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The dielectric constant of a bonded lattice model for water

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Abstract. The formula for the dielectric constant of a liquid, derived by Onsager, is modified to take account of the effect, on molecular orientations in water, of hydrogen bonding. This is achieved by using the lattice model of Bell. By a suitable choice of parameters, isobars are obtained for the dielectric constant as a function of temperature. These are in fair agreement with experiment and illustrate well the important role of hydrogen bonding.

1. Introduction

A water molecule has a permanent dipole moment which we denote by ξ_p and a static polarisability which we denote by α . A simple equation for the temperature dependence of the static dielectric constant ϵ^* of a fluid of such molecules is that of Debye (1912). This equation is based on the assumption that the molecules are independent apart from the effect on molecular orientations arising from a uniform internal field. The calculation of this internal field, due originally to Lorentz (1909), assumes a uniform polarisation of the fluid. Owing in part to the inadequacy of this assumption, Debye's equation is unable to account for the dielectric constant of dense fluids. Onsager (1936) therefore sought a new model for the polarisation of liquids. He chose to represent the molecule as a point dipole at the centre of a spherical cavity of volume V_0 . By this means he was able to obtain a form for the molecular polarisation which took into account its non-uniformity in the neighbourhood of a molecule. His equation can be expressed in the form

$$\frac{(\epsilon^* - 1)(2\epsilon^* + 1)}{\epsilon^*} = \frac{3h(\alpha/V_0; \epsilon^*)}{v} \left(\frac{\xi_p^2 h(\alpha/V_0; \epsilon^*)}{3\epsilon_0 kT} + \alpha \right), \quad (1.1)$$

where

$$h(x; y) = \left[1 - \frac{2x}{3} \left(\frac{y-1}{2y+1} \right) \right]^{-1}, \quad (1.2)$$

v being the volume per molecule, ϵ_0 the permittivity of free space, k Boltzmann's constant and T the absolute temperature. Onsager's equation is better than Debye's for predicting the static dielectric constant of liquids. Both equations do, however, fail to take account of the effect on molecular orientations of local non-electrostatic forces. This omission is particularly important in the case of water because of the presence of hydrogen bonding. This bonding has a strong correlating effect on the

molecular orientations of neighbouring molecules and must be a primary cause of the high static dielectric constant of liquid water.

The first attempt to take detailed account of local forces was that of Kirkwood (1939). His equation contains a term dependent on the correlation between the orientation of a molecular dipole and the orientations of the dipole moments of neighbouring molecules. A number of authors (Oster and Kirkwood 1943, Pople 1951, Haggis *et al* 1952, Bruk-Levinson *et al* 1971, Jansoone and Franck 1972) have used Kirkwood's equation to obtain formulae for the dielectric constant of water.

An alternative to the approach which uses Kirkwood's equation is that in which some modification of Onsager's equation is made, in order to take account of the effects of hydrogen bonding. This has been done by Hobbs *et al* (1966) using a model for liquid water in which a certain percentage of the molecules retain an ice-like structure. The purpose of our work is also to obtain a generalisation of Onsager's equation. To do this we adapt the three-dimensional lattice model of Bell (1972). His work, based on a body-centred cubic lattice structure with a simple directional-bonding model for the water molecule, was successful in providing isobars with the characteristic density maximum of liquid water. It is interesting to know whether, in a suitably modified form, it is able to provide a satisfactory model for dielectric properties.

2. The lattice model

We consider a body-centred cubic lattice of N sites and volume V_s per site. We suppose that M of the sites are occupied by the centres of molecules, with $M \leq N$, there being at most one molecule per site and the remaining $N - M$ sites being vacant. Each molecule has four bonding directions (or arms) pointing to the vertices of a regular tetrahedron. In the water molecule two bonding directions are associated with the nuclei of the hydrogen atoms and two with lone 2p-electrons. A hydrogen bond is formed between the bonding arms of two molecules when one arm is that associated with a hydrogen nucleus and the other is that associated with a lone 2p-electron. In our model the asymmetry of the bond is represented by taking two arms of each molecule as 'positive' and two as 'negative'. The bonding arms of a molecule on a given lattice site are directed towards four nearest-neighbour sites (see figure 1) and

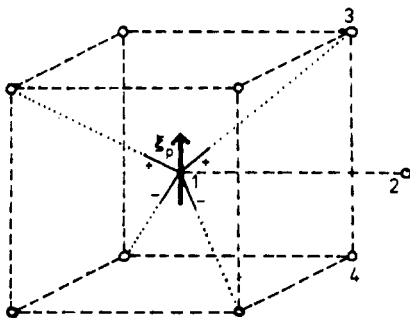


Figure 1. Sites on the body-centred cubic lattice showing a molecule on site 1 in one of its twelve orientational states. Sites 1-4 represent a typical tetrahedron of sites used as a basis for the Guggenheim and McGlashan (1951) approximation.

twelve distinct molecular orientations are therefore possible. A bond is formed between a pair of molecules on neighbouring sites if and only if a positive arm of one molecule and a negative arm of the other lie along the line of centres, directed in each case to the other molecule of the pair. Unlike the two-dimensional triangular lattice model of Bell and Lavis (1970) and Lavis (1973, 1975, 1976) there exists in the model of Bell (1972), and in the present modification of that model, the possibility of each site of the lattice being occupied and each molecule being fully bonded.

Let the molecules be labelled with an index j for $j = 1, 2, \dots, M$. The permanent dipole moment of the j th molecule is $\xi_p^{(j)}$ where $|\xi_p^{(j)}| = \xi_p$, and we suppose that the direction of the dipole moment bisects the angle between the positive arms of the molecule. Associated with any permitted direction of the dipole moment there will be two orientational states differing from each other by a rotation through 90° . Let the assembly be subject to an external electric field $\mathcal{E}_e = \mathcal{E}_e \hat{k}$, where \hat{k} is a unit vector parallel to one set of edges of the cube formed by the eight nearest neighbours of a lattice site. Let the molecular dipoles be in some orientational state $\{\xi_p^{(j)}\}$, not necessarily that of thermodynamic equilibrium. An important part of the development of models for the dielectric properties of assemblies of molecules is the calculation of the electric field experienced by the molecules. For the Debye equation the polarisation \mathcal{P} of the medium surrounding the molecules is assumed to be uniform. A simple electrostatic calculation (see e.g. Böttcher 1952, p 177) then shows that the field at any molecule, in the absence of polarisability ($\alpha = 0$), is the Lorentz field $\mathcal{E}_e + \mathcal{P}/3\epsilon_0$. The alternative Onsager development, which we adopt, does not suppose a uniform polarisation. Instead it assumes that each molecule is in a spherical cavity of volume V_0 and that the medium exterior to the cavities is at equilibrium with dielectric constant ϵ_m^* . The field $\mathcal{E}_m^{(j)}$ in the medium in the vicinity of the j th molecule is then related to the corresponding polarisation $\mathcal{P}_m^{(j)}$ by the equation

$$\mathcal{P}_m^{(j)} = \epsilon_0(\epsilon_m^* - 1)\mathcal{E}_m^{(j)} \tag{2.1}$$

