SOME PROBLEMS IN THE ELECTRONIC STRUCTURE OF MOLECULES

Thesis Submitted

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INTRODUCTION

Scientists have long noted that water, common in the sense that it is the only abundant liquid on our planet, is most uncommon in its properties. Water has a greater heat of vaporization than analagous inorganic or organic liquids, its specific heat is exceeded only by that of ammonia and of some ionic salts, its surface tension only by some fused salts and liquid metals, and its dielectric constant, among pure liquids, only by hydrogen cyanide. When water is compared to the hydrides of the other elements in the same column of the periodic table it is found to exhibit an anomalously high melting point, boiling point, and heat of vaporization.

Ice, no less than water, shows unusual properties. Its mode of melting is the most familiar example: ice is one of the rare pure solids which floats on its melt. Like many of the apparently anomalous properties of ice and water, this is not merely a freak of nature, of interest only to scientists, but a phenomenon essential to life on earth. In 1913 L.J. Henderson wrote,

> "And so it would be with lakes, streams, and oceans were it not for the anomaly and the buoyancy of ice. The coldest water would continually sink to the bottom and there freeze. The ice, once formed, could not be melted, because the warmer water would stay at the surface. Year after year the ice would increase in winter and persist through the summer until eventually all or much of the body of water, according to the locality, would be turned to ice." *

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* Quoted in Edsall and Wyman (1958)

Because the properties of water and ice are of considerable interest not only to chemists and physicists, but to biologists and geologists as well, an enormous volume of research has been devoted to their study. In 1940 Dorsey published a monograph entitled The Water-Substance summarizing the results of 2,172 investigations concerning all three phases of water, and since then, according to Chemical Abstracts, there have been roughly 12,500 papers about water, 2,500 about water vapour, and 800 about ice. Apparently, there have been more than 17,000 scientific studies of H_2O. Needless to say, a fairly comprehensive qualitative understanding of the properties of water has emerged, and the beginnings of a quantitative description have been made.

In an effort to extend this description we have chosen to study water in the solid state as the structure of ice is largely known. The greater part of this thesis will be concerned with intermolecular forces in ice and some associated physical properties. We will not take the usual line of attack in such studies, which has been to calculate the hydrogen-bond energies; instead we shall initially concern ourselves with induced electric dipole moments occurring in ice, and secondarily in hydrogen-bond energies. In Chapter I we will emphasize the importance of the deforma-

tion that an ice molecule experiences owing to the proximity and orientation of its neighbours. Largely by means of classical electrostatics we will compute the average dipole moment of an ice molecule and we will find that it is substantially greater than the moment of an H_2O molecule in the vapour. In Chapter 2 we will interpret the dielectric constant of single crystals of ice, the dielectric constant at high frequencies, and the energy of sublimation of ice in terms of the calculated dipole moment. Chapter 3 will be devoted to a study of proposed mechanisms of molecular reorientation in ice.

CHAPTER ONE

The Dipole Moment of An Ice Molecule

A. Introduction.

In the numerous studies of intermolecular forces in ice, one can find no detailed consideration of the distortion of a molecule by its neighbours. This is surprising for two reasons: for one, forces between polar molecules are sensitive to charge distributions and one would expect that an investigation of distortion of the charge of an H_2O molecule would be essential for an accurate calculation of intermolecular forces in ice. Secondly, the dipole moment of a molecule, the most important indication of its charge distribution, is more simply related to observables than is the coulombic intermolecular energy. This energy is equal to the difference of the observable energy of sublimation and other energy terms which are difficult to estimate. In contrast, the dipole moment is related not only to the dielectric constant, but also to the absolute intensity of infra-red absorption. Unfortunately, the latter is to date an unobserved observable, but there is hope that it will not remain so for long.

In this chapter we shall attempt to make an accurate estimate of the dipole moment of H_2O in ice. We shall begin by mentioning previous suggestions that the dipole moment of

water is enhanced in the solid state, but we will delay more detailed discussion of previous work until we have calculated our value of the dipole moment.

B. Previous calculations of the dipole moment of H_2O in ice and water.

The increased value of the dipole moment of a molecule in passing from vapour to condensed states is not a new idea. Onsager(1936) estimated this enhancement in polar liquids by approximating the charge distribution of a molecule by a point dipole located at the centre of the molecule. The molecule is considered to be spherical and surrounded by a continuous dielectric characterized by the macroscopic dielectric constant and refractive index. His theory is sketched briefly in Appendix A. The enhancement of the moment of a molecule is brought about by the environment of a molecule, which is modified from random arrangement by the field arising from the molecule's permanent moment. Onsager's model leads to a ratio of $|\vec{m}|$, (the dipole moment of a molecule surrounded by its neighbours), to $|\vec{\mu}_o|$, (the dipole moment of an isolated molecule), given by

$$\frac{|\vec{m}|}{|\vec{\mu}_o|} = \frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)} \qquad (I\text{-}1)$$

where n is the refractive index, and ϵ the dielectric constant of the condensed state. Both Powles(1952) and Harris

and Alder(1953) have used equation (I-1) to estimate the value of the dipole moment in ice, and they find that the vapour moment of 1.84 D is increased to about 2.2 D in ice. Of course the approximation of taking neighbouring molecules as a continuum is inadequate for ice, where hydrogen bonds constrain the neighbours to assume specific orientations with respect to the central molecule.

Kirkwood(1939) estimated the dipole moment of H_2O in liquid water by considering the effect of the dipolar fields of neighbouring molecules on the dipole moment of the central molecule. He assumed the central molecule to be tetrahedrally coordinated to four nearest neighbours by rigid bonds, which, however, allow free rotation of the neighbours. He found that the average electric field strength arising from the neighbours increases the moment of the central molecule to about 2 D. Later, Oster & Kirkwood(1943) generalized Kirkwood's approach in such a way that non-integral numbers of neighbours could be considered, and they used data from X-ray diffraction to estimate the number and the distance to the central molecule of the neighbours. Their modified approximation gives a value for the dipole moment of the central molecule of 2.3 D at $0^{\circ}C$.

Until recently, the only calculation of the dipole moment of H_2O in ice which took into account the locations of neighbouring molecules was by Verwey(1941). He used a formal

point charge model of H_2O to calculate the electric field strength at a central H_2O molecule arising from its four nearest neighbouring molecules. Verwey's results are unsatisfactory owing to a number of factors: he took the neighbouring molecules to be in positions which are not consistent with evidence of the structure of ice; he neglected the electric field arising from neighbours other than the nearest four; and he neglected the additional electric field arising from the neighbours owing to their polarization by the central molecule. Surprisingly, there is a fortuitous cancellation of errors in his calculation and his answer is not as far from our value as might be expected. We shall discuss Verwey's calculation in greater detail in section E of this chapter.

Recently suggestions have been made that the dipole moment of ice is greater than former estimates had indicated. C.A. Coulson and D. Smith* made preliminary calculations on the dipole moment of ice which indicated that a thorough investigation of this topic might be fruitful. Soon after we began such an investigation, Onsager and Dupuis(1962) reported an estimate of the dipole moment of H_2O in ice made from dielectric constant data. The authors made use of an expression derived by J.C. Slater for the electric susceptibility of KH_2PO_4 above the Curie point. Assuming that the

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* Private communication from Professor Coulson.

expression, omitting the term for the orthorhombic symmetry of KH_2PO_4, is an adequate description of hexagonal ice, they get for the dipole moment of H_2O in ice:

$$|\vec{m}| = \sqrt{\frac{kT(\epsilon_o - \epsilon_\infty)}{4\pi N'}} \qquad (I\text{-}2)$$

where ϵ_∞ is the dielectric constant at high frequency and N' is the number of molecules per unit volume of ice. Substituting experimental values of the dielectric constant of ice measured by Auty and Cole(1952) they find $|\vec{m}| = 2.94$ D for -10.8°C. The authors believe however that the temperature variation of the dielectric constant above -40°C. indicates an even greater value of the average dipole moment, as large as 3.67 D. This value, approximately twice the dipole moment of water vapour, is based upon the assumptions that Slater's statistical method of computing the dielectric susceptibility is correct; that his expression, symmetric in all coordinates if the orthorhombic correction is omitted, may be applied correctly to hexagonal ice; and that the authors' interpretation of the temperature variation of the dielectric constant is valid. We do not feel able to estimate the magnitude of possible errors in this analysis, but prefer to attempt to calculate the dipole moment from more basic principles.

C. Method of the calculation.

At the outset of our calculation we must choose a convenient model to represent the charge distribution of H_2O. A general type of model is used with small variations by Bernal & Fowler(1933); Magat(1936); Verwey(1941); Rowlinson(1951); Bjerrum(1951); Pople(1951); Campbell(1952); and Cohan et al(1962). It consists of a small number of formal point charges, adjusted in space and magnitude to produce the observed dipole moment. For our purpose this method presents several difficulties. To begin with, although some of these models seem more reasonable than others, it is difficult to find grounds for selecting a 'best' model, and this is disturbing because our results are sensitive to slight changes in the parameters of these models. A second difficulty arises at a stage in our calculation where we must represent the charge distribution of a H_2O molecule distorted by the field of its neighbours. This is similar to the first difficulty but even harder to resolve because we have even fewer criteria for the selection of one representation over another.

A third disadvantage is that these models, though constructed to have the experimental dipole moment, have unreasonable values for the higher moments. Often they predict higher moments of the wrong sign, or moments likely

to be in error by a factor greater than ten. Coulson(1957) has pointed out yet another serious drawback of most of the formal charge models: they neglect the large contribution of the lone-pair electrons to the total dipole moment.

Because of these difficulties with point charge models we have chosen to represent the charge distribution of the H_2O molecule by a multipole expansion. It is well known that the potential of an electric field at an external point arising from an arbitrary distribution of charges may be represented by the sum of the potentials of the charge, dipole, quadrupole, octupole, etc. associated with the charge distribution. We can avoid the problems involved in using point charge models with this multipole expansion method but it is not without difficulties of its own. The most severe difficulty is that although the dipole moment of an isolated water molecule is well established, the higher moments are in doubt. In the absence of experimental values we have decided to use values computed from the best available wave functions for water. A second difficulty is that we have no confidence that our multipole expansion of the potential will converge to the potential of a water molecule when only the first few terms of the expansion are retained. In fact, it is known that convergence is assured only if there is no overlap between the charge clouds of adjacent molecules (Coulson 1959). As we know that this is not the case in ice, probably the

best we can hope for is that the first few terms in our multipole expansion of the potential are an asymptotic representation of the true potential.

Our calculation of the dipole moment of an ice molecule has three stages. In the first, we choose the appropriate values of dipole, quadrupole, and octupole moments of water for use in a multipole expansion. The moments we want are those associated with a water molecule, undistorted other than to have a valence angle equal to the one observed in ice. In the second stage we will calculate the electric field strength, $\vec{E}$, at the nucleus of the oxygen atom of a central molecule arising from the fields of its neighbouring molecules, which are approximated by multipole expansions, using the multipoles determined in stage one. In this stage we will constrain all the molecules to be non-polarizable. In the third stage we will release the constraints on the neighbours and allow them to be polarized by the fields of the central molecule and other neighbours. The polarized neighbours will, of course, have increased multipole moments, and will in turn produce a greater field at the central molecule tending to additionally enhance its moment. This process will continue until there is an equilibrium field $\vec{E}^*$ acting at the nucleus of the central molecule, and from this, and the molecular polarizability of ice, we will calculate $\vec{m}$, the moment of the central molecule.

D. Calculation of the dipole moment of H_2O in ice.

Stage 1: The dipole, quadrupole and octupole moments associated with a water molecule with valence angle of 109° 28'.

The dipole moment of water vapour is a well established quantity. Of those values listed in L.G. Wesson's(1948) compendium of dipole moments, that of Sanger et al(1932), 1.842 ± .008 D, is ascribed the greatest accuracy. The authors used the standard Debye method, measuring the dielectric constant of the vapour over a range of temperatures and densities. As the value of 1.84 D has been corroborated by Groves and Sugden(1935), Hurdis and Smyth (1942) and Golden et al.(1948), we shall take it as the correct value. The last value was measured by the Stark effect, and the others by the Debye method.

The higher moments present a more difficult problem as there are no experimental values available. In fact, the only complete set of quadrupole moment values for water in the literature are those of Duncan and Pople(1953), computed from wave functions. The authors have "hybridized" Slater atomic orbitals to produce the experimental dipole moment and H-O-H angle, and then have computed the quadrupole moments. As there are now more accurate wave functions for water available, we have decided that it would be useful to compute the quadrupole and octupole moments associated with the more accurate wave functions. Dr. Robert Glaeser has kindly carried out these calculations

on two sets of wave functions, the SCF functions of Ellison and Shull(1955) and the bond-orbital wave functions involving seven configuration-interactions (henceforth denoted c.i.7) of McWeeney and Ohno(1960).

a. Glaeser's calculations of $\Theta_{\alpha\beta}$ and $R_{\alpha\beta\gamma}$.

Before describing Dr. Glaeser's calculations we must define the quadrupole moment, $\Theta_{\alpha\beta}$, and the octupole moment, $\Omega_{\alpha\beta\gamma}$, associated with a charge distribution. The quadrupole and octupole moments can be expressed as quantities which are more convenient for calculations. They are the second moment of charge and the third moment of charge defined respectively as:

$$Q_{\alpha\beta} = \int \rho \, r_\alpha \, r_\beta \, d\tau \qquad \text{(I-3)}$$

$$R_{\alpha\beta\gamma} = \int \rho \, r_\alpha \, r_\beta \, r_\gamma \, d\tau \qquad \text{(I-4)}$$

where ρ is the total charge density of the molecule, and r_α, r_β, and r_γ can be x, y, or z. The relations of the quadrupole and the octupole moments to these quantities are given respectively by

$$\Theta_{\alpha\beta} = \frac{1}{2}(3 Q_{\alpha\beta} - Q_{\gamma\gamma} \delta_{\alpha\beta}) \qquad \text{(I-5)}$$

$$\Omega_{\alpha\beta\gamma} = \frac{1}{2}(5 R_{\alpha\beta\gamma} - R_{\alpha\delta\delta} \delta_{\beta\gamma} - R_{\beta\delta\delta} \delta_{\gamma\alpha} - R_{\gamma\delta\delta} \delta_{\alpha\beta}) \qquad \text{(I-6)}$$

where $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$, $\delta_{\alpha\beta} = 0$ if $\alpha \neq \beta$, and repeated suffices imply summation, so that, for example, $\delta_{\alpha\alpha} = \delta_{xx} +$

$\delta_{yy} + \delta_{zz} = 3$. Here, and elsewhere in this thesis, the notation and definitions of multipole moments are essentially those of Buckingham(1959).

A judicious choice of axes causes several components of the second and third moments of charge of water to vanish. Except where noted, we will always choose the bisector of the H-O-H angle as the z-axis, the perpendicular to the plane of the molecule through the oxygen nucleus as the x-axis, and the mutual perpendicular to these as the y-axis. This coordinate system is illustrated in Figure 1. Using this system Q_{xx}, Q_{yy}, and Q_{zz}, are the only non-vanishing $Q_{\alpha\beta}$'s; and $R_{xxz} = R_{xzx} = R_{zxx}$, $R_{yyz} = R_{yzy} = R_{zyy}$ and R_{zzz} are the only non-vanishing $R_{\alpha\beta\gamma}$'s. Later it will be convenient for us to define $Q_A = Q_{zz} - Q_{xx}$, $Q_B = Q_{zz} - Q_{yy}$, $R_A = R_{zzz} - 3R_{xxz}$ and $R_B = R_{zzz} - 3R_{yyz}$.

Dr. Glaeser's calculation of the second and third moments of charge was carried out using the definitions I-3 and I-4, substituting the appropriate ρ. In the case of the Ellison and Shull SCF molecular orbital wave functions, the electronic contribution to ρ is the sum of the squares of the occupied orbitals. Ellison and Shull determined the form of the orbitals by a complete SCF calculation in which molecular orbitals were formed

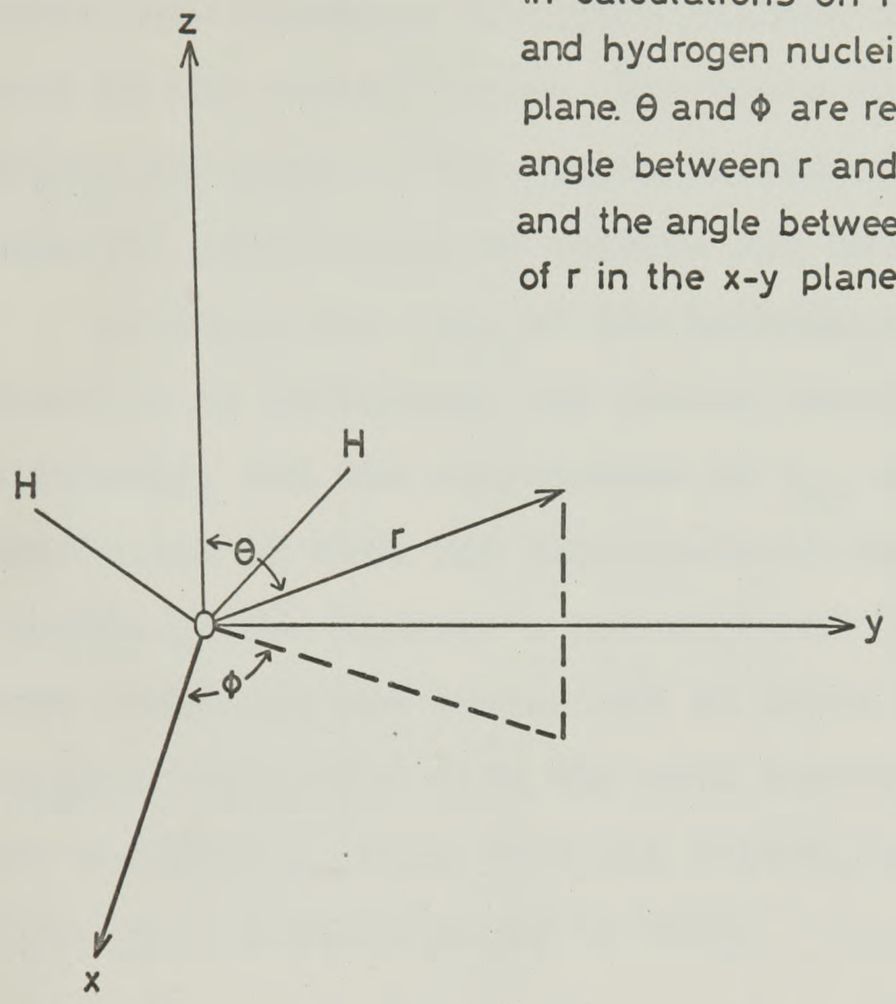


Figure 1. Co-ordinate systems used in calculations on H_2O. The oxygen and hydrogen nuclei are in the z-y plane. θ and ϕ are respectively the angle between r and the z-axis, and the angle between the projection of r in the x-y plane and the x-axis.

from linear combinations of symmetry orbitals possessing the same symmetry type, and the coefficients were calculated by Roothaan's(1951) method. The symmetry orbitals are linear combinations of Slater atomic orbitals taken so as to belong to irreducible representations of the symmetry group of H_2O. Using their coefficients, the calculation of the electronic contribution to $Q_{\alpha\beta}$ and $R_{\alpha\beta\gamma}$ becomes one of evaluating integrals of products of atomic orbitals with terms such as x^2. The nuclear contribution to $Q_{\alpha\beta}$ and

$R_{\alpha\beta\gamma}$ is easily computed and added to the electronic contributions to get $Q_{\alpha\beta}$ and $R_{\alpha\beta\gamma}$. The values of all but the first non-vanishing multipole moments depend on the origin used in the calculations. For these calculations the origin is taken at the oxygen nucleus as this simplifies both the computation of moments and the multipole expansion.

Although the form of the McWeeney-Ohno c.i.7 wave function is different, the charge densities are expressed similarly, and the computation of $Q_{\alpha\beta}$ and $R_{\alpha\beta\gamma}$ follows the same lines as with the Ellison-Shull wave functions. The results of Dr. Glaeser's calculations for both sets of wave functions are summarized in Table 1. The dipole moments associated with the wave functions are also given for reference. Note that all values, except where noted, refer to a valence angle of 105°.

TABLE 1.

Multipole Moments associated with H_2O having a 105° valence angle.

Wave Function	Moment	Value
Ellison and Shull	μ_z	1.52 10^{-18} esu cm
	Q_{xx}	-6.509 10^{-26} esu cm^2
	Q_{yy}	-5.240
	Q_{zz}	-5.481
	$R_{xxz}, R_{xzx}, R_{zxx}$	-1.322 10^{-34} esu cm^3
	$R_{yyz}, R_{yzy}, R_{zyy}$	-0.571
	R_{zzz}	-2.566
McWeeny and Ohno	u_z	1.78* 10^{-18} esu cm
c.i.7	Q_{xx}	-6.556 10^{-26} esu cm^2
	Q_{yy}	-5.172
	Q_{zz}	-5.505
	$R_{xxz}, R_{xzx}, R_{zxx}$	-1.355 10^{-34} esu cm^3
	$R_{yyz}, R_{yzy}, R_{zyy}$	-0.494
	R_{zzz}	-2.746

* This value refers to tetrahedral valence angle.

b. Comparison of Glaeser's quadrupole values with those in the literature.

