Influence of electric field on the hydrogen bond network of water

S. J. Suresh and A. V. Satish
Unilever Research India, Hindustan Lever Research Centre, 64 Main Road, Whitefield, Bangalore 560066, India
A Choudhary
Indian Institute of Technology, Powai, Mumbai 400076, India

(Received 21 October 2005; accepted 6 December 2005; published online 16 February 2006)

Understanding the inherent response of water to an external electric (E)-field is useful towards decoupling the role of E-field and surface in several practically encountered situations, such as that near an ion, near a charged surface, or within a biological nanopore. While this problem has been studied in some detail through simulations in the past, it has not been very amenable for theoretical analysis owing to the complexities presented by the hydrogen (H) bond interactions in water. It is also difficult to perform experiments with water in externally imposed, high E-fields owing to dielectric breakdown problems; it is hence all the more important that theoretical progress in this area complements the progress achieved through simulations. In an attempt to fill this lacuna, we develop a theory based on relatively simple concepts of reaction equilibria and Boltzmann distribution. The results are discussed in three parts: one pertaining to a comparison of the key features of the theory vis a vis published simulation/experimental results; second pertaining to insights into the H-bond stoichiometry and molecular orientations at different field strengths and temperatures; and the third relating to a surprising but explainable finding that H-bonds can stabilize molecules whose dipoles are oriented perpendicular to the direction of field (in addition to the E-field and H-bonds both stabilizing molecules with dipoles aligned in the direction of the field).

© 2006 American Institute of Physics.

DOI: 10.1063/1.2162888

I. INTRODUCTION

The internal structure of water in electric fields is thought to play an important role in several important phenomena/processes, such as the well-known salting-in and salting-out effects, gating of biological ion channels, and electrochemical processes. Despite substantial progress made in the past, what exactly is the internal structure of water in these situations, as well as what governs it, are still widely debated research topics. For example, while some studies have supported the view of structure making and structure breaking by ionic solutes, others have not. Similarly, in the case of water near charged surfaces, while experiments reveal disruption of the H-bond network, simulations show that the H-bond network is largely intact.

In order to be able to clearly describe the role of the electric (E)-field on the internal structure of water without complications arising from the presence of a surface, simulations have been performed in the past on bulk water at field strengths comparable to that existing in the solvation shells of ions and near charged electrodes. Alper and Levy observed large nonlinear effects associated with molecular polarization between $\sim 1 \times 10^9$ and $\sim 2 \times 10^{10}$ V/m. Kiselev and Heinzinger observed a monotonic increase in the average number of H-bonds per molecule as the field strength was increased from 0 to $2 \times 10^{10}$ V/m. Sutmann obtained a similar result up to a field strength of $4 \times 10^{10}$ V/m. They also observed a phase transition into an ordered, icelike structure stabilized through H-bonds at a field strength of $\sim 3 \times 10^{10}$ V/m. Using a different molecular model, Yeh and Berkowitz found a similar phase transition to take place at a lower field strength of $\sim 10^{10}$ V/m.

Despite the reasonable progress on the simulation front, a comprehensive theoretical analysis of the above problem is still pending. Existing models (e.g., Ref. 18) are too simplistic in their treatment despite the fact that the general theoretical framework for treating fluids in E-fields was laid down several decades ago. The principal difficulty with water has been in dealing with the combined effect of hydrogen (H) bond interactions and dipole interactions in an E-field. These two interactions are coupled in a complex manner; for example, H-bonds must break prior to molecular rotation and new bonds must form post rotation. The problem is further complicated by the local or the microscopic field experienced by a molecule being different from the applied field due to polarization effects. It is the goal of the present paper to account for these effects using principles of statistical mechanics.

Substantial theoretical development has taken place in recent times towards describing H-bond interactions in the absence of E-field. Of particular relevance to the present paper is the work by Veytsman, Wertheim, and Stell and Zhou. Despite the approaches followed by each of them being different, the final equations describing the equilibrium properties of water were found to be similar in...
form. The results for the internal structure (e.g., fraction of unbonded association sites) as well as macroscopic thermodynamic properties (e.g., phase behavior, heat of mixing) have been extensively validated against both experimental and simulation data. More recently, these approaches have been extended to understand the behavior of water molecules near a solid wall. Inclusion of effects induced by an external electric field has also been achieved, but only in the context of liquids whose molecules possess one proton donor and one proton acceptors site each. Such liquids are relatively simpler to treat for two reasons: the H-bonded donor and acceptors site each. These liquids are referred to as \( \text{H}_2\text{O}^+ \) and \( \text{H}_2\text{O}^- \).

Our model for water.