We suppose that $\mathcal{E}_m^{(j)}$ arises from the interaction of the dipole field of the j th molecule and the external field on the dielectric medium. In the absence of molecular polarisability a short electrostatic calculation† gives

$$\mathcal{E}_i^{(j)}(\alpha = 0) = \frac{3\epsilon_m^*\mathcal{E}_e}{2\epsilon_m^* + 1} + \frac{2(\epsilon_m^* - 1)\xi_p^{(j)}}{3V_0\epsilon_0(2\epsilon_m^* + 1)} \tag{2.2}$$

for the field $\mathcal{E}_i^{(j)}(\alpha = 0)$ experienced by the j th molecule. Equation (2.2) must now be modified to take account of the molecular polarisability α . This can be done using a summation method similar to that of Coulson and Eisenberg (1966). The details of the calculation are contained in appendix 2 and the result is

$$\mathcal{E}_i^{(j)} = h(\alpha/V_0; \epsilon_m^*) \left(\frac{3\epsilon_m^*\mathcal{E}_e}{2\epsilon_m^* + 1} + \frac{2(\epsilon_m^* - 1)\xi_p^{(j)}}{3V_0\epsilon_0(2\epsilon_m^* + 1)} \right), \tag{2.3}$$

where h is the function defined in equation (1.2).

The total dipole moment of the j th molecule is given by

$$\xi^{(j)} = \xi_p^{(j)} + \alpha\epsilon_0\mathcal{E}_i^{(j)} \tag{2.4}$$

† The details of this and subsequent calculations are given in an unpublished appendix which can be obtained by writing to the authors. This appendix will henceforth be referred to as appendix 2, to distinguish it from the published appendix 1.

and we define the total electric moment of the assembly

$$\Theta = \sum_{j=1}^M \xi^{(j)} \quad (2.5)$$

From equations (2.3)–(2.5) this gives

$$\Theta = h(\alpha/V_0; \epsilon_m^*) \left(\frac{3\alpha\epsilon_0 M \epsilon_m^* \mathcal{E}_e}{2\epsilon_m^* + 1} + \sum_{j=1}^M \xi_p^{(j)} \right). \quad (2.6)$$

The field $\mathcal{E}_i^{(j)}$ can be expressed in terms of the total dipole moment $\xi^{(j)}$ by using equations (1.2), (2.3) and (2.4). We have

$$\mathcal{E}_i^{(j)} = \frac{3\epsilon_m^* \mathcal{E}_e}{2\epsilon_m^* + 1} + \frac{2(\epsilon_m^* - 1)\xi^{(j)}}{3\epsilon_0 V_0 (2\epsilon_m^* + 1)}. \quad (2.7)$$

The first and second terms in equation (2.3) are the directing and reaction fields acting on the *permanent* dipole moment. (For a discussion of these fields see Böttcher (1952).) The first and second terms in (2.7) can be regarded as the corresponding fields acting on the *total* dipole moment.

We shall throughout this work suppose that, if a molecule has its permanent dipole moment oriented perpendicular to the external field, then it is equally likely to be in any one of the states with this orientation. This implies that the electric moment must be of the form $\Theta = \Theta \hat{k}$. We define the conditional probability $\psi(l)$ that a site is occupied by a molecule in a particular state with $\hat{k} \cdot \xi_p = l\xi_p$, for $l = -1, 0, +1$, given that it is occupied by a molecule. These probabilities satisfy the normalisation condition

$$1 = 2\psi(+1) + 8\psi(0) + 2\psi(-1). \quad (2.8)$$

It is clear that

$$\hat{k} \cdot \left(\sum_{j=1}^M \xi_p^{(j)} \right) = 2M\xi_p(\psi(+1) - \psi(-1)). \quad (2.9)$$

We define the dimensionless parameters $\alpha^* = \alpha/V_s$ and $\nu = V_s/V_0$, the reduced external field $\mathcal{E}_e^* = (V_s\epsilon_0\mathcal{E}_e)/\xi_p$ and the reduced electric moment per molecule $\eta = \Theta/(\xi_p M)$. From equations (2.6) and (2.9) we have

$$\frac{1}{2} \left(\frac{\eta}{h(\alpha^*\nu; \epsilon_m^*)} - \frac{3\alpha^* \epsilon_m^* \mathcal{E}_e^*}{2\epsilon_m^* + 1} \right) = \psi(+1) - \psi(-1). \quad (2.10)$$

To obtain from equation (2.10) the required expression for the dielectric constant of water we must calculate the thermodynamic equilibrium values of $\psi(+1)$ and $\psi(-1)$. To do this we construct a statistical mechanical model which takes account of the effects of hydrogen bonding. In the course of this work we need the contribution $e_s(\mathcal{E}_e^*, \{\psi(l)\})$ per molecule to the internal energy, which arises from electrostatic effects. This is not difficult to obtain. The details of the calculation are given in appendix 2 and the final form is

$$e_s(\mathcal{E}_e^*, \{\psi(l)\}) = -2\mathcal{E}_e^* B(\epsilon_m^*)(\psi(+1) - \psi(-1)) + C(\epsilon_m^*), \quad (2.11)$$

where

$$B(\epsilon_m^*) = \frac{3\sigma h(\alpha^*\nu; \epsilon_m^*)\epsilon_m^*}{2\epsilon_m^* + 1} \quad (2.12a)$$

and

$$C(\epsilon_m^*) = \frac{\nu \sigma h(\alpha^* \nu; \epsilon_m^*)(1 - \epsilon_m^*)}{3(2\epsilon_m^* + 1)}, \quad (2.12b)$$

the parameter $\sigma = \xi_p^2/(\epsilon_0 V_s)$ having the dimensions of energy.

