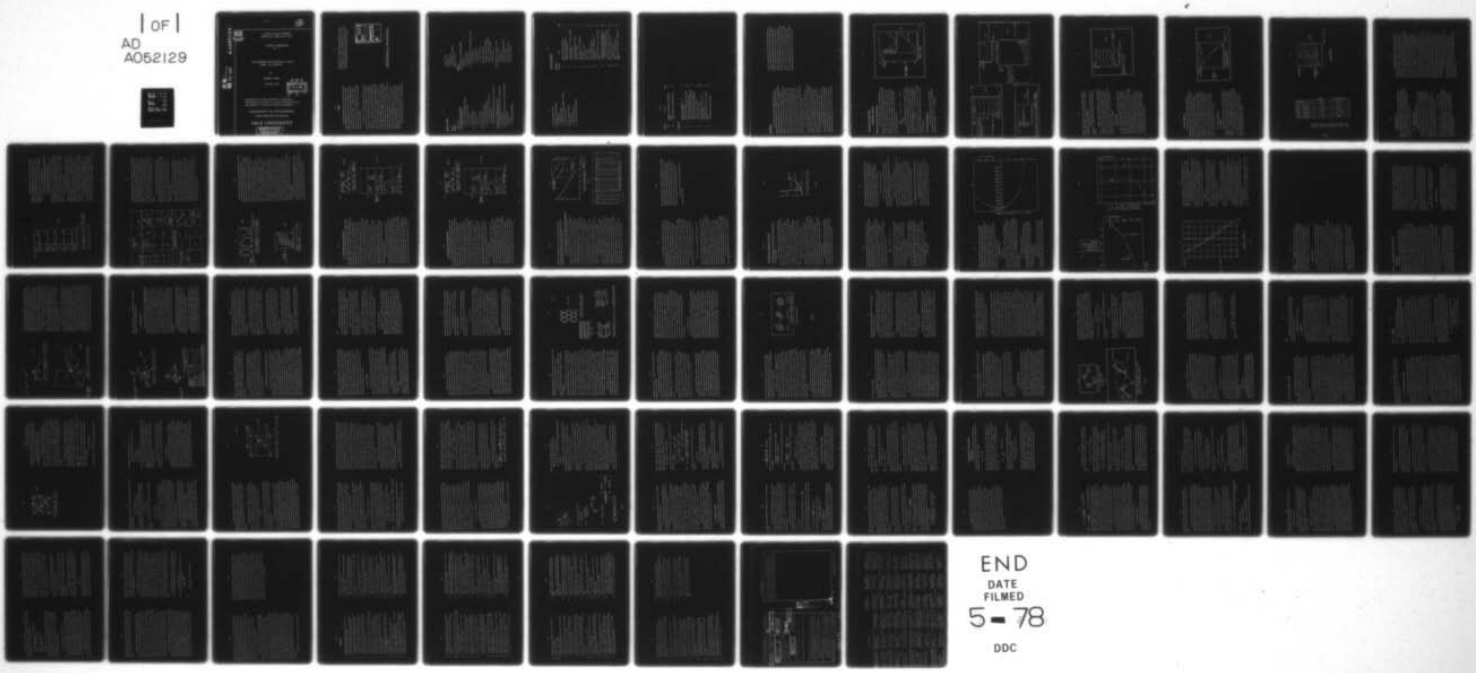
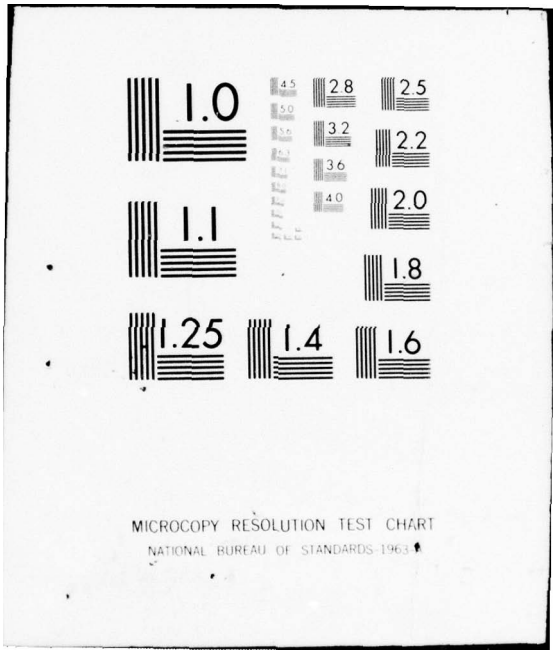
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THE PROPERTIES AND STRUCTURE OF LIQUID WATER : AN OVERVIEW

by

EUGENE H TRINH

November 1977

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SUMMARY

Liquid water presents one of the greatest challenges to those specialized in the Physics of Liquids. Its many unusual properties have not yet been rationalized in terms of a rigorous structural model, although considerable effort has been devoted to the subject. A quantitative treatment is not within our reach at the present time, but a reasonable qualitative understanding of the physical processes occurring in water has been obtained.

This work is an attempt to present an overview of the field of liquid water. The first chapter contains a summary of some of the known thermodynamic, transport, and molecular properties of liquid water. The supercooled and superheated liquid ranges are also considered due to the relatively recent results and renewed interest in these uneasily accessed states of the liquid. The second chapter presents a review of the various theoretical models dealing with the structure of water. The semi-empirical "ad-hoc" models, the lattice and cell models are described together with the various methods of integral equations and computer simulations. The results of a few representative works are summarized in an attempt to arrive at a general picture of the present status of this field. This work is by no means exhaustive, and many existing models and methods have not been mentioned. To include them all would definitely be a task outside the scope of this contribution.

This constitutes the first part of a thesis dealing with

the properties of supercooled and superheated liquid water. The second part, covered in a companion report*, concerns the experimental measurement of the sound velocity in supercooled and superheated water under atmospheric pressure.

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* Technical Memorandum No. 3. Office of Naval Research Publication. Yale University, by E.H. Trinh (Nov. 1977).

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GENERALITIES

The fact that our present knowledge of the liquid state compares unfavorably with our understanding of the solid or gaseous phases should not be surprising. The necessary approximations permissible for the latter two phases are simply not adequate for the description of the interactions between the molecules in the liquid state which are not localized on a regular lattice as in a solid, or are not so far apart that their interactions can be neglected as in vapors. Much progress has been achieved, however, in the case of simple liquids (Argon) and of 'model' liquids (Hard-Spheres, Lennard-Jones) thanks to the use of large scale computers. On the other hand, a rather limited amount of detailed information is available for liquids with more intricate potentials of interaction such as water.

That one should have a scientific interest in water could perhaps be justified only by the fact that life as we know it, would not exist without it. Its importance as a life sustaining medium for all living organisms and as a building block for organic macro-molecules has been well established. Industrial applications, such as the processes of polymerization, depend very much on the knowledge of the properties of water.

Our present incomplete understanding results not only from an insufficient amount of reliable data and the inadequacy of present theoretical methods, but also from the difficulties encountered in the synthesis of a picture of the structure of water from very diverse sources of information. Data resulting

from X-ray and neutron scattering, infrared and Raman spectroscopy, acoustic and dielectric relaxation studies, quantum mechanical and classical statistical mechanical calculations as well as computer simulation, must first be rigorously analyzed and then interpreted in terms of common concepts. One cannot hope for expertise with all these different methods, but it is possible to build a tentative picture of what water appears to be like on the basis of present generally accepted results. Such is the motivation for the first part of this thesis, which deals with past and more recent work by various searchers studying the problem of the structure of water.

THE PROPERTIES OF LIQUID WATER

I- Thermodynamic properties

A Specific volume and thermal expansion.

That the solid phase of water is lighter than its liquid phase is a rare enough phenomenon, even though some solids with open modes of packing share this property, as in the case of Germanium. The really outstanding fact is that water has a minimum in molar volume (a maximum in density) at 3.98 C above its melting point under one atmosphere. Under higher pressure the temperature of maximum density has been found by Kell[3] to vary linearly and negatively :

$$\left(\frac{\delta T}{\delta P}\right)_{\rho_{MAX}} = -0.020 \pm 0.0003 \quad {}^{\circ}C/BAR$$

The temperature dependence of the specific volume at atmospheric and under elevated pressure, is depicted in figures 1 and 2 respectively. Figure 3 shows the dependence of the coefficient of thermal expansion on pressure at several temperatures. Up to 40 C, $\alpha_p = (\delta v/\delta T)_p/v$ also behaves anomalously as the pressure is increased. For most liquids, there is a monotonic decrease of α_p with increasing pressure, as shown in the 80 C curve in figure 3.

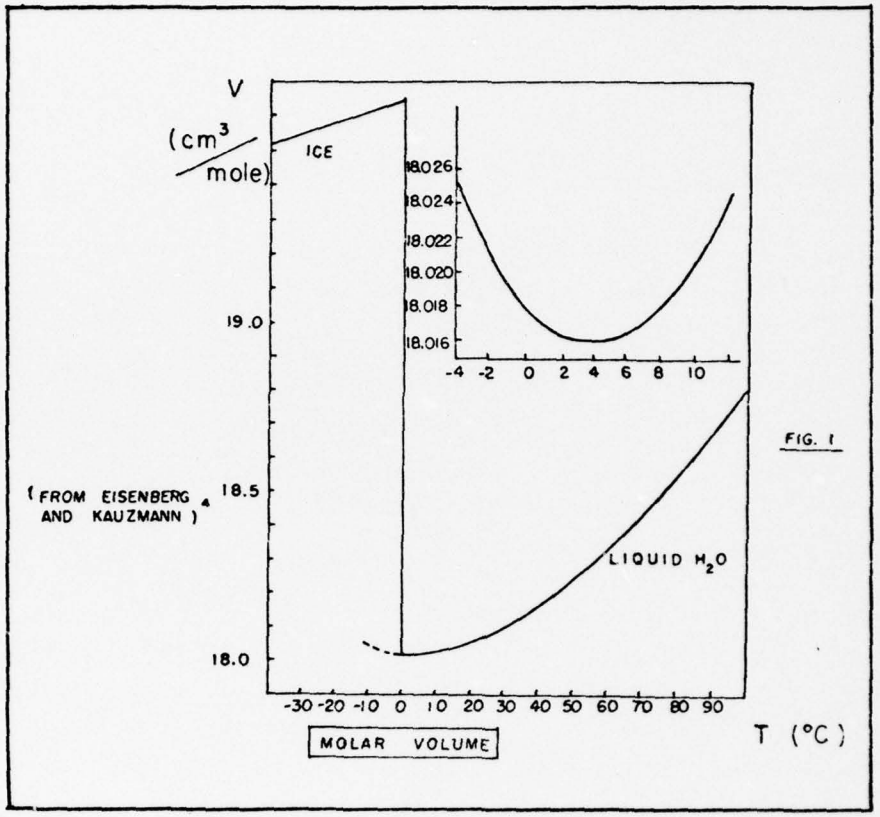


FIG. 1

B Isothermal compressibility.

For most liquids, the coefficient of isothermal compressibility increases monotonically with increasing temperature. In liquid water, $\beta_T = -(\delta v/\delta P)_T/v$

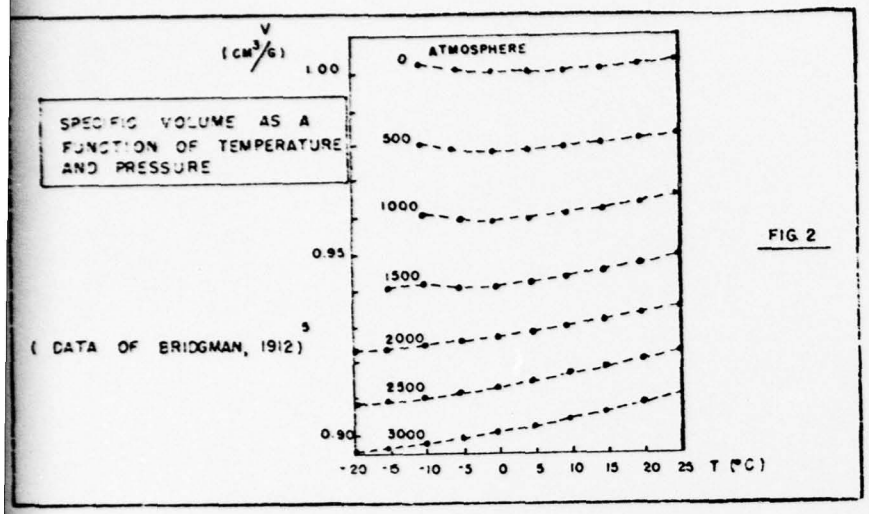


FIG. 2

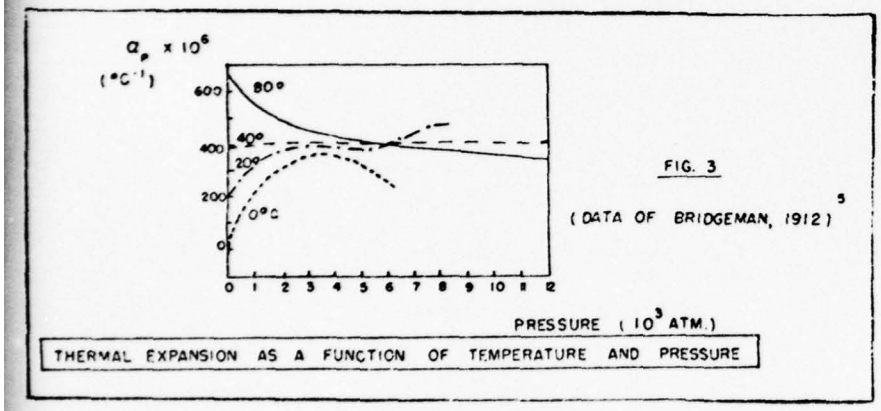


FIG. 3

(DATA OF BRIDGEMAN, 1912)[5]

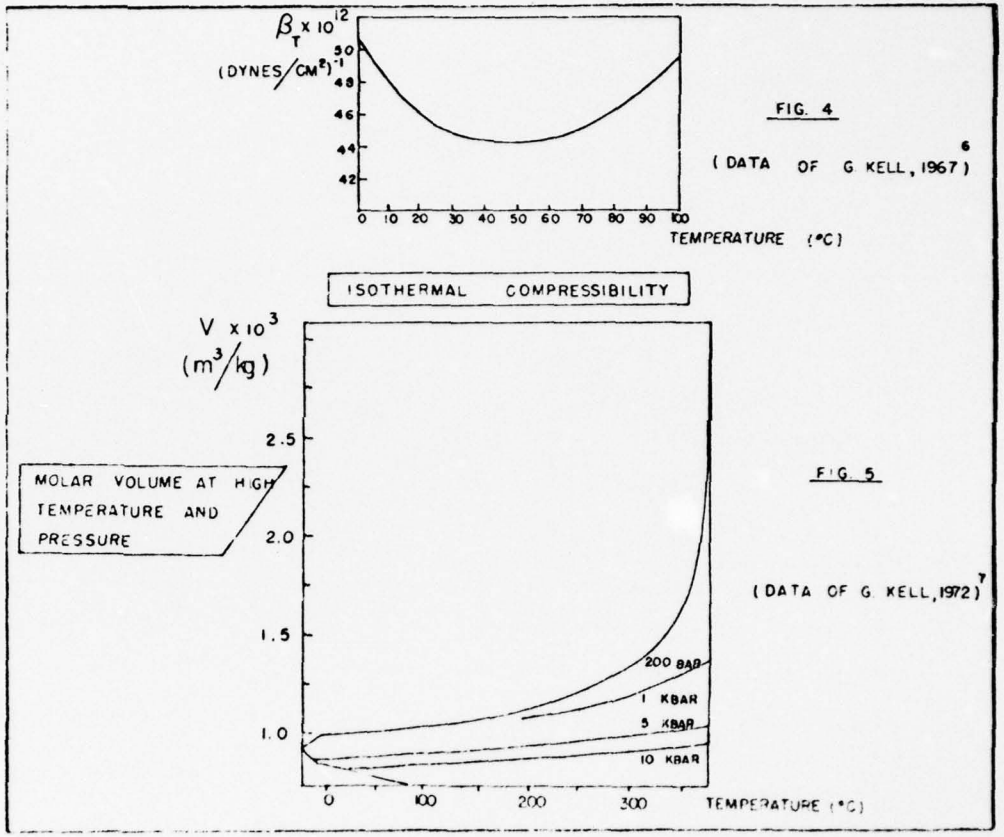


FIG. 4

(DATA OF G KELL, 1967)[6]

FIG. 5

(DATA OF G KELL, 1972)[7]

displays a minimum value at 46 C under atmospheric pressure. This is shown in figure 4, which is a plot of β_T as a function of temperature under one atmosphere.

As the pressure is raised, the minimum of β_T is displaced to a higher temperature and the minimum becomes less marked.

Figure 5 depicts the high pressure, high temperature behavior of the molar volume of water. The stable liquid range is shown up to the critical point. An observation can be made readily : the molar volume of liquid water behaves similarly to most liquids in the region of high temperatures and pressures. The anomalous phenomena seem to occur only in the region of moderate temperature and pressure.

C Sound velocity

Together with the unusual behavior displayed by the density and compressibility, the sound velocity is also anomalous in liquid water. Figure 6 displays the temperature dependence of sound velocity in distilled water under one atmosphere. The maximum value at 74.5 C is the salient feature considering the fact that in most other liquids the sound speed decreases monotonically as the temperature is raised. Smith and Lawson (1954)[8] have measured the sound speed as a function of pressure at different temperatures. Some of the results are reproduced in figure 6 . One effect of pressure, it is revealed, is to drive the temperature of the maximum value up, and to decrease its sharpness.