It is surprising that, although the dipole moments associated with the two wave functions differ considerably, the second and third moments of charge are nearly identical. Even more surprising is that the second moments of charge are within 6% of the corresponding values calculated by Duncan and Pople(1953) (Q_{xx} = -6.547, Q_{yy} = -5.480, Q_{zz} = -5.801). Since the outer regions of the wave functions are weighted very heavily in the calculation of the higher moments, the near equivalence of the higher moments may be an indication that the outer regions of the Ellison-Shull and the McWeeny-Ohno wave functions are nearly identical, and not very different from the outer regions of the Duncan-Pople functions. As the Duncan-Pople functions are made up of simple combinations of Slater orbitals, which are well known to be inaccurate in the outer regions, the near equivalence of higher moments may indicate that they are all in error.

There have been very few experimental estimates of quadrupole moments of water. Rowlinson(1951) correlates the second virial coefficient of steam to its second moment of charge, but he makes several questionable assumptions. He supposes that a triangular model of an H_2O molecule may be described by one quadrupole moment. This is true only if a particular origin is chosen. He then carries out his

expansion from an origin different from the one which causes one of the quadrupole moments to vanish, and it is therefore unlikely that his estimate of the one non-vanishing quadrupole moment is at all accurate.

Buckingham(1957) estimates the value of the quantity (Q_A+Q_B) for water to be $3.9\ 10^{-26}$ esu cm^2 from the difference of enthalpies ofhydration of K^+ and F^- ions. This value is approximately five times the one obtained from Glaeser's calculations.* Buckingham's estimate is based on a model in which a water molecule interacts with an ion located along its dipolar axis. Assuming the interactions of the water molecule with the K^+ and F^- ions are identical except for the opposite direction of the dipolar axis in the two cases, the ion-dipole energies of interaction are identical, and it is possible to evaluate (Q_A+Q_B). Of course, such a model is bound to be oversimplified, and there may be causes of different enthalpies of hydration of K^+ and F^- other than unequal ion-quadrupole energies. Vaslow(1963) has used Buckingham's estimate of (Q_A+Q_B) in calculations of ion-water interaction. He has made calculations with three separate sets of Q_A and Q_B values, the sum of each set being equal to 3.9×10^{-26} esu, but has not considered any case in

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* Buckingham's Q's refer to the centre of mass of the water molecule as the origin, whereas Glaeser's Q's refer to the oxygen nucleus as origin, so that the values are not strictly comparable. In fact, the correction for change of origin slightly increases the disparity.

which Q_B is negative, as Glaeser has found. We have found that, taking the ratio of Q_A to Q_B computed by Glaeser and the sum of Q_A and Q_B calculated by Buckingham, the fields arising from the quadrupole moments are unreasonably large. This suggests that Buckingham's value of (Q_A+Q_B) may be too great.

From the foregoing discussion we conclude that, at the present time, the quadrupole and octupole moments of water calculated by Glaeser are probably the most accurate values available.

c. Values of the moments associated with an unpolarized ice molecule.

Neutron diffraction studies (Peterson and Levy, 1957) indicate that the valence angle of water in D_2O ice is very nearly tetrahedral,* as opposed to steam where it is 104° 31' (Darling and Dennison, 1940). The first step in computing the enhancement of the dipole moment of an ice molecule must be to enlarge the valence angle of a steam molecule to 109° 28' and use the moments associated with this distorted molecule in our multipole expansion. Obviously it is artificial to separate this distortion from other distortions which we consider in Stage 2, but we do so for facility of computation.

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* These studies have also provided accurate O-D distances (1.01Å)

The change of dipole moment with valence angle is simply related to an observable quantity, the absolute intensity of infra-red absorption, but unfortunately no careful study of absolute intensities of water vapour absorption has been made. We must therefore estimate this quantity from calculations. McWeeny and Ohno(1960) have computed μ_o from seven wave functions for both 105° and 109° 28', and μ_o is an average of 0.06 D greater for the smaller angle. On the basis of this result and the experimental value of μ_o of steam (1.84 D) we will take μ_o of ice to be 1.78 D. This happens to be the same value calculated from the McWeeny-Ohno c.i.7 wave function for the tetrahedral angle.

The fields arising from higher moments of an ice molecule are a small percentage of the total field. For this reason we will neglect the small changes which will occur in the second and third moments of charge when the valence angle is enlarged. Hence, the moments which we shall use in our multipole expansion in Stage 2 are simply those in the lower half of Table 1.

2. Stage 2: the electric field strength, $\vec{E}$, at an ice molecule arising from non-polarizable neighbouring molecules.

In this stage we shall first develop the explicit form of our multipole expansion of the field. Then we shall consider the structure of ice to determine the location and

orientation of the point multipoles, and finally we shall compute the field strength at the oxygen nucleus of an arbitrary central molecule.

a. The multipole expansion.

Let us consider the potential V at a point P(X,Y,Z), distance r from the origin, arising from the charge distribution $\rho(x',y',z')$ occupying a volume $d\tau$ near the origin. This is given by

$$V = \int \frac{\rho}{R'} \, d\tau, \qquad \text{(I-6)}$$

where R' is the distance between the point of observation P, and the position P'(x',y',z') of the element of charge $\rho d\tau$:

$$R' = \left[(X-x')^2 + (Y-y')^2 + (Z-z')^2\right]^{\frac{1}{2}}$$

Since P is fixed, R' is a function of the variables x', y', and z', and we may expand 1/R' in a Taylor series near the origin. This gives

$$V = \int \rho \left[\frac{1}{r} + \left(\frac{\partial(1/R')}{\partial r'_\alpha}\right)_0 r'_\alpha + \frac{1}{2!}\left(\frac{\partial^2(1/R')}{\partial r'_\alpha \partial r'_\beta}\right)_0 r'_\alpha \, r'_\beta + \frac{1}{3!}\left(\frac{\partial^3(1/R')}{\partial r'_\alpha \partial r'_\beta \partial r'_\gamma}\right)_0 r'_\alpha \, r'_\beta \, r'_\gamma + \cdots\right] d\tau \qquad \text{(I-7)}$$

where, as before, r'_α, r'_β, and r'_γ can be x', y', or z', and the 0 subscripts indicate that the derivatives must be evaluated at the origin.

The derivatives are easily found. They are:

$$\left[\frac{\partial(1/R')}{\partial r'_\alpha}\right]_0 = \frac{r_\alpha}{r^3} \qquad \text{(I-8)}$$

$$\left[\frac{\partial^2(1/R')}{\partial r'_\alpha \partial r'_\beta}\right]_0 = (3r_\alpha r_\beta - r^2\delta_{\alpha\beta})/r^5 \qquad \text{(I-9)}$$

$$\left[\frac{\partial^3(1/R')}{\partial r'_\alpha \partial r'_\beta \partial r'_\gamma}\right]_0 = 3\left[5r_\alpha r_\beta r_\gamma - r^2(r_\alpha\delta_{\beta\gamma} + r_\beta\delta_{\gamma\alpha} + r_\gamma\delta_{\alpha\beta})\right]/r^7 \qquad \text{(I-10)}$$

where r_α, r_β, and r_γ can be X, Y, or Z and $\delta_{\alpha\beta} = 0$ if $\alpha \neq \beta$, and $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$. Substituting equations I-8, I-9, and I-10 into I-7 and making use of the definitions of the multipole moments, we get

$$V = \int \frac{\rho}{r}\, d\tau + \frac{\mu_\alpha r_\alpha}{r^3} + \frac{1}{2}\frac{Q_{\alpha\beta}}{r^5}(3r_\alpha r_\beta - r^2\delta_{\alpha\beta}) + \frac{1}{2}\frac{R_{\alpha\beta\gamma}}{r^7}\left[5r_\alpha r_\beta r_\gamma - r^2(r_\alpha\delta_{\beta\gamma} + r_\beta\delta_{\alpha\gamma} + r_\gamma\delta_{\alpha\beta})\right] + \ldots \qquad \text{(I-11)}$$

Up to this point the discussion has been general; we now consider the case of water. We know that for water the formal charge and all multipole moments in equation I-11 vanish except for those listed in Table I. This means

$$V = \frac{\mu_z Z}{r^3} + \frac{1}{2r^5}\left[Q_{xx}(3XX-r^2) + Q_{yy}(3YY-r^2) + Q_{zz}(3ZZ-r^2)\right]$$

$$+ \frac{1}{2r^7}\left[3R_{xxz}(5XXZ-r^2Z) + 3R_{yyz}(5YYZ-r^2Z) + R_{zzz}(5Z^3-3r^2Z)\right]$$

$$+ \ldots \qquad \text{(I-12)}$$

We can simplify equation I-12 and transform it to spherical polar coordinates using the following relations:

$X^2+Y^2+Z^2 = r^2$; $X = r \sin\theta \cos\phi$;

$Z = r\cos\theta$; $Q_A = Q_{zz} - Q_{xx}$; $Q_B = Q_{zz}-Q_{yy}$,

$R_A = R_{zzz} - 3R_{xxz}$; and $R_B = R_{zzz} - 3R_{yyz}$;

where ϕ and θ are the angles shown in Figure 1. This gives our final equation for the electrostatic potential:

$$V = \frac{\mu_z \cos\theta}{r^2} + \frac{1}{2r^3}\left[Q_A(1-3\sin^2\theta\cos^2\phi) + Q_B(3\cos^2\theta + 3\sin^2\theta\cos^2\phi - 2)\right] +$$

$$+ \quad \frac{1}{2r^4}\left[R_A\,(\cos\theta - 5\sin^2\theta\cos^2\phi\cos\theta)\right.$$

$$\left. + R_B(5\sin^2\theta\cos^2\phi\cos\theta + 5\cos^3\theta - 4\cos\theta) + \ldots\right] \quad \text{(I-13)}$$

It is now a simple matter to calculate the electric field $\vec{E}$ from $\vec{E} = -\vec{\nabla}V$. The components of $\vec{E}$ in spherical coordinates are:

$$E_r = \frac{2\mu\cos\theta}{r^3} + \frac{3}{2r^4}\left[Q_A(1-3\cos^2\phi\sin^2\theta)\right.$$

$$\left. + Q_B(3\cos^2\theta + 3\sin^2\theta\cos^2\phi - 2)\right]$$

$$+ \frac{2}{r^5}\left[R_A(\cos\theta - 5\sin^2\theta\cos^2\phi\cos\theta) + \right.$$

$$\left. R_B(5\sin^2\theta\cos^2\phi\cos\theta + 5\cos^3\theta - 4\cos\theta\right] + \ldots \quad \text{(I-14)}$$

$$E_\theta = \frac{\mu\sin\theta}{r^3} + \frac{3}{r^4}\left[Q_A(\cos^2\phi\sin\theta\cos\theta) + Q_B(\cos\theta\sin\theta\sin^2\phi\right]$$

$$+ \frac{1}{2r^5}\left[R_A(10\cos^2\phi\sin\theta\cos^2\theta + \sin\theta - 5\cos^2\phi\sin^3\theta)\right.$$

$$+ R_B(15\cos^2\theta\sin\theta + 5\cos^2\phi\sin^3\theta - 4\sin\theta -$$

$$\left. 10\cos^2\phi\sin\theta\cos^2\theta\right] + \ldots \quad \text{(I-15)}$$

$$E_\phi = \frac{3}{r^4}\left[\sin\theta\cos\phi\sin\phi\,(Q_B - Q_A)\right]$$

$$+ \frac{5}{r^5}\left[\sin\theta\cos\theta\cos\phi\sin\phi\,(R_B - R_A)\right] + \ldots \quad \text{(I-16)}$$

When we put $Q_A = Q_B$ and $R_A = R_B$, equations I-13, I-14, I-15, and I-16 reduce to the corresponding simpler equations which Buckingham(1959) has derived for the case of axially

symmetric charge distributions.

Our method of representing the electric field in an ice crystal composed of non-polarizable H_2O molecules is to place the multipole expansion described by equations I-14, I-15, and I-16 at each lattice point of the crystal. The origin of each expansion is the corresponding oxygen nucleus, and the z-axis of each expansion is the dipolar axis of the corresponding ice molecule. We are therefore able to compute the resulting electric field once we know the positions and orientations of the ice molecules.

b. The structure of ice.

The relative positions of the oxygen atoms in ice are firmly established. Barns(1929) studied single ice crystals by X-ray methods and arrived at the structure shown in Figure 2.* The principle characteristic of this structure is that each oxygen atom is at the centre of a regular tetrahedron, having four oxygen atoms at the corners, each 2.76 Å from the central atom. The space group is P $6_3/mmc$, with four atoms at $\pm|1/3, 2/3, z_o;\ 2/3, 1/3, \frac{1}{2}+z_o,|\ z_o$ being very nearly 1/16 (Peterson & Levy, 1957).

The positioning of the hydrogen atoms was a matter of dispute for a number of years but now seems fairly certain.

---

* Figure 2 is an adaptation of a diagram in a paper by P.A. Owston(1958).

Barnes(1929) suggested that ice molecules are ionized to form 2 $H^+ + O^=$, with the H^+ ions located midway between two $O^=$ ions, along their line of centres. Bernal and Fowler (1933) pointed out that such a structure is unreasonable in the light of infra-red and Raman spectra. The vibrational spectrum of ice is so similar to that of steam that it indicates H_2O molecules must be intact in the solid as they are in the vapour. Bernal and Fowler proposed a scheme of regular orientation of ice molecules (i.e. regular location of hydrogen atoms about the oxygen atoms) at low temperatures, and a non-regular arrangement for temperatures just below the melting point. The particular regular arrangement they suggest for lower temperatures has a net dipole moment and should lead to piezo- and pyro-electric properties which are not observed (Owston, 1958).

Pauling(1935) argued persuasively that the orientations of ice molecules are non-regular even at temperatures approaching 0^oK. His method was to show that the assumptions of non-regular orientations predict the observed value of the residual entropy. It is convenient to follow Pauling in numbering his assumptions:

> (1) The orientations of adjacent ice molecules are such that only one hydrogen atom (or rather hydrogen nucleus) lies along each oxygen-oxygen axis.
>
> (2) Ice molecules are intact, and the two hydrogen nuclei bonded to a given oxygen atom are hydrogen-

bonded to two of the four first-neighbour oxygen atoms.

(3) Under ordinary conditions the interaction of non-adjacent molecules is not such as to appreciably stabilize any one of the many configurations satisfying the preceding conditions with reference to the others.

At low temperatures the residual entropy, S_o, is given by $S_o = k \ln W$, where W is the number of configurations accessible to the crystal, and is computed as follows: if there are N molecules in a mole of ice, and if each hydrogen nucleus along a hydrogen-bond has a choice of two positions, one near one oxygen atom and the other near the other, then there are 2^{2N} configurations in the crystal. Many of these are ruled out by the assumption that ice molecules are intact. This assumption permits the four hydrogen nuclei about a given oxygen atom to assume only 6 of the 2^4 possible configurations. Thus the total number of permitted configurations is $W = 2^{2N}(6/16)^N = (3/2)^N$, and the residual entropy is $S_o = k \ln W = 0.805$ e.u. This is in excellent agreement with the experimental value, $S_o = 0.82 \pm 0.15$ e.u. (Giauque & Ashley, 1933 and Giauque & Stout, 1936). Recently, several more rigorous calculations of the residual entropy of ice have been made (e.g. DiMarzio & Stillinger, 1964), but all confirm that Pauling's calculation is correct to within 1%.

If the energy differences between permitted configurations are small compared to kT at very low temperatures,

then a fortiori, the differences are small at temperatures near the melting point. Hence, ice molecules under ordinary conditions are randomly oriented, other than obeying the restrictions of assumptions (1) and (2). This random structure of ice is often known as the "statistical structure".

No experimental data on ice are in conflict with the implications of the statistical structure, and many lend support to it. The high dielectric constant of ice (Auty & Cole, 1952), and the narrowing of nuclear magnetic absorption lines (Kume & Hoshino, 1961) show that ice molecules are constantly changing in orientation at temperatures above -60°C. Neutron diffraction studies of D_2O ice (Peterson & Levy, 1957) indicate that the $(3/2)^N$ permitted configurations of the statistical structure occur with roughly equal frequency, as Pauling predicted.

For completeness we mention that for a number of years Pauling's proposal of the statistical structure was not generally accepted. Dissatisfaction with it was based on a calculation by Bjerrum(1951), who, using a formal point charge model for an ice molecule, found that certain configurations of molecules are more stable than others. Even at the melting point, the differences in energy of the configurations are enough to strongly favour a highly ordered structure. This led Rundle(1955) and others to

attempt to devise structures for ice which would favour the electrostatically stable configurations of Bjerrum, as well as possess the observed residual entropy. However, in 1956 Pitzer and Polissar found that contributions to the energy arising from neighbouring molecules neglected in Bjerrum's calculation substantially reduced the energy differences which he had found, and the statistical model was again generally accepted.

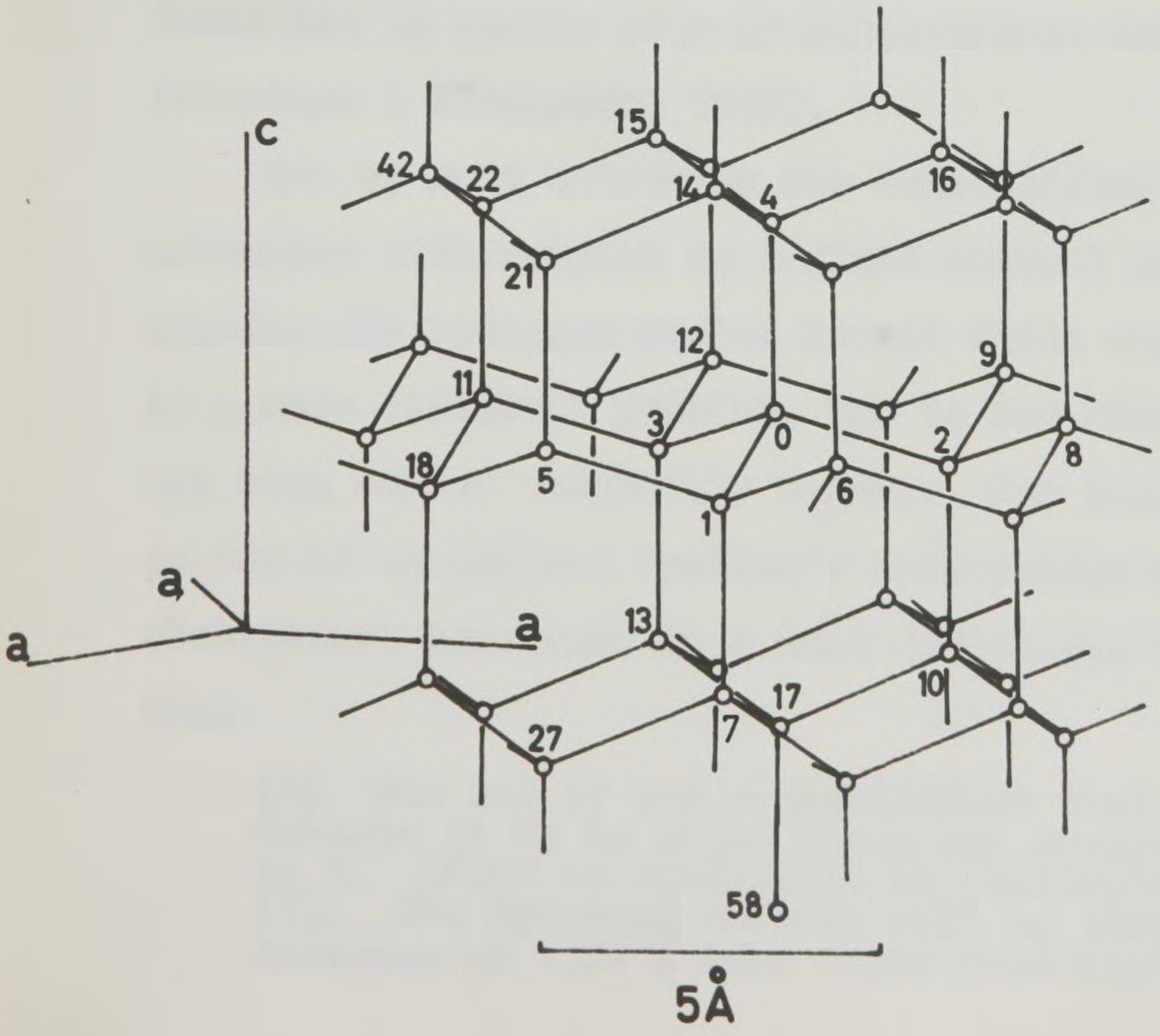
c. Positions and orientations of neighbours with respect to a central molecule in ice.

Having discussed the structure of ice, we are able to determine the location and orientation of neighbours with respect to a fixed central molecule. We will begin by locating the neighbouring oxygen atoms and later we will determine the positions of the corresponding hydrogen nuclei, which will fix the orientations of the neighbouring molecules.