3. The first-order approximation





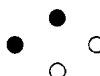





As indicated at the beginning of § 2 a bond will be formed between a pair of molecules on neighbouring sites if and only if the line between the molecules is occupied by the negative arm of one molecule and the positive arm of the other. The interaction energy of a bonded pair of molecules is $-(w+z)$ with $z \geq 0$ and $w > 0$. In all other cases with a pair of molecules occupying neighbouring sites the interaction energy is $-z$ and we neglect interaction energies for molecule pairs which do not occupy neighbouring sites. On the basis of these interactions alone the ground state of the system, for all pressures, would be one in which every site of the lattice is occupied ($M = N$) and the molecules form two interpenetrating fully-bonded structures of the ice I(c) type. In order for our model to be water-like we need to provide for the possibility of a low-density ice I(c) structure ($M = N/2$) being the stable ground state at low pressures. This we do, following Bell (1972), by including a positive energy $u/3$ associated with the occupation of any triad of sites where two second-neighbour sites share a common first neighbour (see figure 1).

As in the work of Bell (1972) the first-order approximation of Guggenheim and McGlashan (1951) will be used based on a tetrahedron of sites (see figure 1). We consider an assembly composed of N groups of sites in order to give the correct number $4N$ of nearest-neighbour pairs. In table 1 we classify the possible occupation states of the basic tetrahedron of sites. The index i is that of Bell (1972). It serves to distinguish between configurations with different non-electrostatic energies $\{e_i\}$. The energies $\{e_i\}$ are listed in table 1, where for every occupied triad of sites we have included an energy u rather than $u/3$. This is to compensate for the fact that the ratio of triads to first-neighbour pairs on the lattice is 3:1 but on the tetrahedron is 1:1. (Two out of every three triads are neglected in the division of the lattice into tetrahedra with sites, but not edges, in common.)

The effect of introducing molecular dipole moments and an external field is to reduce the degeneracies associated with the configurations as compared to those of Bell. We need to distinguish between different configurations with the same index i according to the number of molecules oriented in particular directions with respect to the external field. As indicated above we shall assume a random distribution with respect to all directions perpendicular to the external field. Configurations are then classified using the integer triplets $(i; r_i, s_i)$, where r_i is the aggregate number of molecules in the direction of the field and s_i is the number of molecules perpendicular to the field. The number of occupied sites corresponding to the configuration $(i; r_i, s_i)$ is independent of r_i and s_i and is denoted by n_i . The numbers of molecules with orientations in the direction of the external field and in the opposite direction to the external field are given respectively by $(n_i + r_i - s_i)/2$ and $(n_i - r_i - s_i)/2$. The degeneracy $\omega(i; r_i, s_i)$ associated with the configuration $(i; r_i, s_i)$ must satisfy the condition

$$\omega(i; r_i, s_i) = \omega(i; -r_i, s_i). \quad (3.1)$$

Table 1. Classification of possible occupation states of the basic tetrahedron of sites.

<i>i</i>	Configuration	n_i	e_i
1		0	0
2		1	0
3		2	0
4		2	$-w - z$
5		2	$-z$
6		3	$-w - 2z + u$
7		3	$-2z + u$
8		4	$-2w - 4z + 4u$
9		4	$-w - 4z + 4u$
10		4	$-4z + 4u$

Explicit listing of all degeneracies would be very space consuming. It would also be unnecessary since we need them only as coefficients in particular functions. These functions are given for future use in appendix 1.

We define the probability $p(i; r_i, s_i)$ that the lattice group is in any one particular state described by $(i; r_i, s_i)$. These probabilities satisfy the normalisation condition

$$1 = \sum_{(i; r_i, s_i)} \omega(i; r_i, s_i) p(i; r_i, s_i) \tag{3.2}$$

and are related to the single site probabilities $\psi(+1)$, $\psi(0)$ and $\psi(-1)$, defined in § 2, by

$$\rho\psi(+1) = \frac{1}{16} \sum_{(i; r_i, s_i)} (n_i + r_i - s_i) \omega(i; r_i, s_i) p(i; r_i, s_i), \tag{3.3a}$$

$$\rho\psi(0) = \frac{1}{32} \sum_{(i; r_i, s_i)} s_i \omega(i; r_i, s_i) p(i; r_i, s_i) \tag{3.3b}$$

and

$$\rho\psi(-1) = \frac{1}{V_s} \sum_{(i;r_i,s_i)} (n_i - r_i - s_i)\omega(i; r_i, s_i)p(i; r_i, s_i), \quad (3.3c)$$

where $\rho = M/N$ is the molecular number density, related to the volume v per molecule by $\rho v = V_s$. From equations (2.8) and (3.3)

$$\rho = \frac{1}{4} \sum_{(i;r_i,s_i)} n_i\omega(i; r_i, s_i)p(i; r_i, s_i). \quad (3.4)$$

We obtain the thermodynamic equilibrium state by considering a system in chemical isolation and in thermal and mechanical equilibrium with its environment, which has absolute temperature T and exerts a pressure P . The thermodynamic potential per molecule for such a system is the chemical potential $\mu(\mathcal{E}_e^*, \{p(i; r_i, s_i)\})$. This is given by

$$\begin{aligned} \mu(\mathcal{E}_e^*, \{p(i; r_i, s_i)\}) \\ = \frac{1}{\rho}PV_s + e_c(\{p(i; r_i, s_i)\}) + e_s(\mathcal{E}_e^*, \{\psi(l)\}) - \frac{1}{\rho}kT \ln g(\{p(i; r_i, s_i)\}) \end{aligned} \quad (3.5)$$

where

$$e_c(\{p(i; r_i, s_i)\}) = \frac{1}{\rho} \sum_{(i;r_i,s_i)} e_i\omega(i; r_i, s_i)p(i; r_i, s_i) \quad (3.6)$$

is the non-electrostatic configuration energy per molecule and the electrostatic contribution $e_s(\mathcal{E}_e^*, \{\psi(l)\})$ to the energy per molecule is given by equation (2.11). The configurational counting factor $g(\{p(i; r_i, s_i)\})$ is calculated according to the method of the Guggenheim and McGlashan approximation. We write