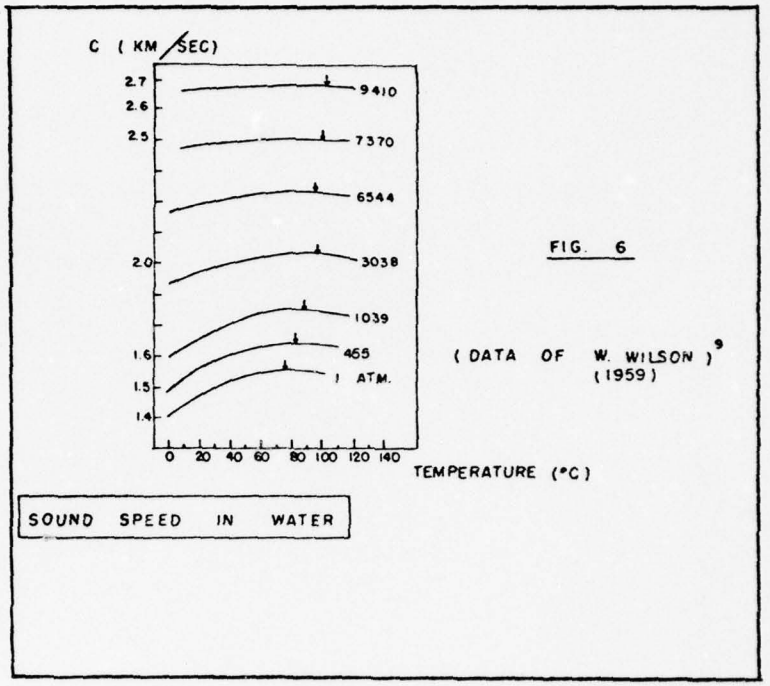


FIG. 6

(DATA OF W. WILSON)[9] (1959)

D - Thermal properties.

The heat capacity of liquid water is large : At constant pressure it has the value of about 18 cal/mole C at 0 C. The temperature variations of the heat capacities at constant pressure and at constant volume are displayed in figure 7. C_p shows a slight minimum at 35 C and C_v is decreasing monotonically. Table I is reproduced from Eisenberg and Kauzmann's [4] book and lists the various changes in internal energy, entropy, and heat capacity upon phase transition. The relatively large increase in heat capacity observed upon fusion is generally attributed to the structural changes possible in the liquid phase. The additional energy involved would be used to either distort or break hydrogen bonds in the liquid.

II- Transport properties.

A - Viscosity

Liquids generally become more viscous when pressure is applied to them. Water is an exception to this rule as figure 8 illustrates. As the pressure increases, the value of the shear viscosity η_s decreases and reaches a minimum for temperatures below 30 C. Davis and Jarzynski [12] have measured the volume viscosity η_v and have found its behavior to be qualitatively similar to the one of η_s. Moreover, the ratio η_v/η_s was found to remain constant within 20 % at all temperatures between 0 C and 90 C, and at pressures up to 1,650 bars.

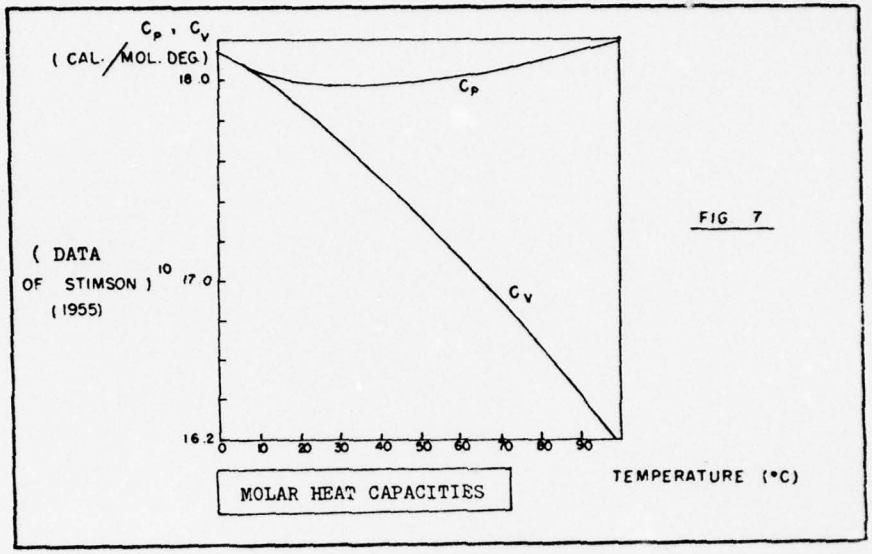
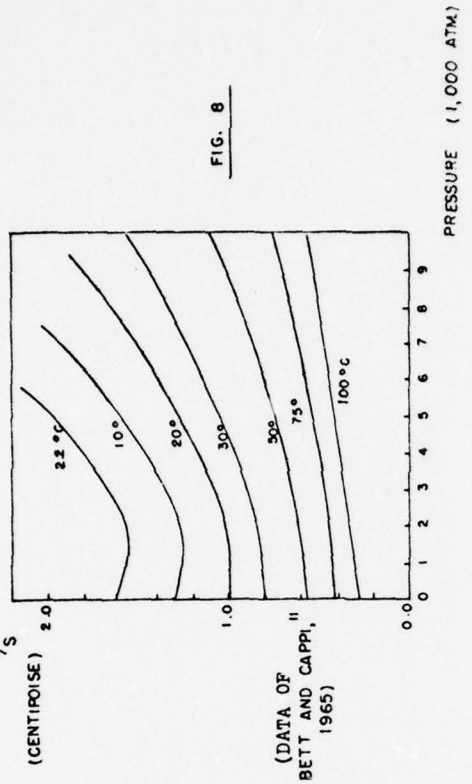


FIG 7

FIG. 8



SHEAR VISCOSITY

	FUSION	VAPORIZATION
TEMPERATURE (°K)	273.15	373.15
δC_p (CAL/MOL °C)	8.911	-10.021
δH (KCAL/MOL.)	1.4363	9.7171
δS (CAL/MOL °C)	5.2581	26.040
δV (CM^3/MOL.)	- 1.621	3.01×10^4
δE (KCAL/MOLE)	1.4363	8.988

PHASE CHANGE PARAMETERS FOR H_2O

TABLE I

B - Heat conductivity

The thermal conductivity of water has an approximately parabolic temperature dependence.[13] It has a maximum value at about 130 C (under saturation conditions), and decreases monotonically up to about 150 C. Most liquids have a continously decreasing heat conductivity as a function of temperature : The behavior of thermal conductivity in water is then also anomalous.

III - Molecular properties.

A - The radial distribution function

Information about the average local structure of water can be obtained through X—ray or neutron scattering experiments. The intensity of the scattered beam is measured as a function of the scattering angle. Structural information is obtained through a modified Fourier transform of the intensity which eventually generates the various functions $\rho_{ij}(R)$ giving the average numbers of atoms of type j situated at a distance R from atom i. In the case of water there are three such functions :

$\rho_{OO}(R)$, $\rho_{HH}(R)$, $\rho_{OH}(R)$ for the various oxygen and hydrogen atoms. Narten and Levy[14] have estimated the contributions of the different types of pairs of atoms from the scattering of X- rays and neutrons. They found that most of the scattering was being done by the O-O pairs while the contributions from the O-H pairs and H-H pairs were only 12% and 2% respectively of the O-O pairs contribution.

Two important qualifications have to be introduced at this point in order to be able to judge the merits of scattering results and their impact on the problem of the structure of water : First, one must keep in mind that X- ray and neutron diffraction experiments are only probes for the average (over a volume large with respect to the molecular dimensions) of the actual instantaneous structural configurations. It is not possible to infer the instantaneous structure. Secondly, the results of a single X- ray or neutron scattering experiment cannot yield the different $\rho_{ij}(R)$ for a heteroatomic substance. In the case of water, three separate experiments involving an emphasis on the three different types of interactions (O-O, O-H, H-H) must be performed for a rigorous measurement of the individual $\rho_{ij}(R)$. In practice only reliable X-ray scattering in water and neutron scattering in heavy water (D_2O) have been performed. Thus, derivation of the radial distribution functions from the experimental results has required the use of models for the local structure of water. One such model used by Narten and Levy employs a single parameter, the remaining inter-atomic dimensions being constrained by the tetrahedral requirement and by known values for interatomic parameters.

The results of Narten and Levy[14] are plotted in figure 9. $G(R) = \rho(R)/\rho_o$ (where ρ_o is the bulk average density of molecules) is the radial distribution function and gives a measure of the local deviation from long range random behavior. The results are for X- ray diffraction in liquid water at equilibrium with its vapor.

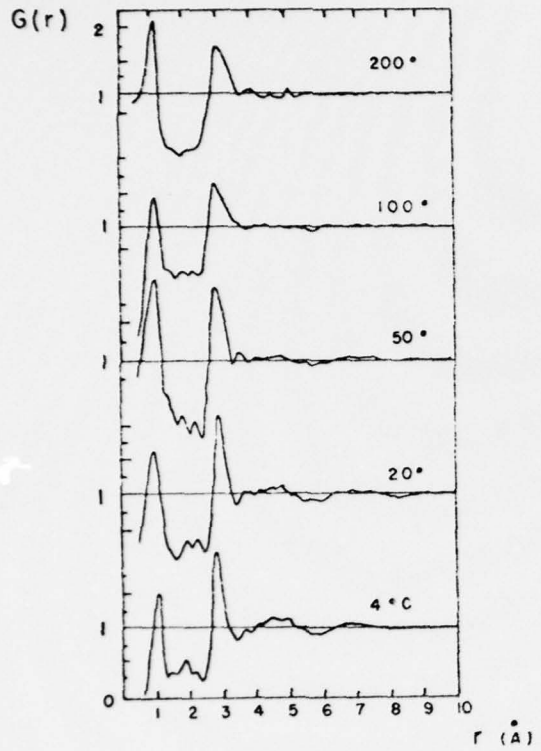


FIG. 9

X RAY CORRELATION FUNCTION $G(r) = \rho(r)/\rho_0$

(Data of Narten and Levy, 1972[14])

The first peak at 1 Å is attributed to the Oxygen-Hydrogen first neighbor interactions. The maximum at 2.9 A reflects the Oxygen-Oxygen, nearest neighbor effect. The two broad peaks at around 4.5 Å and 7 Å depict second and higher neighbor interactions. The small structures between 3.5 Å and 4.0 Å are not assigned any structural meaning.

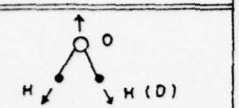
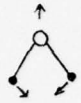
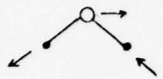
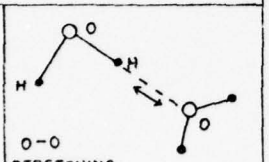
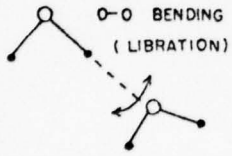
B - The evidence from Infrared and Raman spectroscopy

1 - The Infrared spectrum of liquid water

Infrared and Raman spectroscopy are very sensitive detectors of the effects of molecular interactions. They reveal the fundamental frequencies of molecular vibrations thus prcting the molecular structure and intermolecular forces. Spectroscopic studies of liquid water are fundamental to the question of solving the problem of the possible classification of different molecular species in terms of their environment.

The normal vibrational modes of isolated water vapor molecules, and of bonded molecules in liquid water and ice are listed in Table II. ν_1 , ν_2 , ν_3 are fundamental intramolecular vibrational frequencies of the isolated vapor molecule. For O-H stretching in pure H_2O vapor they are 3651 cm^{-1}, 1595 cm^{-1}, and 3755 cm^{-1} respectively. In the condensed phases the molecules are bonded to one another and additional intermolecular vibrations are introduced. These modes are also described in Table II.

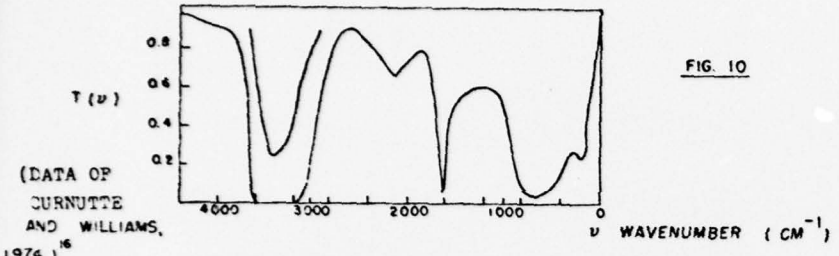
An important consequence of the hydrogen bonds between molecules, however, is their effect upon the frequencies of intramolecular vibrations. In particular, hydrogen bonding tends to shift the infrared and Raman spectral components characteristic of

ν (cm^{-1}) WATER VAPOR	INTRAMOLECULAR MODES ν LIQUID	ν ICE I	MODE
H_2O 3651 HOD 2720 D_2O 2666	O-H STRETCHING 3415 O-D STRETCHING 2495 (30 C)	3200 (H_2O)	 SYMMETRIC STRETCHING ν_1
H_2O 1595 HOD 1402 D_2O 1172	1650	1650	 BENDING ν_2
H_2O 3755 D_2O 2789	3415 2495	3200	 ASYMMETRIC STRETCHING ν_3
INTERMOLECULAR MODES			
ROTATIONAL SPECTRUM OF WATER VAPOR IN 50 – 1200 cm^{-1} RANGE	200	60 230	 O-O STRETCHING
	680	840	 O-O BENDING (LIBRATION)

O-H stretching modes to lower frequencies and the H-O-H bending mode to higher frequencies. For a detailed treatment of the spectroscopic study of the hydrogen bond, one can refer to the book by Pimental and Mc Clellan.[15] Thus, in liquid water the frequencies of both stretching modes are estimated to be around 3420 cm^{-1}. This is lower than the corresponding frequency in the vapor state but larger than the one in ice. This reflects the relative strength of the hydrogen bond in the two condensed phases : The molecules in ice are more strongly bonded to one another.

A typical infrared spectrum obtained from a thin layer of liquid water is reproduced in figure 10. The various absorption bands correspond to the various intramolecular modes (at 3400 cm^{-1}, 1650 cm^{-1}) and intermolecular modes (at 680 cm^{-1}, 200 cm^{-1}). Some combination modes are present (2120 cm^{-1}, 4000 cm^{-1}) ; they result from the association of intra and intermolecular vibrations.

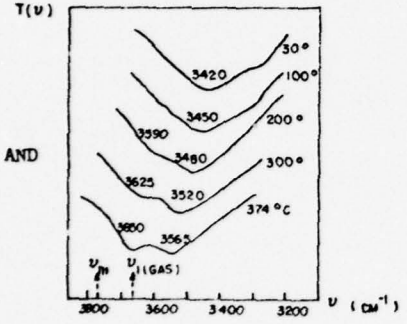
The variation with temperature of the degree of hydrogen bonding can be obtained through the observation of shifts in vibrational frequencies with temperature change. Such a study is shown in figure 11. Raising the temperature seems to drive the frequencies to higher values ; a trend towards the free molecule state. Either weakening or breaking of hydrogen bonds could provide an explanation of such a phenomenon. More quantitative studies can be made in the infrared overtone range ; one may refer to the article by W.A. Luck[18] for more details on the estimates of the degree of hydrogen bonding under various conditions.



(DATA OF CURNUTTE AND WILLIAMS, 1974)[16]

FIG. 10

SPECTRAL TRANSMISSION IN A 10 μM LAYER OF LIQUID WATER AT 25 °C IN THE INFRARED



(DATA OF SAUVAGNE AND JOSIEN, 1974)[17]

FIG. 11

INFRARED ABSORPTION IN THE O-H STRETCHING REGION

Because of its ability to probe the instantaneous environment of the water molecule, vibrational spectroscopy has been invoked to prove or disprove opposite viewpoints in the mixture versus continuum controversy. In particular the interpretation of infrared and Raman spectra has been the center of debates relating to the possibility of differentiating the molecular environments from the shape of the spectral bands. The vibrational band of the O-H stretching mode has been particularly well studied. The fact that the infrared spectral band for such a mode is singly peaked argues for a continuum model. Such a continuous distribution in frequency of the light intensity exiting from a water sample contradicts mixture models which advocates a small number of molecular arrangements. Indeed, if the instantaneous configurations of the molecules of the liquid can be classified in a discrete and finite way, the spectral distribution of the light intensity would reflect such discreteness. In addition, the O-H (uncoupled) stretching band in the liquid is considerably wider than that in ice. This widening of the band has been taken to reflect the greater variation in intermolecular distances in the liquid state. This would result in an increased variation in potential which would affect the intramolecular vibrational frequency.

Proponents of the mixture model have attempted to explain the shape of the spectral band by decomposing it into a small number of Gaussian distributions, each of these being characteristi of a particular molecular configuration. Unfortunately, such decomposition cannot be achieved in a unique fashion.

2 - The Raman spectrum of liquid water.

Water is a very intense absorber in the infrared range. This renders experimental measurements difficult because very thin layers of water are often required. Under these circumstances Raman spectroscopy methods seem to have an advantage over infrared techniques. However, the experimental difficulties encountered with liquid water have not yet been completely mastered, and some disputes over experimental results exist.[19] One of the most important recent contributions from Raman studies deals with the possibility of distinguishing between different types of molecules. These results seem to indicate the presence of broken hydrogen bonds. Such evidence is reproduced in figure 12 a, which describes the temperature dependence of the Raman absorption band due to O-D stretching in a solution of D_2O in H_2O. The existence of an "isosbestic" frequency (common point of intersection for all the curves) is taken as evidence for the presence of different molecular types with opposite temperature dependence.

Possibly even more revealing are the results of stimulated Raman scattering experiments. The fundamental difference between stimulated and spontaneous Raman scatterings is the characteristic threshold nature of the former type. Selective excitation for Raman scattering becomes feasible, and the possibility of obtaining direct evidence for the existence of different species of molecules arises. Such testimony to the presence of differentiable molecular types has been given by Walrafen[20] and is illustrated by figure 12b. In this case, the introduction of CLO_4^- ions has the structure breaking effect of reducing

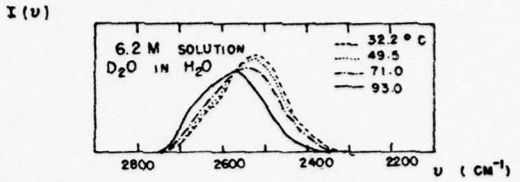
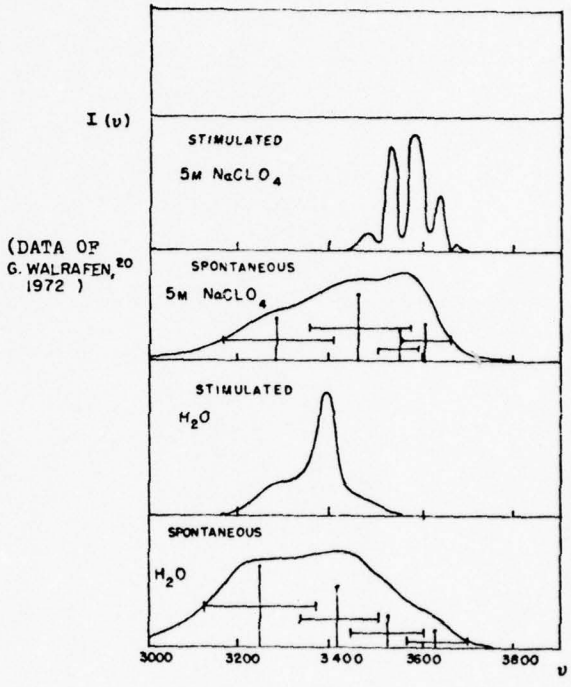


FIG 12 a

RAMAN INTENSITY AS A FUNCTION OF FREQUENCY AT VARIOUS TEMPERATURES



(DATA OF G. WALRAFEN,[20] 1972)

FIG. 12 b

2 - The Raman spectrum of liquid water.