We choose an arbitrary oxygen atom as the "central atom", say the one labelled O in Figure 2. Since atoms not near a surface of the crystal are identical with respect to surrounding oxygen atoms, it makes no difference which one we choose. We shall call the four oxygens adjacent to the central molecule "first neighbours" (labelled 1, 2, 3, and 4 in Figure 2), the twelve other oxygen atoms adjacent to the first neighbours "second neighbours" (labelled 5, 6, ... 16 in Figure 2), and so forth. Obviously some third

FIGURE 2.

Structure of ordinary ice. The c-axis is parallel to the sides of the page. Oxygen atoms are shown as open circles; hydrogen atoms are not shown. The line between two oxygen atoms represents one O—H····O bond. The numbers refer to molecules discussed in the text.



neighbours are adjacent to more than one second neighbour (e.g. 17 and 18), whereas others are adjacent to only one second neighbour (e.g. 27), so that the number of neighbours of each type will not continue to rise by factors of three. By constructing a stick-and-ball model of ice, it is a simple matter to count the number of each type of neighbours, and to compute their distances from the central atom. Such results for ordinary ice are shown in the upper half of Table 2. The lower half of Table 2 contains corresponding results for cubic ice, which we shall discuss briefly in the next chapter. This form of ice exhibits tetrahedral coordination like ordinary, hexagonal ice, but the oxygen atoms have the configuration of the carbon atoms in diamond. Cubic ice is stable only at temperatures below -110°C. (Blackman & Lisgarten, 1957).

Now we must determine the orientations of the ice molecules with respect to a fixed central molecule by placing the hydrogen nuclei around these oxygen atoms. This is a more difficult problem, and to our knowledge, it has not been solved completely before. Our task will be easier if we restate Pauling's assumptions regarding the statistical structure in a form convenient for our determination:

> (1) The sum of the probabilities that a hydrogen nucleus is to be found along any oxygen-oxygen axis is 1. (This is equivalent to Pauling's assumption (1). The hydrogen nucleus will be located at a distance of 1.01 Å (the "near position") from one

Table 2

Number of neighbouring molecules to an arbitrary "central" molecule in ice and their distances from the central molecule.

Neighbours	Number	Distance from central molec.
Hexagonal ice:		
1st	4	2.76 10^{-8}cm
2nd	12	4.51
3rd H-bonded to 3 2nd's	1	4.60
" " 2 "	9	5.28
" " 1 2nd	6	6.44
" " 1 "	9	6.95
4th " " 2 3rd's	7	7.36
" " 2 "	9	7.80
" " 1 "	28	various
5th " " 2 4th's	36	various
Cubic ice:		
1st	4	2.76
2nd	12	4.51
3rd H-bonded to 2 2nd's	12	5.28
" " 1 2nd	12	6.95
4th " " 2 3rd's	6	7.36
" " 2 "	12	7.80
" " 1 3rd	25	various

of the oxygen atoms.)

(2) The sum of the probabilities that hydrogen nuclei are located at a distance of 1.01 Å from any given oxygen atom, along the four oxygen-oxygen axes towards adjacent atoms is 2. (This is equivalent to Pauling's assumption (2); it implies H_2O molecules are intact and neglects the very small concentration of ionized molecules.)

(3) There are no constraints on the positions of hydrogen nuclei about a given oxygen atom other than assumptions (1) and (2) and the constraints imposed by the hydrogen nuclei already placed about the oxygens adjacent to the given oxygen atom.

We start by arbitrarily placing one of the two hydrogen nuclei associated with oxygen atom 0 1.01 Å along the oxygen-oxygen axis (in the near position) between atoms 0 and 1 and the other in the near position along the axis between atoms 0 and 3. In other words, we arbitrarily assign the orientation of molecule 0 just as we arbitrarily chose its location above. We could have chosen any of the five other orientations for molecule 0; all give the same final result.

Now we are able to calculate the probable positions of all other hydrogen nuclei in the crystal by applying our assumptions (1), (2), and (3). A schematic diagram of an ice crystal, Figure 3, will assist us in making this calculation. Oxygen atoms are represented by circles; the number in each circle is the number of the oxygen atom in Figure 2 which it represents, and the line between two circles represents the axis between the two oxygen atoms.

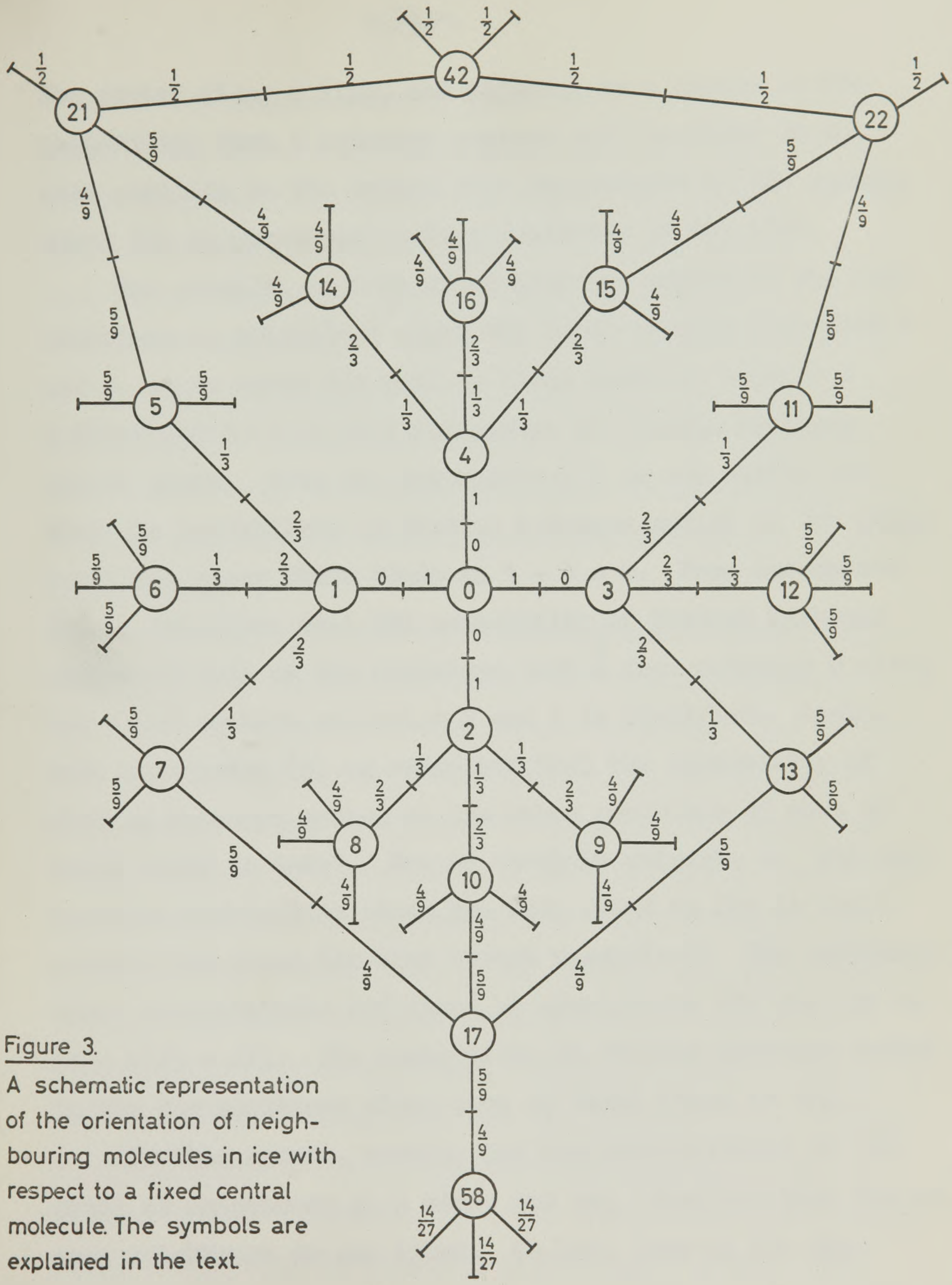


Figure 3.

A schematic representation of the orientation of neighbouring molecules in ice with respect to a fixed central molecule. The symbols are explained in the text.

The number along a line, and adjacent to a circle is the probability that a hydrogen nucleus will be found in the near position to the oxygen atom represented by the circle, along the oxygen-oxygen axis represented by the line.

For example, we have fixed hydrogen nuclei in the near positions to molecule 0 along the bonds towards molecules 1 and 3, so we write 1's next to these bonds to signify a probability of 1, i.e. a certainty, of finding hydrogen nuclei there. From our assumption (1) we can easily see that the probability of finding hydrogen nuclei on the other positions along these bonds is 1 - 1 = 0. From assumption (2) we calculate that the probability of finding hydrogen nuclei in each of the positions 1.01 Å from molecule 0 along the bonds towards molecules 2 and 4 is (2-2)/2=0. Again, from assumption (1) we calculate that the probability of finding hydrogen nuclei on the other positions of each of these bonds is 1-0=1. Now we consider molecule 1: its only hydrogen probability which has been fixed so far is the 0 probability along the bond toward molecule 0. The remaining three probabilities are fixed by assumptions (2) and (3) as (2 - 0)/3 = 2/3. The probability of finding hydrogen nuclei in the far positions along each of these bonds is 1/3.

In this manner, working out the probabilities of one shell of neighbours at a time, one can calculate them for as many neighbours as one likes. We have done so for the

nearest 121 neighbours to a fixed molecule in ordinary ice (all first, second, third, and fourth neighbours, and all fifth neighbours shared by two fourth neighbours), and for the nearest 58 neighbours in cubic ice (all first, second, and third neighbours, and all fourth neighbours shared by two third neighbours). Figure 3 shows a small portion of these results for ordinary ice. We shall spare the reader the confusion of the full diagram for the 121 neighbours, which would take four additional pages to present with even minimal clarity, and content ourselves with making a comment about Figure 3.

It is apparent that the further a molecule is from the central molecule, the more likely it is to be oriented randomly with respect to the central molecule. For example, the hydrogens of molecule 42 - one of the nearest fourth neighbours - shown at the top of Figure 3, are found with equal probability in each of its near positions. This means that it is equally likely to be found in each of its six possible orientations, and on the average its dipole will make no contribution to the electric field tending to polarize the central molecule. Similarly, the maximum deviation from a value of $\frac{1}{2}$ for the probability of finding a hydrogen nucleus in a near position to molecule 58, another fourth neighbour, is 1/18. Among many sixth neighbours the maximum deviation from $\frac{1}{2}$ is only 1/324. This

increasing randomness of orientation of more distant neighbours assures us that the total contribution to the field from molecules more than a few molecular diameters from the central molecule is negligible. This can be clearly seen in the results.

d. The calculation of $\vec{E}$, the electric field tending to polarize the central molecule, when the molecules are constrained to be non-polarizable.

Having obtained equations I-14, I-15, and I-16, and a knowledge of the positions and orientations of the neighbouring molecules, the computation of $\vec{E}$ is a matter of numerical evaluation. The contribution to $\vec{E}$ from the dipole moments associated with neighbouring molecules was evaluated with the assistance of the Mercury Computer at the Oxford University Computing Laboratory. Input data consisted only of the coordinates of the neighbours with respect to the central molecule and the hydrogen probabilities, as computed in the previous section. A simple programme calculated the probability of finding each neighbour in each of its six possible orientations, and then evaluated the first terms of equations I-14, and I-15, for each neighbour, weighting the contributions from the various orientations. These results are given in the first column of Table 3.

Table 3.

Contributions to $\vec{E}$, the electric field strength at the oxygen nucleus of a central molecule in ice, arising from neighbouring molecules in their average configurations. All figures are in units of 10^6 esu cm^{-2}.

	Dipole	Quadrupole	Octupole	Total
First Neighbours	0.2260	0.0828	-0.0007	0.3081
Second Neighbours	0.0432	0.0010	-	0.0442
Third Neighbours	0.0179	-	-	0.0179
Shared Fourth Neighbours	0.0048	-	-	0.0048
Total	0.2919	0.0838	-0.0007	0.3750

The contributions to $\vec{E}$ arising from the quadrupole and octupole moments associated with neighbouring molecules are shown in the second and third columns of Table 3. The field from the quadrupole moments, over 20% of the total field, is by no means negligible, although the field from quadrupoles farther than the first neighbours is less than 0.5% of the total. The very small value of the field arising from the octupole moments associated with the first neighbours, may, perhaps, be misleading. Octupoles of

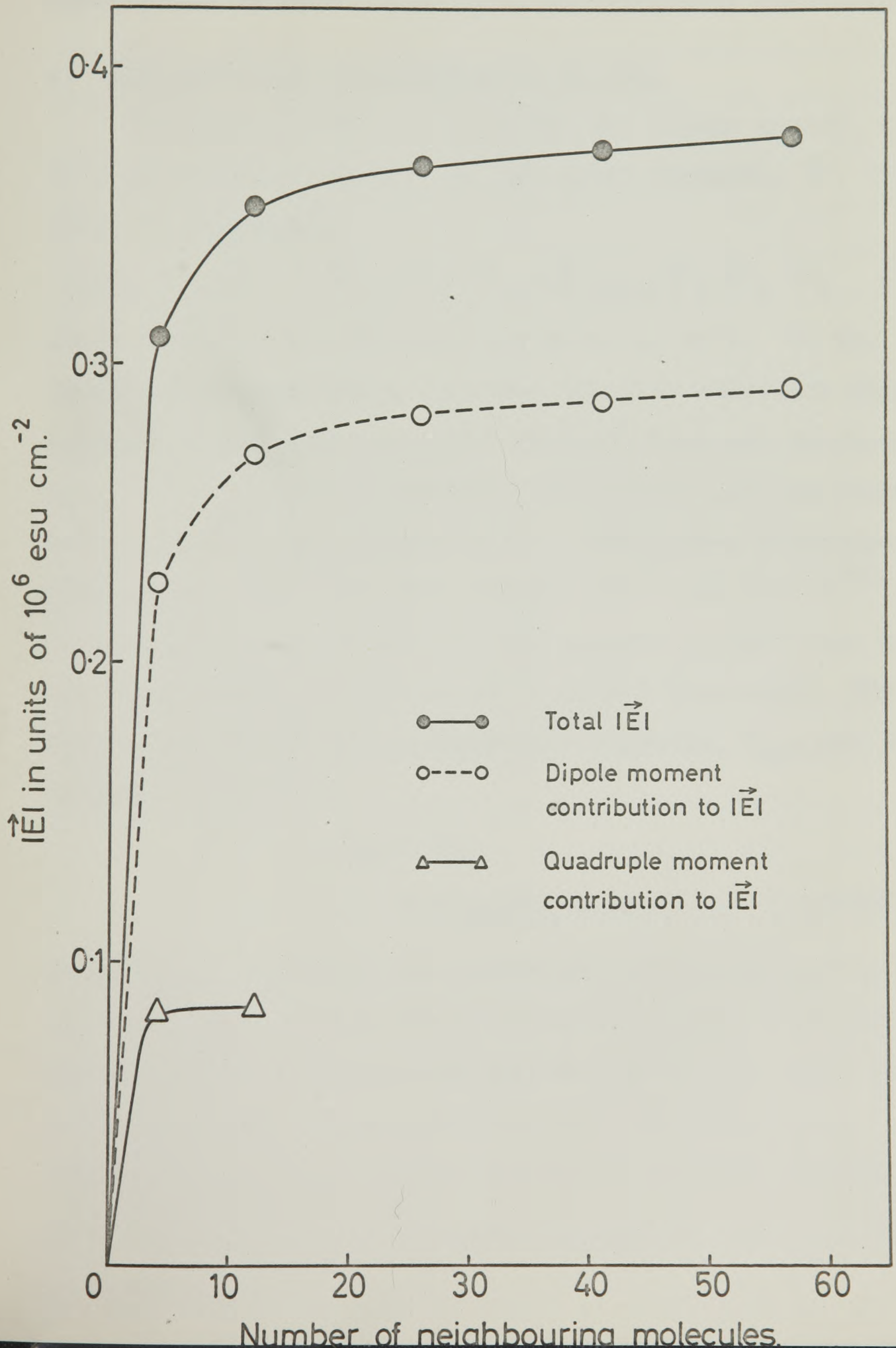
single first neighbours produce contributions to $\vec{E}$ as large as $+0.0179\ 10^6$ esu cm^{-2}, but these are opposed by slighly larger contributions of opposite sign from other first neighbours, so that the average $\vec{E}$ from the octupoles nearly vanishes. The contributions to $\vec{E}$ are shown graphically in Figure 4.

The direction of $\vec{E}$ is the same as that of the dipole moment of the central molecule. This is expected because the central molecule is likely to position itself in such a way as to minimize the energy of interaction of its dipole moment in the field arising from its neighbours. If we had found any other direction, it would have thrown doubt on our assumption of the statistical structure of ice. Because $\vec{E}$ has the direction of the permanent moment of the central molecule, the induced moment, $\vec{\mu}'$, will have the same direction as the permanent moment.

3. Stage 3: <u>the average electric field strength, $\vec{E}^*$, acting at the oxygen nucleus of an ice molecule, arising from its polarizable neighbours</u>.

Up to this point we have assumed that ice molecules are not distorted by the electric fields of neighbouring molecules. Of course, this is not the case: the charge distributions of real ice molecules are distorted by neighbouring molecules, and their multipole moments are altered. Accordingly, we must consider these effects in our

Figure 4. Contributions to $|\vec{E}|$, the value of the electric field strength at a central molecule in ice, arising from neighbouring molecules in their average configurations.



calculation. We begin by discussing the most important description of this distortion, the molecular polarizability.

a. The molecular polarizability of ice.

Buckingham(1959) has expanded the dipole moment, m_α, of a polarizable molecule in the field strength, $\vec{E}^*$, arising from its neighbours

$$m_\alpha = \mu_o + \alpha_{\alpha\beta} E^*_\beta + \tfrac{1}{2}\beta_{\alpha\beta\gamma} E^*_\beta E^*_\gamma + \tfrac{1}{6}\gamma_{\alpha\beta\gamma\delta} E^*_\beta E^*_\gamma E^*_\delta \quad \text{(I-17)}$$

where Greek letter suffices can be x, y, or z. Of the tensorial coefficients, $\alpha_{\alpha\beta}$, the familiar molecular polarizability, is the only one about which we have any knowledge. $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are "hyperpolarizabilities" and are significant only for large values of $\vec{E}^*$. Buckingham estimates that β and γ for water are roughly 10^{-30} esu and 10^{-36} esu respectively, and if this is so, neglect of them will cause our final value of $\vec{m}$ to be about 0.03 D too small. The quadrupole moment of a polarizable molecule, $T_{\alpha\beta}$, may be written similarly

$$T_{\alpha\beta} = \Theta_{\alpha\beta} + A_{\gamma:\alpha\beta} E^*_\gamma + \ldots \quad \text{(I-18)}$$

where $A_{\alpha:\alpha\beta}$ describes the quadrupole moment induced in the molecule by $\vec{E}^*$. We have no knowledge of this coefficient either, so we are forced to neglect the change in $\vec{E}^*$ arising from the induced quadrupole moments. Hopefully this change is not large because the field strength arising from the undistorted quadrupole moments is less than 25% of the total of $\vec{E}$.

The molecular polarizability, $\alpha_{\alpha\beta}$, is in general given by a second rank tensor, which is symmetric for non-optically active molecules, and diagonal when the components are taken to be the polarizabilities along the principal axes of the molecule. If we call the polarizabilities along the principal axes of water (see Figure 1) α_{xx}, α_{yy}, and α_{zz}, then the mean of these components, $\bar{\alpha}$, is the average polarizability, deduced from the Lorenz-Lorentz equation:

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}). \qquad \text{(I-19)}$$

Since, as we noted in Stage 2, $\vec{E}$ in ice has the direction of $\vec{\mu}_o$ (the z direction in Figure 1), α_{zz} is the only component of $\alpha_{\alpha\beta}$ needed to describe the distortion of an ice molecule.

Dorsey(1940) reports that the most reliable value for $\bar{\alpha}$ of steam is $1.59\ 10^{-24}$ cm^3. Verwey(1941) and others have used this and similar values for α_{zz} of ice. This, of course, is justified only if it is assumed that $\bar{\alpha} = \alpha_{zz}$, and if α_{zz} has the same value for steam and ice. We will discuss both of these assumptions, beginning with the latter.

In general, the change of molecular polarizability with density is poorly understood. Brown(1956) discusses a number of rigorous calculations of polarizabilities of atomic and molecular assemblies using concepts other than the hyperpolarizabilities mentioned above. Some indicate

that the polarizability of an individual molecule ceases to be a useful concept at high densities. In any case, the basic theory of polarizabilities is not thoroughly enough developed to be of use here.

Unfortunately, differences in the polarizability of H_2O in its three phases are especially difficult to understand. The difficulty arises from the anamalous behaviour of the refractive indices of liquid water and ice, the observable from which α is derived. Usually the dielectric constant of a substance at high frequencies of the applied field, ϵ_∞, is very nearly equal to the square of its refractive index at optical frequencies, n^2. However, for both ice and water ϵ_∞ is significantly greater than n^2. One explanation given for this discrepancy (Eg. Cartwright & Errera, 1936) is that the distortion polarizability of H_2O is increased in the condensed phases owing to an increase in the so-called atomic polarizability. In section C of the next chapter we discuss this problem in detail, and conclude that the best data available suggests that the difference $\epsilon_\infty - n^2$ in ice is not the result of increased distortion polarizability, and that the correct value of n^2 for use in calculating is 1.77, the value of n^2 of ice in the near infra-red.