$$g(\{p(i; r_i, s_i)\}) = \frac{g_0(\{\rho\psi(l)\})N!}{\prod_{(i;r_i,s_i)} [\{Np(i; r_i, s_i)\}]^{\omega(i;r_i,s_i)}} \quad (3.7)$$

and impose the condition

$$\begin{aligned} & \frac{N!}{[\{N\rho\psi(+1)\}]^2[\{N\rho\psi(0)\}]^8[\{N\rho\psi(-1)\}]^2[N(1-\rho)]!} \\ & = \sum_{\{p(i;r_i,s_i)\}} g(\{p(i; r_i, s_i)\}), \end{aligned} \quad (3.8)$$

where the summation is over all $\{p(i; r_i, s_i)\}$ compatible with (3.2) and (3.3) with fixed values of $\{\psi(l)\}$ and ρ . It can be shown that the summation on the right-hand side of (3.8) can be approximated by its largest term. This is given (see appendix 2) by

$$p(i; r_i, s_i) = (\psi(+1))^{1(n_i+r_i-s_i)}(\psi(0))^{s_i}(\psi(-1))^{1(n_i-r_i-s_i)}\rho^{n_i}(1-\rho)^{4-n_i}, \quad (3.9)$$

and from equations (2.11), (3.5)–(3.9) we have

$$\begin{aligned} \mu(\mathcal{E}_e^*, \{p(i; r_i, s_i)\}) \\ = \frac{1}{\rho}PV_s - 2\mathcal{E}_e^*B(\epsilon_m^*)(\psi(+1) - \psi(-1)) + C(\epsilon_m^*) \\ + \frac{1}{\rho} \sum_{(i;r_i,s_i)} \omega(i; r_i, s_i)p(i; r_i, s_i)[e_i + kT \ln p(i; r_i, s_i)] \end{aligned}$$

$$-3kT[2\psi(+1)\ln\psi(+1)+8\psi(0)\ln\psi(0)+2\psi(-1)\ln\psi(-1)+\ln\rho+(\rho^{-1}-1)\ln(1-\rho)]. \quad (3.10)$$

We minimise the chemical potential with respect to $\{p(i; r_i, s_i)\}$ and ρ at constant \mathcal{E}_e^* , P and T . The variables $\{\psi(l)\}$ are given by (3.3). The details of the calculations are given in appendix 2. A compact form for the results is in terms of the new variables θ , ϕ and χ , the function F defined by equation (A.15) or (A.16) and the parameters $\{\beta_i\}$ defined in equation (A.14). We have

$$\langle p(i; r_i, s_i) \rangle = \frac{\beta_i \exp(r_i\theta + s_i\phi + n_i\chi)}{F(\{\beta_i\}; \theta, \phi, \chi)} \quad (3.11)$$

$$\langle \psi(+1) \rangle = \exp\left[\frac{4}{3}\left(\theta - \frac{\mathcal{E}_e^* B(\epsilon_m^*)}{4kT}\right)\right] (4G(\mathcal{E}_e^*, \theta, \phi))^{-1}, \quad (3.12a)$$

$$\langle \psi(0) \rangle = \exp\left(\frac{4}{3}\phi\right) / (4G(\mathcal{E}_e^*, \theta, \phi)) \quad (3.12b)$$

$$\langle \psi(-1) \rangle = \exp\left[-\frac{4}{3}\left(\theta - \frac{\mathcal{E}_e^* B(\epsilon_m^*)}{4kT}\right)\right] (4G(\mathcal{E}_e^*, \theta, \phi))^{-1} \quad (3.12c)$$

and

$$\langle \rho \rangle = 1 - \left(\frac{\exp(PV_s/kT)}{F(\{\beta_i\}; \theta, \phi, \chi)}\right)^{1/3} \quad (3.13)$$

where

$$G(\mathcal{E}_e^*, \theta, \phi) = \cosh\left[\frac{4}{3}\left(\theta - \frac{\mathcal{E}_e^* B(\epsilon_m^*)}{4kT}\right)\right] + 2 \exp\left(\frac{4}{3}\phi\right). \quad (3.14)$$

Substituting from equations (3.11)–(3.14) we have the equilibrium expression for the chemical potential

$$\begin{aligned} \mu(\mathcal{E}_e^*, \{\langle p(i; r_i, s_i) \rangle\}) \\ = C(\epsilon_m^*) + kT \left[4\chi - 3 \ln\left(\frac{\langle \rho \rangle}{4(1-\langle \rho \rangle)}\right) + 3 \ln G(\mathcal{E}_e^*, \theta, \phi) \right]. \end{aligned} \quad (3.15)$$

Equation (3.13) relates the four variables $\langle \rho \rangle$, θ , ϕ and χ at constant \mathcal{E}_e^* , P and T . In order to completely determine these variables we need three more equations. These are given by substituting from (3.11) into (3.4) and from (3.12) into (3.3). We have

$$4\langle \rho \rangle = \frac{F_3(\{\beta_i\}; \theta, \phi, \chi)}{F(\{\beta_i\}; \theta, \phi, \chi)} \quad (3.16)$$

$$\frac{\sinh\left[\frac{4}{3}\left(\theta - \frac{\mathcal{E}_e^* B(\epsilon_m^*)}{4kT}\right)\right]}{G(\mathcal{E}_e^*, \theta, \phi)} = \frac{F_1(\{\beta_i\}; \theta, \phi, \chi)}{F_3(\{\beta_i\}; \theta, \phi, \chi)} \quad (3.17)$$

and

$$\frac{2 \exp\left(\frac{4}{3}\phi\right)}{G(\mathcal{E}_e^*, \theta, \phi)} = \frac{F_2(\{\beta_i\}; \theta, \phi, \chi)}{F_3(\{\beta_i\}; \theta, \phi, \chi)}, \quad (3.18)$$

where the functions F_1 , F_2 and F_3 are defined in equations (A.17)–(A.21).