![Our model for water.](FIG. 1)

**II. THEORY**

Each water molecule is assigned two proton donor sites (referred to as \( d_1 \) and \( d_2 \)) and two proton acceptor sites (referred to as \( e_1 \) and \( e_2 \)). The tetrahedral arrangement of these sites, the H-bond, the dipole moment vector \( (\vec{\mu}) \), and the \( E \)-field vector \( (\vec{E}) \) are schematically shown in Fig. 1. A site of type \( d_1 \) belonging to a molecule is allowed to H-bond with that of type \( e_1 \) of another molecule, provided the two sites are proximal, and the O-\( d_1 \) axis of the first molecule and \( e_1 \)-O axis of the second molecule are collinear. The energy released upon the formation of a H-bond is assumed to be independent of the type of donor \( (d_1 \) or \( d_2 \)) or acceptor site \( (e_1 \) or \( e_2 \)) involved. Also, the bonding probability at any given site is assumed to independent of whether other sites on the same molecule are bonded or not.

The energy of a molecule in an \( E \)-field depends on two angles, the dipolar angle \( (\theta) \) with respect to the field axis, and the angle of rotation \( (\Phi) \) of the molecule about the dipole moment axis (see Fig. 1). The former angle governs the torque experienced by the molecule due to \( E \)-field, and hence determines the dipole energy. The latter angle, at a given \( \theta \), governs the angular orientation of the four H-bonding axes of the molecule with respect to the field axis, and hence governs its H-bond interaction. Our goal now is to evaluate the fraction of molecules \( x_{[\theta,\Phi]} \) in orientation \( (\theta,\Phi) \). This is achieved by focussing our attention on the monomeric or the unbonded water molecules, as detailed below. The probability that a molecule in orientation \( (\theta,\Phi) \) is unbonded is the probability that all its four association sites are simultaneously unbonded. Hence, if \( Y \) represents the nonbonding probability at a site, the fraction of unbonded molecules in orientation \( (\theta,\Phi) \) is

\[
x_{[\theta,\Phi]} = x_{(\theta,\Phi)} Y_1 Y_2 Y_3 Y_4,
\]

where angles \( \alpha_1, \alpha_2, \alpha_3, \) and \( \alpha_4 \) are the angular orientations of the O-\( d_1 \), O-\( d_2 \), \( e_1 \)-O, and \( e_2 \)-O axes (all with respect to the field axis), respectively. These angles are fixed by the tetrahedral geometry and the angles \( (\theta,\Phi) \) through the following equations:

\[
\alpha_1 = \cos^{-1}[-\sin(\theta)\sin(54.73^\circ)\cos(\Phi) + \cos(\theta)\cos(54.73^\circ)],
\]

\[
\alpha_2 = \cos^{-1}[+\sin(\theta)\sin(54.73^\circ)\cos(\Phi) + \cos(\theta)\cos(54.73^\circ)],
\]

\[
\alpha_3 = \cos^{-1}[-\sin(\theta)\sin(54.73^\circ)\sin(\Phi) + \cos(\theta)\cos(54.73^\circ)],
\]

\[
\alpha_4 = \cos^{-1}[+\sin(\theta)\sin(54.73^\circ)\sin(\Phi) + \cos(\theta)\cos(54.73^\circ)].
\]

An alternative method to evaluate the same fraction of unbonded molecules is based on Onsager’s theory, modified to include H-bonding interactions. As per Onsager’s theory, the molecule is treated as a dipole at the center of a spherical cavity of molecular dimensions in a continuous medium of static dielectric constant \( \epsilon_r \). The radius \( a \) of this cavity is defined by the assumption that \( (4/3)\pi a^3 n_a = V \), where \( V \) is the volume of the system. The internal or the microscopic field \( (\mathbf{F}) \) (which is different from the applied field) that a molecule experiences is assumed to comprise of two parts: a cavity field which would be produced in the empty cavity by the external applied field, and a reaction field set up in the cavity by the polarization which the dipole induces in its surroundings. The importance of including the reaction field has been elucidated in earlier treatments as well. Following Onsager’s method, the final expression for the internal field is given by the expression

\[
\mathbf{F} = \frac{3\epsilon_0}{(2\epsilon_0 + 1)} \mathbf{E} + \frac{2(\epsilon_0 - 1)}{(2\epsilon_0 + 1)\epsilon_0} \frac{\mathbf{p}}{a^3},
\]

where \( \epsilon \) is permittivity in vacuum, and \( \mathbf{p} \) is the total moment of the molecule. The two terms on the right side of Eq. (3) represent the cavity and reaction fields, respectively.
The dipole moment of water in the liquid phase, \( \mathbf{p} \), is expressed as a vector sum of permanent dipole moment, \( \mathbf{\mu} \), and the moment \( \alpha' \mathbf{F} \) induced in the molecule by the local field, 
\[
\mathbf{p} = \mathbf{\mu} + \alpha' \mathbf{F}.
\] 
(4)

The magnitude of \( \mu \) in the present study is taken to be that in the vapor phase \([1.854 \ \text{D} \ (\text{Ref. 38})]\). \( \alpha' \) is the polarizability of the molecule, which was defined by Onsager in terms of the internal refractive index \( r \) by the relationship 
\[
\frac{\alpha'}{\varepsilon_0 r^2} = \frac{(r^2 - 1)}{(r^2 + 2)}.
\] 
(5)