The Lorenz-Lorentz equation relates the molecular polarizability and refractive index of gases and non-polar

molecules in cubic crystals. It is given by

$$\frac{n^2-1}{n^2+1} = \frac{4\pi}{3} N' \bar{\alpha} \qquad \text{(I-20)}$$

where N' is the number of molecules per unit volume. It is well known that this equation fails for polar liquids and solids in applied fields of radio frequencies because, among other factors, it takes no account of the opposition of the fields of their dipoles to the applied field. However, at optical and near infra-red frequencies the permanent dipoles or ionic charges of a substance seem to have little effect on its polarization by the applied field, and the substance may be treated as if it is composed of non-polar molecules (Bottcher, 1952, p. 289). In support of this interpretation are the results of Tessman and Kahn(1953). They find that the Lorenz-Lorentz equation gives good values for the electronic refraction of a number of ionic crystals. In the absence of a more rigorous theory for molecular crystals we accept this interpretation for ice, and insert 1.77 for n^2 in equation I-20. We find

$$\bar{\alpha} = 1.59\ 10^{-24}\ \text{cm}^3 \qquad \text{(I-21)}$$

which is identical to the value of $\bar{\alpha}$ for steam reported by Dorsey(1940).

Recently W.H. Orttung(1963) has calculated $\bar{\alpha}$ of liquid water from another relation of n^2 and $\bar{\alpha}$. This is Bottcher's equation:

$$\frac{12\pi n^2 N'}{(n^2-1)(2n^2+1)} = \frac{1}{\bar{\alpha}} - \frac{2n^2-1}{a^3(2n^2+1)} \qquad \text{(I-22)}$$

where a is called the molecular radius and is considered to be independent of temperature. A derivation of this equation is given in Appendix A. Orttung has plotted the left-hand side of equation I-22 against $(2n^2-1)/(2n^2+1)$, and has found that his data do not fall along a straight line. He has computed $\bar{\alpha}$ and a, by drawing a tangent to a relatively straight portion of the curve. The resulting values of $\bar{\alpha}$ for various optical frequencies fall between 1.34 and 1.36 10^{-24} cm^3. Although Orttung gives his results for $\bar{\alpha}$ to seven significant figures, he does not mention that they differ in the second from the value of $\bar{\alpha}$ of the vapour. In contrast to Bottcher's equation, the Lorenz-Lorentz equation gives values of $\bar{\alpha}$ approximately equal to 1.48 10^{-24} cm^3 in this frequency range, nearly the vapour value, and nearly the value of $\bar{\alpha}$ for ice obtained from the Lorenz-Lorentz equation. That the Lorenz-Lorentz equation produces a more likely result in this case than Bottcher's equation is not surprising. The former relation is based on the model of a cubic crystal which is probably a better approximation to liquid water than is the model of a continuous environment at one molecular diameter from the molecule under consideration, the basis of the latter.

The assumption of the equality of $\bar{\alpha}$ and α_{zz} is probably

not greatly in error. It is possible to deduce the relations of $\bar{\alpha}$ to its components only when the Kerr constant and the degree of depolarization of Rayleigh-scattering are known in addition to $\bar{\alpha}$ (Bottcher, 1952). To our knowledge neither of these quantities has been measured for water vapour or ice. Orttung and Meyers(1963) have measured the Kerr constant of liquid water and have derived a value of the quantity $\left[\alpha_{zz}-\frac{1}{2}(\alpha_{xx}+\alpha_{yy})\right]$ equal to 0.019 using J.A. Pople's correlation parameter for water. Their result is no doubt quite approximate, but it does indicate that the anisotropy of polarizability of water is very small. If we assume $\alpha_{xx}=\alpha_{yy}$, we find that taking $\bar{\alpha}=\alpha_{zz}$ does not introduce a significant error. Hence, we shall take

$$\alpha_{zz}=\bar{\alpha} = 1.59\ 10^{-24}\ cm^3 \qquad (I-23)$$

b. <u>The value of $\vec{m}$, the moment of an ice molecule</u>.

Having obtained values for $\vec{E}$, α_{zz}, and $\vec{\mu}_o$, it is an easy matter to calculate $\vec{E}^*$ and $\vec{m}$. When we relax the constraint of non-polarizability which we have imposed on the ice molecules in our calculation of Stage 2, the field strength $\vec{E}$ will induce an average additional moment equal to $\alpha_{zz}\ \vec{E}$ at the oxygen nucleus of each molecule. Since $\vec{E}$ has the direction of $\vec{\mu}_o$, this additional moment has the direction of both. Let us write the additional moment as $\alpha_{zz}(\vec{E}_d+\vec{E}_h)$ where $\vec{E}_d$ is the contribution to $\vec{E}$ arising from

the dipoles associated with neighbouring molecules, and $\vec{E}_h$ is the contribution to $\vec{E}$ arising from the higher moments associated with neighbouring molecules. From the first terms of equations I-14 and I-15 we know that $\vec{E}_d$ is proportional to $\vec{\mu}_o$, that is,

$$\vec{E}_d = c\vec{\mu}_o, \qquad \text{(I-24)}$$

where c is the constant of proportionality. Hence, we can write the additional moment as $\alpha_{zz}c(\vec{\mu}_o + \frac{\vec{E}_h}{c})$.

Of course, the average additional moment will give rise to an average additional electric field at each oxygen nucleus equal to $\alpha_{zz}c^2(\vec{\mu}_o + \frac{\vec{E}_h}{c})$, and this new field will produce an additional moment in the direction of $\vec{\mu}_o$ equal to $\alpha^2_{zz}c^2(\vec{\mu}_o + \frac{\vec{E}_h}{c})$. This process will continue, and we can express $\vec{m}$ as a series:

$$\vec{m} = \vec{\mu}_o + \alpha_{zz}c(\vec{\mu}_o + \frac{\vec{E}_h}{c}) + (\alpha_{zz}c)^2 (\vec{\mu}_o + \frac{\vec{E}_h}{c})$$
$$+ (\alpha_{zz}c)^3 (\vec{\mu}_o + \frac{\vec{E}_h}{c}) + \ldots$$
$$= \vec{\mu}_o (1 + \frac{\vec{E}_h}{\vec{E}_d}) \left[\frac{1}{1 + \frac{\vec{E}_h}{\vec{E}_d}} \right.$$
$$\left. + [\alpha_{zz}c + (\alpha_{zz}c)^2 + (\alpha_{zz}c)^3 + \ldots] \right] \qquad \text{(I-25)}$$

Since $(\alpha_{zz}c)^2$ is less than unity we can sum the infinite progression, giving

$$\vec{m} = \vec{\mu}_o \left(1 + \frac{\vec{E}_h}{\vec{E}_d}\right) \left[\frac{1}{1 + \frac{\vec{E}_h}{\vec{E}_d}} + \frac{\alpha_{zz} c}{1 - \alpha_{zz} c} \right]$$

Substituting equation I-24 we find

$$\vec{m} = \vec{\mu}_o + \frac{\alpha_{zz} \vec{\mu}_o (\vec{E}_d + \vec{E}_h)}{\vec{\mu}_o - \alpha_{zz} \vec{E}_d}$$

or

$$\vec{m} = \vec{\mu}_o + \frac{\alpha_{zz} \vec{\mu}_o \vec{E}}{\vec{\mu}_o - \alpha_{zz} \vec{E}_d} \qquad \text{(I-26)}$$

Inserting our values of α_{zz}, $\vec{\mu}_o$, $\vec{E}$, and $\vec{E}_d$ into equation I-26 we find the average value of the dipole moment of an ice molecule to be,

$$\vec{m} = 2.59\ 10^{-18} \text{ esu cm} \qquad \text{(I-27)}$$

Hence the average value of the field strength arising from the neighbouring molecules is

$$\vec{E}^* = 0.507\ 10^{6} \text{ esu cm}^{-2} \qquad \text{(I-28)}$$

This is roughly 150,000,000 volts cm^{-1}, or nearly the field strength which would arise from a monovalent ion placed on the dipolar axis at a distance of one of the nearest neighbours.

E. Discussion of error, comparison with results from other models, and discussion of the possibility of extending these calculations.

The three stages in our calculation where errors are the

most likely to arise are in our assumptions of a model of H_2O from which we calculate $\vec{E}$, in our assumption of the statistical structure of ice, and in our choice of a value of α_{zz}. The last is the most worrisome because of the paucity of pertinent experimental data. However, our assumptions regarding polarizability (neglect of hyperpolarizabilities, quadrupole polarizability, and anisotropy of polarisability) have always been made in such a way as to slightly underestimate $\vec{m}$, so that we have confidence that our value, if in error, is a minimum value.

Although we have given evidence for accepting the statistical structure we must point out that other structures would produce different values of $\vec{m}$. It is possible to arrange the hydrogen nuclei of an ice crystal to produce moments as small as 1.9 D and as great as 3.1 D. However, barring a major deviation from the statistical structure, or a large change of the polarizability of water between phases, we feel that the value of the dipole moment of an ice molecule is slightly greater than 2.59 D but probably not greater than 2.75 D. We feel that the value of 3.67 D suggested by Onsager and Dupuis(1962) is impossibly large.

Earlier we discussed reasons for believing that a multipole expansion is a better representation of the charge distribution of water than formal point charge models. It is interesting, nevertheless, to consider the values of $\vec{m}$ which

are predicted by various point charge models. Considering the effects of only the first neighbours, we have computed the moment of an ice molecule using two models, each adjusted to give a dipole moment of roughly 1.84 D. (see figure 5).

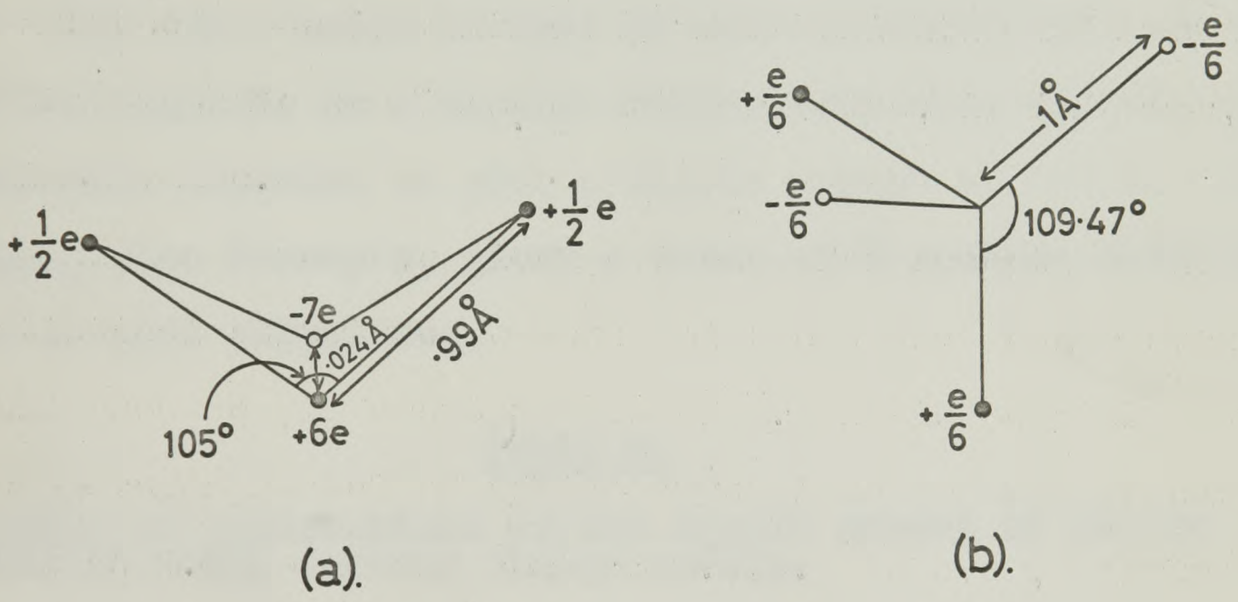


Figure 5. Formal point charge models for H_2O. (a) One of Verwey's models, with charges of +6e on the oxygen nucleus, where e is the electronic charge, +½e on each hydrogen nucleus, and -7e at a point along the dipole axis 0.024Å from the oxygen nucleus. (b) Bjerrum's model for an ice molecule with point charges of e/6 situated at the vertices of a regular tetrahedron, inscribed in a sphere with a radius of 1Å. Two point charges are positive, and two are negative.

The first is one of two models proposed by Verwey(1941). The author states that this model produces a value of $\vec{m}$ in equal to 2.45 D. In repeating his calculation we find that his result is based upon two erroneous assumptions: that the hydrogen nuclei of the neighbours are not placed statistically,

but according to the non-random model proposed by Bernal and Fowler(1933) for ice at lower temperatures; and that the neighbouring molecules are not polarizable. His result is given in Table 4, along with the result which is obtained using his model and assuming that the hydrogen nuclei are statistically arranged and that neighbouring molecules have the same polarizability as the central molecule.

The other model is that of Bjerrum(1951) who represents an ice molecule as a regular tetrahedron with charges at its verticies adjusted to give a dipole moment of 1.9 D. This model, like Verwey's, gives a value of $\vec{m}$ greater than the one we have calculated.

Table 4.

Results of calculations of the dipole moment of an ice molecule using various charge models.

Model	Comments	$\vec{m}$
Multipole expansion	Statistical hydrogens	2.59 D
Verwey's	Bernal-Fowler hydrogens Non-polarizable neighbours	2.45
"	Statistical hydrogens and polarizable neighbours	3.17
Bjerrum's	Statistical hydrogens	2.86

It must be remembered that when neighbours beyond the first are considered, these values of $\vec{m}$ will be even greater. Apparently, both these models overestimate the field strength

arising from moments higher than the dipole. This is not surprising since both have significant quantities of charge concentrated at large distances from the oxygen nucleus.

The results of this chapter are not encouraging as far as similar calculations with wave mechanical models of water are concerned. They indicate that it will be necessary to take into account the perturbation of each molecule by its neighbours - not only the nearest four neighbours but, for good accuracy, at least the nearest thirty.

CHAPTER TWO

The Relation of Physical Quantities to the Dipole Moment of Ice.

In this chapter we relate the value of the dipole moment of ice calculated in Chapter I to three physical quantities of ice: energy of sublimation, dielectric constant of single crystals, and dielectric constant at high frequencies. These values do not assure us that we have calculated an accurate value of the dipole moment; however, none is inconsistent with our value, and, more important, each supports one or more of our assumptions.

A. The energy of sublimation of ice.

1. The coulombic contribution to the energy of sublimation.

There have been numerous calculations of the energy of sublimation of ice; we will discuss the more interesting of these after we have made a calculation of our own. We will compute the coulombic contribution to the sublimation energy, using the values of the multipole moments of Chapter I. Like Rowlinson(1951) and Smith(1959) we will treat the coulombic contribution to the sublimation energy as the interaction of point multipole moments situated at the oxygen nuclei of the ice lattice. As our approach to this computation is not, by and large, original, we will not describe it in undue detail.

A derivation of an expression for the coulombic inter-

action of two charge distributions has been given by Margenau(1931, 1939). The first charge distribution is taken near the origin, and gives rise to a potential V at an external point P. V is then given by our equation I-11. The second charge distribution ρ_2 is placed near P at a second origin, and the energy of coulombic interaction of the two distributions is given by

$$U_{12} = \int \rho_2 V \, d\tau_2 \qquad \text{(II-1)}$$

Assuming that no element of charge $\rho_2 d\tau_2$ is further from the origin of the second distribution than the origin of the first charge distribution, it is possible to develop II-1 in a Taylor series:

$$U_{12} = \int \rho_2 \left[V_{o2} + \left(\frac{\partial V}{\partial r'_{2\alpha}}\right)_{o2} r'_{2\alpha} + \frac{1}{2!}\left(\frac{\partial^2 V}{\partial r'_{2\alpha}\partial r'_{2\beta}}\right)_{02} r'_{2\alpha} r'_{2\beta} + \cdots \right] \qquad \text{(II-2)}$$

where the notation is the same as in section I-B-2 except that the subscript 2 refers to the second charge distribution, and the subscript 02 means "taken at the origin of the second charge distribution." Hence, $\rho(x'_2, y'_2, z'_2)d\tau_2$ is an element of charge near origin 2, and $r'_{2\alpha}$ and $r'_{2\beta}$ can be x'_2, y'_2, or z'_2. Expressions for V_{02} and its derivatives are obtained from equation I-11.

The substitution of the multipole moments of the second charge distribution is carried out as in our derivation in

Chapter I, except that the work is simplified if we take the z-axes of the two distributions to lie along the line between their origins and in the direction from the first, towards the second origin. Completing these operations, we can write the energy of interaction

$$U_{12} = U_{mm} + U_{mQ} + U_{QQ} + U_{mR} + \cdots \qquad \text{(II-3)}$$

where U_{mm} is the contribution to the energy arising from the interaction of the dipole moments associated with the two distributions, U_{mQ} is the contribution arising from the interaction of the dipole moment associated with one distribution with the quadrupole moment associated with the other, etc. The explicit forms of the first three terms of U_{12} are:

$$U_{mm} = \frac{1}{r^3}\left[m^1_x m^2_x + m^1_y m^2_y - 2m^1_z m^2_z\right] \qquad \text{(II-4)}$$

$$U_{mQ} = \frac{3}{2r^4}\left[m^2_z (Q^2_{xx} + Q^2_{yy} - 2Q^1_{zz}) - m^1_z (Q^2_{xx} + Q^2_{yy} - 2Q^2_{zz}) + 2(m^2_x Q^1_{xz} + m^2_y Q^1_{yz} - m^1_x Q^2_{xz} - m^1_y Q^2_{yz})\right] \qquad \text{(II-5)}$$

$$U_{QQ} = \frac{3}{4r^5}\left[Q^1_{\alpha\alpha} Q^2_{\alpha\alpha} - 5(Q^1_{zz} Q^2_{\alpha\alpha} + Q^2_{zz} Q^1_{\alpha\alpha}) - 15 Q^1_{zz} Q^2_{zz} + 2(Q^1_{xx} Q^2_{xx} + Q^1_{yy} Q^2_{yy} + 16 Q^1_{zz} Q^2_{zz} + 2Q^1_{xy} Q^2_{xy} - 8Q^1_{xz} Q^2_{xz} - 8Q^1_{yz} Q^2_{yz})\right] \qquad \text{(II-6)}$$

where r is the distance between the origins of the charge distributions (the oxygen nuclei), m^2_x, for example is the x component of the dipole moment associated with the second charge distribution, and $Q^1_{\alpha\alpha} = Q^1_{xx} + Q^1_{yy} + Q^1_{zz}$.

It is possible to evaluate II-4, II-5, and II-6 for each two neighbouring ice molecules once the multipole moments in the molecule-fixed axes of Figure 1 have been transformed to the new axes, in which the line through the oxygen nucleus is the z-axis. The first three entries in the second column of Table 5 are these terms for ice in its statistical configuration, and with m taken to have the value of μ_o of ice. This means that the U_{mm} term, for example, represents four different U_{mm}'s weighted according to their frequency of occurrence. The first three entries in the third column are the corresponding terms with m taken to have the value of the dipole moment of an ice molecule as calculated in Chapter I. The difference of the two entries in the same row is an indication of the energy gain of mutual polarization of the molecules. Of course, the magnitude of the U_{mQ} and U_{QQ} terms in the third column are smaller than their true values because we have used undistorted quadrupole moments for both columns. Note that all energies in the Table 5 are expressed in kcal per mole of hydrogen-bond.

For second and further neighbours a similar evaluation of U_{12} is a prodigious job, and we do not feel that the

Table 5.

Coulombic contribution to the energy of hydrogen-bonds in ice.

Term	$m = \mu_o = 1.78$ D	$m = 2.59$ D
First neighbours:		
U_{mm}	-1.446 kcal/mole H-bd	-3.060 kcal/mole H-bd
U_{mQ}	-1.057	-1.465
U_{QQ}	-0.321	-0.321
Other neighbours:		
2nds	-0.283	-0.558
3rds & 4ths	-0.197	-0.287
Energy to polarize molecules	0.0	+1.482
Total U_{12}	-3.304	-4.209 kcal/mole H-bd

accuracy of the calculation warrants the labour. Instead we have followed Buckingham(1959) and put II-2 in an alternate form. V_{02} is the potential at the origin of the second charge distribution, arising from the first distribution. Similarly, $(\partial V/\partial r_\alpha)_{02}$ is the α component of the field strength from distribution one acting at the second origin, $E^*{}_\alpha{}^1$, but with reverse sign,

$$\left(\frac{\partial V}{\partial r_\alpha}\right)_{02} = -E^*{}_\alpha{}^1 \qquad \text{(II-7)}$$

Likewise

$$\left(\frac{\partial^2 V}{\partial r_\alpha \partial r_\beta}\right)_{02} = -E'{}_{\alpha\beta}{}^{*1} \qquad \text{(II-8)}$$

where $E'{}_{\alpha\beta}{}^{*1}$ is the $\alpha\beta$ component of the derivative of the field strength from distribution one acting at the second origin.