Consider now the case where $\mathcal{E}_e^* = 0$. It follows from equation (A.22) that (3.17) has a solution $\theta = 0$ and from (A.25) that (3.18) has a solution $\phi = 0$. From (3.17)

$$\theta \sim \frac{\mathcal{E}_e^* B(\epsilon_m^*)}{4kT} (1 + 3f(\{\beta_i\}; \chi)) \tag{3.19}$$

as $\mathcal{E}_e^* \rightarrow 0$, where

$$f(\{\beta_i\}; \chi) = \left(\frac{4F_3(\{\beta_i\}; 0, 0, \chi)}{3F_{11}(\{\beta_i\}; 0, 0, \chi)} - 3 \right)^{-1} \tag{3.20}$$

and

$$F_{11} = \frac{\partial F_1}{\partial \theta} = \frac{\partial^2 F}{\partial \theta^2}. \tag{3.21}$$

Substituting in equations (3.12a) and (3.12c)

$$\langle \psi(+1) \rangle \sim \frac{1}{12} \left(1 + \frac{\mathcal{E}_e^* B(\epsilon_m^*)}{kT} f(\{\beta_i\}; \chi) \right) \tag{3.22a}$$

and

$$\langle \psi(-1) \rangle \sim \frac{1}{12} \left(1 - \frac{\mathcal{E}_e^* B(\epsilon_m^*)}{kT} f(\{\beta_i\}; \chi) \right), \tag{3.22b}$$

and hence from equations (2.10) and (2.12a)

$$\langle \eta \rangle \sim \frac{3h(\alpha^* \nu; \epsilon_m^*) \epsilon_m^* \mathcal{E}_e^*}{2\epsilon_m^* + 1} \left(\frac{\sigma h(\alpha^* \nu; \epsilon_m^*) f(\{\beta_i\}; \chi)}{3kT} + \alpha^* \right). \tag{3.23}$$

In the limit as the external electric field tends to zero, the static dielectric constant ϵ^* arising from the molecular dipoles is given by

$$\langle \eta \rangle \langle \rho \rangle \sim (\epsilon^* - 1) \mathcal{E}_e^* \tag{3.24}$$

and imposing the consistency condition

$$\epsilon_m^* = \epsilon^* \tag{3.25}$$

we have from equation (3.23)

$$\frac{(\epsilon^* - 1)(2\epsilon^* + 1)}{\epsilon^*} = 3\langle \rho \rangle h(\alpha^* \nu; \epsilon^*) \left(\frac{\sigma h(\alpha^* \nu; \epsilon^*) f(\{\beta_i\}; \chi)}{3kT} + \alpha^* \right). \tag{3.26}$$

Equation (3.26) is the generalisation of Onsager's equation which takes account of the effects of hydrogen bonding. From equations (A.27) and (3.20)

$$f(\{1\}; \chi) = 1 \tag{3.27}$$

and in this case, where all interaction energies are set equal to zero, equation (3.26) reduces to (1.1).

The variables $\langle \rho \rangle$ and χ which feature in equation (3.26) are obtained as a solution of equations (3.13) and (3.16) with $\theta = \phi = 0$. To obtain the liquid-vapour phase transition we use Maxwell's rule and equation (3.15) with $G(0, 0, 0) = 3$.

It will be observed that, throughout our calculations of the equilibrium state, we have treated ϵ_m^* as a constant, applying the consistency condition (3.25) only at the final stage of the work. The result of this assumption is that, in the zero electric field

limit, equations (3.13) and (3.15) are equivalent to equations (4.5) and (4.2) respectively of Bell (1972), the term $C(\epsilon_m^*)$ in equation (3.15) being a constant which affects only the zero point of the chemical potential. An alternative treatment would be to assume that $\epsilon_m^* = \epsilon_m^*(\rho, T)$ in equation (3.10). Equation (3.13) would then contain the partial derivative of ϵ_m^* with respect to ρ . After application of the consistency condition this partial derivative could be obtained by differentiating equation (3.26). This in turn would produce the partial derivative of χ with respect to ρ which would have to be derived by differentiating equation (3.16). Although this treatment would be physically more satisfactory in that it would lead to an electrostatic effect on the isobars, it would be very much more complicated. Our method which is equivalent to neglecting $C(\epsilon_m^*)$ in equation (2.11) can be regarded as an approximation to this more difficult work.

4. Results and discussion

The main purpose of this work is to obtain, for our model, curves of the dielectric constant of liquid water against temperature along isobars. Equation (3.26), which is our equation for the dielectric constant, contains the variables $\langle \rho \rangle$ and χ . The values of these variables at fixed values of the reduced temperature $T^* = (kT/w)$ and the reduced pressure $P^* = (PV_s/w)$ are obtained from equations (3.13) and (3.16) (with $\theta = \phi = 0$). A consequence of our assumption that ϵ_m^* is a constant is that the isobars of our model are exactly those of Bell (1972) with the same values of the critical point parameters and the same liquid–vapour transition temperature at fixed pressure.

One difficulty associated with the use of a lattice model, like that of Bell, is that the pressure and temperature are given in reduced form. Comparison with experiment involves calculation of the energy parameter w and the volume per site V_s . We also need to assume some values for the energy ratios (z/w) and (u/w) . Bell calculated four points on the reduced temperature scale; the critical temperature T_c^* , the liquid–vapour transition temperature T_b^* , and the temperatures T_ρ^* and T_κ^* at which the density is maximum and the compressibility is minimum, respectively, along an isobar†. The last three of these are, of course, functions of pressure and all four are dependent on the ratios (z/w) and (u/w) . The strategy adopted by Bell was, for a number of different values of (z/w) and (u/w) :

- (i) to calculate the reduced atmospheric pressure P_a^* using the formula

$$P_a^* = P_c^*(P_a/P_c) \quad (4.1)$$

where P_a and P_c are the experimental values of the atmospheric and critical pressures respectively;

- (ii) to calculate T_b^* , T_ρ^* and T_κ^* along the isobar $P^* = P_a^*$.

Of the three values of the pair $(z/w, u/w)$ chosen by Bell, in only one case, that of $z/w = 2.0$, $u/w = 1.25$, was $T_\rho^* < T_b^*$. Since this condition is essential for our work, these are the values for the energy ratios which we have chosen. In table 2 we list the reduced critical temperature and pressure together with the reduced atmospheric pressure, derived from equation (4.1), and the phase transition and density maximum temperatures on the isobar.

† A further point on the reduced temperature scale would be obtained by the introduction of long-range ordering and the calculation of the liquid–solid phase transition temperature, as has been done in the case of the two-dimensional triangular model of Bell and Lavis (1970) by Lavis (1973). This work is underway.

Table 2. Experimental data required for the present calculations together with the results of the calculations.