Water is a very intense absorber in the infrared range. This renders experimental measurements difficult because very thin layers of water are often required. Under these circumstances Raman spectroscopy methods seem to have an advantage over infrared techniques. However, the experimental difficulties encountered with liquid water have not yet been completely mastered, and some disputes over experimental results exist.[19] One of the most important recent contributions from Raman studies deals with the possibility of distinguishing between different types of molecules. These results seem to indicate the presence of broken hydrogen bonds. Such evidence is reproduced in figure 12 a, which describes the temperature dependence of the Raman absorption band due to O-D stretching in a solution of D_2O in H_2O. The existence of an "isosbestic" frequency (common point of intersection for all the curves) is taken as evidence for the presence of different molecular types with opposite temperature dependence.

Possibly even more revealing are the results of stimulated Raman scattering experiments. The fundamental difference between stimulated and spontaneous Raman scatterings is the characteristic threshold nature of the former type. Selective excitation for Raman scattering becomes feasible, and the possibility of obtaining direct evidence for the existence of different species of molecules arises. Such testimony to the presence of differentiable molecular types has been given by Walrafen[20] and is illustrated by figure 12b. In this case, the introduction of CLO_4^- ions has the structure breaking effect of reducing

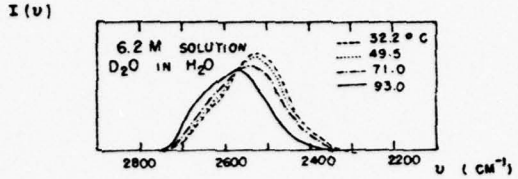
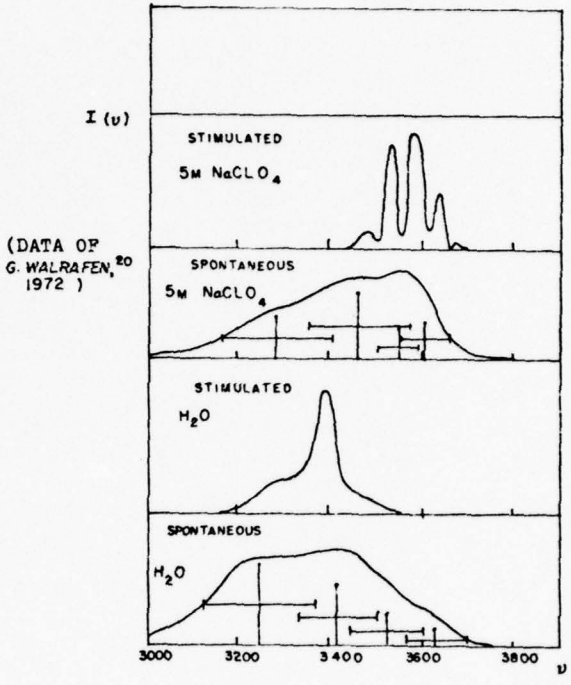


FIG 12 A

RAMAN INTENSITY AS A FUNCTION OF FREQUENCY AT VARIOUS TEMPERATURES



(DATA OF G. WALRAFEN,[20] 1972)

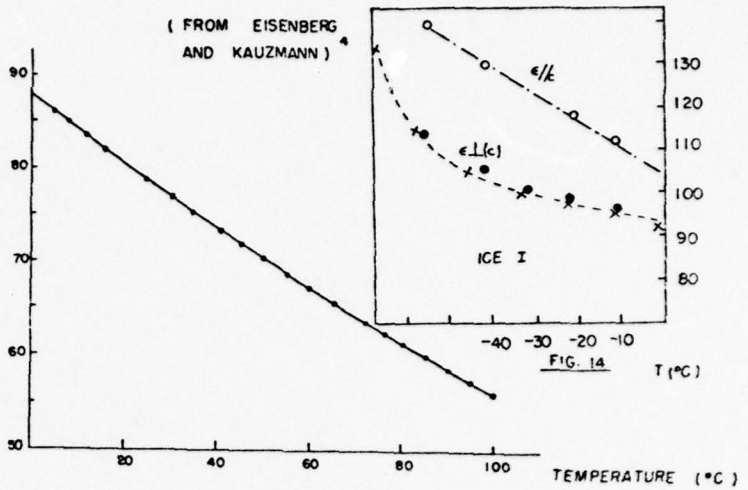
FIG. 12 B

the number of hydrogen bonds. In such a solution of $NaClO_4$ in H_2O, exclusive excitation of non-hydrogen bonded molecules by stimulated Raman scattering seems to be obtained.

C - The static dielectric constant and dielectric relaxation

At 25 C under one atmosphere the static dielectric constant of liquid water has the value of 79 ; this is anomalously large for a liquid. One factor that could explain such a high dielectric constant is the high spatial correlation between the tetrahedrally coordinated molecules. Under the influence of an electric field the neighboring molecules at the different points of the tetrahedron orient their dipole moments parallel to the molecule at the center of the tetrahetron, thus contributing to an increased induced polarization of the center molecule. Some experimental values for the temperature variations of the static dielectric constant ϵ_0 are reproduced in figure 13. The graph includes values for Ice Ic with the electric field both parallel and perpendicular to the C axis of the crystal.

An approximate evaluation of a macroscopic rate for molecular reorientations is possible through the study of the frequency dependence of the dielectric constant. When a static or low frequency field is applied to the liquid, the molecules have the time to adjust their orientation according to the direction and magnitude of the field. As the frequency of the oscillating field is increased, less and less time is allotted to the molecules for reorientation. Consequently, the value of the dielectric constant decreases ; for very high frequencies the value of the dielectric constant, denoted by ϵ_∞ , falls to around 4.5.



STATIC DIELECTRIC CONSTANT (MALMBERG AND MARRIOTT, 1956 [21])

FIG 13

T	ϵ_0	ϵ_∞	τ	α
0 °C	88.3	4.44	1.79×10^{-11}	0.014
10	84.1	4.10	1.26	0 014
20	80.4	4.23	0.93	0.013
30	76.8	4.20	0.72	0 012
40	73.2	4.16	0.58	0.009
50	70.0	4.13	0.48	0. 013
60	66.6	4.21	0.39	0. 011
75	62.1	4.49	0.32	—

DIELECTRIC CONSTANT AND RELAXATION TIME

(COLLIE ET AL.[22])

For some liquids the macroscopic rate of molecular reorientation given by dielectric relaxation can be described by a single relaxation time τ_D . Liquid water is essentially such a case. However, there is strong evidence for the existence of a small spread in relaxation time which could be caused by a number of different relaxation times very close together. Table III presents some results of microwave measurements giving the dielectric constant, the main relaxation time, and the spread denoted by α. It must be noted that τ_D is a macroscopic manifestation of the molecular motion and cannot be taken as the individual molecule rotation time, which should be somewhat shorter.

The theory of rate processes gives the temperature dependence for cases with a single relaxation time as :

$$2\pi/\tau_D = \omega_s = C \exp(\Delta S^*/R) \exp(\Delta E^*/RT)$$

where ΔS^* and ΔE^* are the entropy change and the activation energy of the relaxation process. From experimental values, an approximate determination of ΔE^* gives a value of about 5 kcal/mole in the case of liquid water. This value is close to what is generally accepted as the energy of hydrogen bonding. Thus, the orientation process for dipole relaxation is likely to involve the breaking of a single hydrogen bond. The different interpretations of the existence of a single relaxation time together with its small spread in terms of hydrogen bond bending or breaking have been considered by Eisenberg and Kauzmann[4] (p.209 in their book).

This concludes our brief survey of the currently available experimental evidence on liquid water in its stable state.

Due to the diversity of the sources of information on the subject, this present treatment has been very incomplete; it is hoped, however, that even such a short presentation may reveal the characteristic properties of liquid water and their relations to the problem of structure while pointing to current areas of debate. For more comprehensive treatises one is invited to refer to the compilations by Franks,[23] Horne,[24] and Luck.[18]

We now turn our attention to the properties of metastable liquid water.

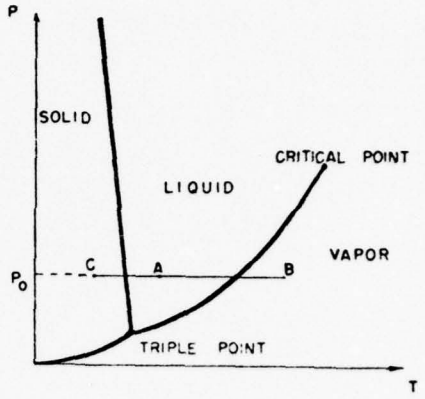
THE PROPERTIES OF METASTABLE LIQUID WATER

I - The thermodynamic description and some basic facts from nucleation theory.

The usual range of the liquid state is determined by the conditions of temperature and pressure at which phase tranformations occur (vaporization or solidification) when the two phases involved are in contact with each other. In the cases when the new phase must appear in the bulk of the original phase, the onset of the transition is often considerably delayed. The liquid can then remain in a state of *metastable equilibrium* where its bulk chemical potential is higher than that of the phase to be nucleated. The surface free energy of the new phase acts in this case as an energy barrier to nucleation.

Figure 15 is a schematic representation of the P-T diagram of water. The three coexistence lines separate the three possible states of the substance. Point A represents a stable state of liquid water. A superheated state can be reached (point B) if the temperature is raised isobarically and the sample remains in the liquid state. This can also be done by reducing the pressure isothermally to reach point B. Similarly, a liquid sample can be supercooled by reducing the temperature under constant pressure to reach the point C.

In the kinetic approach to the problem of homogeneous nucleation the phase transformation is viewed as resulting from the growth to macroscopic size of "critical" embryos (or "nuclei") of the new phase in the midst of the original phase.



P-T PHASE DIAGRAM OF WATER

FIG 15

As a result of density fluctuations, small embryos of the new phase are formed. Because of the constant attachment and detachment of molecules, these embryos are not in equilibrium, except when they reach the "critical" size at which point they are in a state of unstable equilibrium and may readily grow to macroscopic size. The equilibrium distributions of the vapor embryos and the work required for their creation have been determined[25] for a superheated liquid. This work is maximum for the formation of a "critical" embryo and can be written

$$W_C = 16\pi\sigma^3 / (P - P_L)^2 \quad ,$$

where σ is the surface tension, P is the pressure in the vapor cavity, and P_L is the pressure in the liquid. The magnitude of W_c varies with the degree of superheating or supercooling . In the case of a supercooled liquid, the expression for W_c is further complicated by the anisotropy of σ and by the nature of the solid surfaces of the embryos.

The "classical" theory of nucleation as formulated by Volmer[26], Becker and Doering[27], and Frenkel[28], among others, provides a way to determine approximately the rate of formation of critical embryos in the steady state regime. Under steady state conditions the net rates at which the different size embryos grow are all equal and their distributions are stationary. The rate of creation of the critical embryos is related to the work of formation through the relation

$$J = C\exp(-W_c/kT) .$$

In the case of supercooled liquids an additional effect is introduced by the viscous forces which tend to impede the rearrangements of the molecules. In general, the description of the rate of critical nuclei formation in supercooled liquids involves an activation energy E_A for molecules crossing the solid-liquid interface. The relation becomes then

$$J = C'(T).\exp(-E_A/kT).\exp(-W_c/kT) .$$

In the constant C' are included factors relating to the attachment and detachment coefficients for the molecules which are often approximated when actual calculations are performed. The coefficient C' is temperature dependant.

Numerous modifications and emendations to the "classical" nucleation theory have been introduced. Their aims have been to correct certain computation errors and oversimplifications which were originally introduced. The basic relation between the work of critical nuclei formation to the rate J is, however, still the common approach adopted. For a more detailed discussion, one may refer to Dunning's review article in the monograph on Nucleation edited by A.C. Zettlemoyer.[29]

II The experimental data on supercooled and superheated water.

Experimental measurements in metastable liquids are difficult to perform because of the stringent requirements of purity and isolation of the samples. It is then not surprising that the amount of available experimental data for thermodynamic parameters of liquids in their supercooled or superheated

states is quite small. In the case of liquid water, however, a growing interest in the supercooled range has produced a respectable bank of thermodynamic data. The superheated state of water, on the other hand, has not been studied extensively. Some experimental parameters relating to the predictions of nucleation theory (tensile strength[30], limit of superheat [2]) have been determined, but virtually no thermodynamic quantities, except for the density, has been measured.

1 - Supercooled water.

a) Density.

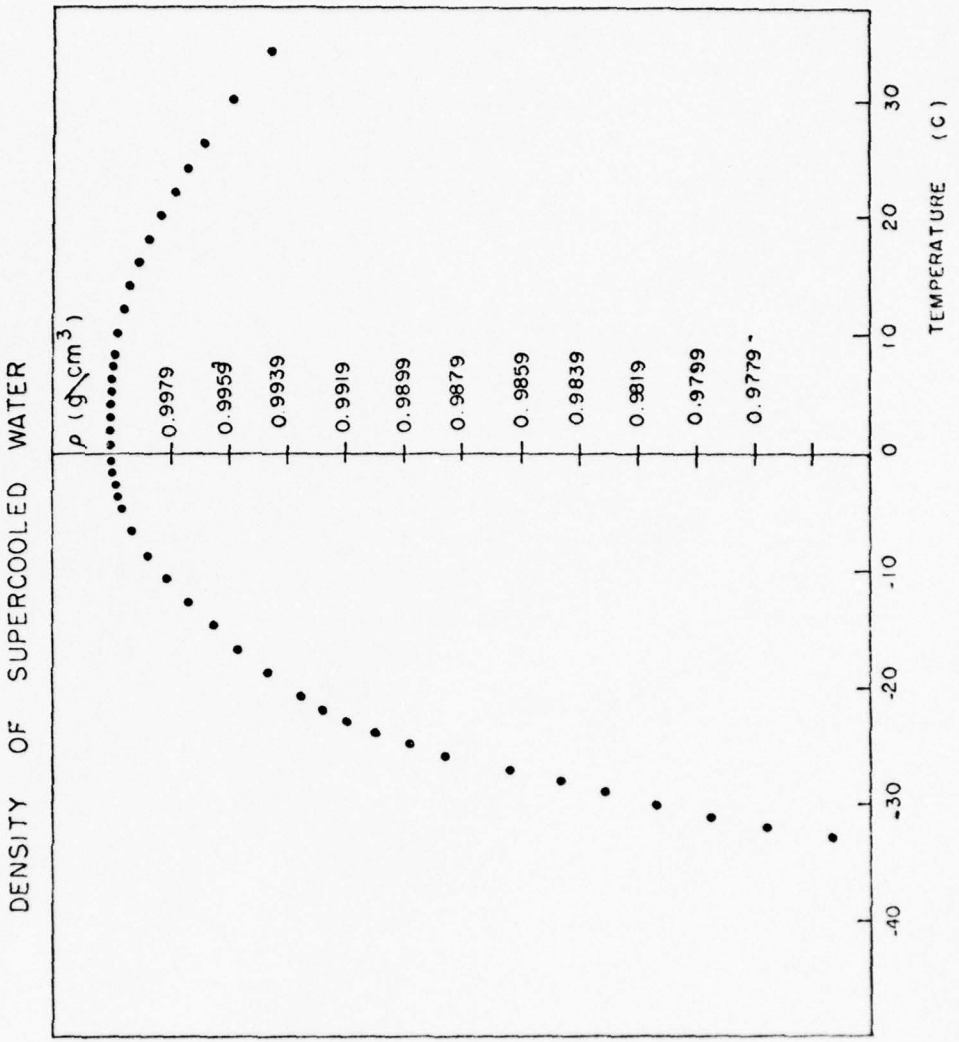
The density has been measured under atmospheric pressure by Zheleznyi[31] down to -34 C and Shuffle and Venugopalan[32] down to -38 C. Figure 16 reproduces Zheleznyi's data as a function of the temperature. An outstanding feature is the accelerating decrease of the density with decreasing temperatures. The coefficient of thermal expansion $\alpha = (\delta V / \delta T)_p / V$ is negative and decreases extremely rapidly.

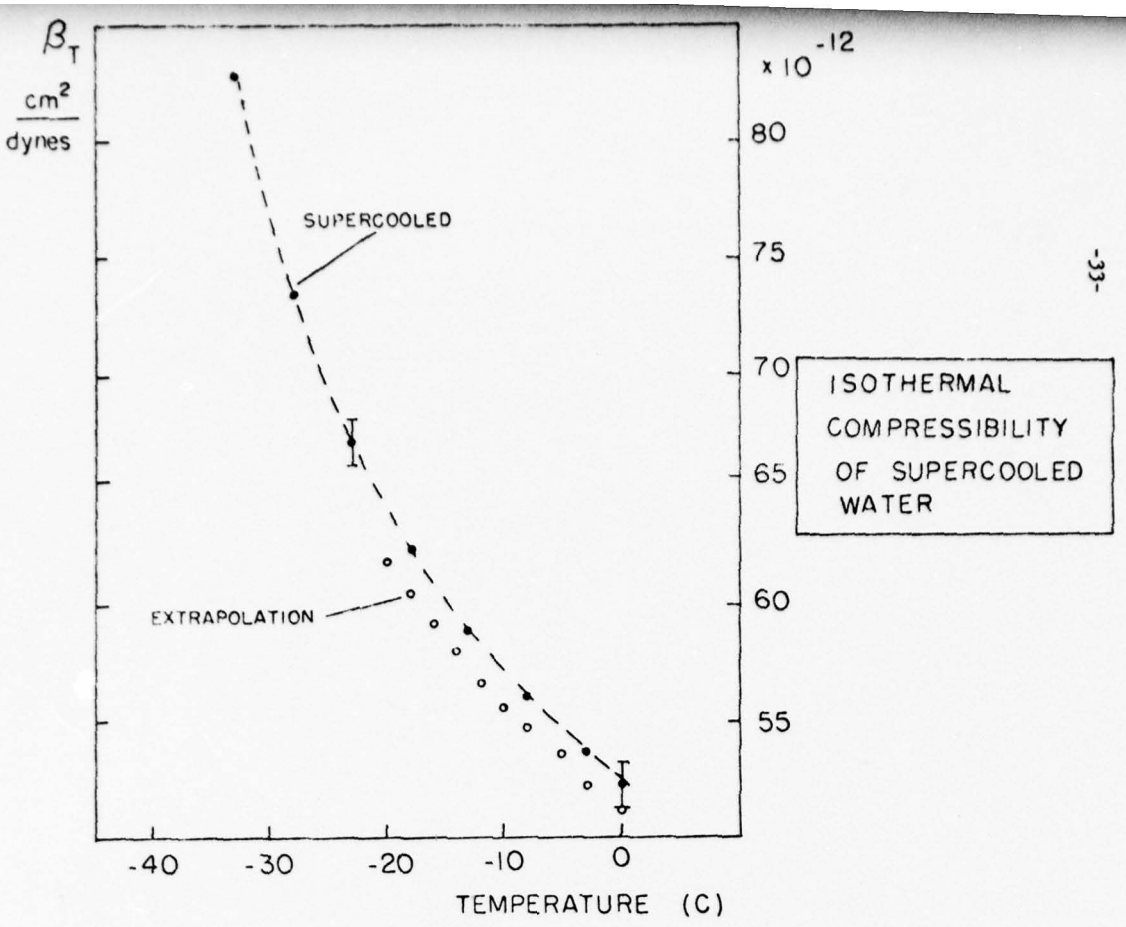
b) Isothermal compressibility.