Substituting II-7, II-8, and the definitions of the multipole moments into II-2, we get

$$U_{12} = q^2 V_{02} - m^2{}_\alpha E^*{}_\alpha{}^1 - \tfrac{1}{2} Q^2{}_{\alpha\beta} E'{}_{\alpha\beta}{}^{*1} - \ldots \qquad \text{(II-9)}$$

In ice the net charge, q, vanishes, and we will neglect all derivatives of the field strength, whose effect at large values of r is not as great as that of the field strength itself. Hence for second and higher neighbours,

$$U_{12} = - m^2{}_\alpha E^*{}_\alpha{}^1 \qquad \text{(II-10)}$$

From the values of $\vec{\mu}_o$, $\vec{m}$, $\vec{E}$, and $\vec{E}^*$ computed in Chapter I it is an easy matter to obtain the entries in the fourth and fifth rows in Table 5.

The entry in the sixth row of Table 5 represents the energy necessary for the polarization of the ice molecules, in increasing their average moments from 1.78 D to 2.59 D. It is equal to $(\mu^\#)^2/(2\bar{\alpha})$, where μ^* is the average induced moment. The last entries, the sums of the two columns, are the total coulombic energies of interaction for the cases of non-polarizable and polarizable ice molecules respectively. Clearly, the mutual polarization of ice molecules increases their cohesion. We have probably underestimated this increase in cohesion because we have neglected distortion of multipole moments other than the dipole, as well as the interaction of the field gradient arising from neighbours beyond the first with the quadrupole moments of the central molecule. The sum of the third column, the value of -4.2 kcal/mole of hydrogen-bond, cannot be compared directly to the energy of sublimation of ice which is the sum of this coulombic energy and several other energies which will be discussed in the next section.

2. Comparisons with results of other authors.

Table 6 summarizes a number of the more interesting calculations of hydrogen-bond energies of ice, along with

the experimental values. The calculations seem to divide naturally into three groups. The first group includes the papers of Bernal & Fowler(1933), Verwey(1941), Bjerrum(1951), and Rowlinson(1951). These authors adopt a formal point charge model which gives rise to a coulombic contribution not very different from the experimental hydrogen-bond energy. The coulombic contribution is then 'corrected' for energy contributions arising from dispersion forces and repulsive forces. The sum of coulombic, repulsive and dispersion energies in all these calculations is near the experimental energy.

The second group includes the works of Coulson and Danielsson(1954), and Tsubomura(1954). These authors emphasize that there are likely to be other contributions to the hydrogen-bond energy which are comparable in magnitude to the coulombic contribution, and that the near identity of the coulombic and experimental energies in ice may be the result of fortuitous cancellation of the other energies. In particular, they are concerned with the contribution to the bond energy called delocalisation energy, caused by a movement of electronic charge in the hydrogen bond $\backslash O_1\text{-}H.....O_2<$ away from O_2. Coulson(1957, 1959) has cited considerable experimental evidence for this effect, including abnormally great intensity of infra-red absorption in hydrogen-bonded compounds, abnormally small oxygen-oxygen distances in

hydrogen-bonded crystals, and non-linearity of hydrogen-bond strengths with the dipole moments of proton acceptors in hydrogen-bonds. Tsubomura's calculations indicate that the delocalization energy in ice is in the range of -8 kcal per mole of hydrogen-bond.

The present work and that of Smith(1959) form a third group. Our results are not inconsistent with those of the second group because delocalization energy, as defined by Coulson(1959), includes the effect of distortion of one molecule by its neighbour. However, in view of the magnitude of the distortion effect, our results do suggest that it may be better to estimate the remaining effects of delocalization starting with some form of distorted wave functions. Our results differ in two respects from those of the first group: in the first place our calculations indicate the importance of considering the effects of distortion, which are largely neglected in the calculations of the first group. Secondly, the magnitude of our calculated coulombic energy, even after the effects of distortion have been included, is considerably smaller than that found by the first group. This discrepancy probably arises in large part from the different representations of the charge distribution of hydrogen atoms in the point charge and multipole expansion models of an ice molecule. The point charge models represent a hydrogen as a positive point charge and tend to overestimate its energy of interaction with the

Table 6.

Results of a number of calculations of hydrogen-bond energies of ice. All entries are in units of kcal. per mole of hydrogen-bond.

Authors	Type of model of ice molec.	Coulombic not including distortion	Repulsive	Dispersion	Distortion or Delocalization	Total
Bernal & Fowler (1933)	Formal pt. charge	-7.1 †	+3.4	-2.0	---	-5.7
Verwey(1941)	"	-6.2 #	+4.2	-2.7	---	-4.7
Bjerrum(1951)	"	-7.2	+3.4*	-2.0*	---	-5.8
Rowlinson(1951)	Formal pt. charge and multipole expansion	-4.7 †	-0.9 ‡‡		-0.2	-5.8
Coulson & Danielsson (1954)						
Tsubomura(1954)	Wave Mechanical				-8.0	
Smith(1959)	Multipole expansion	-3.02			-0.68	
Present work	"	-3.3 †††			-0.9 †††	

Experimental values: 0°K ..... -5.9*
273°K ..... -6.1*

* Taken from Bernal & Fowler(1933)
† Includes 2nd neighbours
‡‡ Includes 1st, 2nd, and 6 3rd neighbours
# Includes some distortion: see section I-E.
††† Includes 1st, 2nd, 3rd, and 16 4th neighbours.

electronic charge of the adjacent oxygen atom. In contrast, the multipole expansions probably underestimate this interaction because of the difficulty of representing the charge distribution of a hydrogen with the first terms of an expansion centred on the oxygen nucleus. The true value of the coulombic contribution is likely to lie between these two models, and its evaluation must await calculations with better representations of water.

3. Comparison of coulombic energies in cubic and ordinary ice.

Earlier (in section I-D-2-C) we mentioned the cubic form of ice which is stable only at temperatures below -110°C. It is interesting to compare the coulombic (including distortion) energy of cubic ice to that of ordinary ice in order to see if it is this energy which is responsible for stabilizing one form with reference to the other. There are grounds for thinking this may be the case: a comparison of the structures of the two forms indicates that relatively long-range forces are the only ones likely to be different. The immediate neighbourhoods of molecules in both forms of ice are quite similar, if both forms are taken to have the statistical structure. The first four neighbours to an arbitrary central molecule in the two forms have identical corresponding positions, and three of the four have identical orientations. Of the twelve second neighbours, only three differ in position

and orientation from their corresponding molecules in the other ice crystal. The equivalence of cell dimensions in the two types of crystals suggests that repulsive forces are similar (Blackman and Lisgarten 1951). In addition, the average volumes per molecule in cubic and hexagonal ice are identical(Blackman and Lisgarten, 1957) so that the free energy of one form is not lower than the other owing to the pressure-volume term. Other than the possibility of difference in entropy of the forms, it seems plausible that their difference in free energy may be largely determined by a difference in coulombic energies.

Contrary to this reasoning, we find only a slight difference in the coulombic energies of the two forms, and the difference favours the ordinary hexagonal form. It is 0.024 kcal/mole of ice, or roughly 5% of kT at 0°C., or 7% of kT at -110°. The difference arises from slighly smaller contributions to $\vec{E}$ from the second and third neighbours in cubic ice. The values of $\vec{m}$, U_{12} and other electrostatic constants for cubic ice are shown in Table 7. They are computed in exactly the same manner as those for ordinary ice.

Table 7

Electrostatic constants of cubic ice.

$\vec{m}$ = 2.58 10^{-18} esu cm	
$\vec{E}$ = 0.3720 10^{6} esu cm^{-2}	
U_{12} = -4.196 kcal/mole of hydrogen bond	
U_{12} (ordinary ice) - U_{12} (cubic ice) = -0.024 kcal/mole of ice	
kT for 0.C.	= 0.54 kcal/mole

Having thrown doubt on the possibility that one of the two forms of ice, both having the statistical structure, is stabilized with respect to the other by coulombic interactions, we can only speculate on the origin of the stability. Perhaps differences in entropy are all-important, or perhaps cubic ice at low temperatures exits in an energetically favourable, non-statistical structure, which gives rise to large coulombic interactions.

B. Dielectric constant of single crystals of ice.

1. Introduction and method of calculation.

The dielectric constant is the observable which is most simply related to the dipole moments and polarizabilities of molecules. Since the theory of the relation of the dielectric constant to these molecular properties has been rather thoroughly developed, we are able to compare the measured values of the dielectric constant of ice to the values predicted by the dipole moment of ice which we have calculated in Chapter I. Unfortunately, such a comparison does not give us a clear indication that our value of the dipole moment of ice is correct, but it does indicate that our method of determining the orientations of neighbouring molecules with respect to a central, fixed molecule is correct.

The relation of dielectric constant to molecular properties which we shall use is Frohlich's equation (1948 and

1958), in its modified form which is suitable for application to anisotropic crystals (Powles, 1955). In the derivation of this equation one considers an ellipsoidal region of dielectric material with axes of length proportional to $\sqrt{\epsilon_i}$, where ϵ_i are the dielectric constants along the principal crystal axes. The ellipsoid, containing N' molecules, is taken to be large compared to molecular dimensions but small compared to the whole specimen of dielectric in which it is embedded. The equation is then given by

$$\frac{(\epsilon_i - 1)(2\epsilon_i + 1)}{3\epsilon_i} = \frac{4\pi N'}{3} \frac{\overline{3m_i m_i^*}}{kT} \qquad \text{(II-11)}$$

where m_i^* is the component along the i^{th} principal crystal axis of the average moment of the whole ellipsoid for a fixed orientation of the central molecule having a dipole moment of value m. $\overline{m_i m_i^*}$ is the average value of the product of m_i and m_i^* for all possible values of m, each value weighted according to its probability of occurrence. Equation II-11 is in C.G.S. esu units, as are all equations dealing with electrostatics in this thesis.

The derivation of II-11 is given in Appendix B; within the context of classical statistical mechanics and electrostatics it contains very few approximations. It is restricted to substances whose dielectric constant is independent of the strength of the applied field for weak fields, and whose

macroscopic dipole moment vanishes in the absence of an applied field. These conditions are fulfilled by many crystals and in particular by ice. A less certain approximation is that the interaction of the dipole moment of the molecule at the centre of the ellipsoid with molecules outside the ellipsoid may be treated as though the molecules outside form a continuum described by the macroscopic dielectric constant. This approximation is better when ellipsoids of greater volume are considered, but, in any case, it is certainly a great improvement over the crucial approximation of the Onsager and Bottcher theories which treatsthe nearest neighbours to a molecule as a continuum. This improved form of approximation was developed by Kirkwood(1939), who was first to apply it to the theory of dielectrics.

Our task in calculating the dielectric constant of single crystals of ice is thus to evaluate the expression $\overline{m_i m_m^*}$ for two cases: where i is the direction of the c-axis and where it is the average of all directions perpendicular to the c-axis (see Figure 2). In doing so we will consider a sphere of dielectric rather than an ellipsoid because the anisotropy of ice is so small that ellipsoids containing the number of molecules we are considering do not deviate from spherical shape by as much as one molecular diameter. Before evaluating $\overline{m_i m_i^*}$ we shall briefly discuss experimental and previous theoretical determinations of the

dielectric constant of ice.

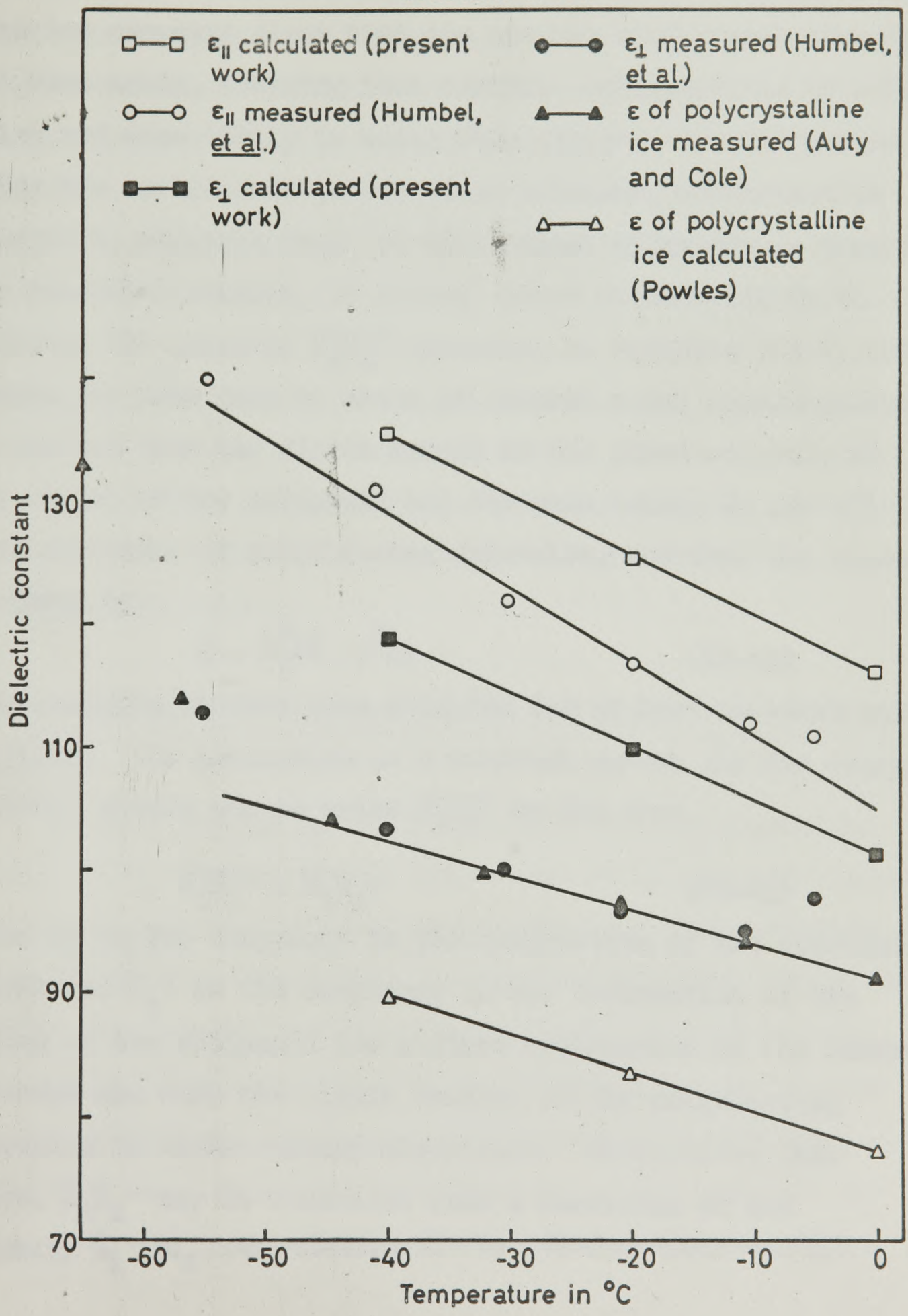
2. Experimental and theoretical determinations of the dielectric constant of ice.

Auty and Cole(1952) have carefully measured the dielectric constant of polycrystalline ice, ϵ, as a function of temperature. They find that ϵ is 91.5 at 0°C. and increases as the temperature is lowered. Their results are shown in Figure 6. Also shown in Figure 6 are the experimental results of Humbel, Jona, and Scherrer(1953) for the dielectric constant of single crystals of ice. They find that the average dielectric constant in directions perpendicular to the c-axis of the crystal, $\epsilon_{\perp}$, is very nearly equal to ϵ measured by Auty and Cole, but that the dielectric constant parallel to the c-axis, $\epsilon_{\parallel}$, is about 14 units greater than ϵ at 0°C. and increases at a somewhat greater rate than ϵ as the temperature is lowered.

In 1952 Haggis, Hasted, and Buchanan used Kirkwood's theory to calculate the dielectric constant of ice. Although this theory is strictly applicable only to liquids of non-polarizable dipoles, the authors obtained a value of ϵ for 0°C. very nearly equal to the experimental value. Considering their approximations, this agreement is probably fortuitous, but it suggests that rigorous applications of statistical mechanical theories of dielectrics to ice may be fruitful.

In the same year Powles(1952) made a detailed application

Figure 6. Experimental and theoretical values of the dielectric constant of ice.



of Frohlich's theory to ice. He calculated ϵ for polycrystalline ice assuming first that ice has the statistical structure, and then again, assuming that certain configurations of molecules are more likely to occur than others. We will not consider his second calculation since evidence, summarized in Chapter I, suggests that the statistical structure is correct. The essential problem, in Powles' first calculation is to evaluate the quantity $\overline{m_i m_i^*}$ appearing in equation II-11, and Powles has done this by means of several major approximations. He assumes that the dipole moment of the fixed molecule at the centre of the ellipsoid has the same value, $\bar{m}$, for all configurations of neighbouring molecules, and that the value is given by

$$\bar{m} = \frac{n^2+2}{3} \, |\vec{\mu}_o| \qquad \text{(II-12)}$$

This relation follows from equation I-1 if $2\epsilon+1$ is taken equal to $2\epsilon+n^2$. The assumption of a constant moment for the central molecule allows one to write $\overline{m_i m_i^*}$ in the form

$$\overline{m_i m_i^*} = \bar{m}_i \bar{m}_i^* \qquad \text{(II-13)}$$

where $\bar{m}_i$ is the component in the i-direction of the constant moment and $\bar{m}_i^*$ is the component in the i-direction of the moment of the ellipsoid for a fixed orientation of the central molecule and with the dipole moments of the neighbouring molecules in their average directions. Then, as we show below, $\bar{m}_i \bar{m}_i^*$ may be evaluated from a knowledge of the quantity $\bar{m}_i^* / \bar{m}_i$ and relation II-12. Powles has computed

$\overline{m}_i^*/\overline{m}_i$ for ice for a group of molecules which includes first and second neighbours, and seven third neighbours to the central molecule. He finds no anisotropy when only first and second neighbours are considered, and a very slight anistropy when the seven third neighbours are included. His results for ϵ of polycrystalline ice are shown in Figure 6. In the next section we shall see that Powles has underestimated the values of $\overline{m}_i^*/\overline{m}_i$ for both crystal axes and that the value of $\overline{m}_i^*/\overline{m}_i$ is considerably different for the a- and c-axes. Powles obtains reasonable values for the dielectric constant only because his assumption of a constant value of the dipole moment of the central molecule introduces a partially compensating error.

3. Calculation of values of $\overline{m}_i^*/\overline{m}_i$ and approximate values of $\overline{m_i m_i^*}$.

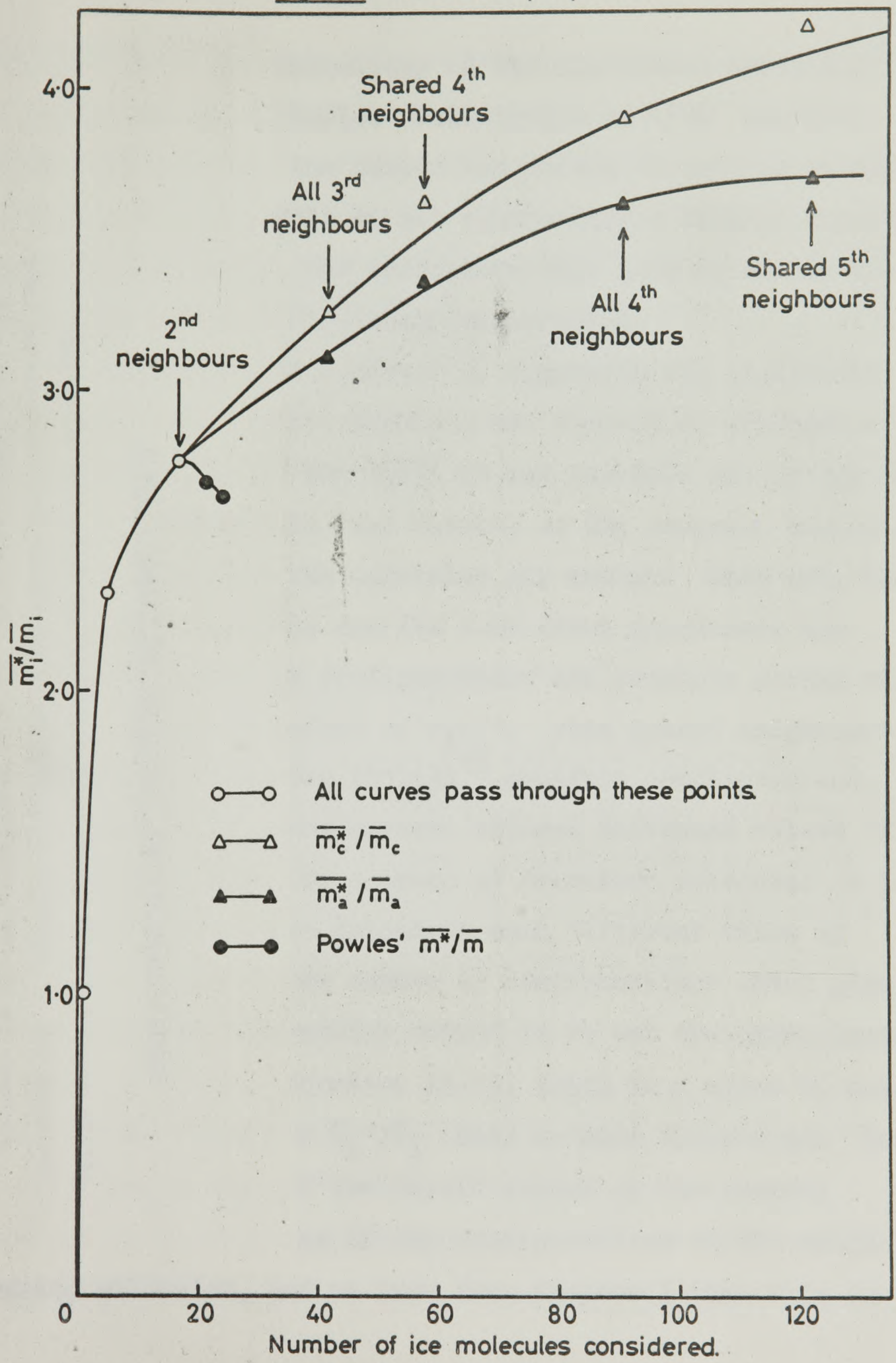
In this section we shall describe the computation of values of $\overline{m}_i^*/\overline{m}_i$ for the a- and c-axes of ice for the nearest 121 neighbours to the central molecule, and an approximate relation of these quantities to the corresponding values of $\overline{m_i m_i^*}$. To compute values of, say, $\overline{m}_c^*/\overline{m}_c$ we must sum the components in the direction of the c-axis of a set of unit vectors having the average orientations of the neighbouring molecules for a fixed central molecule. This problem has been essentially solved in section I-D-2-C where a method

was presented for finding the average orientation of neighbouring molecules for a fixed orientation of the central molecule. Using this method the computation of $\bar{m}_i^*/\bar{m}_i$ is merely a matter of numerical evaluation.

