

THE DIELECTRIC CONSTANT OF LIQUID WATER AND VARIOUS FORMS OF ICE ACCORDING TO SIGNIFICANT STRUCTURE THEORY

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Communicated May 27, 1966

The electrostatic problem in treating hydrogen bonding and other dipolar liquids is to relate properly the molecular properties of the liquid molecules to the fundamental electrostatic equation $(\epsilon - 1)/4\pi = P/E$. Here ϵ is the dielectric constant of the liquid, P the polarization of the dielectric, and E the field intensity. The solution of the basic problem for homogeneous media with a sphere of dielectric constant ϵ_2 in a surrounding medium of dielectric constant ϵ_1 leads to the expression for the field,¹ F , inside the sphere

$$F = \frac{3\epsilon_1}{2\epsilon_1 + \epsilon_2} E. \quad (1)$$

Onsager,^{2, 3} and Kirkwood⁴ have called this the cavity field. In Onsager's excellent treatment of the problem of dipolar liquids, account was taken of long-range interactions between the dipole in the central cavity and the surrounding medium. In Kirkwood's approach the short-range interactions between nearest neighbors also were considered. In particular, on introduction of the internal dielectric constant, n^2 , and the assumption of spherical isotropically polarizable molecules, Onsager obtained

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = 4\pi \frac{N}{V} \left(\frac{\mu^2}{3kT} \right) \left(\frac{n^2 + 2}{3} \right)^2. \quad (2)$$

Here n is the refractive index appropriate to electronic and atomic polarizability, N is Avogadro's number, V is the molar volume of the liquid at temperature T , k is the Boltzmann constant, and μ the value of the permanent dipole moment characteristic of the isolated molecule.

In his derivation of equation (2), Onsager neglected short-range order. He assumed all angles between the molecular dipole and the applied field to be equally likely aside from the orientation energy in the local field. This postulate makes equation (2), as it stands, inapplicable to ice or water. This assumption cannot be even approximately true for a perfect single crystal of ice I. The dipole of a water molecule points from the oxygen atom to the midpoint between its two hydrogen atoms. There are six ways of selecting which two of the four neighboring hydrogen atoms in ice I are to belong to the central oxygen atom, and these six ways correspond to the water dipole pointing in the plus and minus direction of each of the three axes of an appropriately chosen rectangular coordinate system. Now if the water dipole were free to take up each of these six positions, the mean value of $\cos^2 \theta'$, where θ' is the angle between the direction of an applied field and the water dipole, would be $1/3$ as it is for free rotation and one would still arrive at equation (2). However, if ice had this sixfold degeneracy, there would be a corresponding entropy per mole of $R \ln 6$ persisting to low temperatures instead of the 0.870 eu observed by Giaouque,⁵ which, as Pauling⁶ points out, closely approximates an en-

trophy of $R \ln 6/4$. Pauling's argument for 6/4 for the degeneracy proceeds as follows. Since neighboring oxygen atoms are equally likely to pre-empt the intermediate hydrogen atom, there is only a chance of $(1/2)^2$ that a particular one of the six orientations of the water dipole be allowed. This gives the degeneracy 6/4 which is in close agreement with experiment. This degeneracy of 6/4 per water molecule allows some randomness of molecular orientation with respect to the direction of maximum polarization for a domain. The result is a decrease in the average component of the dipole moment, $\mu \cos \theta$, in the direction of maximum polarization of the domain.

Accordingly, the model discussed below differs from the Onsager model in one essential respect, namely, the method of obtaining the polarizability attributable to the permanent dipoles. In Onsager's model this polarizability, $\frac{\mu^2}{3kT} \left(\frac{n^2 + 2}{3} \right)^2$, is obtained by space averaging $\mu \cos \theta$ over all possible values of the angle θ . This assumes that the relative population of dipole vectors is not constrained by short-range directional interactions and leads to an incorrect value of this polarizability in cases where the dominant forces are directional short-range interactions. Kirkwood attempted to account for the short-range directional interactions by introduction of a correlation factor between a central molecule and nearest neighbors, but again it was assumed that the central dipole was free to orient in a local field, F .