The coefficient of isothermal compressibilty β_T has been measured by Speedy and Angell[33] down to -26 C. Their results are reproduced in Figure 17 and reveal a slightly higher value for β_T at low temperatures than that determined from an extrapolation of data above 0 C.

c) Specific heat.

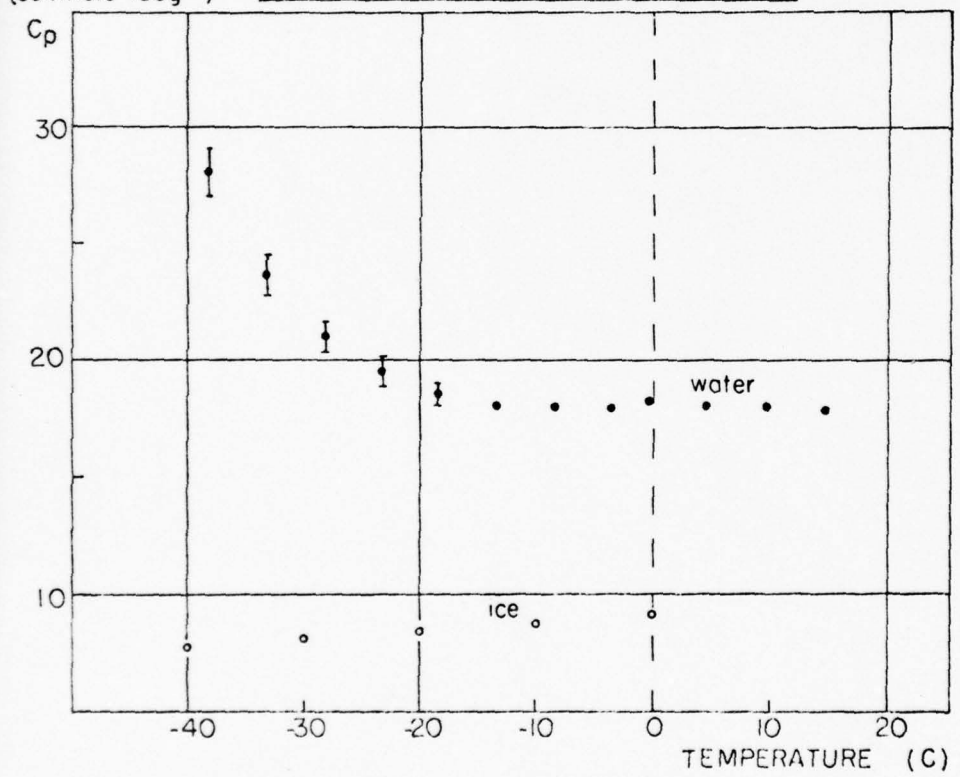
Rasmussen and MacKenzie[34] and Angell et al.[35] have measured the specific heat at constant pressure C_p (isopiestic heat capacity) in water supercooled to -38 C by means of emulsions.

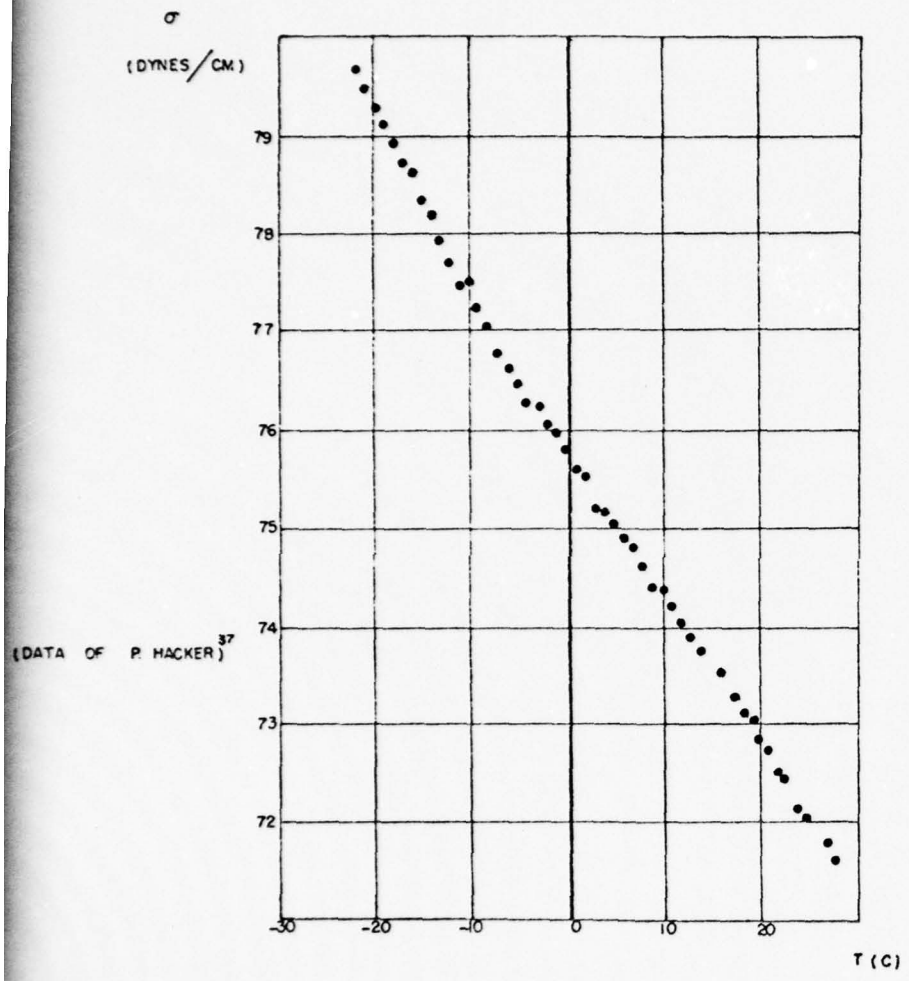




ISOTHERMAL COMPRESSIBILITY OF SUPERCOOLED WATER

ISOPIESTIC SPECIFIC HEAT IN SUPERCOOLED H_2O [35]





SURFACE TENSION

FIG. 19

The results of Angell et al. are reproduced in figure 18. An anomalous increase in C_p below -15 C can be observed. The calculation of the specific heat under constant volume (C_v) reveals that it remains relatively constant down to -38 C.

This phenomenon has been given two different interpretations: The first involves a thermodynamic singularity at -45 C, and the second invokes the concept of precrystallization. A discussion of an interpretation for the temperature dependence of C_p will be offered in the last chapter of the companion report.

d) Viscosity.

Hallett[36] has measured the viscosity of water down to -24 C. The results show a smooth continuation of the data in the stable range, although the rate of increase of the viscosity with falling temperature is larger than that determined simply from an extrapolation of the data above 0 C.

e) Surface tension.

P.Hacker[37] has been able to determine the surface tension down to -24 C. A slight but abrupt change in the temperature coefficient may be detected at about -5 C (see Fig. 19).

f) The self-diffusion coefficient and proton relaxation time.

The self-diffusion coefficient has been determined by H. Pruppacher[38] down to -20 C and by Gillen et al.[39] down to -31 C. An interpretation of this data has been offered recently by Ricci et al.[40] who have generalized the Macedo-Litovitz[41] theory of diffusion by incorporating the influence of the average number of broken hydrogen bonds.

The temperature and pressure dependence of the longitudinal proton relaxation time (T_1) have been recently studied by Lang and

Lüdemann[42]. An anomalous increase in T_1 with an initial increase in pressure under isothermal conditions has been detected in the temperature range between +20 and -66 C. The experimental data have been fitted with an empirical two-exponential relation developed by Hindman.[43] The anomalous pressure dependence of T_1 has been attributed to pressure effects on the random hydrogen bonded network present in liquid water at these low temperatures.

2- Superheated Water.

Chukanov and Skripov[44] and Kell and Whalley have measured the density of superheated water under moderate and high pressures. Data at atmospheric pressure have been obtained through an extrapolation. According to their results, the temperature and pressure behavior of the density in superheated water is qualitatively similar to that of the stable liquid above room temperature.

The sound velocity has been measured in liquid water above 100 C but under saturation conditions.[45] Although the liquid is not superheated in these circumstances, it is expected that the temperature dependence of the sound velocity thus measured is not very different from that found in the superheated liquid, at least at temperatures not very much higher than 100 C.

What has been listed above is essentially the currently available experimental information on metastable liquid water. In the next chapter we will consider the theoretical treatment of the problem of the structure of water.

CHAPTER II THE STRUCTURE OF LIQUID WATER: THEORY

I INTRODUCTION

The nature of one of the main controversies in the theory of the structure of liquid water reveals the general state of affairs in this field. Indeed, the debate about such a fundamental question as to whether the molecular aggregations in water can be classified in a discrete or continuous manner in terms of the energy of hydrogen bonding, betrays the modest progress which has been achieved since Roentgen first proposed his speculations about the existence of a mixture of "icelike" and "un-icelike" components. The unusual thermodynamic properties, specifically the PVT properties, were the principal reasons for the proposal of such a theory, and they remain today the conceptual basis of the various ad-hoc structural models involving the idea of a mixture of discrete components. Empirical structural models were also proposed within the 'continuum' framework and generally met as much success as the 'mixture' models in accounting for the various thermodynamic anomalies found in water. In this approach the instantaneous environment of a water molecule is seen as varying not in a discrete way but in a continuous manner.

An alternate way of undertaking the theoretical study of the structure of water is to start from the basic principles of statistical thermodynamics and to derive a partition function for the system under study. The rigorous solution of the appropriate equations, however, remains a quite insurmountable task

because of the complexity of the potential of interaction between the many water molecules. The adoption of the assumption of pairwise additivity for the interaction potential has led to some progress in both of the available methods for research. The first method, based on the solution of the integral equations involving the pair distribution function, has provided some useful insights into the structural properties of liquid water. The alternate path comprises either the Monte Carlo or the Molecular Dynamics approaches and has revealed itself to be more fruitful.

In this part of the thesis a review of works on water structure is attempted. Evidence from both theoretical and experimental sources employing various methods is examined. A tentative picture of the present status of the field is thus proposed.

We proceed by first considering the properties of the water molecule and of the all important hydrogen bond.

A THE WATER MOLECULE

The apparent simplicity of an isolated water molecule conceals the wealth of intricate interactions and anomalous phenomena found in the molecular aggregations of the liquid state.

The equilibrium configuration of an isolated water vapor molecule is depicted in Figure 1. The molecular properties of water can be obtained by both theoretical and experimental means. Within the framework of the Born-Oppenheimer and

(DATA OF BENEDICT ET AL., 1956)[46]

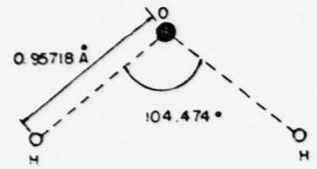


FIG. 1

EQUILIBRIUM CONFIGURATION OF A WATER VAPOR MOLECULE

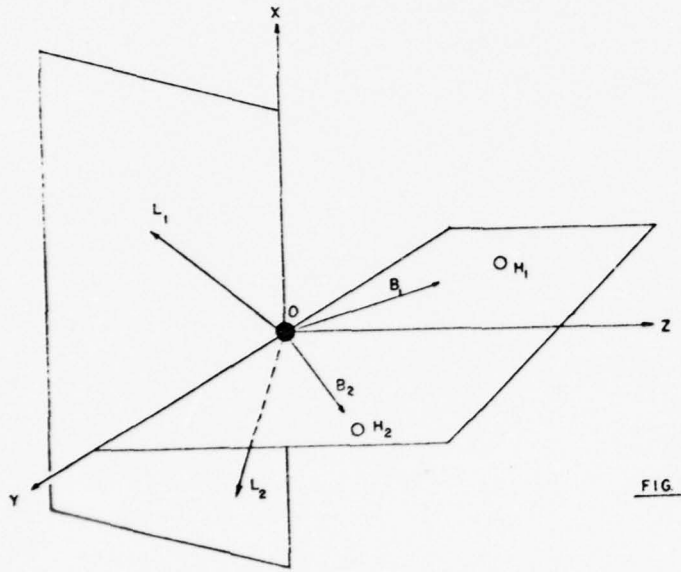


FIG 2

(FROM EISENBERG AND KAUZMANN,)[4] 1969, p.25

DIRECTION OF BONDING ORBITALS IN WATER

Molecular Orbitals approximations, extended Hartree-Fock calculations have been performed to yield reasonably accurate wave functions from which geometrical, energetic, and electrical parameters can be deduced. The agreement between these quantum mechanical results and the values obtained experimentally are generally good. In some instances, as in the cases of the anisotropic polarizability, the molecular orbitals calculations have provided results not yet available through experimentation.

The values of some parameters of the H_2O molecule are listed in Table I. For a short but comprehensive review of the results of Molecular Orbitals theory applied to water, one may refer to the article by P. Shuster.[47] Extensive listings of the molecular properties of water are compiled in the works of Dorsey[48], Eisenberg and Kauzmann[4], and in the series of monographs on Water edited by Franks[12].

The charge distribution of the water molecule can reveal much about the structure of water in its condensed phases. It is the characteristic configuration of the electronic charge distribution that leads to hydrogen bonding and tetrahedral coordination. This distribution is schematically depicted in Figure 2. The theory of Molecular Orbitals advocates the hybridization of the 2s and 2p orbitals of the oxygen atom. Because of this hybridization, the lone pair of the electrons belonging to the Oxygen has two lobes situated symmetrically with respect to the plane of the oxygen and hydrogen atoms. These lobes make an approximately tetrahedral angle (about 104 ^{o} in the vapor molecule) with the lobes that are involved in valence bonding with the Hydrogen atoms. Tetrahedral coordination in ice and liquid

TA OF LA PLACA AND POST, 1960,
D BRILL, 1962)[49]

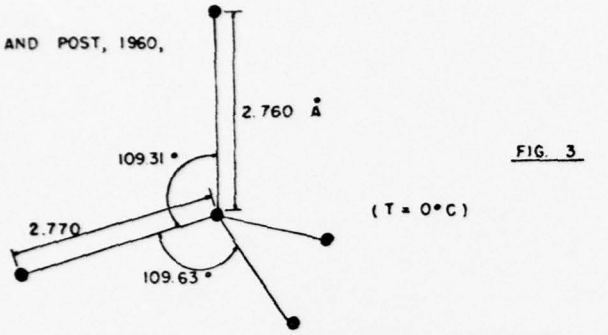
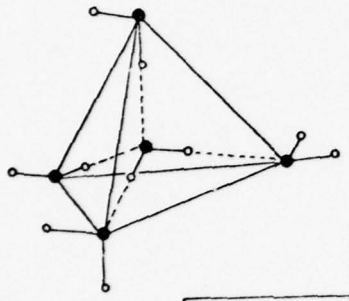


FIG. 3

POSITION OF THE OXYGEN ATOMS IN ICE I



FROM F STILLINGER, 1976)

HYDROGEN BONDED TETRAHEDRAL COORDINATION

Moments of inertia $\times 10^4$ g.cm	I_x = 5.6698 I_y = 1.8384 I_z = 3.8340
Bond length	$\bar{r}$ = 0.9575 $\times 10^{-8}$ cm
Bond angle	104.074°

EQUILIBRIUM GEOMETRICAL PARAMETERS FOR THE H_2O MOLECULE

water, which seems now to be an undisputed fact, is a direct consequence of this charge distribution.

B THE HYDROGEN BOND

The lone pair hybrids can effect a hydrogen bond with the protons of any two other water molecules. Figure 3 illustrates the resulting tetrahedral coordination found in ice I. The hydrogen bond is the result of a mostly electrostatic interaction between the molecules. However, other effects, such as delocalization (or distortion of electron clouds), repulsion due to the overlap of electron clouds, and dispersion forces due to the induced polarization caused by the instantaneous charge distribution, are also present. For more details one may consult the works by Coulson[50]. Theoretical quantum mechanical studies of the hydrogen bond have been performed, and detailed reviews of these works can be found in the articles by C.N.R. Rao[51] and P. Shuster[52].

The important geometrical parameters here are the numbers of hydrogen bonded molecules around a given single molecule, and the value of the O-O angle between two bonded molecules. These parameters are of crucial importance in the discussion of the properties of the 'mixture' and 'continuum' models.

Quantum mechanical studies of water dimers, trimers, and polymers have indicated that the energy of hydrogen bonding for a water molecule depends upon the number of hydrogen bonds in which this particular molecule is already engaged. Specifically, the energy of the H-bond in a trimer is greater than that in a

dimer. This tends to imply that hydrogen bonding in water is a cooperative phenomenon involving more than two molecules. This cooperative property is a consequence of the non-additivity of the potential energy of interaction among the molecules forming the liquid.

An additional remark should be made concerning the energy of hydrogen bonding. There is no agreed definition of this quantity, and this concept has been applied in different ways in the computations by different authors. Eisenberg and Kauzmann have listed a few possible definitions[53]. In evaluating the predictions of specific works, care should be used to choose the appropriate definition.