The numerical evaluation was carried out with the assistance of the Mercury Computer at the Oxford University Computing Laboratory, and the results are shown in Figure 7. They show that when molecules beyond the second neighbours are considered, anisotropy in the values of $\bar{m}_i^*/\bar{m}_i$ exists, and that values are greater for the c-axis than for the a-axis.* The curves have been drawn only through points which represent complete shells of neighbours because groups of molecules with incomplete shells are not likely to be spherical. Points are also shown for groups containing all fourth neighbours shared by two third neighbours, and all fifth neighbours shared by two fourth neighbours. As expected, these points lie above the curves because the orientations of molecules shared between two inner molecules are more fully constrained than are the orientations of molecules bonded to a single inner molecule. The value of $\bar{m}_a^*/\bar{m}_a$ is apparently reaching an asymptote of about 3.75. The value of $\bar{m}_c^*/\bar{m}_c$ is still increasing when 120 neighbouring molecules have been considered, but 4.3 does not seem an unreasonable estimate of its asymptotic value. Since for 0°C. $(\epsilon_{\parallel} - \epsilon_{\perp})/E_{\parallel} = 0.15$ and $(4.30 - 3.75)/4.3 = 0.13$, these results look hopeful for a

* This computor programme was also applied to data for cubic ice. In this case the values of $\bar{m}_i^*/\bar{m}_i$ show no anisotropy.

Figure 7 Values of $\overline{m_i^*}/\overline{m_i}$ of ice.



calculation of the anisotropy of the dielectric constant.

The results of Powles' calculation of $\overline{m}^*/\overline{m}$ are also shown in Figure 7; the reason his points do not lie on the curve may be the result of his considering a slighly lopsided group of molecules. His conclusion that 2.65 is nearly an asymptotic value of $\overline{m}^*/\overline{m}$ seems unwarranted.

We must now find a method of computing the quantities $\overline{m_i m_i^*}$ which we need to calculate the dielectric constants. An exact calculation of the $\overline{m_i m_i^*}$ is not feasible for groups of molecules greater than five because of the enormous number of configurations that the molecules may assume. When only the fixed central molecule and its four first neighbours are considered, eightyone configurations are possible giving rise to eight different values of $m_i m_i^*$. When second neighbours are included, there are $(81)(3)^{12}$ possible configurations, giving rise to at least several hundred different values of $m_i m_i^*$. Hence, even for a group of seventeen molecules it is out of the question to calculate each different value of $m_i m_i^*$, and to count the number of configurations which give rise to it. An alternative method is to use the approximate relation of Powles (equation II-13) which is a means to relate $\overline{m_i m_i^*}$ to the values of $\overline{m}_i^*/\overline{m}_i$ which we have calculated. But II-13 is valid only if the dipole moment of the central molecule is independent of the configurations of the neighbouring molecules, and we know from Chapter I that this is

certainly not the case. The solution to this dilemma which we have adopted is first to compute exact values of the quantities $\bar{m}_i \bar{m}_i^*$ for a group of five molecules, and also for a large group of molecules. We denote these quantities $\left[\bar{m}_i \bar{m}_i^*\right]_5$, and $\left[\bar{m}_i \bar{m}_i^*\right]_\infty$ respectively. Then we compute nearly exact values of $\left[\overline{m_i m_i^*}\right]_5$, and from these quantities we derive approximate values for $\left[\overline{m_i m_i^*}\right]_\infty$.

We will illustrate these calculations with the case of components in the direction of the c-axis. First we compute $\left[\bar{m}_c \bar{m}_c^*\right]_5$; it is given by

$$\left[\bar{m}_c \bar{m}_c^*\right]_5 = \bar{m}^2 \left(\bar{m}^*_c/\bar{m}_c\right) \cos^2 e_c \qquad \text{(II-14)}$$

$$= \bar{m}^2 \left(\bar{m}^*_c/\bar{m}_c\right)/3$$

where $\cos^2 e_c$ is the square of the cosine of the angle between the c-axis and the dipole moment of the central molecule and always has the value 1/3 in ice. Substituting into II-14 with data for $\bar{m}_c^*/\bar{m}_c$ from Figure 7, and with a value for $\bar{m}^2$ from data in Table 3 and equstion I-26, we get

$$3\left[\bar{m}_c \bar{m}_c^*\right]_5 = (2.40)^2(2.33) = 13.4 \qquad \text{(II-15a)}$$

In the same way, using our asymptotic value of $\bar{m}_c^*/\bar{m}_c$ and our value of $\bar{m}$ from Chapter I, we find

$$3\left[\bar{m}_c \bar{m}_c^*\right]_\infty = (2.59)^2(4.30) = 28.8 \qquad \text{(II-15b)}$$

The calculation of $\left[\overline{m_c m_c^*}\right]_5$ is more difficult. We must compute each of the eight possible vablues of $m_c m_c^*$ and weight each by the percentage of the total eightyone configurations which give rise to it. We can write $3\left[\overline{m_c m_c^*}\right]_5$ in the form

$$3\left[\overline{m_c m_c^*}\right]_5 = \frac{1}{\sum N_j} \sum_{j=1}^{8} N_j \left(\overline{m}_c^*/\overline{m}_c\right)_j m^2_j \qquad \text{(II-16)}$$

where N_j is the number of configurations giving rise to a given value of m, denoted m_j, and $\left(\overline{m}_c^*/\overline{m}_c\right)_j$ is the corresponding value of $\overline{m}_c^*/\overline{m}_c$, and where $\sum N_j = 81$. Evaluating II-16 by the methods of Chapter I we find

$$3\left[\overline{m_c m_c^*}\right]_5 = 10.6 \qquad \text{(II-17)}$$

Now we add second neighbours and find an expression for $\left[\overline{m_c m_c^*}\right]_{17}$. For each of the eight sets of configurations of first neighbours giving rise to a dipole moment m_j, there are 3^{12} configurations of second neighbours, which give rise to n different values of m, denoted m_{jk}, each value arising from N_{jk} different configurations. Then

$$3\left[\overline{m_c m_c^*}\right]_{17} = \frac{1}{\sum N_j \sum N_{jk}} \sum_{j=1}^{8} \left[\sum_{k=1}^{n} N_{jk} \left(\overline{m}_c^*/\overline{m}_c\right)_{jk} m^2_{jk}\right] \qquad \text{(II-18)}$$

where $\sum N_j = 81$, $\sum N_{jk} = 3^{12}$, and $\left(\overline{m}_c^*/\overline{m}_c\right)_{jk}$ is the resulting value of $\overline{m}_c^*/\overline{m}_c$ for a given m_{jk}.

We simplify II-18 by means of two rather crude assumptions

which amount to assuming that the moment of the central molecule is independent of the orientations of the second neighbours. The first is that the relative average values of the dipole moments associated with each of the eight sets of configurations of first neighbours are not altered by the addition of the second neighbours, but are merely increased in proportion to the increase in the value of $\bar{m}$. That is, for each j, m^2_{jk} may be replaced by

$$m^2_{jk} = (m_j)^2 \frac{\left[\bar{m}^2\right]_{17}}{\left[\bar{m}^2\right]_5} \qquad \text{(II-19)}$$

The second assumption is the same as the first but is made for the quantities $(m_c^*/m_c)_{jk}$: for each j,

$$\left(\frac{\bar{m}_c^*}{\bar{m}_c}\right)_{jk} = \left(\frac{\bar{m}_c^*}{\bar{m}_c}\right)_j \frac{\left[\bar{m}_c^*/\bar{m}_c\right]_{17}}{\left[\bar{m}_c^*/\bar{m}_c\right]_5} \qquad \text{(II-20)}$$

Substituting II-19 and II-20 into II-18, and using II-16, we get

$$3\left[\overline{m_c m_c^*}\right]_{17} = 3\left[\overline{m_c m_c^*}\right]_5 \frac{\left[\bar{m}_c \bar{m}_c^*\right]_{17}}{\left[\bar{m}_c \bar{m}_c^*\right]_5} \qquad \text{(II-21)}$$

Repeating this line of reasoning for the addition of third, and higher neighbours, we can write

$$3\left[\overline{m_c m_c^*}\right]_\infty = 3\left[\overline{m_c m_c^*}\right]_5 \frac{\left[\overline{m_c \bar{m}_c^*}\right]_\infty}{\left[\overline{m_c \bar{m}_c^*}\right]_5} \qquad \text{(II-22a)}$$

Then, from equations II-22a, II-15a, II-15b, and II-17, we find

$$3\left[\overline{m_c m_c^*}\right]_\infty = 10.6\ (28.8)/(13.4) = 22.7 \qquad \text{(II-22b)}$$

The calculation of the corresponding quantities which refer to the a-axis is identical to this, and $(3/2)\left[\overline{m_a m_a^*}\right]_\infty$ is given by

$$(3/2)\left[\overline{m_a m_a^*}\right]_\infty = 19.8 \qquad \text{(II-23)}$$

4. Results and discussion.

The dielectric constant in the direction of the c-axis, $\epsilon_{\parallel}$, is easily evaluated from relation II-22 and equation II-11. The average dielectric constant in directions perpendicular to the c-axis, $\epsilon_{\perp}$, is similarly evaluated, except that an additional factor of $\frac{1}{2}$ must be inserted in the right-hand side of II-11 to account for the averaging. Both these quantities are plotted against temperature in Figure 6. At 0°C. the calculated values are roughly 10% greater than the experimental values, but the calculated anisotropy is very close to the observed value.

Our derivation of the quantities $\overline{m_i m_i^*}$ has involved such approximate treatment that we do not believe the absolute values of our calculated diectric constants are any guide to the accuracy of the value of the dipole moment of ice calculated in Chapter I. However, the anisotropy in the values of the $\overline{m}_i^*/\overline{m}_i$ seems to have some interest in itself. First, an explanation of the anisotropy of the dielectric constant emerges naturally from a consideration of the structure of an ice crystal, without having to introduce ad hoc assumptions such as the assumption of Granicher et al. (1957) that the external field exerts a bias in certain directions on the motion of lattice defects. Second, in computing the anisotropy we have used the same method employed in Chapter I to determine the orientations of neighbouring molecules with respect to a central fixed molecule Since the magnitude of the calculated anisotropy is in accord with experiment we have additional reason to believe this method correct. Third, our result, that $\overline{m}_a^*/\overline{m}_a$ reaches an asymptotic value more rapidly than $\overline{m}_c^*/\overline{m}_c$, suggests that for the full long-range order of an ice crystal in the direction of the c-axis to be realized, larger crystallites must be entact than for the full long-range order in the perpendicular directions to be complete. Disturbances in lattice order, such as defects or dislocations, may, then, have a greater effect on the value of $\varepsilon_{\parallel}$ than on $\varepsilon_{\perp}$. Since,

as we shall discuss in Chapter III, an important type of lattice defect in ice is thought to arise from thermal agitation, it seems reasonable that $\epsilon_{||}$ depends more strongly on temperature than $\epsilon_{\perp}$. This, of course, is the experimental result.

C. Dielectric constant of ice at high frequencies.

1. Previous interpretations of the value of the high frequency dielectric constant of ice and water.

Earlier (section I-D-3-a), we mentioned the anomalous value of the dielectric constant of ice at high frequencies of the applied field. In fields of sufficiently high frequency, permanent dipoles of molecules are unable to reorient themselves, and for most substances the high frequency dielectric constant, ϵ_∞, is only very slightly greater than the square of the optical refractive index, n^2. This is not the case for ice, where the value of ϵ_∞, between -66° and 0°C., (Auty & Cole, 1952) is 3.1 and the value of n^2 is 1.77. For water the value of ϵ_∞ is 5.1 ± 1, and may be slightly temperature dependent (Hasted and El Sabeh, 1953).

The lack of reliable data for the refractive indices of ice and water at wavelengths between the near infra-red and the centimetre region has impeded the interpretation of these ϵ_∞-n^2 values. Furthermore, attempts to compare previous interpretations of these values are confusing because the interpretors have not always been explicit in designating

the molecular phenomena responsible for the values. However, we can generally classify previous interpretations according to two types, not necessarily mutually exclusive. The first ascribes the difference $\epsilon_\infty - n^2$ to a distortion polarization. Early proponents of this explanation were Cartwright and Errera, who in 1936 derived values for the refractive index of ice and water in the infra-red from reflection and absorption measurements. They found that water and ice exhibit an absorption band (at 500cm^{-1} for water), not exhibited by water vapour, which is accompanied by an increase in refractive index. They suggested that the increase in refractive index is due to an atomic polarization which arises from intermolecular forces, and Cartwright(1936) cited evidence that hindered rotations of molecules are involved. The term "atomic polarization" is not used by these authors in its usual sense, to denote a polarization arising from the relative displacement of the nuclei of an individual molecule, but apparently in a more general sense, not explicitly defined, having to do with the relative displacements of molecules in a lattice. The values of atomic polarization which they derive for ice and water are much greater than known values of atomic polarization for molecules of comparable molecular weights, except for those of ionic salts where large values of atomic polarization arise from relative displacement of ions. More recently Hill(1963) and Hallam

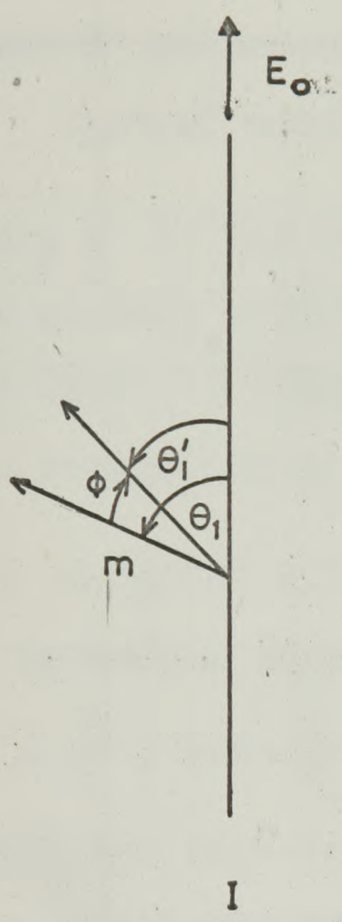
(1963) have also described the values of $\epsilon_\infty - n^2$ of water to a "distortion polarization".

The other interpretation of the large values of $\epsilon_\infty - n^2$ of ice and water, is that they result from some form of molecular rotation which persists at higher frequencies than the usual mode of molecular reorientation. Haggis, Hasted, and Buchanan(1952) suggest that the value of ϵ_∞ of water is greater than ϵ_∞ of ice because water molecules bound to others by one or no hydrogen-bonds may be able to reorient themselves at higher frequencies than those bound by two or more hydrogen-bonds. An explanation of the value of $\epsilon_\infty - n^2$ of ice has been proposed by Onsager and Dupuis(1962). They suggest that ice molecules are able to twist slightly in the ice lattice and partially oppose the external field with the fields of their dipole moments, and they suggest that this twisting is associated with the strong absorption of ice near $800cm^{-1}$ found by Zimmermann and Pimentel(1962). This explanation may be basically the same in substance as that of Cartwright and Errera but more directly stated.

The suggestion that ϵ_∞ is greater than n^2 in ice owing to small twistings of the molecules seems quite reasonable when we compute the angle of rotation needed to produce the observed value of $\epsilon_\infty - n^2$. For this purpose we adopt an argument used by Debye(1929) in demonstrating that the observed dielectric constant of ice in a field strength of

one volt/cm could arise from a 180° rotation of one molecule in every five million. Debye simply employed the fundamental equation of electric polarization (equation A-1a of Appendix A), substituting appropriate values of the dielectric constant, molar volume, and macroscopic field. Using the same approach, and our knowledge of the structure of ice, we find that in a high frequency field of 300 volts/cm the observed value of $\epsilon_\infty - n^2$ is obtained if the average angle between the directions of the dipole moment of an ice molecule and the external field is decreased by 3×10^{-6} radians. Apparently, minute angular deviations from equilibrium directions are sufficient to account for this effect.

On the basis of this calculation we adopt the following hypothesis to account for the discrepancy of ϵ_∞ and n^2: when an electric field of high frequency is applied to an ice crystal, the thermal motions of the molecules are slightly biased by their tendency to align their moments with the external field. The average deviation of a molecule from its equilibrium direction is determined by the strength of the external field tending to twist it away from the direction, and the nature of the restoring forces tending to maintain the orientation of the molecule. In the next two sections we shall derive an expression for $\epsilon_\infty - n^2$ based on this hypothesis and evaluate it approximately.



2. An expression for $\epsilon_\infty - n^2$.

Consider a macroscopic sphere of ice to which we apply a weak high frequency field. This field gives rise to a macroscopic field, E_o, within the sphere, reversing direction too rapidly for the mechanism of complete reorientation to take place. Instead, according to our hypothesis, each molecule twists so that the angle between the equilibrium direction of its moment and E_o is decreased by an angle ϕ. Then, if in the absence of a field, the moment, m, of an ice molecule forms an angle θ_1 with a given direction, when a

field is applied in that direction, the angle decreases by to θ'_1 (see I). Hence, from the fundamental equation of electric polarization (equation A-1a of Appendix A) we get

$$\epsilon_\infty - n^2 = 4\pi N' \frac{\bar{m}}{E_o} \left[\overline{\cos\theta'_1 - \cos\theta_1}\right] \qquad \text{(II-24)}$$

where N' is the number of molecules per unit volume, $\bar{m}$ is the average value of the dipole moment of an ice molecule, and $\overline{\cos\theta'_1 - \cos\theta_1}$ is the average value of the difference in the cosines of θ'_1 and θ_1. Using the relation

$$\theta_1 - \theta'_1 = \phi \qquad \text{(II-25)}$$

it is easily shown that

$$\epsilon_\infty - n^2 = 4\pi N' \frac{\bar{m}}{E_o} \left[\sin\theta_1 \overline{\sin\phi} + \cos\theta_1 \overline{\cos\phi} - \cos\theta_1\right] \qquad \text{(II-26)}$$

where the bars denote average values.

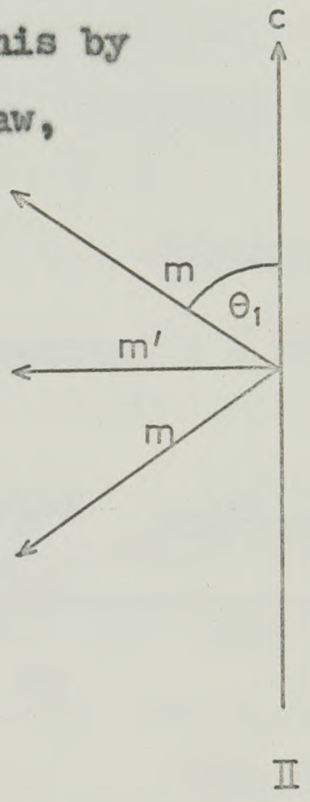
Since the approximate evaluation of our final expression is most conveniently carried out for a macroscopic field in the direction of the c-axis, we will take E_o to have this direction, denoting it E_c, and find an expression for $\epsilon_\infty - n^2$ in the c-direction, denoted $\left[\epsilon_\infty - n^2\right]_c$. It is also helpful to note that the dipoles of all ice molecules form an angle θ_1 with the c-axis of $\pm \cos^{-1}\sqrt{1/3}$, an equal number having each sign. Then it simplifies our algebra, and in no way alters our result, if we consider all ice molecules to be perpendicular to the c-axis and to have an average moment $\bar{m}'$ where $\bar{m}' = \bar{m} \sin\theta_1 = \bar{m}\sqrt{2/3}$ (see II). Then,

$$\left[\epsilon_\infty - n^2\right]_c = 4\pi N' \frac{\bar{m}}{E_c} \overline{\sin\phi} \cong 4\pi N' \frac{\bar{m}'}{E_c} \bar{\phi} \qquad \text{(II-27)}$$

where the last equality is a valid approximation because ϕ is a small angle.