The model suggested by the present authors is that the Bernal and Fowler⁷ and Bjerrum⁸ proposals for the structure of water (see Fig. 1), and by implication many

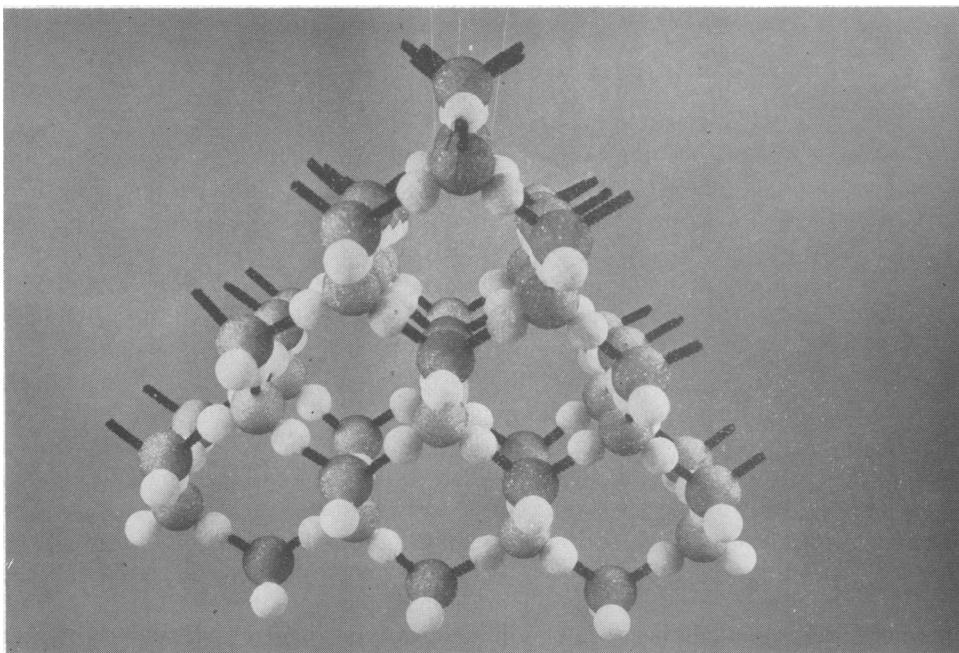


FIG. 1.—This model of the structure of ice was kindly supplied to us by Dr. Melvin E. Zandler. The small balls represent hydrogen atoms, while the big balls represent oxygen atoms. We see that the direction of every dipole points in the same direction—outward and down. Thus the projection of each dipole $\mu \cos \theta$, along the direction of maximum polarization for such a domain, is μ itself.

other hydrogen-bonding liquids and solids, be introduced immediately into the evaluation of the average dipole moment in the field direction attributable to permanent dipoles. This is done by assuming the following:

(1) Solid or liquid water is made up of a mosaic of roughly bricklike domains with the dipoles in a particular domain having an average resultant moment $\mu \cos \theta$ along the direction of maximum polarization for the domain while the direction of maximum polarization of neighboring domains is rotated through 180° with respect to the first. For perfect tetrahedral bonding, $\cos \theta$ approaches its maximum value of 1, while for bent hydrogen bonds⁹ $\cos \theta$ is correspondingly smaller.

(2) When an electric field is applied to the system, the directions of maximum polarization of domains orient in the field until all domains are either lined up with the field or against it. Further, these domains with their directions of maximum polarization oriented in the direction of the field increase in volume at the expense of domains oppositely oriented until equilibrium is attained. The resulting mean dipole moment for solidlike molecules is then

$$\mu = \frac{\frac{\mu \cos \theta F}{kT} - \frac{-\mu \cos \theta F}{kT}}{\frac{\mu \cos \theta F}{kT} + e} = \frac{\mu^2 \cos^2 \theta F}{kT} \quad \text{provided } \frac{\mu \cos \theta F}{kT} \ll 1. \quad (3)$$

Here F is the local field. Thus for ice and the solidlike part of water the factor $\frac{\mu^2}{3kT}$ in equation (2) must be replaced by $\frac{\mu^2 \cos^2 \theta}{kT}$, while for the gaslike portion the factor $\frac{\mu^2}{3kT}$ is retained since such molecules oriented freely in the local field, F .¹⁰

(3) The interface between domains in the mosaic is made up of Bjerrum faults, vacancies, and related mismatch structures.

According to the significant structure theory of liquids,¹¹ the fraction of molecules having solidlike character is V_s/V , where V_s is the molar volume of the solidlike structure in the liquid and V is the volume of the liquid at the temperature of observation. The remaining fraction of the molecules, $(V - V_s)/V$, is gaslike.