II THE EMPIRICAL MODELS FOR THE STRUCTURE OF WATER

The great majority of the earlier models were based on empirical evidence. The typical procedure was a physically intuitive postulation of the existence of certain types of molecular environments. Calculations of the properties of the resulting fictitious substance were carried out through statistical mechanical methods complemented by various assumptions. A varying number of undetermined parameters could be adjusted to obtain the best fit to experimental data. Although very reasonable agreements have been obtained in many cases, this procedure has been amply criticized because of the failure to provide satisfactory accounts for many properties other than the ones the various models had been specifically designed to simulate. In addition, because this approach does not have any firm theoretical foundation, it allows too great a freedom in interpreting the existing

physical evidence. In other words, it has been found that too many intuitively postulated molecular structures can be made to agree with experimental observations. Consequently, in some cases this has led to drastic oversimplifications which may have been a significant contributing factor to the origin of the heated controversy about the respective claims of the 'mixture' and 'continuum' models.

Striving for a more rigorous approach, some workers have attempted to adapt the cell and lattice theories to the problem of water structure. While this path provides a more theoretically satisfying point of view, it has not yet been shown that this approach can be physical enough to be useful. The main drawback is the postulation of a regular lattice in order to describe a fluid.

Computer simulation as applied to the study of water structure eliminates the need for the postulation of any a priori structure and, in theory, should allow for a more rigorous statistical mechanical treatment. In practice, other kinds of approximations must be made and their consequences have not yet been fully appraised.

In this section the empirical or ad-hoc models are treated first and the different aspects of the 'mixture' and 'continuum' models are discussed. The cell and lattice models are examined next, and finally the integral equations and the computer simulation methods are treated.

Many reviews of the works on water structure have appeared in the literature[54]; consequently, most of the achievements and

weaknesses of the earlier models are now fairly well documented. The purpose of this chapter is not to contribute any new argument or to expose any new development, but rather to attempt to link into one whole unit what could be found in separate chapters written by different authors emphasizing particular viewpoints. The implications of experimental data and theoretical results obtained through diverse methods are emphasized in an effort to obtain a general picture of the present state of knowledge. Completeness and detailed thoroughness are of course not claimed because of the vastness of the area under study and of the limited personal expertise of the author.

A THE MIXTURE MODELS

The most obvious characteristic property of liquid water leading to the idea of a mixture of several molecular components is the temperature behavior of its specific volume. At the simplest level, a mixture of two components differing in their density can account for the characteristic maximum in density. The denser component is usually associated with non-hydrogen bonded water molecules and the other component with hydrogen bonded molecules with tetrahedral coordination.

In a review article, Nemethy[55] has clarified the distinctions between the various types of'mixture' models. According to him, water can be considered a molecular mixture in three senses.

— Firstly, the water molecules can be assembled in different structures characterized, for example, by their modes of packing. The liquid can be considered a mixture of these structures which instantaneously occuppy different regions in

space.

— *Secondly, water molecules* can be differentiated by the number of hydrogen bonds they engage in. There can be, for example, five different species, each with no hydrogen bond, one hydrogen bond, and so on up to four hydrogen bonds.

— Thirdly, a clear classification of water molecules in terms of the number of hydrogen bonds is not necessary to have a mixture. It suffices that a continuous process of bond forming and bond breaking exists, thereby varying the environment of a given water molecule.

The various structural models may possess some or none of these characteristics. Such a classification is methodological and relates only to the concept of a mixture; it is, however, useful in clarifying the distinctions between 'mixture' and 'continuum' models. A'continuum'model is then defined as one which cannot have any of the above three characteristics.

1 The two-state models.

Conceptually, the simplest type of model in the mixture framework is the two-state model. Some of the more important work was done by Hall[56], Grojtheim and Krogh Moe[57], Davis and Litovitz[58], Marchi and Eyring[59], and Franck and Quist[60]. All of these models include the postulate that liquid water reflects the additive properties of two constituents: One with extensive hydrogen bonding and resembling very much the structure of ice, and the other with little or no hydrogen bonds and having the characteristic of a close-packed structure.

A major objection to this approach stems from the implicit assumption that each of the structures is of very large extent, as required by the thermodynamic treatment used in the description of these structures. This feature cannot be reconciled with the results of low angle X-ray scattering experiments which probe distances on the order of a few molecular diameters. These experimental results do not give any indication of long range structural inhomogeneity which must be present if two extended structures are mixed. On the other hand, even if these structures were assumed to be of small size, this would lead to a large proportion of the molecules in the vicinity of interfaces between the components. The properties of such molecules may not reflect the characteristics of the bulk of either structure. In addition, some of the two-state models postulate the existence of water molecules which are either completely hydrogen bonded (4 bonds) or completely unbonded. The absence of partially bonded molecules appears to be an unrealistic feature.

In spite of these shortcomings, satisfactory semi-quantitative calculations of macroscopic parameters based on these models have been obtained. Comparison of these results with experimental data has been done with the help of adjustable parameters. In each case these parameters have been assigned a specific physical significance (for example the energy of hydrogen bonding, or the free volume available to a single molecule, etc...). In the case of the simple two-state models, however, the true nature of these parameters may not remain the

same as that assigned by their various authors. The numerical values given to them by the constraint of fitting experimental data may be the result of some kind of averaging process.

To illustrate the procedure involved in extracting information from postulated models, a few of the more significant works are examined briefly.

Grojtheim and Krogh Moe[57] have achieved a reasonable fit to the molar volume data by postulating the following straightforward additive property

$$V = V_B + x(V_A - V_B) .$$

The subscript A indicates an ice-like structure due to complete bonding of the molecules in the liquid. B refers to a close-packed fluid structure associated with unbonded molecules. $2N_0$ bonds (N_0 is Avogadro's number) are formed in one mole of water, the molar volume is then equal to V_A. Thus, x denotes here the ratio of the number of bonds present to the possible total number. For V_A an analytical expression is derived from an extrapolation of the volume data of ice. V_B is given by an empirical equation applicable to 'normal' liquids and representing the volume behavior of water above 170 C. The parameters (3 in all) are adjusted so that agreement is obtained with data at a given temperature.

Besides the general defects of a two-state model, this particular scheme has also the drawback of advocating the presence of an extended ice structure in the liquid. Fletcher[61], however, has estimated that a cluster of 100 to 200 molecules would be

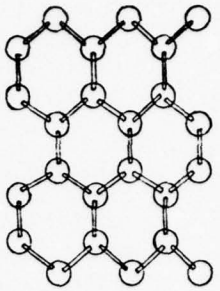
appropriate for crystal nucleation in water supercooled to -40 C, a result inconsistent with this particular model.

Davis and Litovitz[58], and Davis and Jarzynski[54] have made use of structural relaxation properties as a basis for a two-state model.

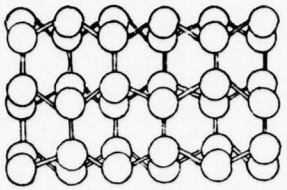
As a result of a perturbation caused in the external conditions of temperature and pressure, as for example during the passage of a sound wave, the molecules of a liquid initially at equilibrium rearrange structurally. The individual molecules shift positions from one type of structure to the other and vice versa. These processes are governed by the law of non-equilibrium thermodynamics, and the finite amount of time required to reach equilibrium again is characterized by the structural relaxation time t_r . Because of the transport of mass and energy involved, there are some relaxational contributions to the coefficients of compressibility and expansivity, as well as to the specific heat of the liquid medium. A sound wave propagating through the medium is damped, with the dissipation described by the energy absorption coefficient α. A book by Herzfeld and Litovitz[88] and volume II of "Physical Acoustics" edited by Mason[89] containing comprehensive treatises on ultrasonic relaxation in liquids may be referred to for more details.

The two structures used by Davis and Litovitz involve "puckered hexagonal rings" found in the ice structure. They are depicted in Figure 4 . An open-packed structure is formed by analogy to the ice I structure, and a close-packed structure is obtained by rotating one layer of hexagonal ring by 60

FIG. 4

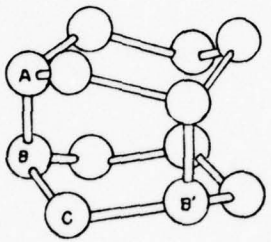


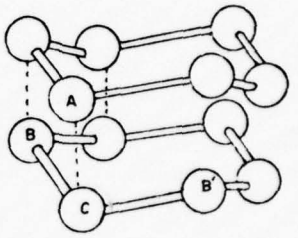
TOP VIEW



SIDE VIEW

POSITION OF O ATOMS IN ICE.
(FROM DAVIS AND LITOVITZ)[58]





OPEN STRUCTURE (FROM DAVIS AND LITOVITZ) CLOSE-PACKED STRUCTURE

degrees above the other. A nearly complete body centered cubic structure is thus obtained.

A reasonable agreement with experimental results from X-ray scattering for the radial distribution function is obtained as well as a qualitative consistency with Raman scattering results. A good fit to the data for expansivity and isothermal compressibility (from less than 1% to 5% error) is possible. The right temperature behavior for the isothermal compressibility is also obtained.

The requirement of the existence of only two types of molecules (four bonded and two bonded) is a weakness of this particular model. The fact that estimates for the specific heats are low suggests the addition of other states; the subsequent rearrangements of these additional entities would contribute to the value of the specific heat. The implied presence of long range order in the liquid is also erroneous.

Franck and Quist[60] have proposed a two-state model based on Pauling's suggestion that the concept of clathrate structures found in the cases of gas hydrates be applied to water. In this scheme, some of the water molecules are bound in a framework which contains cavities where unbonded molecules can be found. Franck and Quist chose a framework made up of 46 molecules and containing 6 spheroidal cavities and two additional smaller cavities. This choice is somewhat arbitrary, and these authors have agreed that a more realistic model would probably have to contain a variety of different framework structures

consistent with physical evidence. Nonetheless, satisfactory agreement with experimental data has been obtained in the temperature range between 0 and 30 C. Molar volume and isothermal compressibility are two properties which have been closely predicted by the model. A 30 % discrepancy in the case of the specific heat has been obtained. The excess molal entropy in the cases involving solutions of non-polar hydrates has also been predicted in a reasonable manner, but the wrong temperature dependence has been given. Franck and Quist have invoked the existence of a third state, intermediate between the framework structure and the monomers, in order to account for the discrepancies. The addition of a third state would significantly complicate the calculations.

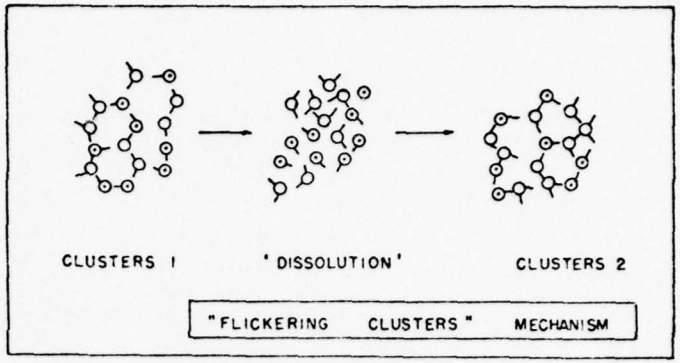
2 The cluster models.

The model proposed by Franck and Quist contains two additional characteristics: It calls for cluster formation and advocates the existence of interstitial molecules. The idea of "flickering clusters", first proposed by Franck and Wen[62], reflects the constant motion of the molecules in the liquid and the continually varying spatial configurations. The postulation of the existence of clusters has the advantage of allowing for the presence of a wide variety of molecular environments. In addition, this would eliminate the problem associated with having a large proportion of molecules situated at the surfaces between different structures present in the simple two-state models. On the other hand, some new questions arise with the assumption of clusters: The descrip-

tion of the species of water molecules cannot be done easily. Consequently, much arbitrariness remains in the description of the various properties of these species, such as their distribution as a function of binding energy.

The cooperative property of the hydrogen bond is of crucial importance in the discussion of cluster formation and dissolution. Since the presence of a hydrogen bond on a water molecule influences the probability that this molecule will form another bond, it is natural to expect that an assembly of many interconnected molecules will be formed. The breaking of a bond similarly affects the cooperative breaking of bonds in neighboring water molecules and results in the dissolution of clusters. Thus, a description of the structure of water would involve the continuous formation and dissolution of molecular clusters, as illustrated in figure 5. The rate at which these clusters form and dissolve could be estimated by considering relaxation time constants. The experimental values for relaxation times are found to be between 10^{-11} to 10^{-13} sec.

One should mention that Perram and Levine[62], on the basis of a statistical mechanical treatment, have criticized the "flickering clusters" scheme. Their interpretation of the consequences of cooperativity favors structural models of the interstitial types. This approach advocates the mixture of a regular solid-like lattice with monomers which can occuppy interstitial (empty) spaces between the regular lattice positions. The monomers are distributed over the vacant sites. It is not obvious, however, that the empty and filled interstitial spaces will disturb the long range



(FROM EISENBERG AND KAUZMANN [4])

FIG. 5

order of such a structure.

An extensive treatment of the cluster model has been given by Nemethy and Sheraga[63]. This work has been subsequently corrected and improved by Vand and Senior[64] and by Hagler et al.[54] Additional models have been proposed by Jhon et al.[87]; in these cases the significant structure theory has been used.

Nemethy and Sheraga have postulated a mixture of clusters of hydrogen bonded molecules (4 species depending upon the numbers of H bonds that they possess) and of monomers. Their work contained various errors which have been corrected at a later stage. Thus, it would more appropriate to examine the later work containing the same assumptions and points of view but which include the correction of errors of analysis and the incorporation of more experimental evidence.

Hagler, Sheraga, and Nemethy[54] have proposed an improved model involving the mixture of clusters of various sizes together with monomers. This theory takes into account the contribution to the entropy made by such a distribution of clusters by considering the various ways to arrange hydrogen bonds in a given cluster. The entropy consideration is expressed by a term containing an adjustable parameter to account for the influence of cluster size. A total partition function is written as the product of the partition functions for external and internal degrees of freedom for each distribution of clusters. The external translational term involves a parameter restricting the rotation of the molecule which is considered as a rigid rotor. For the internal modes of vibration, the frequencies used are

taken from data obtained by Walrafen with the assumption of independence from cluster size.

The maximum deviations from experimental values are claimed to be 4.3 % for the free energy, 4 % for the enthalpy, and 2.4 % for the entropy. The values calculated for the heat capacity are said to be up to 20 % higher than experimental values. The hydrogen bond energy is calculated to be between 2.54 and 2.62 kcal/mole between 0 and 60 C. The median size of the clusters is given at 11.2 molecules per cluster at 0 C and 5.6 molecules at 60 C.

The main weaknesses of the model have been pointed out by the authors and concern the sizes of the clusters and their influence on the remaining properties, such as the energy of H-bond and the frequencies of internal vibrations. A major fault of this model is still the neglect of any explicit cooperative effect. This is reflected by the single value given to the H-bond enrgy E_H . This cannot be so if the bond strength varies with the number of bonds which are present. An improved version of this model has been proposed by Lentz, Hagler, and Sheraga[54].

3 Interstitial models.

An interstitial model was proposed by Danford, Narten, and Levy[65] on the basis of results of X-ray scattering in liquid water. Samoilov had already suggested in 1946 that, as a result of the melting process, water molecules were displaced into the cavities present in the ice I structure. This seems to be supported by the fact that there is a peak in the radial distri-

bution function at the approximate distance where a void should be located in the ice I structure.

In the model of Narten et al. the interstitial sites of the ice I lattice are occupied by monomers. This lattice is also allowed to expand isotropically with rising temperature. A large numbers of parameters (7) is employed in the fit to the data for the radial distribution function and the molar volume. Comparison between calculated thermodynamic parameters and experimental data suggests that this model is too "solid-like" to account fully for the properties of a liquid.

Many other empirical models which could be included in the mixture class exist in the literature. The ones mentioned above, however, illustrate the various approaches and types of specific structures used. Next, we shall consider the 'continuum' approach.

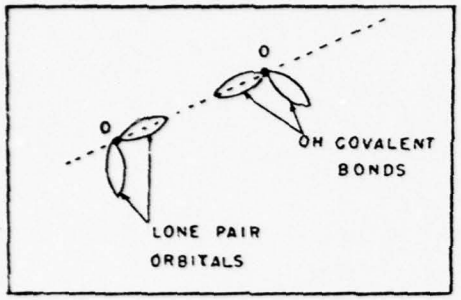
B THE CONTINUUM APPROACH

A continuum model for liquid water could perhaps be considered as the limiting case of the mixture model in the event that the number of the different molecular species becomes infinite. Under these conditions, the environment of the molecules cannot be subdivided into a discrete number of different types. In particular, the energy of hydrogen bonding does not take a number of discrete values corresponding to the discrete number of broken and intact bonds . Instead, this energy varies continuously, reflecting the continuous distributions of bond lengths and bond angles. Thus, at room temperature and under atmospheric

pressure, liquid water is viewed as a completely hydrogen bonded molecular aggregate. The environment of the individual molecules is characterized by continuously distributed values for the bond lengths and bond angles. No criterion exists which could qualify a hydrogen bond as being broken.

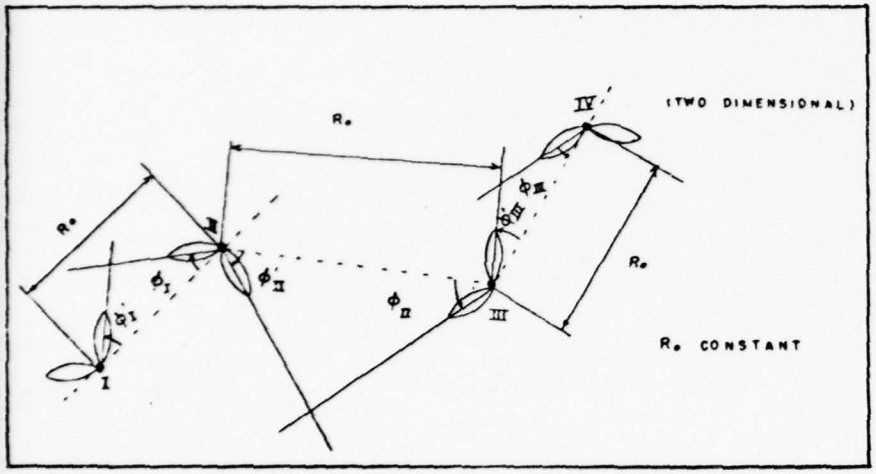
The major work expounding a continuum model was proposed by Pople.[66] This model attempts to explain the characteristic properties of liquid water by considering the effects of the distortion of the individual hydrogen bonds. A completely bonded molecular aggregate is postulated as representative of the liquid structure. To account for the breakdown of long range order upon fusion, the four hydrogen bonds around each molecule are considered to bend independently. This model contains the assumption that the distance to the nearest neighbor from any molecule remains fixed. Thus, due to hydrogen bond bending, the number of second and higher order neighbors changes with the external conditions of temperature and pressure. A hydrogen bond is considered undistorted when the directions of the lone pair orbitals of one molecule and one of the O-H bonds of another molecule are colinear and coincide with the line joining the O atoms. Figure 6a illustrates this configuration while figure 6b describes the distorted bonds geometry. The angles ϕ and ϕ' describe the deviation due to bending from the O-O line for the lone pair orbital and the O-H bond, respectively.