We have reduced the calculation of $\epsilon_\infty - n^2$ to a calculation of $\bar{\phi}$, and we do this by statistical mechanics. By Boltzmann's law,

$$\bar{\phi} = \frac{\int_{\phi=\pi/2}^{-\pi/2} e^{-\Delta U/kT} \, \phi \, d\phi}{\int_{\phi=\frac{\pi}{2}}^{\frac{-\pi}{2}} e^{-\Delta U/kT} \, d\phi} \qquad \text{(II-28)}$$



where ΔU is the energy change caused by rotating an ice molecule an angle ϕ from its equilibrium orientation. ΔU has two components. First, the interaction energy of the dipole of the molecule in the external field is changed by an amount $-mE_o(\cos\theta'_1 - \cos\theta_1)$, or for the case of the c-axis and our approximations, $-m'E_c\phi$. The other component is the increase in energy owing to changes in bond-lengths and -angles, including those of hydrogen-bonds, during the rotation. We will assume that the restoring forces involved are proportional to the angle of rotation, so that this contribution to the

energy can be expressed as $\frac{1}{2} K\phi^2$. For the moment we will be deliberately vague about the nature of K, but will return to this question below. We also assume that the forces between molecules are not such that the twisting of the moment of a molecule towards the c-axis causes an additional twisting of the molecule or its neighbours in any direction perpendicular to the plane of the moment and the c-axis. Hence we can write ΔU in the form

$$\Delta U = \tfrac{1}{2} K\phi^2 - \bar{m}' E_c \phi \qquad \text{(II-29)}$$

Substituting II-29 into II-28, and letting $A = \bar{m}' E_c / K$ and $x = \phi - A$, we find

$$\bar{\phi} = \frac{A \int_{x=\pi/2-A}^{\pi/2-A} e^{-Kx^2/2kT}\, dx + \int_{x=\pi/2-A}^{\pi/2-A} x e^{-Kx^2/2kT}\, dx}{\int_{x=\pi/2-A}^{\pi/2-A} e^{-Kx^2/2kT}\, dx} \qquad \text{(II-30)}$$

Hence, when $A \ll \pi/2$ and $kT/K \ll 1$, both of which are true in the present case for moderate temperatures and field strengths,

$$\bar{\phi} = A = \bar{m}' E_c / K \qquad \text{(II-31)}$$

Thus, from II-27

$$\left[\epsilon_\infty - n^2\right]_c = 4\pi N' \frac{\bar{m}'^2}{K} \qquad \text{(II-32)}$$

Apparently, under these circumstances, $\epsilon_\infty - n^2$ is

independent of temperature excluding the small temperature dependence of N', $\bar{m}'$, and K; but is proportional to $\bar{m}^2$ and inversely proportional to K. A relation of this general form has been suggested by R.H. Cole(1961) on the basis of experimental values of $\epsilon_\infty - n^2$ for several substituted benzenes, which are proportional to the square of the dipole moments of the compounds. Another encouraging point about the form of this equation is that it suggests a possible reason for the greater value of $\epsilon_\infty - n^2$ of water than that of ice the oxygen-oxygen distance of nearest neighbours has a value of 2.76Å in ice, but in water at 15° has an average value of 2.90Å, and increases to 3.05Å at 83°. It seems reasonable to speculate that these longer hydrogen-bonds have smaller bending and stretching force constants and will hence give rise to greater values of $\epsilon_\infty - n^2$. Of course, the larger value of N' of water will contribute slightly to this increase.

3. An approximate evaluation of $\left[\epsilon_\infty - n^2\right]_c$.

To evaluate II-32 we must know the force constants which describe all the deformations which accompany the twisting of ice molecule toward the direction of the applied field. In the absence of such detailed knowledge we will, by a number of crude approximations, relate K to k_θ, the force constant describing the bending of the O....H-O bonds, which

has been deduced by Zimmermann and Pimentel(1962) from spectroscopic data.

When the moment of an ice molecule rotates by an angle ϕ towards the c-axis, the two hydrogen bonds in the plane of $\vec{m}$ and the c-axis are bent by an angle θ (see III). By trigonometry,

$$\sin\phi = \frac{b'\sin\theta}{a+b} = \frac{b'\sin(\pi-\theta)}{a+b}$$

Since ϕ and $\pi-\theta$ are small angles,

$$\phi \simeq \frac{b(\pi-\theta)}{a+b)} = \frac{1.75}{2.76}(\pi-\theta) \qquad \text{(II-33)}$$

Neglecting the energy arising from the distortion of the electron lone pairs of these hydrogen bonds, and neglecting the energy increase owing to the very much smaller bending of the other two hydrogen-bonds of this molecule, we can write the energy of twisting as

$$\tfrac{1}{2} K\phi^2 = 2\,\tfrac{1}{2} k_\theta (\pi-\theta)^2$$

Using relation II-33, we get

$$K = 2\left(\frac{2.76}{1.75}\right)^2 k_\theta \qquad \text{(II-34)}$$

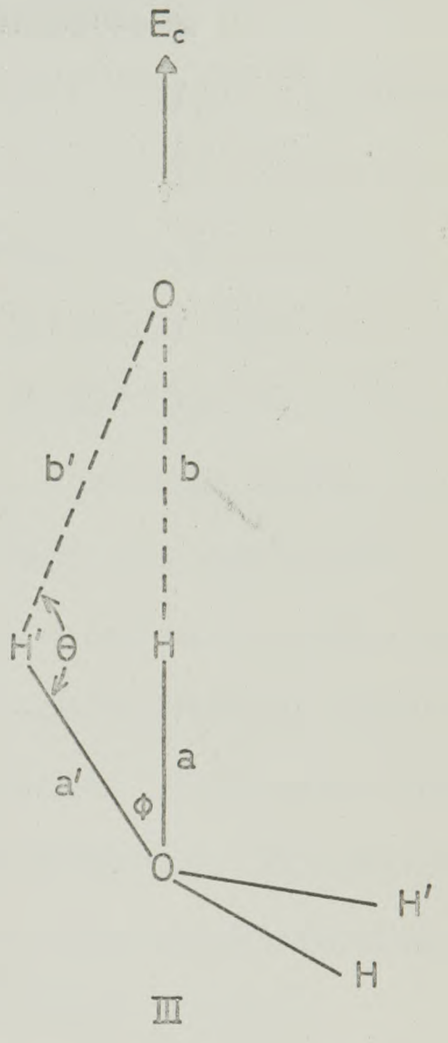
Using this value of K to calculate the root mean square value of ϕ at 0°C., we find it to be 5.7°, a reasonable value.

We are now in a position to find $\left[\epsilon_\infty - n^2\right]_c$. Combining II-34 and II-32 and substituting appropriate values of the constants for 0°C. ($N' = 3.07\ 10^{22}$ molecules/cm^3, $\bar{m} = 2.59$ D, and

$k_\theta = 0.085\ 10^5$ dynes/cm, we get

$$\left[\epsilon_\infty - n^2\right]_c = \frac{4\pi N' \bar{m}^2}{3k_\theta (2.76/1.75)^2} = 0.23$$

This is a good deal less than the experimental value of $\epsilon_\infty - n^2$ (=1.3), perhaps owing to our crude estimate of K. There is the possibility that our value of K is an overestimate, thereby reducing the calculated value of $\epsilon_\infty - n^2$, in spite of the strain energies we have neglected in making the estimate. One possible reason for this is that the twisting of one molecule towards the c-axis may assist the twisting in that direction of its neighbours.



We believe that the results of this section indicate that the discrepancy between ϵ_∞ and n^2 of ice may arise from the bias of thermal motions of molecules by the applied high frequency field; but greater confidence in this hypothesis must await either accurate measurements of the refractive index of ice in the far infra-red region, or an accurate knowledge of the potential function describing the

motions of an ice molecule in the lattice. Until such time we feel that it is more reasonable to ascribe the $\epsilon_\infty - n^2$ values to molecular twisting than to a "distortion polarization" which has no apparent atomic explanation.

CHAPTER THREE

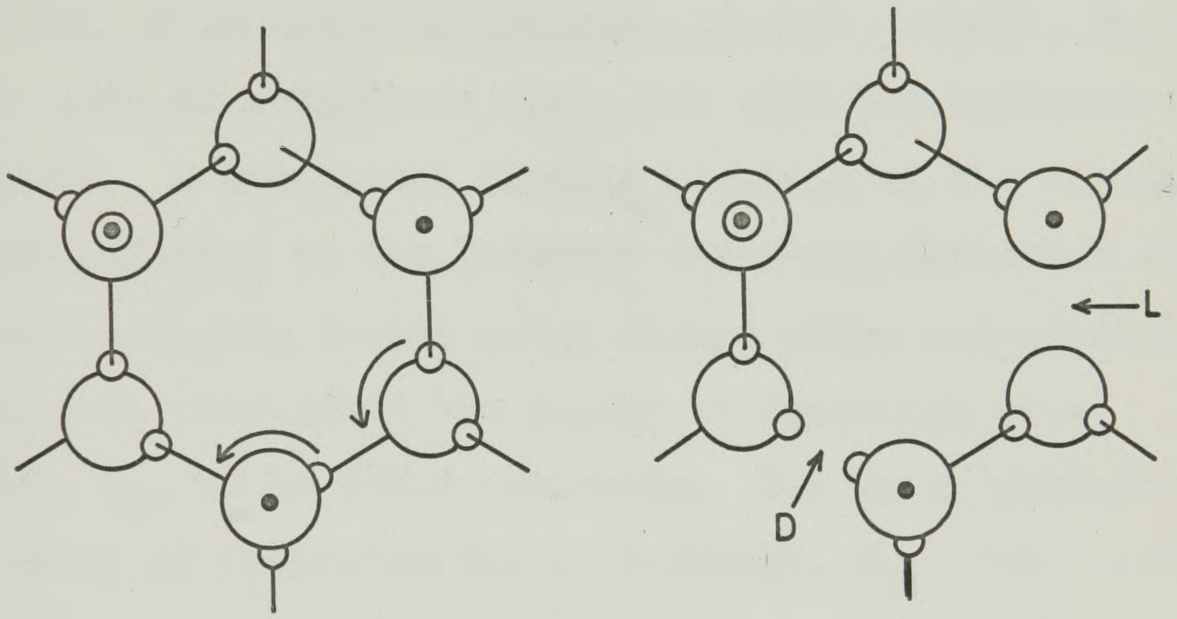
Energy of Formation of Orientational Defects in Ice.

A. Introduction and previous suggestions about the nature of orientational defects in ice.

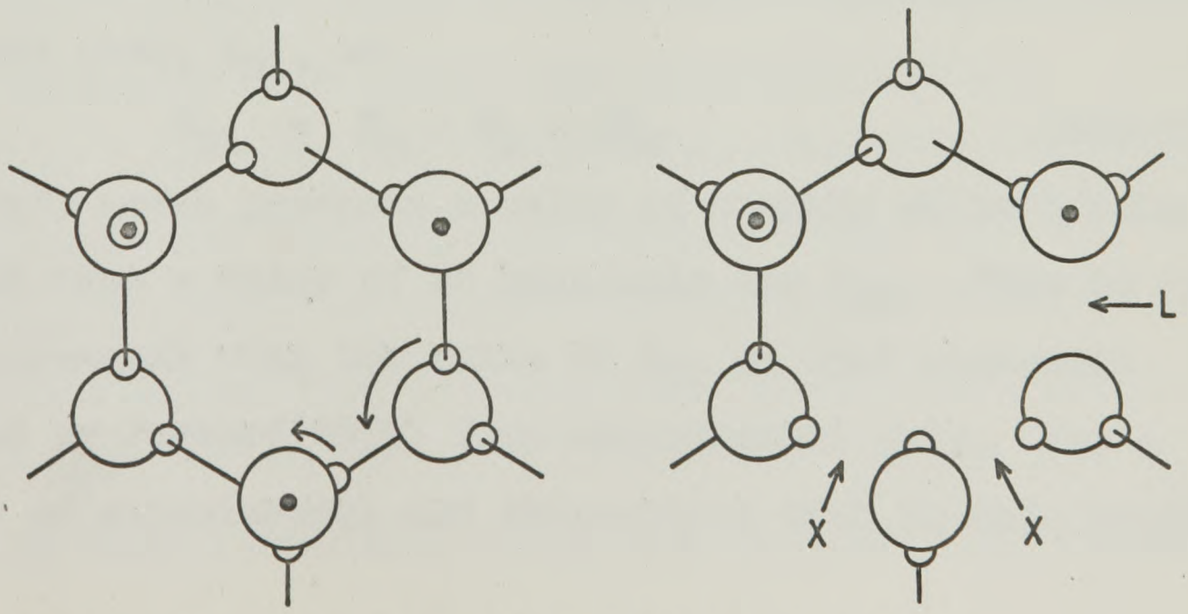
During the past fifteen years it has become apparent that the electrical properties of ice cannot be entirely explained by the existence of ionic defects, in which a proton jumps from one oxygen along a hydrogen bond to its neighbour forming an H_3O^+ cation and an OH^- anion, and by subsequent proton jumps. For example, the high value of the dielectric constant of ice indicates that ice molecules experience reorientation in the presence of an applied field, but attempts to devise mechanisms of reorientation involving only proton jumps have not been successful. Bjerrum(1951) pointed out that proton jumps produce either no net polarization in the crystal, or polarization in the wrong direction. Another example is the direct current conductivity. Granicher et al.(1957) showed that protons are the sole charge carriers during conductivity in ice, and that ice has a time-independent direct-current conductivity. But examination of a model of ice shows that once a proton has followed a given path towards the cathode, no other proton may take the same path. Hence, the time-independence of conductivity indicates that there must be some other mechanism to reorient the ice molecules, allowing another proton to follow the

Figure 8.

Formation of proposed orientational defects in ice. Oxygen atoms are represented by the larger spheres, hydrogen atoms by the smaller ones, and hydrogen-bonds by the lines. The c-axis is perpendicular to the plane of the paper. If the water molecule nearest the top of the page in each group of six is considered to be number 3 in Figure 2, then, proceeding clockwise, the others are numbers 0, 1, 5, 18, and 11.



a) Formation of a pair of D- and L- defects in ice



b) Formation of a pair of X- and L- defects in ice

same path.

Bjerrum(1951) introduced the concepts of D- and L-orientational defects which, when considered with the ionic defects, can account for these properties. A pair of D- and L- defects is formed (Figure 8a) when thermal movements cause an ice molecule to rotate through 120° around one of its O--H...O axes thus leaving one pair of neighbour O....O atoms with no intervening hydrogen atom (L-defect), and another pair of neighbours O-H...H-O with two hydrogens (D-defect). A subsequent similar rotation of the appropriate molecule adjacent to the L-defect separates these two defects. Bjerrum, using his formal point charge model discussed in section I-E, calculated the energy of formation of a D-defect, E_D, to be 6 ± 0.9 kcal/mole. His model predicts the same energy of formation for an L-defect, E_L. Since the formation of a pair of D- and L-defects necessitates breaking two normal hydrogen-bonds, each with an energy of formation, E_N, it is possible to write the total energy of formation of a defect pair, E_{DL}, as

$$E_{DL} = E_D + E_L - 2E_N \qquad \text{(III-1)}$$

Bjerrum's model predicts a value of roughly -6 kcal/mole for E_N, and thus a value of 24 kcal/mole for E_{DL}. This is in fair agreement with the value of E_{DL} of 15.7 kcal/mole deduced by Jaccard(1959) from experimental data. For a review of experimental and theoretical work on this topic,

complete through 1961, the reader is referred to Granicher (1963).

In the last two years there have been several calculations which indicate that if D-defects exist at all, they must exist in a form quite different from that depicted in Figure 8a. Cohan et al.(1962), computed E_D using an elaborate point charge model, and found a value considerably greater than Bjerrum's. They also discovered that E_D is reduced if the two molecules forming the defect are rotated as rigid bodies, in such a way that the distance between two hydrogen atoms, H_1 and H_2 in $(O\text{-}H_1 \ldots H_2\text{-}O)$ is increased. Depending on the axis of rotation, the position of minimum energy corresponds to a rotation of each molecule by 20° to 30°.

A point charge model, however, does not seem to be the best model of an ice molecule with which to compute E_D. The reason for this is that the energy of interaction of two non-bonded hydrogen atoms at such close range is likely to arise primarily from strong spin coupling, and not primarily from coulombic interaction. Moreover, as the strong repulsive energy from spin coupling falls off exponentially with increasing hydrogen-hydrogen distance, and as the energy of coulombic interaction is inversely proportional to the distance between the charges, it is unlikely that a coulombic model will predict the true

position of minimum energy for a deformation of the defect.

For this reason Dunitz(1963) has estimated the interaction energy of hydrogen atoms H_1 and H_2 in a D-defect from several semiempirical energy functions for the interaction of two non-bonded hydrogen atoms. One of the functions which he has used is that of Hendrickson(1961):

$$E(r) = 10^4 \exp(-4.6r) - 49.2/r^6 \qquad \text{(III-2)}$$

where E(r) is the interaction energy in kcal/mole, and r is the distance between the hydrogen atoms in Å. The first term on the right-hand side of III-2 represents the repulsive energy of the hydrogens owing to spin-coupling, and the second term represents the attractive energy owing to dispersion forces. Using III-2, Dunitz has found a value of about 60 kcal/mole for E_D, where he has taken r=0.8 Å, which is roughly the distance between the two adjacent oxygen nuclei minus twice the O-H bond distance. On the basis of this calculation Dunitz concludes that the existence of the D-defect, at least in the form shown in Figure 8a, is improbable.

In place of the D-defect, Dunitz proposes another sort of defect, called the X-defect which he calculates to have a much lower energy of formation. An X-defect is formed (Figure 8b) when one ice molecule rotates about an O-H...O axis through 60°, and the adjacent molecule rotates through 120°, thus creating one L-defect and also placing a hydrogen

atom along the vacated O...O direction. The X-defect is the configuration with a hydrogen atom located symmetrically between two O...H-O bonds. Hence, the one hydrogen-hydrogen interaction of the D-defect, is replaced by two in the X-defect, each at a distance of about 1.3Å. Dunitz suggests that the three molecules forming the X-defect may rotate as rigid bodies, increasing the two hydrogen-hydrogen distances to 1.7Å. Using this model and equation II-2, Dunitz estimates the energy of formation of the X-defect, E_X, to be 10 kcal/mole.

We believe that Dunitz has neglected a significant contribution to E_X. In contrast to the molecules forming a D-defect, both of which are linked to three adjacent ice molecules by normal hydrogen-bonds, the central molecule in an X-defect has only one hydrogen bond definitely intact. In Figure 8b this is the hydrogen-bond which points toward the bottom of the page. The two hydrogen bonds in the regions denoted X in Figure 8b, if they exist at all, are formed between O-H bonds of the side molecules, and electron lone-pairs of the central molecule. However, unlike the normal situation in which the axes of the electron lone-pairs coincide with the axes of the O-H bonds, here the axes form angles of 54.7°. To our knowledge there are no examples of hydrogen-bonds known in which the direction of the O-H bond of the hydrogen donor forms such a great angle with the

electron lone-pair of the hydrogen acceptor. To the contrary, it is thought (Hamilton, 1961) that the large deviation (40°) from linearity of the O-H...N hydrogen-bond in crystals of dimethylglyoxime may arise from the tendency of the O-H bond to be directed toward the lone-pair orbital of the nitrogen atom. Hence, there is the possibility that consideration of the two abnormal hydrogen-bonds in the X-defect may increase Dunitz's estimate of E_X by as much as 10 kcal/mole; that is, to double it. Rather than make a rough estimate of this effect, we have decided to consider the D-defect in greater detail, and have found that it probably has a lower energy of formation than the X-defect, even ignoring the effects of the abnormal hydrogen-bonds of the X-defect.

B. <u>The energy of formation of a D-defect, taking into account changes of bond-lengths and bond-angles in the region of the defect</u>.

In 1963 the author and Professor C.A. Coulson pointed out that if changes in bond-lengths and -angles in the neighbourhood of a D-defect are considered, the $H_1 \ldots H_2$ repulsive energy is considerably less than that calculated by Dunitz. These changes, which we shall refer to as a "relaxation" of the lattice, occur with relative ease owing to the relatively weak bonding in the neighbouring hydrogen-bonds.