Calculation of Dielectric Constants.—In the light of the foregoing discussion and the evidence from significant structure theory¹¹ that the fraction V_s/V of the molecules of a liquid has solidlike properties and the remaining fraction $(V - V_s)/V$ has gaslike properties, we expect the dielectric constant of water to be given by

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = 4\pi \frac{N}{V} \left(\frac{n^2 + 2}{3} \right)^2 \left[\frac{V_s \mu^2 \cos^2 \theta}{V kT} + \frac{V - V_s}{V} \frac{\mu^2}{3kT} \right]. \quad (4)$$

For ice, one has

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{3\epsilon} = 4\pi \frac{N}{V_s} \frac{\mu^2 \cos^2 \theta}{kT} \left(\frac{n^2 + 2}{3} \right)^2. \quad (5)$$

For convenience in actual calculations, equations (4) and (5) may be rearranged to give

$$\epsilon = \frac{n^2}{2} + \frac{n^4}{2\epsilon} + 6\pi N \cos^2 \theta \left(\frac{\mu^2}{k} \right) \left(\frac{n^2 + 2}{3} \right)^2 \left(\frac{1}{VT} \right) \left[\frac{V_s}{V} \left(1 - \frac{1}{3 \cos^2 \theta} \right) + \frac{1}{3 \cos^2 \theta} \right] \quad (6)$$

and

$$\epsilon = \frac{n^2}{2} + \frac{n^4}{2\epsilon} + 6\pi N \cos^2 \theta \left(\frac{\mu^2}{k} \right) \left(\frac{n^2 + 2}{3} \right)^2 \left(\frac{1}{V_s T} \right). \quad (7)$$

The value of $\cos^2 \theta$ can be determined as a parameter by evaluation at a single temperature using experimental quantities for the other factors in equation (7). The small deviation of $\cos^2 \theta$ from unity reflects (1) any approximations in our model, (2) approximations in the value used for μ and n , and (3) deviations from tetrahedral structures due to bending of hydrogen bonds, and finally (4) some decrease in polarization in a domain because of the degeneracy of 6/4 per molecule.

As an application of equation (6), the calculated values of the dielectric constant of water are compared in Table 1 with observed values at several temperatures. In the calculation the one parameter, $\cos^2 \theta$, is taken as 0.964 and μ as 1.84 debyes for both light and heavy water. The fact that for all forms of ice and water the values found for $\cos^2 \theta$ are nearly equal to unity is an extremely satisfying result.

For comparison, Oster and Kirkwood^{4b} obtained, using the Kirkwood correlation parameter, the data shown in Table 2.

Judging from the data in Table 2 for the small temperature interval involved, the Kirkwood correlation parameter gives a poorer agreement with the temperature coefficient than that given by equation (6). Also, the Oster-Kirkwood model, which assumes free rotation about the hydrogen bond of the nearest neighbors of a central molecule, seems to be less appropriate for water than our model of water as a mosaic of domains.

TABLE 1
COMPARISON OF CALCULATED AND OBSERVED VALUES OF THE DIELECTRIC CONSTANTS OF LIGHT AND HEAVY WATER

T, °K	ϵ_{obs}^a	ϵ_{calc}	H ₂ O		
			$V_{b,c}$	V_{sc}	n^{2d}
273	88	88	18.0	17.85	1.78
373	56	60	18.8	17.7	1.74
473	35	38	20.8	17.7	1.64
573	20	22	25.3	17.7	1.51
T	ϵ_{obs}^e	ϵ_{calc}	D ₂ O		
			V_c	V_{sc}	n^{2d}
278	85.8	85.3	18.11	17.88	1.78
293	80.1	80.9	18.13	17.85	1.78
313	73.1	75.4	18.20	17.85	1.77
333	66.7	69.8	18.36	17.85	1.76

^a Values for 273°K and 373°K were taken from Malmberg, C. G., and A. A. Maryott, *J. Res. Natl. Bur. Std.*, **56**, 1 (1956); and for 473°K and 573°K from *Natl. Bur. Std. (U.S.), Circ. 514* (1951), p. 2.

^b Calculated from densities given in the American Institute of Physics *Handbook* (New York: McGraw-Hill Book Co., 1963), 2nd ed., pp. 2-147.

^c Values are taken from ref. 11b.

^d Value at 273°K from footnote b above, pp. 6-90, and values at other temperatures were calculated from the molar refraction values of 3.66 cc using molar volumes given in the fourth column.

^e The values are taken from Collie, C. H., M. B. Hasted, and D. M. Ritson, *Proc. Phys. Soc. (London)*, **60**, 145 (1948).