Rigorously, the energy of a bent bond depends not only on the ϕ and ϕ' angles, but also on the azimuthal angular deviations and on the relative orientation of the remaining parts



TWO FULLY HYDROGEN BONDED MOLECULES
(UNDISTORTED BONDS)

FIG 6a



DISTORTED HYDROGEN BONDS BETWEEN A CENTRAL MOLECULE AND THREE NEAREST NEIGHBORS

FIG 6b

of the molecules. In order to simplify the analysis, Pople has assumed that the energy of the H-bond is symmetrical in the azimuthal direction and is additive with respect to the angles ϕ and ϕ'. The possibility of bond stretching is also neglected, leading to the constant O-O distance denoted by R_o. Consequently, the azimuthal variations average out and the expression for the bond energy can be written as

$$E = F(\phi') + F(\phi) \quad .$$

An explicit form of the function $F(\beta)$ is taken as

$$F(\phi) = F_o - g\cos\phi \quad .$$

The constant g is called the hydrogen bond bending constant and it is given by

$$g = (d^2F/d\beta^2)_{\phi=0} \quad .$$

Using classical statistics as a first approximation, Pople has calculated the average bond-bending angle. This was found to be equal to 26 and 30 degrees at 0 and 100 C respectively.

1 The Radial Distribution Function.

The RDF has been calculated using the formalism of this model. With the help of four adjustable constants, a reasonable agreement is obtained with the data of Morgan and Warren[67] for the distribution of the oxygen atoms. An important feature of the model is that it allows the collapsing(towards the central molecule)of molecules belonging to the second and third coordination shells. This is consistent with the value of 4.4 for the coordination number of the first shell, and with the higher density in the 3.5 Å region when compared with the density of ice.

2 The Variations of the Density upon Fusion.

A semi-quantitative treatment has provided an explanation for the density increase at the melting point of ice. This anomalous phenomenon is attributed to the collapse of the structure in the second and third coordination shells. An estimate for the density increase due to the displacement of molecules in the second and third shell toward the center molecule was found to be 0.29 g/cm^3 . This compares favorably with the figure of 0.22 g/cm^3 obtained by substracting from the true density of water at 0 C (0.9999 g/cm^3) the density that would be found had the liquid retained an ice structure (0.78 g/cm^3). The average hydrogen bond length was taken to be 2.90 $\mathring{A}$ from the data of Morgan and Warren.

3 The Static Dielectric Constant.

The temperature dependence of the dielectric constant has been successfully predicted by this model in the region between 0 and 83 C. The absolute magnitude, however, has been found to be too low by about 20 %. This was believed to have been caused by the neglect of contributions to the electrostatic field by molecules beyond the nearest four neighbors. An improved agreement is obtained when molecules beyond the nearest four are considered.

4 Thermal Energy.

Eisenberg and Kauzmann[68] have shown that the distorted hydrogen bond model of Pople could also provide an explanation for the value of the thermal energy of liquid water. They have determined the vibrational and configurational contributions to

the internal energy by assuming a distorted bonded structure. A relation between the shift of the frequency of the maximum of the uncoupled O-H stretching band and the energy of hydrogen bonding was adopted. More distorted bonds were taken as causing higher frequencies. The configurational energy calculated with the help of this relation was found to correspond very closely to the experimental values. Hence, a continuum model has been shown to be consistent with the known experimental thermal properties of liquid water.

Another model based on distorted hydrogen bonds has been proposed by Bernal[69]. In this case, the four coordinated molecules were given hydrogen bonds which could be considerably distorted. The molecules were supposed to be linked in an irregular network of rings. Bernal has reported a general agreement between calculations based on such a random network model and measured radial distribution functions.

This concludes the treatment of the empirical models for liquid water. Lattice and cell models are considered next.

III THE STATISTICAL THEORIES OF WATER

Some of the methods used in the study of simple monatomic liquids have been extended to treat the additional problems encountered in the case of water. Such an enterprise has been partly motivated by the desire to establish the theory of this liquid on firmer theoretical foundations since much arbitrariness has been thought to exist in the various schemes employing empirical methods.

Two possible approaches can be taken: The first one starts from the study of molecular interactions to search for an explanation of the macroscopic properties of the liquid from the characteristics of the forces acting between the individual molecules. This approach leads to the method of integral equations whose solutions are closely related to the diverse molecular distribution functions. The thermodynamic parameters can then be derived from these distribution functions in a straightforward manner. The second method deals with the description of an approximate structure of the liquid from which the various macroscopic parameters are derived by statistical mechanical methods. The origins of such a structure in terms of the molecular forces are not investigated until the structural problem has been solved.

The various structures used as starting points are always very similar to those found in the solid state(crystalline or amorphous). The method of lattice statistics, which has been found very successful in the theory of solids, is used together with various approximations and a small number of adjustable parameters.

A survey of a few lattice models found in the literature is now presented. The method of the distribution functions will be treated in the following section.

A THE LATTICE THEORY OF LIQUID WATER

1) GENERALITIES.

Because of the small change in volume upon fusion and the small value of the latent heat of fusion compared to the heat of sublimation, many of the structural characteristics of the solid state are thought to persist in the liquid phase. One such characteristic property is the presence of a regular lattice network on which the molecules are distributed. To satisfy the requirement of long range disorder found in the fluid phase, some irregularity is introduced in the forms of vacancies existing at lattice sites, of interstitial molecules between lattice positions, and of a disordered distribution of hydrogen bonds between the molecules.

By analogy with the solid state, the molecules of the liquid are viewed as occupying positions within a 'free volume' (or cell) centered at each lattice or interstitial position. The molecules are thus confined for a period long compared to the vibrational period, but migrate to other positions after a time of the order of 10^{-11} sec. Experimental data are in support of this view since the measured molecular diffusion time constants are up to two orders of magnitude larger than the vibrational periods.

A monograph on the lattice theories of the liquid state

by J.A. Barker[70] covers the main assumptions, achievements, and shortcomings of such theories; it may be referred to for more details on the subject.

2) THE MODEL OF GIBBS AND FLEMING

A first treatment introduced by Fleming and Gibbs[71] is based on the structure of gels. The liquid in this case is viewed as a three dimensional network resulting from random polymerization through hydrogen bonds. This structure allows for the existence of molecules with four, three, two, and one hydrogen bonds which are constantly forming and breaking in a cooperative manner. Unfortunately, due to the lack of adequate mathematical tools, this model has only been discussed qualitatively. Its merits and weaknesses cannot be evaluated on any comparative basis.

Fleming and Gibbs[72] have also extended the methods of the lattice gas to the problem of the structure of water. As usual in these cases, the full configurational space is divided into a finite but large number of "cells". Each cell describes the position of a molecule in the three dimensional space and its orientation in the total $8\pi^2$ orientational space. The latter property is given by a set of parameters associated with each lattice position. The orientational parameter in the i^{th} cell is denoted by α_i and it can have discrete values corresponding to the m regions in orientational space available to the molecule: $\alpha_i = 0,1,2,\ldots,m$. Usually $\alpha_i = 0$ indicates an empty cell. Thus, the instantaneous configurations of N molecules can be given by a set of parameters (α_i) , i= 1,2,3,....M. M is the total number of cells making up the whole system, and one must have M>N.

There are $\frac{M!\ m^N}{N!\ (M-N)!}$ distinct sets (α_i) that can be distinguishable.

The partition function is then evaluated by summing over all the possible sets after having made some suitable assumptions concerning the molecular potential of interaction.

In the model of Fleming and Gibbs, the body centered cubic structure (BCC) has been chosen to provide the regular array over which the water molecules are distributed. This BCC lattice can be decomposed into two interpenetrating cubic lattices (the structure of ice I_c is cubic, while that of ice I is hexagonal). In each cell, a water molecule is allowed to have any one of 12 distinct orientations (α_i= 1,2,...,12 for a given i), each one of which has the molecule pointing its O-H direction or lone pair electrons direction towards the vertices of one of the tetrahedral cubic sub-lattices. Figure 7 describes such a structure. It is also assumed that each lattice site cannot be occupied by more than one molecule.

In order to evaluate the partition function, several additional assumptions are made. Only pair interaction between molecules which are nearest neighbors is considered. In this case, the magnitude of this pair interaction potential is only allowed three distinct values depending upon the mutual orientation of the neighboring molecules. The interaction potential is then given by

$$V_{\alpha\alpha'} = \begin{cases} -E_B & \text{if } \alpha \text{ and } \alpha' \text{ correspond to orientations leading to hydrogen bonding,} \\ -e_1 & \text{if rotation of one of the molecules is sufficient to allow hydrogen bonding,} \end{cases}$$

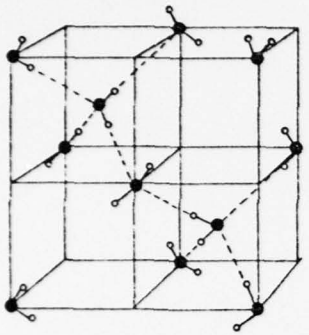


FIG. 7

BODY CENTERED CUBIC LATTICE USED BY FLEMING AND GIBBS

$-e_2$ if rotation of both molecules is needed to allow hydrogen bonding.

The numerical values of E_B, e_1, e_2 are kept adjustable in order to coincide with numerical values determined experimentally.

The Grand Partition function is written

$$\Xi = \sum' \exp\left[-\beta \sum_{R_1,\alpha_1}\left[U^{int} - \mu - \frac{1}{\beta}\ln(v_c/\Lambda^3)\right] n_{\alpha_1}(\underline{R}_1)\right]$$
$$\exp\left[-\tfrac{1}{2}\beta \sum_{\underline{R}_1,\underline{R}_2,\alpha_1,\alpha_2} V_{\alpha_1\alpha_2}(\underline{R}_1-\underline{R}_2) n_{\alpha_1}(\underline{R}_1) n_{\alpha_2}(\underline{R}_2)\right],$$

where U^{int} is an internal kinetic energy (vibrational or rotational motions), $n_\alpha(\underline{R})$ is the number of molecules at the lattice site situated at $\underline{R}$ and with orientation α (one must have $n_\alpha = 0$ or 1, and $\sum_\alpha n_\alpha \leq 1$), μ is the chemical potential, $V_{\alpha_1\alpha_2}(\underline{R}_1-\underline{R}_2)$ is the pair interaction energy, $\Lambda = \frac{\beta h^2}{(2m\pi)^{1/2}}$ is the thermal 'wavelength' arising from the contribution of the translational kinetic energy. The symbol Σ' denotes the sum over all the allowed states of the system.

Calculations of the thermodynamic parameters are made to two orders of approximation. The first order is the Mean Field Approximation (MFA) which simplifies considerably the problem by replacing the potential acting on a molecule by the average potential due to the presence of its neighbors. In this case

$$\sum_{\substack{\underline{R}_1,\underline{R}_2 \\ \alpha_1,\alpha_2}} V_{\alpha_1\alpha_2}(\underline{R}_1-\underline{R}_2) \longrightarrow \sum_{\alpha',\underline{R}'} V_{\alpha\alpha'}(\underline{R}-\underline{R}')\langle n_{\alpha'}(\underline{R}')\rangle = \frac{1}{12}\sum_{\alpha',\underline{R}'} V_{\alpha\alpha'}(\underline{R}-\underline{R}')n,$$

where $n = \frac{\langle M\rangle_0}{M}$, which is the average density of particles per lattice site in the case of no potential energy of interaction (V=0). The MFA yields

$$kT_c = \tfrac{1}{4}(E_B + 5e_1 + e_2)$$
$$n_c = \tfrac{1}{2}$$

at the critical point. The values of the energy parameters are

adjusted in order to reproduce the experimental critical temperature. The result gives

$$E_B = 4.65 \text{ kcal/mole}$$

$$e_1 = e_2 = 7.2 \cdot 10^{-2} \text{ kcal/mole} .$$

Using experimental values for the nearest neighbor separation, Fleming and Gibbs have derived the following critical parameters

$$\rho_c = 0.699 \text{ g/cm}^3$$

$$P_c = 783 \text{ atmospheres} .$$

There is a sizeable discrepancy with respect to the experimental figures

$$\rho_c = 0.325 \text{ g/cm}^3$$

$$P_c = 218 \text{ atmospheres} .$$

An equation of state has also been derived from the Grand Partition function, but in view of the total neglect of any angular correlation effect in the MFA, no comparison has been made with experimental results. The second and third virial coefficients have also been calculated with good result for the former and unsatisfactory result for the latter. This is not surprising in view of the fact that the third virial coefficient reflects three body and higher interactions.

The next step, the Second Order Approximation (SOA) has yielded better results. The calculations involved in the SOA are significantly more involved than in the MFA; one is invited to refer to the original article for the details.

A significant achievement of this treatment is the prediction of a density maximum under both atmospheric pressure and saturation conditions. Under atmospheric pressure, the temperature of the maximum density is located below 0 C. Subsequent

calculations have located it at about -50 C .

The critical parameters are determined to be

$T_c = 739$ C ,

$\rho_c = 0.353 \text{ g/cm}^3$,

$P_c = 478$ atmospheres.

They are still in substantial disagreement with experimental values.

The internal energy, the Gibbs free energy, and the isothermal compressibility are also calculated. The agreement with experimental values for the free energy is reasonable, but the computed isothermal compressibility fails to display a minimum in its temperature variations.

A significant advantage of this model is pointed out by Fleming and Gibbs: it is its ability to treat the liquid-gas phase transition. No solid-liquid transition is predicted, however.

3) THE MODEL OF BELL

Bell and Lavis[73] have treated the problem of a simple two-dimentional model of the interstitial type. Under constant pressure, density maxima have been predicted in the liquid and supercritical states for some appropriate values of the ratio e/w. Here -e is the interaction energy between two non-hydrogen bonded first neighbors, and -(e+w) is the energy betwwen two bonded first neighbors on a triangular two-dimensional lattice. The first order or quasi-chemical approximation is used by considering the system as an assembly of basic groups of lattice sites. In this case such a basic group is formed by a triangular configuration.

Three dimensional models have been subsequently proposed by Bell[74] and Bell and Salouta[75]. The latter article describes a model which has the advantage of being capable of providing an exact solution, thus rendering possible the comparison of results from various approximation schemes and the appraisal of their quality.

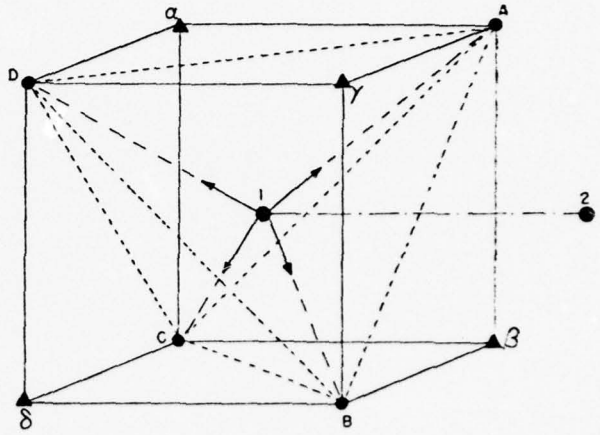
In the first model Bell has made use of a BCC lattice similar to Fleming and Gibbs'. In addition, a non-additive interaction is introduced between molecules on three simultaneously occupied sites at the vertices of a right isosceles triangle. The energy of such a three-body interaction is given by

$$V^{(3)} = \frac{1}{3}u \quad .$$

As in the two dimensional model, two bonded nearest neighbors have an interaction energy -(e+w), while two unbonded nearest neighbors interact with energy -e. u is an energy parameter to be adjusted in combination with w.

In this case the basic group of sites is a tetrahedron with four sites at its vertices. This is depicted in figure 8. These vertices are ABCD. The two interpenetrating tetrahedrally coordinated diamond lattices making up the BCC lattice are formed by the sites ABCD and αβγδ in figure 8. A perfect solid lattice would be formed if all the molecules were located on either one of the tetrahedral sub-lattices. The absence of long range order in the liquid, however, implies that the molecules should be distributed over the lattice sites belonging to both tetrahedral arrays. Under these circumstances, regions with primarily occupation of one sub-lattice would display a short range order. This order

FIG 8



TETRAHEDRAL GROUPING OF SITES IN BELL'S MODEL

is disturbed by vacancies on the first sub-lattice and the occupation of sites on the second sub-lattice. The molecules belonging to one sub-lattice are hydrogen bonded but are not bonded to molecules belonging to the second sub-lattice. Bell also assumes that the volume per lattice site v_o remains constant. He also does not allow for any hydrogen bond distortion.

The method of Guggenheim and McGlashan is used to derive the Helmholtz free energy. This method provides an approximate relation between the number of configurations on the lattice, denoted by g, and the probability of occurrence of a configuration i taken by the basic group of molecules, denoted by P_i. This relation is given by

$$\ln g = \ln g_o(\varrho) - M \sum_i w_i P_i \ln P_i .$$

There are 10 possible distinct configurations for the tetrahedral group (i = 1,2,...,10). In this equation w_i is the statistical weight of the configuration i, M is the number of lattice points, $\varrho = N/M$ is the number of molecules per lattice site, and $g_o(\varrho)$ is the value of g that would be correct in the case of a random distribution on the lattice structure (i.e. at $T = \infty$).

The configuration Helmholtz free energy is given by

$$F_{conf} = E_{conf} - kT \ln g = N f_{conf}(\varrho, P_i),$$

and

$$f_{conf} = \sum_i e_i w_i P_i + kT \sum_i w_i P_i \ln P_i - 3kT \varrho \ln\left(\frac{\varrho}{12}\right) + (1-\varrho)\ln(1-\varrho).$$

The equilibrium state at constant T,V, and N is obtained through the minimization of f_{conf} with respect to P_i.