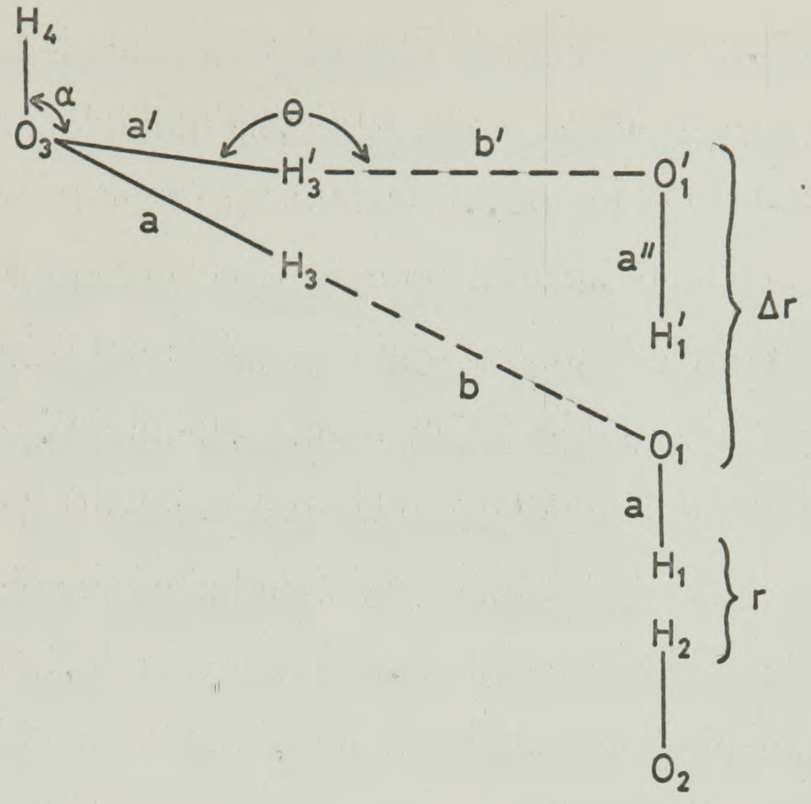


Figure 9. Changes in bond-lengths and -angles in the neighbourhood of a D-defect shown schematically. The actual lengths and angles are given in the text.

If no relaxation occurs in a D-defect, then the two hydrogen atoms are at a separation of about 0.78 Å (O_1-H_1...H_2-O_2 in Figure 9). We have confirmed the result of Dunitz that their repulsive interaction energy in this case is roughly 60 kcal/mole.

Let us now allow relaxation to occur: O_1 moves a distance Δr to O'_1, and O_2 a similar distance in the opposite direction to O'_2. In addition the length of the bond O_1-H_1 is compressed from a to a". If we assume that O_3 is fixed, then the O_3-H_3...O_1 angle is relaxed from 180° to θ, and the H_4-O_3-H_3 angle from 109.47° to α. The

O_3-H_3...O_1 distance is reduced from (a+b) which is 2.76 Å, to (a'+b'). Similar relaxations occur in the other adjacent molecules.

We now seek the values of a', a", b', e, and α which minimize the total energy. This total energy comprises the H'_1...H'_2 repulsive energy, twice the H_1'-O_1' compression energy, and six times the various H_4-O_3-H_3'...O_1' bending and compression energies. We calculate the H...H repulsive energy from Hendrickson's(1961) semi-empirical potential (equation III-2). The force constants which we use are those derived from spectroscopic data by Zimmermann and Pimentel(1962). They are k(O_3-H_3...O_1 compression) = 0.155, k(O_3-H_3...O_1 bending) = 0.085, and k(H_4-O_3-H_3 bending) = 0.56, all in units of 10^5 dynes/cm. We have derived a value of k(O-H compression) = 8.07 10^5 dynes/cm from data of Nakamoto et al.(1955).

The resulting minimum energy is 5.19 kcal per mole of D-defect, and it occurs when r=1.80 Å, Δr=0.50 Å, a-a" = 0.01 Å, a' = 0.99 Å, b' = 1.66 Å, e = 169.75°, α = 105.47°. If we now also allow O_3 and the five other first-neighbour oxygen atoms to O_1 and O_2 to relax, this energy will be even lower.

It is of interest to know whether the energy of a D-defect in its relaxed position is further decreased if the two molecules forming the defect are rotated as rigid bodies

so that the $H_1'...H_2'$ distance is increased further. We are not able to deal with this problem accurately as it involves force constants that we do not know. However, from equation III-2 we find that such rotations result in no more than small decreases in energy. For a 5° rotation of each molecule the decrease is 0.1 kcal/mole, and for a 15° rotation it is 0.5 kcal/mole. Hence, if we were able to compute the increase in strain energy for these rotations we would probably find that the angle of rotation producing a minimum in the sum of repulsive and strain energies is not large.

In summary, it appears that relaxation has the effect of reducing the sum of the repulsive and strain energies in a D-defect from about 60 kcal/mole to about 5 kcal/mole, and it is clear that the existence of such defects cannot be ruled out. It is difficult to estimate the energy of a relaxed X-defect, but even if the sum of the repulsive and strain energies is negligible, the energy of the two abnormal hydrogen-bonds may make this defect less favourable than the relaxed D-defect.

APPENDIX A

Comparison of Bottcher's theory of dielectrics to the theories of Debye and Onsager, and derivation of equations used in the text.*

Bottcher's theory, as all theories of dielectrics, is based on the fundamental equation of electric polarization,

$$\epsilon - 1 = \frac{4\pi \vec{M}_E}{V' \vec{E}_o} \qquad \text{(A-1a)}$$

where $\vec{M}_E$ is the dipole moment of a volume V' of the dielectric in the direction of a uniform macroscopic field, $\vec{E}_o$. Bottcher follows both Debye and Onsager in considering $\vec{M}_E$ to consist of two terms, one representing the contributions of permanent moments of the molecules of the dielectric, and the other, the contributions of induced moments. Equation A-1a is then written

$$\frac{\epsilon - 1}{4\pi} \vec{E}_o = N' \left[\bar{\alpha} \vec{E}_i + \bar{\vec{\mu}}_o \right] \qquad \text{(A-1b)}$$

where $\vec{E}_i$ is the internal field strength acting on a molecule, $\bar{\vec{\mu}}_o$ is the average value of the permanent dipole moment of the molecules in the direction of $\vec{E}_o$, N' is the number of molecules per unit volume, and other symbols are the same as those used in the text. All three of these theories take

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* The general approach used in this appendix is that of Bottcher(1952).

$$\vec{\mu}_o = \frac{\mu_o^2}{3kT} \vec{E}_r \qquad (A\text{-}2)$$

where $\vec{E}_r$ is the average field strength exerting a torque on a molecule, called the directing field by Bottcher; the theories differ only in their expressions for $\vec{E}_i$, and $\vec{E}_r$.

The Debye theory takes the well known Lorentz field $E_o(\frac{\varepsilon+2}{3})$, as both the internal and directing fields. The Onsager and Bottcher theories differ from this in two respects: first, they recognize that the internal field differs from the Lorentz field because of the effect of the dipole moment of a molecule on its environment. The effect is to orient neighbouring molecules so that they produce field $\vec{E}^*$ in the direction of the moment of the molecule. Obviously $\vec{E}_i$ must then be a function of temperature and of the dipole moments of the neighbouring molecules. The second difference is that these theories take into account that at low frequency values of the applied field, $\vec{E}^*$ has the same direction as $\vec{\mu}_o$ and thus cannot produce a torque on the central molecule. This is to say that the directing field, $\vec{E}_r$ is smaller than the internal field, $\vec{E}_i$ by an amount equal to the average value of $\vec{E}^*$,

$$\vec{E}_r = \vec{E}_i - \overline{\vec{E}^*} \qquad (A\text{-}3)$$

The most drastic approximations in the Onsager and Bottcher theories come in the calculation of $\vec{E}^*$ and $\vec{E}_r$.

Both theories assume that the charge distribution of a molecule may be described as a point dipole located at the centre of the molecule, which is supposed to be spherical and surrounded by a continuous dielectric characterized by the macroscopic dielectric constant, ϵ. With these assumptions one finds

$$\vec{E}^* = \frac{f}{1 - \bar{\alpha} f} \vec{\mu}_o \qquad \text{(A-4)}$$

where $f = \frac{2\epsilon - 2}{a^3(2\epsilon + 1)}$ and a is the radius of the molecule.

For interest we can compare the value of $\vec{E}^*$ which we have computed for ice to the value which is given by equation A-4. Taking $\vec{\mu}_o = 1.78\ 10^{-18}$esu, $\bar{\alpha} = 1.59\ 10^{-24}$ cm^3, $a = 1.38\ 10^{-8}$ cm, which is half the distance between two oxygen atoms in ice, and $\epsilon = 95$ for -10°C. (Auty & Cole, 1952), A-4 gives $E^* = 1.6\ 10^6$esu. This value is over three times as great as the one which we have calculated, $E^* = 0.5\ 10^6$esu.

The relation between $\vec{\mu}_o$ and $\vec{m}$, the dipole moment of a molecule surrounded by its neighbours, as given by the Onsager and Bottcher theories follow from equation A-4 and the definition of $\vec{m}$,

$$\vec{m} = \vec{\mu}_o + \bar{\alpha}\vec{E}^* \qquad \text{(A-5)}$$

Substituting A-4 into A-5, and using the definition of f, we find

$$\frac{|\vec{m}|}{|\vec{\mu}_o|} = \frac{1}{1 - \frac{\bar{\alpha}(2\epsilon - 2)}{a^3(2\epsilon + 1)}} \qquad \text{(A-6)}$$

Onsager eliminated $\bar{\alpha}$ and a from A-6 by assuming that the molecules fill all space,

$$\frac{4\pi a^3 N'}{3} = 1 \qquad \text{(A-7)}$$

and that the refractive index is related to the molecular polarizability by the Lorenz-Lorentz equation,

$$\frac{n^2-1}{n^2+1} = \frac{4\pi N'}{3}\bar{\alpha} \qquad \text{(A-8)}$$

The result is equation I-1 of the text,

$$\frac{|\vec{\mu}|}{|\vec{\mu}_o|} = \frac{(n^2+2)(2\varepsilon+1)}{3(2\varepsilon+n^2)}$$

The device of a spherical cavity in the dielectric is also used by Onsager and Bottcher to calculate the directing field, $\vec{E}_r$. $\vec{E}_r$ is a function of the cavity radius, the macroscopic field $\vec{E}_o$, and the dielectric constant, and is given by

$$\vec{E}_r = \frac{3\varepsilon}{(1-f\bar{\alpha})(2\varepsilon+1)}\,\vec{E}_o \qquad \text{(A-9)}$$

where f has the same meaning as in A-4. $\vec{E}_i$ is now determined by equations A-3, A-4, and A-9. Substituting the resulting expression for $\vec{E}_i$ into equation A-1 and eliminating $\vec{E}_r$ from A-9 and A-2 and substituting the resulting value of $\frac{\vec{r}}{\mu_o}$ into A-1 one gets the fundamental equation of Bottcher's theory:

$$\frac{(\varepsilon-1)(2\varepsilon+1)}{12\pi\varepsilon}\,\frac{N'}{1-f\bar{\alpha}}\left[\bar{\alpha}+\frac{\mu_o^2}{3kT(1-f\bar{\alpha})}\right] \qquad \text{(A-10)}$$

A-10 is a slightly generalized version of Onsagar's fundamental equation. The latter may be obtained from A-10 by inserting A7 and A-8 into A-10.

The most interesting applications of Bottcher's theory are to non-polar molecules, and to polar molecules subjected to an external field of optical frequency. For both these cases $\vec{E}_i = \vec{E}_r$; in the former case because $\vec{E}^* = 0$, and in the latter because the average value of $\vec{E}^*$ in every direction is 0. Equation A-10 can then be written in the form

$$\frac{12\pi\epsilon N'}{(\epsilon-1)(2\epsilon+1)} = \frac{1}{2} - \frac{(2\epsilon-2)}{a^3(2\epsilon+1)} \qquad \text{(A-11)}$$

In the case of an external field in the optical frequency range, ϵ must of course be replaced by n^2.

APPENDIX B

Derivation of Frohlich's equation for dielectrics, and Powles' extension of the equation for anisotropic dielectrics.*

Frohlich, in his theory of dielectrics, considers the moment $\vec{M}_E$ appearing in the fundamental equation of electric polarization (A-1a) to be the average electric moment in the direction of the external electric field of a macroscopic spherical region of dielectric. The sphere, of volume V', is large compared to molecular dimensions, but small compared to the whole dielectric in which it is embedded. The essential problem is to relate $\vec{M}_E$ to the moments of the molecules inside the sphere, and Frohlich does this by classical statistical mechanics.

Owing to thermal fluctuations there is a probability

$$\frac{e^{-U(X,\, E_o)/kT}}{\int e^{-U(X,\, E_o)/kT} dX} \qquad (B\text{-}1)$$

of finding the assembly of particles inside the sphere with a set of displacements between X and X+dX. X represents a set of displacement vectors of the particles from their positions of lowest energy, and $U(X,E_o)$ is the potential energy of the assembly in the configuration X, in the presence of the field $\vec{E}_o$. Hence, M_E is given by

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* The derivations of this section follow those of Frohlich (1948 and 1959) and Powles(1955).

$$M_E = \frac{\int M(X) \cos\theta \, e^{-U(X, E_o)/kT} \, dX}{\int e^{-U(X, E_o)/kT} \, dX} \qquad (B\text{-}2)$$

where θ is the angle between $\vec{M}$ and $\vec{E}_o$.

This expression for M_E can be simplified by expanding $U(X,E_o)$. Since the dielectric surrounding the sphere is characterized by the dielectric constant ϵ, the interaction of the dipoles inside the sphere with $\vec{E}_o$ is given by a well known theorem of electrostatics as $-M(X)E_o \cos\theta \, 3\epsilon/(2\epsilon+1)$. Therefore, in the presence of a field $\vec{E}_o$,

$$U(X, E_o) = U(X) - M(X) E_o \cos\theta \frac{3\epsilon}{2\epsilon+1} \qquad (B\text{-}3)$$

Substituting B-3 into B-2, expanding the righthand side of B-2 in a Taylor series in E_o, and retaining only the first two terms (the first term vanishes), one finds

$$M_E = \frac{3\epsilon}{2\epsilon+1} \frac{E_o J}{kT} \int M^2(X) \cos^2\theta \, e^{-U(X)/kT} \, dX \qquad (B\text{-}4)$$

where

$$\frac{1}{J} = \int e^{-U(X)/kT} \, dX \qquad (B\text{-}5)$$

The justification for retaining only the first two terms is the well known experimental result that the dielectric constant is independent of the applied field strength except for very strong fields.

After averaging the value of M_E for all orientations of the dielectric material (that is, all values of θ), one substitutes B-4 into equation A-1a, finding

$$\epsilon - 1 = \frac{4\pi}{3V'} \frac{3\epsilon}{2\epsilon+1} \frac{\overline{M^2}}{kT} \qquad \text{(B-6)}$$

where

$$\overline{M^2} = J \int M^2(X) e^{-U(X)/kT} \, dX \qquad \text{(B-7)}$$

$\overline{M^2}$ is the mean square of the polarization of a sphere of the dielectric embedded in a large specimen of the same material in the absence of a macroscopic field.

The remaining task is to relate $\overline{M^2}$ to the moments of the molecules inside the sphere; this is done as follows: if $\vec{m}(x_j)$ is the dipole moment of the j^{th} of the N' molecules inside the sphere, then

$$\vec{M}(X) = \sum_{j=1}^{N'} \vec{m}\,(x_j) \qquad \text{(B-8)}$$

Hence, from B-7

$$\overline{M^2} = \sum_{j=1}^{N'} J \int \vec{m}\,(x_j)\, \vec{M}(X) e^{-U(X)/kT} \, dX \qquad \text{(B-9)}$$

In the j^{th} term of this expression, the integration is carried out in two steps, first over the whole of the sphere except the j^{th} molecule (volume element dX_j), and then over this molecule (volume element dx_j). Carrying out the first step one writes

$$\overline{M^2} = \sum_{j=1}^{N} \int \vec{m}(x_j).\vec{m}^*(x_j)\, p(x_j)\, dx_j \qquad (B\text{-}10)$$

where

$$\vec{m}^*(x_j) = \frac{\int \vec{M}(X) e^{-U(X)/kT}\, dX_j}{\int e^{-U(X)/kT}\, dX_j} \qquad (B\text{-}11)$$

and

$$p(x_j) = \frac{\int e^{-U(X)/kT} dX_j}{\int e^{-U(X)/kT} dX} \qquad (B\text{-}12)$$

$\vec{m}^*(x_j)$ represents the average moment of the whole sphere for a fixed set at x_j displacements of the j^{th} molecule leading to a moment $\vec{m}(x_j)$, and $p(x_j)$ is the probability of finding the j^{th} molecule with moment $\vec{m}$. Carrying out the second step, one writes

$$\overline{M^2} = N' \overline{\vec{m}.\vec{m}^*} \qquad (B\text{-}13)$$

where $\overline{\vec{m}.\vec{m}^*}$ is the average value of the product $\vec{m}.\vec{m}^*$ taking into account all possible values of $\vec{m}$, and weighting them according to the probability of finding each value. Finally B-13 is inserted in B-6, giving

$$\frac{(\varepsilon-1)(2\varepsilon+1)}{3\varepsilon} = \frac{4\pi N'}{3} \frac{\overline{\vec{m}.\vec{m}^*}}{kT} \qquad (B\text{-}14)$$

which is Frohlich's equation.

In Powles' extension of Frohlich's theory to anisotropic crystals, instead of a spherical region in the dielectric,

an ellipsoidal region having principal axes of length proportional to $\sqrt{\epsilon_i}$ is chosen, where ϵ_i are the dielectric constants along the principal crystal axes. The macroscopic field is not taken in an arbitrary direction but along each crystal axis in turn. We will denote it by $\bar{E}^i_o$. The derivation then proceeds with few differences from Frohlich's derivation.

The interaction of the dipoles in the ellipsoid with $\bar{E}^i_o$ is now given by $-M(X)\bar{E}^i_o\, 3\epsilon_i/(2\epsilon_i+1)$. The expression for M_E in the anisotropic theory is identical to B-4 except that ϵ_i replaces ϵ, and that $\cos^2\theta$ is now unity. All subsequent steps are similar to the derivation of the isotropic equation except that there is now no need to average M_E for all orientations of the specimen. The resulting equation is

$$\frac{(\epsilon_i-1)(2\epsilon_i+1)}{3\epsilon_i} = \frac{4\pi N'}{3}\,\frac{\overline{3m_i m_i^*}}{kT} \qquad \text{(B-15)}$$

where m_i and m_i^* are the components in the i-direction of $\vec{m}$ and $\vec{m}^*$ for the ellipsoidal region.

ABSTRACT

The greater part of this thesis is concerned with intermolecular forces in ice and some associated physical properties.

Chapter I: The Dipole Moment of an Ice Molecule

The average induced electric dipole moment of an ice molecule is computed. The charge distribution of an ice molecule is represented by a multipole expansion. The value of the dipole moment used in the expansion is taken from experimental measurements on water vapour, and the values of the quadrupole and octupole moments are taken from calculations on wave functions.

The electric field strength of an arbitrary central molecule arising from neighbouring molecules is computed from a knowledge of the structure of ice, and the multipole expansions of the charge distributions of the neighbours. This has necessitated the development of a method for finding the probable orientation of each neighbouring molecule with respect to the fixed central molecule. The nearest 121 neighbours to the central molecule have been considered. From this electric field strength, and the value of the polarizability of ice, the dipole moment of an ice molecule is calculated. It is found to be $2.59\ 10^{-18}$ esu cm, a considerable increase over the dipole moment of water vapour,

$1.84\ 10^{-18}$ esu cm.

Chapter II: The Relation of Physical Quantities to the Dipole Moment of an Ice Molecule.

The value of the dipole moment of an ice molecule calculated in Chapter I is related to the coulombic contribution to the energy of sublimation of ice, the dielectric constant of single crystals of ice, and the high frequency dielectric constant of ice. Treating the coulombic contribution to the energy of sublimation as the interaction of the multipole moments of the ice molecules, it is shown that neglect of the induced moments will result in an underestimate of this contribution by at least 1.8 kcal/mole of ice.

Frohlich's theory of dielectrics is used to compute the dielectric constants parallel and perpendicular to the direction of the c-axis of a single ice crystal. Approximate methods are used to evaluate the expressions, and the calculated values are roughly 10% above the observed values. However, the calculated anisotropy of the dielectric constant at $0^{\circ}C$. agrees favourably with the experimental value.

An expression is derived for the difference of the high frequency dielectric constant and the optical refractive index of ice. This difference is proportional to the square of the dipole moment of an ice molecule, inversely proportional to the force constant which describes the twisting of an ice molecule in an electric field, and independent of

temperature. The expression is evaluated approximately using experimental force constants, and is found to give a value of the difference which is too small, but of the same order of magnitude as the observed value.

Chapter III: Energy of Formation of Orientational Defects in Ice.

Previous calculations of the energy of formation of orientational defects in ice are critically discussed. The energy of formation of Bjerrum's D-defect is calculated, assuming that bond-lengths and bond-angles in the region of the defect may be deformed. It is found that these deformations reduce the energy of formation of the D-defect from 60 to about 5 kcal/mole.

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