Experimental data ^a	Critical point data (z/w) = 2.0, (u/w) = 1.25
$T_c = 647.30$ K	$T_c^* = 1.3537$
$T_b = 373.15$ K	$P_c^* = 0.0516$
$T_\rho = 277.15$ K	On the atmospheric isobar
$P_c = 2.21 \times 10^7$ N m ⁻²	$P_a^* = 0.00024$
$P_a = 1.01 \times 10^5$ N m ⁻²	$T_b^* = 0.5879$
$\xi_p = 6.14 \times 10^{-30}$ C m	$T_\rho^* = 0.4927$
$\alpha = 21.11 \times 10^{-30}$ m ³	
Derived quantities	
$w = 65.99 \times 10^{-22}$ J	$V_s = 15.39 \times 10^{-30}$ m ³
$(\sigma/w) = 41.88$	$\alpha^* = 1.37$

^a From Eisenberg and Kauzmann (1969).

To calculate the energy parameter w and the volume V_s per site we use the equations

$$w = kT_c/T_c^* \quad (4.2)$$

and

$$V_s = wP_c^*/P_c. \quad (4.3)$$

The necessary experimental data, together with the results of our calculations are given in table 2. It is difficult to make a direct comparison with experiment for w , but V_s can be compared with the value 16.01×10^{-30} m³ derived from the body-centred cubic structure of ice I(c) and the value 18.77×10^{-30} m³ derived from the maximum in the radial distribution function of liquid water (see Eisenberg and Kauzmann 1969, pp 83 and 159 respectively). To complete our set of fixed parameters we need values for (σ/w) and α^* . For the permanent dipole moment and polarisability of the water molecule we use values derived from experiment. These are given in table 2, together with the results of our calculations.

Using the values for the reduced boiling and maximum density temperatures, together with their experimental values given in table 2, we calculate a reduced freezing temperature $T_f^* = 0.4887$. Atmospheric isobars for the static dielectric constant are obtained in the range $[T_f^*, T_b^*]$ of reduced temperatures for varying values of the parameter $\nu = V_s/V_0$. Equating this range of reduced temperatures with the experimental range [273.15 K, 373.15 K] we display our results in figure 2, together with the experimental curve for the static dielectric constant derived from the values of Malmberg and Maryott (1956). As the value of ν increases (and thus for fixed V_s the value of V_0 decreases) our curve rises to higher values at all temperatures. For $\nu = 0.505$ we have a curve within 6% of the experimental values for the whole temperature range. In this context it is interesting to note that Onsager (1936) chose a cavity of volume equal to the volume per molecule. This, in our notation, corresponds to $\nu = \langle \rho \rangle$. The value $\nu = 0.505$ is quite close to the molecular number density

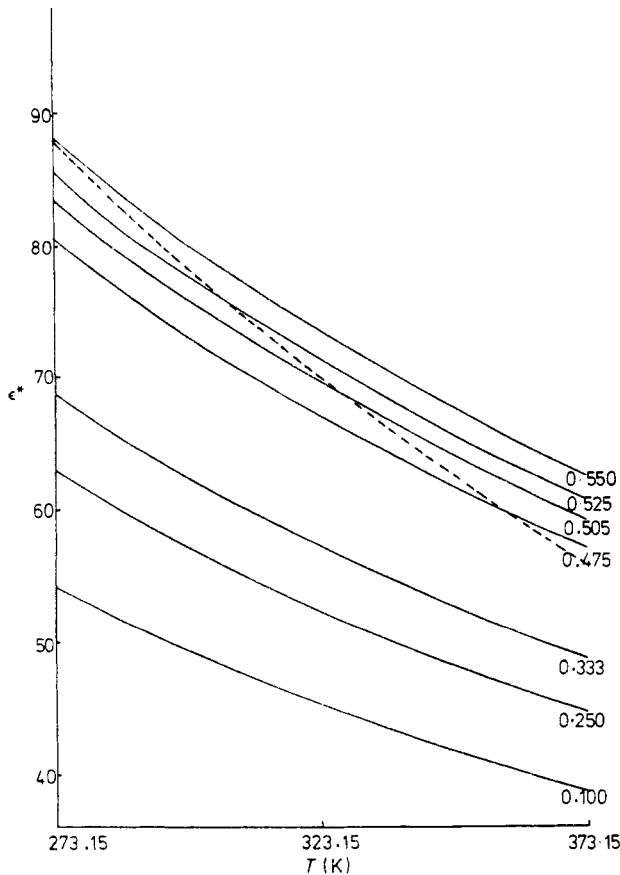


Figure 2. Curves for the static dielectric constant, plotted against absolute temperature along the atmospheric isobar for various values of the parameter $\nu = V_s/V_0$. The broken curve represents the experimental results of Malmberg and Maryott (1956).

predicted by our model (see Bell 1972, figure 2). Since our model effectively provides an equation of state relating pressure, density and temperature, we are able to obtain isotherms for the dependence of the dielectric constant on the pressure. A selection of these curves is shown in figure 3. As is to be expected the dielectric constant is a monotonically increasing function of pressure.

In figure 4 our curve (with $\nu = 0.505$) for the dielectric constant against temperature, along the atmospheric isobar, is displayed together with the experimental curve and the theoretical curves derived by other authors. With the exception of the curve of Hobbs *et al* (1966) all these results have been obtained by application of Kirkwood's equation (Kirkwood 1939). Oster and Kirkwood (1943) applied Kirkwood's equation to the problem of the dielectric constant of water, taking into account the effect on the orientation and polarisation of a molecule of only the shell of first-neighbour molecules. Pople (1951) applied Kirkwood's equation to his own distorted hydrogen bond model. He took into account the effects of the first three shells of nearest neighbours on the molecular orientation, but restricted the contribution to molecular polarisation to the shell of first neighbours. His results have since been modified by Eisenberg and Kauzmann (1969) to include the effects of the first three