Calculations for the number density $\varrho = N/M$ as a function

of the reduced temperature kT/w (w is the energy of hydrogen bond) at given values of the reduced pressure PV/w have been performed. The reduced isothermal compressibility, coordination number, and reduced chemical potential have also been determined. These calculations have been done with several values of the energy parameters e/w and u/w. In the range for which $2u/w = \frac{1}{2} + e/w$, a density maximum and a compressibility minimum have been predicted in the temperature variations of these parameters. The best fit to experimental data is also obtained for this constraint of the energy parameters. The agreement with experimental data for the properties computed is good. The disappearance of the density maximum at pressure higher than a value P_o (larger than the critical pressure) is also predicted. The coordination number under low pressure in the liquid phase is found to lie between 4 and 5 in the temperature range between the density maximum and the boiling point. No evidence for a solid-liquid phase transition has been obtained.

In a more recent paper, Bell and Sallouta have modified the basic structural model in order to obtain an exact solution. This was done by placing the interstitial sites between the primary lattice sites along the bonds between the molecules. If an interstitial site is unoccupied, the two neighboring molecules are considered to be hydrogen bonded and their interaction energy is -w. In the opposite case, they are unbonded and their interaction energy becomes -e.

Exact computations have been performed with this model together with zeroth and first order approximations in the framework

of the Ising model. Two-dimensional lattice structures given by a honeycomb framework and a plane square lattice have been treated and exact solution have been obtained. The three dimensional diamond lattice has also been treated and solved exactly. The exact results have been compared to both the zeroth and first order approximations. It has been found that for appropriate values of the ratio of the energy parameters e and w, density maxima and compressibility minima can be obtained together with a qualitative agreement with the experimental vapour-liquid phase diagram. In all the cases, the first order treatment, which is equivalent to the Guggenheim-McGlashan scheme mentioned in the preceding section, has been found to give results in good agreement with the outcome of exact calculations.

4) THE MODEL OF WERES AND RICE

Another approach to the problem of water structure is provided by the cell model of Weres and Rice[76]. In this case the structure of the liquid is believed to be governed by a finite number of basic structural entities which are determined by the different distributions of molecules over a cell composed of 15 lattice points located at the sites of a BCC structure. These distributions are constrained by the geometrical restrictions imposed by the strength and directional characteristics of the hydrogen bonds. Both completely and incompletely bonded molecules are allowed in this model. The probabilities of occurrence of the various basic cell configurations are the determining factors of the structure of the whole system.

An effective pair potential of interaction developed by

Ben-Naim and Stillinger[77] (the BNS potential) is used in the calculations of the various cell partition functions. This pair potential includes two factors: an isotropic interaction represented by the usual Lennard-Jones 6-12 potential, and an angularly dependent electrostatic interaction. This BNS potential is written

$$V(\underline{x}_1,\underline{x}_2) = V_{LJ}(R_{12}) + S(R_{12})V_{elec}(\underline{x}_1,\underline{x}_2),$$

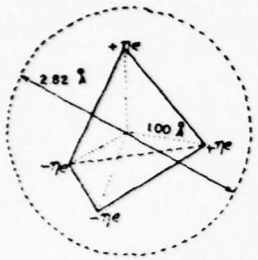
where $V_{LJ}(R_{12})$ is the Lennard-Jones potential, V_{elec} is the electrostatic potential, and $S(R_{12})$ is the switching function designed to avoid any divergence as two molecules approach each other. Figure 9 describes the potential and the configuration of the static charges (Bjerrum model) at the origin of the electrostatic interaction. The higher neighbor interactions are neglected, but a correction factor is introduced in the form of a 'communal entropy' based on the vibrational contribution and determined by quantum mechanical methods.

The evaluation of the partition function involves the determination of the contributions from the statistics arising from the association of the molecules to form the macroscopic system, as well as the calculation of the partition function for the individual basic cells.

The number of possible configurations of the basic cells Ω necessary to build the entire system is given by the method of lattice statistics

$$\Omega = \frac{(N/\rho)!}{N_1[N(1/-1)]!} \times \frac{(4N\rho)!}{(NP_h)![N(4\rho-P_h)]!} \times \frac{N!}{(NP_2)!(NP_3)!(NP_4)!} \times$$

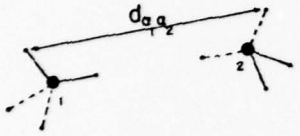
$$\left[12(P_h/4)^2\right]^{NP_2} \left[8(P_h/4)^3\right]^{NP_3} \left[2(P_h/4)^4\right]^{NP_4} \left(\frac{1-\rho}{1-P_h/4}\right)^{N(4-2P_h)}$$



$$U(1,2) = V_{LJ}(R_{12}) - S(R_{12})\,V_{HB}(1,2)$$

$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

$$V_{HB}(1,2) = (\eta e)^2 \sum_{\substack{a_1=1 \\ a_2}}^{4} \left[\frac{(-1)^{a_1+a_2}}{d_{a_1 a_2}(1,2)}\right]$$



$$S(R_{12}) : \text{SWITCHING FUNCTION} : \begin{cases} 0 & \text{FOR } 0 \le R_{12} \le R_1 \\ \dfrac{(R_{12}-R_1)^2(3R_2-R_1-2R_{12})}{(R_2-R_1)^3} & \text{FOR } R_1 \le R_{12} \le R_2 \\ 1 & \text{FOR } R_2 \le R_{12} \le \infty \end{cases}$$

BNS EMPIRICAL POTENTIAL FOR WATER

FIG 9

where: N: the total number of molecules,

NP_h: the total number of hydrogen bonds,

ϱ: the fraction of occupied states,

P_i: the fraction of molecules with i hydrogen bonded neighbors (i=2,3,4).

The evaluation of the basic cell partition function involves various approximations and methods. One is invited to refer to the original paper for the details of the treatment. The main assumptions and arguments are summarized below.

The interactions between a molecule and its neighbors further than the nearest ones are treated in the dielectric continuum approximation: The molecules situated outside a 4 Å sphere centered on the molecule of interest are replaced by a dielectric medium.

As a first approximation, the translational and rotational degrees of freedom of the molecules in the cell are treated as independent harmonic oscillators. Their driving potential is approximated by a quadratic function in the deviation from the equilibrium positions (i.e. the lattice positions in the configuration of ideal hydrogen bonding). The magnitude of the vibrational frequencies, however, are such that a quantum mechanical treatment is deemed necessary. Because the dimensions of the cell are allowed to vary linearly with temperature in order to account for thermal expansion, the harmonic oscillators' frequencies are calculated separately at each different temperature.

Some difficulty arises due to the fact that the BNS potential has been derived on exclusively classical considerations. An ad-hoc modification of it is introduced to achieve a better fit

between the experimental and calculated values for the average and maximum vibrational frequencies.

The relations between the thermodynamic parameters and the set of parameters P_i are derived, and the minimization of the free energy provides the equilibrium distribution.

The temperature variations of the principal thermodynamic and structural properties are evaluated between 0 and 100 C. The computed variations of the Gibbs free energy, the enthalpy, and the entropy are in good agreement with the experimentally determined values. The error in each case is estimated to be within 10%. A larger error (25 %) is found in the case of the heat capacity. The number of hydrogen bonds per molecule is determined to be 1.35 and remains nearly constant between 0 and 100 C. The mean number of nearest neighbors is nearly constant at 4.7 and is very close to the experimental value of 4.5. The figures for the density are reasonably close to reality except towards low temperatures where no maximum can be detected.

Weres and Rice have estimated that the largest error is due to the neglect of the correlation in the motion of neighboring molecules. A few possible modifications of this model in order to improve its predictions have been proposed by Stillinger[86], one may refer to his article for their enumeration.

5) THE MODEL OF O'REILLY

A model possessing the ability to provide a reasonable treatment of the dynamical properties of liquid water has been proposed by O'Reilly.[78] This work proceeds at several levels of approxi-

mation. On the lowest order of accuracy, liquid water is regarded as a quasi-hard sphere fluid. An expression for the work required for the creation of a 'vacancy' in the liquid is derived from the scaled particle theory of Reiss et al.[87]. This is given by

$$W(\underline{r}) = \frac{4}{3}\pi \underline{r}^3 P + K_o + 4\pi \underline{r}^2 \sigma (1 - \frac{2\delta}{r}) ,$$

for a cavity of radius $\underline{r}$ and volume V_m at a temperature T and a pressure P, and where

$$K_o = kT\left[-\ln(1-y) + 4.5(\frac{y}{1-y})^2\right] - \frac{\pi P \sigma^3}{6} ,$$

$$4\pi r^2 \sigma_o = kT(\frac{r}{\sigma})^2\left[\frac{12y}{1-y} + 18(\frac{y}{1-y})^2\right] - 2\pi P \sigma \underline{r}^2 ,$$

$$y = \frac{n\sigma^3\rho}{6} \qquad (\ \sigma = 2.82\ \text{Å}\ ,\ \text{collision diameter of } H_2O\ ) ,$$

and

$$\frac{2\delta}{\underline{r}} = \frac{\sigma}{2r}\left[\frac{6y/(1-y) + 18\left[y/(1-y)^2\right] - (\pi P\sigma^3/kT)}{6y/(1-y) + 9\left[y/(1-y)\right]^2 - (\pi P\sigma^3/kT)}\right] .$$

The probability that a vacancy exists at a molecular site is given by

$$P_v = \exp(\ W/kT\ ) .$$

To the next order of approximation, the short range order of the liquid is regarded as being derived from the structure of the FCC (face-centered-cubic) lattice found in ice VII. The density is computed by

$$\rho = \rho_s(\ 1 - \exp\ (W/kT)) ,$$

where ρ_s is the density of ice VII at one atmosphere. The experimental temperature dependence of the density is fitted to within 0.1% between -20 and 250 C.

The isothermal compressibility is computed in a self-consistent manner by using the expression for the density and W.

A minimum in the compressibility-temperature curve is determined at 35 C.

In the third order of approximation, the liquid is attributed the structure of ice Ic. Two such ice Ic lattices can be fitted into the lattice structure of ice VII. Thus in this level of approximation, the water molecules are viewed as occupying an ice Ic sublattice and 30% of the remaining sites (on the other ice Ic sublattice). These latter sites are considered to be the interstitial sites.

There exist now two probabilities for a vacancy: P_o is the probability for vacancy of an ordinary site, and P_1 is the probability for vacancy of an interstitial site. They are related by

$$P_v = \frac{P_o + P_1}{2} \quad .$$

An equilibrium constant is then defined as $K = \frac{1-P_o}{1-P_1}$.

A mean energy barrier height for molecular rotation is derived in terms of K, P_v, and two energy parameters e_o and e_1. This is given by

$$\delta E = \left[(e_o - e_1) + \left(\frac{1-K}{1+K}\right)^2 (e_o + e_1)\right] (1-P_v) \ .$$

The rotational correlation time T_2 is defined as

$$T_2 = \int_0^\infty \langle Y_2^o(\theta(t)) Y_2^o(\theta(0)) \rangle \, dt \ ,$$

where $Y_2^o(\theta) = \frac{1}{2}\left(\frac{5}{4\pi}\right)^{\frac{1}{2}} (\cos\theta - 1)$,

and where θ is the angle between a fixed direction in space and a fixed direction in the water molecule. T_2 can be calculated under the assumption that the water molecule is a spherical top by

$$T_2 = \frac{\langle\theta^2\rangle^{\frac{1}{2}}}{4(1-\lambda_2)} \left(\frac{\pi I}{2kT}\right)^{\frac{1}{2}} \frac{kT}{\delta E} \cdot \exp(\delta E/kT) \ ,$$

where $I = 1.92 \times 10^{-40}$ g.cm^2 is the mean moment of inertia , and $\lambda_2 = \exp(-\langle\theta^2\rangle)$.

The viscosity η can be calculated through

$$T_2 = \frac{V_m \eta}{kT} \left(\frac{2^{\frac{1}{2}}}{1-\lambda^2}\right) \exp(-W/kT) \ .$$

The deuteron spin-lattice relaxation time can be derived by using

$$\frac{1}{T_1} = \frac{3}{8}\left(\frac{e^2qQ}{h/2\pi}\right)^2 \tau_2 \quad , \quad \left(\frac{e^2qQ}{h/2\pi} = 213 \text{ Hz}\right).$$

The coeficient of self diffusion is derivable from the viscosity by

$$D = \frac{kT}{4\pi a \eta} \ , \text{ where } a = \sigma/2 = 1.41 \text{ Å} \ .$$

The computed temperature dependence of T_1, η ,and D are in good agreement with experimental data. The pressure dependence of T_1 and D can also be derived from the model, and they agree with the experimental evidence. The oxygen-oxygen pair correlation function was also determined ($g_{oo}(R)$) under conditions analogous to those used in Molecular Dynamics computer simulations. A good agreement was then obtained with the results of Rahman and Stillinger[79] at atmospheric pressure and under 22 kBars. Only two adjustable parameters were used in the fit.

6) THE "BOND LATTICE" MODEL OF ANGELL

A relatively simple, yet successful structural model for liquid water was introduced by C. A. Angell in 1970.[80] The initial assumption of the model is that the liquid will settle into a "tightly connected random tetrahedral network structure" if it

could be cooled down without the onset of crystallization. A random quasi-lattice structure is thus defined for the liquid.

A second lattice is defined with respect to this point lattice and is called the "bond lattice". Each site on this lattice is situated between the sites of the point lattice, i.e. on the lines of the hydrogen bonds connecting the molecules. The ground state of such a bond is postulated as being when the bond is "on". The breaking of the bond corresponds to an elementary "excitation".

Because of the strains due to the totally connected network, in the event of the breaking of a bond, the molecules reorient themselves cooperatively, seeking a less strained configuration.

The methods of lattice statistics allow the calculation of the equilibrium distribution of broken bonds over such a random network. The result is given by

$$n_x = 2N\,(1+\exp(e/kT))^{-1} = \frac{2N}{1+\exp(e/kT)}\ ,$$

where n_x is the number of broken bonds, N the number of H_2O molecules, and e is the energy associated with the breaking of a bond.

This expression has been evaluated under the assumption that the interaction between the lattice elements can be neglected, i.e. a broken bond has no effect on the neighboring bonds. This treatment also assumes that a hydrogen bond can be classified as on or off in a discrete manner.

The configurational heat capacity is given by

$$C_v = Nk\,(e/kT)^2 N_x(1-N_x) \quad \text{where } N_x = \frac{n_x}{2N}\ .$$

Because there is a change in the vibrational frequency distribution upon breaking a bond, the excitation must be changed to $e - Ts_x$, where s_x is the net increase in lattice entropy upon excitation.

The configurational heat capacity per mole then becomes:

$$C_v = 2R\,(dE/RT).N_x(1-N_x),$$

where $N(e-Ts_x) = dE+PdV-TdS$.

The parameters dE and dS are fixed by calculating the configurational heat capacity of water obtained by using the vibrational contribution in ice. One finds dE = 1.9 kcal/mole of bonds, and TdS = 4.8 cal/ mole. They agree with values provided by Eisenberg and Kauzmann to within 5% at all the temperatures considered (250 K to 400 K).

A maximum in the density is also obtained on the basis of the calculated negative values of the expansivity at 0 C.

By way of the Vogel-Tamman-Fulcher fit of the viscosity data and a postulated probability of molecular rearrangements due to fluctuations in N_x, Angell has obtained a very good fit of the temperature dependence of the viscosity. The values calculated for the relaxation time in water also compare well with the experimental values for dielectric relaxation time. The pressure dependence of the viscosity is also in qualitative agreement with experimental evidence.

An improvement of this first order approximation is suggested by Angell and could include the effect of the cooperative behavior of the water molecules. Such a scheme is analogous to the *Ising problem with interacting neighboring particles.*

From the results of the lattice and cell models it can be concluded that, although the basic postulation of a solid-like lattice structure seems to be an extremely rough approximation when one is concerned with a fluid, it has been possible to simulate the principal anomalous phenomena exhibited by liquid water. Such an outcome confirms our qualitative view of these phenomena even though it reveals that the methods employed are incomplete, or worse, inadequate. The main problem remains that of the statistical mechanical treatment of cooperative phenomena as applied to the interactions between the water molecules. A cleverly designed intermolecular potential may eventually provide an approximate treatment, although it is doubtful whether a pair potential, even with quantum effects accounted for, could achieve this task.

B The method of Integral equations.

1) Generalities

A rigorous statistical treatment of the structure of a macroscopic system would require the exact evaluation of the quantum mechanical partition function

$$Q_{qm} = \sum_i e^{-\beta E_i} \quad .$$

This sum is over all the possible states of the system with the appropriate energy levels E_i . However, almost invariably the difficulties involved in the computation of Q_{qm} are insurmountable. A first approximation is often taken in the physics of liquids leading to the replacement of Q_{qm} by the classical partition function Q_{cl}

$$Q_{cl} = \frac{1}{h^{3N} N!} \int \ldots \int d\underline{p}^N \, d\underline{R}^N \, e^{-\beta H} \quad ,$$

defined for a system of N spherical particles with the hamiltonian represented by H. $\underline{P}$ and $\underline{R}$ are the momentum and position coordinates. One has for the hamiltoman

$$H(\underline{P}^N, \underline{R}^N) = \sum_{i=1}^{N} \frac{P_i^2}{2m} + U_N (\underline{R}^N) \quad ,$$

where $U_N (\underline{R}^N)$ is the total potential energy of the configuration $\underline{R}^N$. For a system of non-spherical particles, one must add the angular coordinates to $\underline{R}^N$; thus : $\underline{X}^N$: $(\underline{R}^N, \underline{\theta}^N)$. $\underline{\theta}^N$ could be represented by the set of Euler angles . After integration over the momenta and after assuming that the internal degrees of freedom are independent of a specific configuration, one obtains

$$Q_{cl} = \frac{q^N}{(8\pi^2)^N \Lambda^{3N} N!} \int\ldots\int d\underline{X}^N e^{-\beta U_N(\underline{X}^N)} ,$$

where $\Lambda = \frac{h}{2\pi(2\pi mkT)^{\frac{1}{2}}}$ is the 'thermal wavelength' and q^N is the partition function for the rotational and internal degree of freedom. In principle, the partition function will allow the derivation of all the thermodynamic parameters. Information about the structure of the liquid is conveyed by the various distribution functions. The computation of these distribution functions can only be accomplished after an appropriate (tractable) potential function for molecular interaction has been chosen. Then, the method of integral equations will provide the means to evaluate these distribution functions.

In the case of liquid water, only the pair distribution function has been treated by this method. Thus, instead of seeking an approximate partition function as was done in the cases involving the empirical models or in the cases dealing with the lattice and cell models, this approach aims to evaluate directly the pair distribution function. Now the elementary entities are the molecules themselves, not a basic cell containing a number of molecules, or types or molecules differing through their hydrogen bonding configurations.