TABLE 2
DIELECTRIC CONSTANT OF WATER AS CALCULATED BY OSTER AND KIRKWOOD

T, °K	273	298	335	356
ϵ_{calc}	84.2	78.2	72.5	67.5
ϵ_{obs}	88.0	78.5	66.1	59.5

TABLE 3
DIELECTRIC CONSTANT OF VARIOUS FORMS OF ICE^{12, 13}

<i>T</i> , °K	ϵ_{obs}	ϵ_{calc}	Constant used
<i>Ice I:</i>			
273	91.5	91.5	Density of Ice I = 0.917 gm/cm ³ $n^2 = 1.72$
262.3	95.0	95.2	
252.2	97.4	98.8	
241	100	103	
228.4	104	109	
216.3	114	115	
<i>Ice III:</i>			
243	117	117	Density of Ice III = 1.155 gm/cm ³ $n^2 = 1.96$
253	—	112.5	
<i>Ice V:</i>			
263	—	133.2	Density of Ice V = 1.258 gm/cm ³ $n^2 = 2.08$
243	144	144	
223	—	156.7	
<i>Ice VI:</i>			
273	—	172	Density of Ice VI = 1.350 gm/cm ³ $n^2 = 2.19$
242	193	193	
223	—	210	

As an application of equation (7), the calculated values of the dielectric constant of various forms of ice are compared in Table 3 with observed values at several temperatures. Unfortunately, we have not sufficient experimental data available for a good comparison except for ice I, which shows excellent agreement with experiment.

In the calculations, the following values of $\cos^2 \theta$ are used

0.977 for Ice I	0.90 for Ice III
0.949 for Ice V	1.138 for Ice VI

Factors Affecting the Dipole Moment in Condensed Phases.—The factor $\left(\frac{n^2 + 2}{3}\right)^2$ corrects for the increase in dipole moment due to induction. The fact that for Ice VI the estimated value for $\cos^2 \theta$ is greater than 1 suggests that a slightly larger value of n^2 would probably be appropriate.

Many solids containing polar molecules show little polarization arising from molecular dipoles in the solid state. This is to be expected if the dipoles are arranged in the solid so that their mean component along the direction of maximum polarization of a domain is small or zero.

When the vapor pressure of a system gets high, the vacancies in the liquid tend to cluster like molecules in the vapor, and the gaslike part of the polarizability should be multiplied by the factor $\sum \frac{1}{n} X_n \left(\frac{\mu_n}{\mu}\right)^2$. Here X_n is the mole fraction of molecules in clusters of n molecules having a resultant dipole moment μ_n .

Relaxation Times.—As Debye¹⁰ showed, the dielectric constant ϵ_2 is a function of frequency and satisfies the equation

$$\epsilon_2 = (\epsilon_0 - \epsilon_\infty) \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (8)$$

where according to absolute rate theory,¹⁴ we write

$$\frac{1}{2\tau} = k' \equiv \frac{kT}{h} \exp^{-\frac{\Delta G^\ddagger}{RT}}. \quad (9)$$

Here ϵ_0 and ϵ_∞ are the dielectric constants at low and high frequencies, and ω is the circular frequency of the applied potential. The relaxation times for ice given by Auty and Cole¹⁵ are $\tau_{\text{H}_2\text{O}} = 5.30 \times 10^{-6} e^{\frac{13,250}{RT}}$ for ordinary ice and $\tau_{\text{D}_2\text{O}} = 7.7 \times 10^{-6} e^{\frac{13,400}{RT}}$ for solid deuterium oxide. Using equation (9) we find $k_{\text{H}_2\text{O}} = 9.4 \times 10^4 e^{\frac{-13,250}{RT}}$ for ordinary ice and $k_{\text{D}_2\text{O}} = 6.5 \times 10^4 e^{\frac{-13,400}{RT}}$ for the specific rates of relaxation of light and heavy ice, respectively.