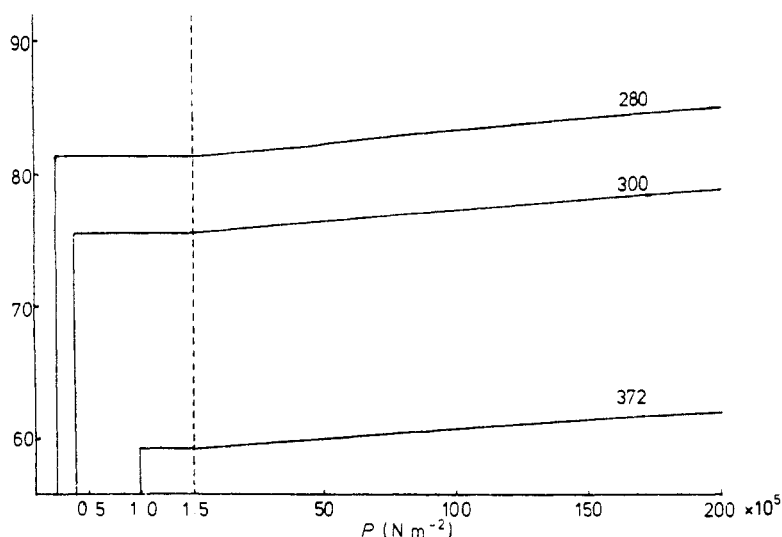


Figure 3. Curves for the static dielectric constant, plotted against pressure along various isotherms. The curves are labelled with their values of absolute temperature and the horizontal axis changes scale at $P = 1.5 \times 10^5 \text{ N m}^{-2}$. The curves drop vertically at the transition to the vapour state.

shells of neighbours on polarisation (see Eisenberg and Kauzmann 1969, figure 4.17, p 190). The resulting curve corresponds well with the experimental curve. Haggis *et al* (1952) apply Kirkwood's equation to a mixture model. They assume that a certain fraction of hydrogen bonds is broken at any given temperature and that the liquid is a mixture of molecules forming 0, 1, 2, 3 and 4 hydrogen bonds. In order to give agreement with experiment they chose the fraction of broken bonds at 273.15 K to be 0.09 and determined the fraction of broken bonds at other temperatures from thermodynamic considerations. This gave a curve for the dielectric constant in good agreement with experiment. More recently Bruk-Levinson *et al* (1971) have applied the potential of Stockmayer (1941) in order to obtain the molecular correlation function of Kirkwood's equation and Jansoone and Franck (1972) have used the approach of Wertheim (1971) based on the mean spherical model. In neither of these cases is the result particularly satisfactory. Finally the work of Hobbs *et al* (1966) should be referred to. This is based on a generalisation of Onsager's equation in which a certain fraction of molecules are assumed to be solid-like and the remaining molecules are assumed to be gas-like. Since they have calculated values of the dielectric constant in the liquid range at only freezing and boiling temperatures, it is difficult to assess their results.

We would not attempt to pretend that we have with our model derived the most accurate theoretical curve for the dielectric constant so far obtained. Indeed the results of Hasted *et al* (1952) and of Pople (1951), modified by Eisenberg and Kauzmann (1969), give good agreement with experiment. The main point about our model is that it is more nearly 'complete' than previous work. We need take from experiment only the critical point data, the freezing, maximum density and boiling temperatures and the values of the dipole moment and polarisability of the molecule. Once this is done the curve for the dielectric constant can be derived. For all

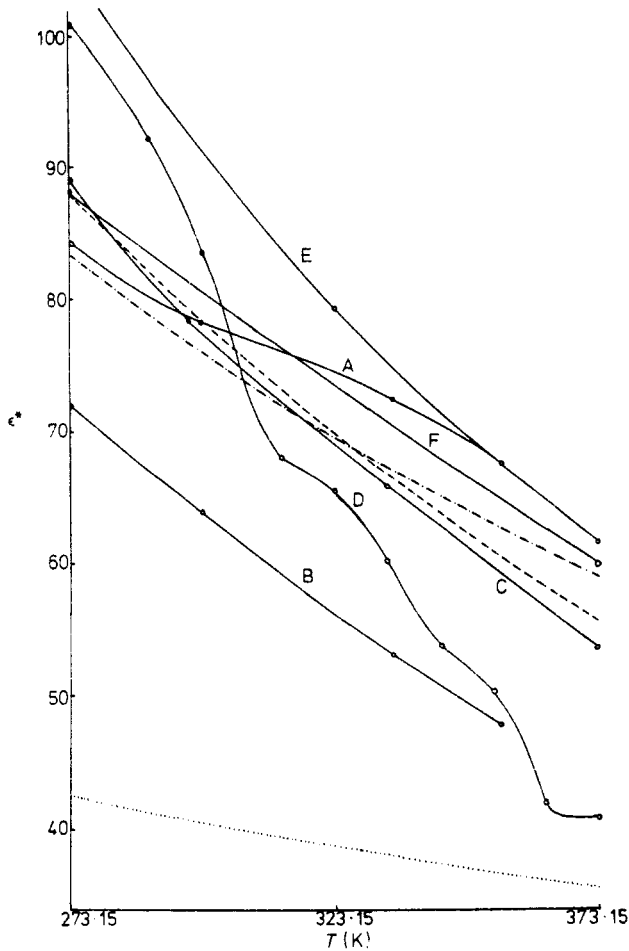


Figure 4. Curves for the static dielectric constant, plotted against temperature along the atmospheric isobar. The broken curve represents the experimental results of Malmberg and Maryott (1956), the chain curve is given by the present work with $\nu = 0.505$, $z/w = 2.0$, $u/w = 1.25$ and the dotted curve is the corresponding curve for the 'pure' Onsager equation. The full curves are the theoretical curves of: A, Oster and Kirkwood (1943); B, Pople (1951); C, Haggis *et al* (1952); D, Bruk-Levinson *et al* (1971); E, Jansoone and Franck (1972); F, Hobbs *et al* (1966).

calculations based on the Kirkwood equation, experimental data (density, number of bonded molecules etc) are needed at successive points along the curve. This also applies to the modified Onsager model of Hobbs *et al* (1966). Another important advantage of our model is that it enables us to distinguish clearly between the effects on molecular orientation of long-range electrostatic forces and short-range bonding interactions. In figure 4 we have, for the sake of comparison, included the curve corresponding to the 'pure' Onsager equation (1.1), where $\nu = V_s/\langle\rho\rangle$ is given, as before, by equation (3.16) with $\theta = \phi = 0$. The difference between the curve for our modified Onsager equation and that of the pure Onsager equation clearly illustrates the important role of hydrogen bonding in producing the high dielectric constant of water.