2) Ben Naim's treatment.

A good deal of work in this aspect of the problem of water structure has been done by Ben Naim.[8] The principles and methods employed have been compiled in his book on "Water and Aqueous Mixtures". We shall consider his methods and some of his results.

The ultimate aim of this approach is the evaluation of the pair correlation function $g^{(2)}(\underline{X}_1, \underline{X}_2)$. This is defined by

$$\varrho^{(2)}(\underline{X}_1, \underline{X}_2) = (\varrho/8\pi^2)^2 \, g^{(2)}(\underline{X}_1, \underline{X}_2) ,$$

where ϱ is the bulk density and $\varrho^{(2)}(\underline{X}_1, \underline{X}_2)$ is the probability density of observing two H_2O molecules in the configuration given by the set of coordinates $(\underline{X}_1, \underline{X}_2)$. $\varrho^{(2)}$ is defined by

$$\varrho^{(2)}(\underline{X}_1, \underline{X}_2) = \frac{N! \int\ldots\int \exp -\beta U_N(\underline{X}_1, \ldots, \underline{X}_N) \, d\underline{X}_3 \ldots d\underline{X}_N}{(N-2)! \int\ldots\int \exp -\beta U_N(\underline{X}_1, \ldots, \underline{X}_N) \, d\underline{X}_1 \ldots d\underline{X}_N} .$$

Here $U_N(\underline{X}_1, \ldots, \underline{X}_N)$ is the effective pair potential of interaction valid for the N particles in the system.

The experimental radial distribution function (RDF) obtained through X-ray or neutron scattering is in effect the angle averaged pair correlation function

$$\bar{g}^{(2)}(\underline{R}_1, \underline{R}_2) = (1/8\pi^2)^2 \int g^{(2)}(\underline{X}_1, \underline{X}_2) \, d\underline{\theta}_1 d\underline{\theta}_2 ,$$

where $(\underline{\theta}_i, \underline{R}_i)$ is equivalent to $(\underline{X}_i)$. $\underline{R}_i$ denotes the spatial coordinates of a fixed point in the water molecule (generally the oxygen atom or the center of mass), and $\underline{\theta}_i$ denotes the Euler angles.

One should state at the outset that the difficulties involved in treating the problem of water is such that at the present time there exist only results of computations based on drastic approximations. In consequence, Ben Naim only claims that the results concern "water-like particles". The hope is that

the degree of similarity between these models and water molecules will allow quantitative predictions not too far from reality.

The first step is the derivation of an effective intermolecular potential that will reproduce the main structural features of liquid water. One choice (Ben Naim's) could be the BNS potential described in the preceding section. This potential function has been subsequently modified by Stillinger[79] who introduced the ST 2 potential in his works in Molecular Dynamics. Both these potentials are derived on entirely classical assumptions. A partial remedy to this defficiency is provided by the potential function introduced by Popkie et al.[82] which includes the contribution from electron correlations.

A fairly complete historical survey of the development of effective pair potential of interaction for water can be found in the doctoral dissertation of M. Mruzik.[83]

To evaluate the pair correlation function, Ben Naim has adapted the Percus-Yevick equation.[84] This equation provides a relation between the pair correlation function and the interaction potential. This equation is written

$$y(\underline{X}_1,\underline{X}_2) = 1 + (\varrho/8\pi^2) \int y(\underline{X}_1,\underline{X}_2) f(\underline{X}_1,\underline{X}_2) \left[y(\underline{X}_3,\underline{X}_2) f(\underline{X}_3,\underline{X}_2) + y(\underline{X}_3,\underline{X}_2) - 1 \right] x d\underline{X}_3 ,$$

where f and y are defined as

$$f(\underline{X}_1,\underline{X}_2) = e^{-\beta U_N(\underline{X}_1,\underline{X}_2)} ,$$

and

$$y(\underline{X}_1,\underline{X}_2) = g^{(2)}(\underline{X}_1,\underline{X}_2) e^{\beta U_N(\underline{X}_1,\underline{X}_2)} .$$

This integral equation must be solved for $y(\underline{X}_1,\underline{X}_2)$ when $f(\underline{X}_1,\underline{X}_2)$

has been given an assumed value.

Because of the large amount of computation necessary to solve this equation, an additional approximation is introduced which conveniently averages out all the angular coordinates and reduces the equation to three dimensions.

3) Evaluation of average thermodynamic functions.

Once the pair correlation is known, one can derive the average thermodynamic functions using certain relations. For the internal energy one has

$$E = 3/2NkT + \tfrac{1}{2} \int d\underline{X}_1 \int d\underline{X}_2 U(\underline{X}_1,\underline{X}_2) \varrho^{(2)}(\underline{X}_1,\underline{X}_2)$$
$$= 3/2NkT + (N\varrho/16\pi^2) \int d\underline{X}_1' U(\underline{X}_1') g^{(2)}(\underline{X}_1') ,$$

where $\underline{X}_1'$ are the reduced coordinates taken with respect to one of the two particles.

The pressure is given by the relation

$$P = kT\varrho - (1/6V) \int d\underline{X}_1 \int d\underline{X}_2 \left[\underline{R} . (\partial U/\partial \underline{R}) \right] \varrho^{(2)}(\underline{X}_1,\underline{X}_2) ,$$

where $\underline{R} = \underline{R}_2 - \underline{R}_1$.

The two relations given above depend upon the choice of the effective pair potential and must be complemented by contributions arising from higher orders interactions for a more accurate treatment. One relation which is valid for all potential functions (i.e. which does not need pairwise additive assumption) is the compressibility equation

$$\vartheta_T = (1/kT\varrho) + (1/kT) \int d\underline{R} \left[g(\underline{R}) - 1 \right] = (1/kT\varrho) + (1/kT) \int \left[g(\underline{R}) - 1 \right] 4\pi R^2 dR .$$

A great advantage of this relation is that it involves only the

radial distribution function $g(\underline{R})$. Once this is known, it becomes possible to calculate ε_T.

4) Some of the results.

The Percus-Yevick equation has not allowed a solution for the regular BNS potential. An additional parameter had to be introduced to control the degree of the electrostatic contribution (or hydrogen bond contribution). The modified BNS potential is written

$$U(\underline{X}_1,\underline{X}_2,\lambda) = U_{LJ}(R_{12}) + \lambda S(R_{12})U_{el}(\underline{X}_1,\underline{X}_2) ,$$

$\lambda=0$ is the rough approximation corresponding to the case of Lennard-Jones particles. As λ is gradually increased to a maximum value of 0.3 (beyond which no solution can be obtained), the agreement between the computed RDF and the experimental one improves significantly. The positions of the first and second peaks in the RDF match reasonably well for $\lambda=0.3$. However, the computed coordination number (number of molecules contained within a sphere of arbitrary radius R_m centered on one of the molecules) is too high (7.4 instead of 4.4 found experimentally).

In conclusion, one could say that the integral equations method may be able to provide some interesting qualitative results concerning the typical mode of packing of the molecules, but that the number of approximations involved at this time prohibits it from being of much use in calculating macroscopic properties. In addition, many of the structural properties exhibited by the "water-like" particles must come from the particular potential of interaction used in the treatment.

C Computer Simulation Studies.

1) Generalities.

An alternative approach to the treatment of the statistical mechanics of the individual molecules making up a macroscopic system exists in the wide ranging possibilities of computer simulation. A significant improvement over the methods mentioned previously arises from the possibility of performing almost exact calculations. The uncertain effects of many assumptions do not have to be contended with. These accurate computations, however, cannot be made for the entire system of N (N is of the order of 10^{23}) molecules. The maximum number of particles considered in such computations does not usually exceed 10^3. Thus, coupled to this method is the inherent assumption that the structural characteristics of liquid water can be derived from the properties of the interactions of molecules situated in the first few coordination shells of a central molecule. This is translated in many cases into an artificially imposed cutoff distance for pair molecular interactions.

Of the available methods of computer simulation, only the Molecular Dynamics approach allows the calculation of kinetic properties. The second method, the Monte Carlo technique, is stricly an equilibrium statistical mechanical method. Both means, however, deal with a small number of particles (10^2 to 10^3 particles) contained in a small volume or 'box', and use periodic boundary conditions in order to avoid the spurious surface effects arising from the small size of the 'box'. Under these conditions, the entire system is viewed as being

made up of many identical 'boxes', one of which is the object of the study. The contributions to the force field at a particular point of the box could include those from particles inside the box as well as those from their mirror images with respect to the box boundaries. The configuration of such a volume is usually taken to be that of a simple cube.

The Molecular Dynamics and Monte Carlo methods differ fundamentally in the way they evaluate the various macroscopic average parameters. The case of the Monte Carlo method is analyzed first.

2) Monte Carlo Simulations.

The size of the volume considered in the simulation is determined by the number of particles and the macroscopic density. For example, in the work of Lie, Clementi, and Yoshemine,[85] 343 molecules are considered. The density is set equal to that of water at 25 C and one atmosphere. The size of the volume (a cube) is 21.73^3 $\mathring{A}^3$.

In the Monte Carlo framework, static properties of the macroscopic system are calculated as ensemble averages over (usually) canonically generated configurations for the n particles in the volume under consideration. Metropolis et al. have devised a way to generate an infinite Markovian chain whose individual steps sample successive configurations with a probability density of the appropriate ensemble. For the case of the canonical (N,V,T) ensemble, this is given by

$$P_{NVT}(\underline{X}_i^N, V, T) = \frac{e^{-\beta U_N(\underline{X}_i^N)}}{N!\, Q_{NVT}} ,$$

where Q_{NVT} is the canonical partition function and U_N the potential of interaction.

An approximation is made in the actual computation because the Markovian chain is interrupted after a finite number of steps. If the total number of steps is not too small, however, the consequence of the approximation is not great unless extremely accurate average values are desired.

We shall now consider some of the results of Monte Carlo simulation by Lie et al[85]. In this instance, the pair interaction potential adopted was derived by Matsuoka et al. through ab-initio calculations. The functional form of such a potential includes many terms and will not be reproduced here. The details may be obtained in the article by Lie et al.

The radial distribution function for each of the O-O, O-H, and H-H interactions have been calculated and compared with experimental data of Narten et al.[14] These experimental results, however, have been derived with both results from X-ray and neutron scattering and a plausible model for the average orientations of pairs of near neighbors molecules. At any rate, the agreement between the computed and the experimental results is very good. The position of the first peak and its height in the $g_{OO}(R)$ function are calculated to be respectively at 2.83 $\mathring{A}$ and 2.48 $\mathring{A}$; the corresponding experimental values being 2.82 $\mathring{A}$ and 2.31 $\mathring{A}$. The comparison for the functions $g_{OH}(R)$ and $g_{HH}(R)$ also gives reasonably good results even though some uncertainty remains about the validity of the experimental figures.

The pressure, heat capacity at constant volume, and the isothermal compressibility are determined. The results are given below together with the experimental values.

$19.5 < (C_v)_{calculated} < 15.9$ cal/mole.deg.

$(C_v)_{exp} = 17.9$ cal/mole.deg.

$(\beta_T)_{calculated} = 53 \times 10^{-6}$ atm^{-1}

$(\beta_T)_{exp} = 46 \times 10^{-6}$ atm^{-1}

These results seem to suggest that the Monte Carlo simulations are able to reproduce the RDF and some of the thermodynamic properties of liquid water, even with the use of a pair potential function. However, progress in this field appears to be closely linked to the improvement of our knowledge of the molecular interaction potential.

3) The method of Molecular Dynamics.

In a Molecular Dynamics study, the classical equations of motion of a small number of particles (n is usually a few hundred) are solved through the use of high speed computers. The evolution in time of the sub-system under study can be monitored continuously by the computer, making it possible to determine the kinetic properties of this group of molecules. The water molecules are considered to be rigid, asymmetric particles with both translational and rotational degrees of freedom.

Initially, the n particles are assigned values for the momenta and positions. The coupled equations of motion for translation and rotation are then solved for each particle with the

use of an effective pair potential, and the new positions and momenta of all the particles are calculated after a time step δt. This procedure is repeated for the next configuration and the next time step. Obviously, this procedure is limited by the calculation time used by the computer and the large amount of information gathered. For liquid water time steps as short as 10^{-16} sec are required due to the strong molecular interactions. Thus, the true total duration of a simulation with 10^4 to 10^5 time steps is usually around 10^{-11} to 10^{-12} sec. This is equal to or longer than the time constants for most kinetic processes on the molecular scale.

A great deal of work in Molecular Dynamics simulation has been accomplished by Stillinger and Rahman.[79] Some of their results are considered here.

A modified version of the BNS potential described in a preceding section, the ST 2 potential, has been used in the Molecular Dynamics study of liquid water under normal and elevated pressures.

In a first study (at a density of 1 g/cm^3) 216 rigid molecules contained in a cubical 'box' of edge length of 18.62 Å have been considered. The temperature is determined from the total kinetic energy of an assumed thermalized system by

$$E_{kin} = 3kT .$$

The four different temperatures at which the runs were made were fixed by four different total energies attributed to the molecules of the system. The total energy must remain constant theoretically, but in practice a rescaling of the momenta was

found necessary in order to satisfy that condition after every 10 time steps. The magnitude of the time increment was 2.1261×10^{-16} sec. for a total running time of 8.10×10^{-12} sec for the longer runs.

Stillinger and Rahman have also determined the nuclear pair correlation functions g_{OO}, g_{OH}, and g_{HH} at four different temperatures. The agreement for $g_{OO}(R)$ between the calculated and the experimental results (of Narten et al.) is good. At almost the same temperature (10 C instead of 4 C), the position of the first peak does not differ by more than 0.01 Å. The peak height from Molecular Dynamics, however, is significantly higher than that from X-ray scattering. A broad peak is obtained through the calculations at around 4.5 Å indicating that some of the tetrahedral structure is preserved. The remaining disagreement between computed and experimental data is tentatively assigned to quantum corrections. The temperature dependence of the RDF is qualitatively similar to the behavior of the experimental RDF.

Molecular Dynamics simulation of water under high pressure (with a density of 1.346 g/cm^3, equal to the density at the triple point of iceVI, ice VII, and liquid water, i.e. at 81.6 C and under 22 kbars) has yielded evidence of a denser packing than at atmospheric pressure by a factor of almost two: The mean number of neighbors out to the position of the first minimum is found to be equal to 10 instead of 5.38 at 97 C and one atmosphere. Stillinger and Rahman reject the possibility of describing the liquid structure at the higher density by a crystal structure analogous to that of ice VII since the coordination number for

that type is only 8. Upon melting, the volume increases, and there does not seem to be a way for interstitial molecules to contribute to an increase in coordination number. Moreover, Stillinger and Rahman do not view the existence of large cavities in ice VII as highly probable.

The evaluation of thermodynamic quantities (C_v, ϱ, β_T) involves an analysis of the consequences of the artificial cut-off point for pair interaction arbitrarily introduced to ease the task of computation. The density of the liquid under saturation conditions exhibits a maximum at 27 C where $\varrho = 1.0047$ g/cm^3 (as opposed to 4 C and 1.0 g/cm^3 found experimentally). The values obtained for C_v (34.7 cal/mole.deg) is too high (the experimental value is 18.0 cal/mole.deg). This discrepancy is also attributed to quantum effects. Under elevated pressure C_v was found to be much lower (C_v=17 cal/mole.deg at 97 C and at a density of 1.346 g/cm^3). This is consistent with the idea that the application of pressure decreases the structural contribution to the specific heat by hindering the molecular rearrangements.

The self-diffusion coefficient can be calculated through the velocity auto-correlation function $\sigma(t)$ which is defined as

$$\sigma(t) = \langle \underline{v}(0) . \underline{v}(t) \rangle ,$$

and one can compute D (the self-diffusion coefficient) with

$$D = \lim_{t \to \infty} \frac{\langle \delta \underline{R}_j(t)^2 \rangle}{6t} ,$$

and

$$\frac{d}{dt} \langle \delta \underline{R}_j(t)^2 \rangle = 2 \int_o^t dt' \langle \underline{v}(0) . \underline{v}(t') \rangle .$$

$\delta\underline{R}_j$ is the displacement of the center of mass of the molecule j during the time t. The values calculated for D are about 30 % larger than those determined experimentally. One interesting effect was obtained in the study under higher pressure: An increase in the density by over 30 % only induces a decrease of slightly more than 10 % in the value of D. In close packed fluids like Argon, such a increase in density results in a drastic reduction in the value of D. This has been interpreted as evidence for the phenomenon of increased fluidity in liquid water with an initial increase of pressure.

Evidence for hydrogen bond breaking with rising temperature under low pressure has been obtained through calculations of the pair interaction distribution function P(V). As the temperature is raised, this distribution shifts to a higher probability of molecular pairs having higher potential energy. This could be interpreted as a decrease in the number of hydrogen bonds due to the higher temperature. However, the results of Molecular Dynamics experiments do not provide any evidence for the presence of two or several different types of structures mixed in the liquid. Stillinger and Rahman have computed the distribution of molecules in terms of their number of hydrogen bonds. With the energy of the hydrogen bond retained as a variable parameter, they have found that in every case such a distribution was singly peaked. A multiply peaked distribution would have to be found in the case of a mixture of distinct types of molecular environments.

In conclusion, it appears that the computer simulation

methods are able to reproduce the essential features of liquid water under low pressure. The Monte Carlo method, with the use of a more accurate potential function, has achieved a better agreement with experimental values for equilibrium properties. The possibilities of the method of Molecular Dynamics are greater. Its achievements cannot yet be fully evaluated, however, because of the lack of rigorously valid experimental data. Quantum corrections to the Molecular Dynamics results may improve their quality, and more extensive studies may confirm the high pressure results. An attractive possibility is the study of phase transitions and the processes of nucleation. Finally, because exact computations can be carried out with these methods, the results they provide could be used as standards for judging those obtained through the use of more approximate techniques.

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This work is an attempt at presenting an overview of the field of liquid water. The first chapter contains a summary of some of the known thermodynamic, transport, and molecular properties of this liquid. The supercooled and superheated liquid ranges are also considered due to the relatively recent interest in these uneasily accessed states. The second chapter contains a cursory review of the various models dealing with the structure of water. The semi empirical "ad-hoc" models are described together with the "lattice" and "cells" models, as well as the methods of integral equations and computer simulations. The results of a few representative works are summarized in an attempt to obtain a general picture of the present status of this field. This work is by no means exhaustive, to include all the existing works is a task outside of the scope of this contribution.

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