A reasonable value for the frequency factor $\frac{kT}{h} e^{\frac{\Delta S^\ddagger}{R}}$ for a simple unimolecular rate constant where the entropy of activation, ΔS^\ddagger , is small is 10^{13} . If we divide 9.4×10^4 by 10^{13} , we obtained 9.4×10^{-9} for the fraction, f , of molecules which are situated so they can rotate from one domain into a neighboring domain better oriented with respect to the field. If, for each domain, only one molecule at a time is so situated that it can migrate to a neighboring domain, the linear dimension of the domain would be about a tenth of a micron. If more molecules can migrate at a time, the volume of the domain would be proportionately larger, and if the entropy of activation, ΔS^\ddagger , is negative, the domain is correspondingly smaller. From this point of view the model seems reasonable. If the reaction coordinate were rotation about an axis normal to the axis of the dipole, the frequency factor would be larger for H_2O than for D_2O by a factor $\sqrt{2}$. The reported frequency factors are at least not inconsistent with this requirement. Manson, Cagle, and Eyring¹⁶ have found 13,800 calories for the activation energy for the rate of growth of microcrystals of ice from supersaturated vapor up to a size where they can be seen. The saturated vapor was seeded with AgCl to nucleate the liquid drops. The rate-determining step is the growth of one ice crystal at the expense of another. This correspondence in activation energies for crystal growth and passage between domains supports our model of the mechanism of dielectric relaxation in ice.

Manson, Cagle, and Eyring¹⁶ interpreted their results to show that a liquid domain of about 40 water molecules must freeze as a unit to form the bridge required in crystal growth. Jhon, Grosh, Ree, and Eyring^{11b} were able to explain the thermodynamic properties and viscosity of water on the assumption that it contained domains of about 46 molecules which changed as a unit from an "ice I-like" to an "ice III-like" state. These findings suggest the expected result that the domains which are hydrogen-bonded together should be much smaller in water than in ice, i.e., liquids lack long-range order.

Because the domains of long-range order in water are much smaller than in ice and because of an abundance of fluidized vacancies in water, we expect that the relaxation time for water will have an f factor much nearer unity and an activation energy about 10,000 calories less than for ice. This is in accord with the value of

$\tau = 0.9 \times 10^{-11}$ reported by Collie, Hasted, and Ritson¹⁷ for water. The relaxation time for D₂O is about $\sqrt{2}$ times as long as for H₂O in qualitative agreement with the findings in ice and with our expectations that the reaction coordinate will approximate a molecular rotation.

Conclusions.—In this paper there are several points to be emphasized. (1) Short-range order in many solids and in hydrogen-bonded liquids prevents the reorientation of a molecular dipole by rotating locally in response to an electric field. However, only under extraordinary circumstances will there be long-range order extending through a macroscopic sample. Consequently, the result of an applied field will be to make those domains grow which are favorably oriented with respect to the field at the expense of the less favorably oriented until a steady state is achieved. (2) Because relaxation involves only molecules at the interface between domains, the relaxation time measures the size of the domains. The lack of sufficient degeneracy, as shown by the entropy, to allow local relaxation supports this point of view. (3) The lack of long-range order in liquids allows one to predict much shorter relaxation times for this state. (4) Significant structure theory by introducing the concept of solidlike and gaslike molecules leads to an explanation of the observed temperature coefficient of the dielectric constant in liquids.

Debye's¹⁹ calculation of the temperature dependence of the dielectric constant of water agrees well with experiment. It consists in assuming that each water molecule is restrained by a local potential field of about $10kT$. The difficulty with this explanation is that the relaxation time should be the reciprocal of a vibrational frequency which is more than an order of magnitude shorter than the experimental value. This forces us to turn to domains as the explanation of relaxation. The observed orientational entropy indicates there is too much local restriction to obtain polarizations of ice and water of the magnitude observed by rotation *in situ*.

Domains with large electric moments would tend to line up parallel and antiparallel just as magnets juxtapose poles of opposite kinds. Our assumption that there are few domains with their direction of polarization oriented at angles intermediate between zero and 180° is justified in this way. The presence of domains with intermediate orientation would lower the polarization and in the limit of complete randomness would lead to a factor of 1/3 multiplying μ^2/kT . This would require that the calculated Onsager field be low by just enough to compensate for this randomness.

Investigators have frequently looked, unsuccessfully, for the domain structure in water which our considerations suggest may be present. The low-angle X-ray scattering in water does not differ appreciably from that found for liquid argon. A fairly broad distribution in domain volume around a mean value of about 46 molecules may explain this discrepancy.

In subsequent publications, the dielectric constants of some of other well-known systems¹⁸ will be investigated using our proposed model in conjunction with the significant structure theory of liquids.

One of the authors (M. S. Jhon) wishes to thank the National Science Foundation for support of this work. Dean Eyring wishes to express his appreciation for the opportunity of discussing some of the above problems with Professor Peter Debye.

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