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Appendix 1

For the molecular configurations on the lattice group, given in table 1, we define the functions

$$\Omega(i; \theta, \phi) = \sum_{r_i, s_i} \omega(i, r_i, s_i) \exp(\theta r_i + \phi s_i) \quad i = 1, 2, \dots, 10, \quad (\text{A.1})$$

where the summation is over all values of r_i and s_i compatible with the particular configuration i . It is clear that

$$\Omega(1; \theta, \phi) = \omega(1; 0, 0) = 1 \quad (\text{A.2})$$

and

$$\Omega(2; \theta, \phi) = 4(2 e^\theta + 8 e^\phi + 2 e^{-\theta}) = 16x(\theta, \phi), \quad (\text{A.3})$$

where

$$x(\theta, \phi) = \cosh \theta + 2 e^\phi. \quad (\text{A.4})$$

Since the two molecules in state 3 are, once placed on a particular pair of sites, free to assume any orientations, we have

$$\Omega(3; \theta, \phi) = 32x^2(\theta, \phi). \quad (\text{A.5})$$

For configuration 4

$$\Omega(4; \theta, \phi) = 4(e^{2\theta} + 4 e^{(\theta+\phi)} + 8 e^{2\phi} + 4 e^{(-\theta+\phi)} + e^{-2\theta}) = 8y(\theta, \phi), \quad (\text{A.6})$$

where

$$y(\theta, \phi) = \cosh 2\theta + 4 e^\phi \cosh \theta + 4 e^{2\phi}. \quad (\text{A.7})$$

The corresponding Ω for configurations 5 to 10 can now be expressed entirely in terms of the functions x and y . We have

$$\Omega(5; \theta, \phi) = 8(8x^2(\theta, \phi) - y(\theta, \phi)), \quad (\text{A.8})$$

$$\Omega(6; \theta, \phi) = 64x(\theta, \phi)y(\theta, \phi), \quad (\text{A.9})$$

$$\Omega(7; \theta, \phi) = 64x(\theta, \phi)(4x^2(\theta, \phi) - y(\theta, \phi)), \quad (\text{A.10})$$

$$\Omega(8; \theta, \phi) = 8y^2(\theta, \phi), \quad (\text{A.11})$$

$$\Omega(9; \theta, \phi) = 16y(\theta, \phi)(8x^2(\theta, \phi) - y(\theta, \phi)) \quad (\text{A.12})$$

and

$$\Omega(10; \theta, \phi) = 8(32x^4(\theta, \phi) - 16x^2(\theta, \phi)y(\theta, \phi) + y^2(\theta, \phi)). \quad (\text{A.13})$$

It is clear that $\Omega(i; 0, 0)$ is identical to the degeneracy ω_i of Bell (1972). In terms of the energies $\{e_i\}$ given in table 1 we define

$$\beta_i = \exp(-e_i/kT) \quad i = 1, 2, \dots, 10, \tag{A.14}$$

and the function

$$F(\{\beta_i\}; \theta, \phi, \chi) = \sum_{(i;r_i,s_i)} \beta_i \omega(i; r_i, s_i) \exp(\theta r_i + \phi s_i + \chi n_i), \tag{A.15}$$

which can also be written

$$F(\{\beta_i\}; \theta, \phi, \chi) = \sum_i \beta_i \Omega(i; \theta, \phi) \exp(\chi n_i). \tag{A.16}$$

We shall also need

$$F_1(\{\beta_i\}; \theta, \phi, \chi)$$

$$\begin{aligned} &= \frac{\partial F}{\partial \theta} = \sum_{(i;r_i,s_i)} \beta_i r_i \omega(i; r_i, s_i) \exp(\theta r_i + \phi s_i + \chi n_i) \\ &= \sum_i \beta_i \Omega_1(\theta, \phi) \exp(\chi n_i), \end{aligned} \tag{A.17}$$

and

$$F_2(\{\beta_i\}; \theta, \phi, \chi)$$

$$\begin{aligned} &= \frac{\partial F}{\partial \phi} = \sum_{(i;r_i,s_i)} \beta_i s_i \omega(i; r_i, s_i) \exp(\theta r_i + \phi s_i + \chi n_i) \\ &= \sum_i \beta_i \Omega_2(\theta, \phi) \exp(\chi n_i), \end{aligned} \tag{A.18}$$

where

$$\Omega_1 = \partial \Omega / \partial \theta \tag{A.19}$$

$$\Omega_2 = \partial \Omega / \partial \phi \tag{A.20}$$

and

$$F_3(\{\beta_i\}; \theta, \phi, \chi)$$

$$\begin{aligned} &= \frac{\partial F}{\partial \chi} = \sum_{(i;r_i,s_i)} \beta_i n_i \omega(i; r_i, s_i) \exp(\theta r_i + \phi s_i + \chi n_i) \\ &= \sum_i \beta_i n_i \Omega(\theta, \phi) \exp(\chi n_i). \end{aligned} \tag{A.21}$$

It is clear, from equation (3.1), that

$$F_1(\{\beta_i\}; 0, \phi, \chi) = 0 \tag{A.22}$$

and using the results that

$$\left(\frac{\partial x}{\partial \phi} \right)_{\theta=\phi=0} = \frac{2}{3} x(0, 0) \tag{A.23a}$$

$$\left(\frac{\partial y}{\partial \phi}\right)_{\theta=\phi=0} = \frac{4}{3}y(0, 0) \quad (\text{A.23b})$$

it is not difficult to show that

$$\Omega_2(i, 0, 0) = \frac{2}{3}n_i\Omega(i; 0, 0), \quad (\text{A.24})$$

from which it follows that

$$F_2(\{\beta_i\}; 0, 0, \chi) = \frac{2}{3}F_3(\{\beta_i\}; 0, 0, \chi). \quad (\text{A.25})$$

From

$$\sum \omega(i; r_i, s_i) = \frac{4!2^{n-s}8^s}{[\frac{1}{2}(n+r-s)]!s![\frac{1}{2}(n-r-s)]!(4-n)!} \quad (\text{A.26})$$

where the summation is over all configurations for which $r_i = r$, $s_i = s$ and $n_i = n$, it can be seen that

$$F(\{1\}; \theta, \phi, \chi) = [1 + 4 e^x (\cosh \theta + 2 e^\phi)]^4. \quad (\text{A.27})$$

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