In the present study, \( r \) is taken to be 1.33 corresponding to that in the visible light frequency. Combining Eqs. (3)–(5), we obtain 
\[
\mathbf{p} = \mathbf{\mu} + \frac{\alpha' \varepsilon_0 \mathbf{E}(r^2 - 1)}{2(\varepsilon_0 + r^2)} + \frac{\alpha' \varepsilon_0 \mathbf{E}}{2(\varepsilon_0 + r^2)}. 
\] 
(6)

In the absence of an external \( \mathbf{E} \)-field, the second term on the right side of Eq. (6) becomes zero. If one then substitutes \( \varepsilon_0 = 80 \) (corresponding to a temperature of 293 K), the calculated liquid-phase dipole moment turns out to be 2.34 D, a value that falls within the lower end of the reported range of 2.3–3.1 D.\(^{39} \)

Now, unlike bonded molecules that are constrained by H-bonds, unbonded molecules are free to rotate in an \( \mathbf{E} \)-field.

The torque exerted by the microscopic (or the internal) field on one such unbonded molecule is given by \( \langle \mathbf{p} \times \mathbf{F} \rangle \), where \( \mathbf{p} \) and \( \mathbf{F} \) are given by Eqs. (6) and (3), respectively. The energy of this dipole in the field is given by the expression 
\[
U_{\theta, \text{monomer}} = \int_0^\theta (\mathbf{p} \times \mathbf{F}) d\theta' = -\frac{\varepsilon_0 (r^2 + 2)}{(2\varepsilon_0 + r^2)} \mu \mathbf{E} \cos(\theta).
\] 
(7)

The probability for an unbonded, monomeric water molecule to be oriented at angle \( \theta \) is given by the Boltzmann factor 
\[
e^{-U_{\theta, \text{monomer}}/kT} = C e^{[\varepsilon(x)(r^2 + 2)/(2\varepsilon_0 + r^2)]} \mathbf{E} \cos(\theta kT),
\] 
where \( C \) is a proportionality constant. In addition, a molecule with angular coordinate \( \theta \) can have its dipole moment axis lie anywhere on the surface of a cone of half angle \( \theta \), caused by the rotation of the dipole about the \( \mathbf{E} \)-field axis. Hence, the fraction of unbonded molecules whose angular coordinates are \( (\theta, \Phi) \) is 
\[
X_{\theta, \Phi} = C e^{[\varepsilon(x)(r^2 + 2)/(2\varepsilon_0 + r^2)]} \mathbf{E} \cos(\theta kT) 2\pi \sin(\theta).
\] 
(8)

Equating Eqs. (1) and (8), we have 
\[
x_{\theta, \Phi} Y_{a_1} Y_{a_2} Y_{a_3} Y_{a_4} = C e^{[\varepsilon(x)(r^2 + 2)/(2\varepsilon_0 + r^2)]} \mathbf{E} \cos(\theta kT) 2\pi \sin(\theta).
\] 
(9)

The proportionality constant \( C \) in Eq. (9) is removed by imposing the constraint, 
\[
\int_0^\pi \int_0^{2\pi} x_{\theta, \Phi} Y_{a_1} Y_{a_2} Y_{a_3} Y_{a_4} d\theta' d\Phi' = 1. \text{ Hence,}
\] 
(10)

where angles \( \alpha_1', \alpha_2', \alpha_3', \) and \( \alpha_4' \) are obtained by substituting \( \theta' \) and \( \Phi' \) for \( \theta \) and \( \Phi \), respectively, in Eqs. (2a)–(2d).

We now evaluate the nonbonding probability, \( Y \), appearing in Eqs. (9) and (10). Consider a site of type, say, \( e_1 \), belonging to molecules whose \( e_1 - O \) axis lies at an angle \( \beta \) with respect to the \( \mathbf{E} \)-field axis (see Fig. 1). Let there be \( N_\beta \) such sites, of which \( m_\beta \) are bonded to acceptor sites of type \( d_1 \), and \( m_\beta \) to sites of type \( d_2 \). The remaining \( N_\beta = N_\beta - 2m_\beta \) (or fraction \( Y_\beta = N_\beta / N_\beta \)) sites would be unbonded. At equilibrium, \( m_\beta \) and \( N_\beta \) are related. To derive this relationship, we adopt the approach proposed earlier\(^{24,25} \) in which H-bonding between two complementary sites, say, \( e_1 \) and \( d_2 \), can be represented by a chemical reaction, 
\[
e_1 + d_2 \rightarrow e_1' \cdots d_2', \tag{11}
\]

The equilibrium criteria for the above reaction can be written as 
\[
\frac{m_\beta}{N_\beta} = e^{-\Delta_{\text{HH}}/kT} \frac{1}{V} P_{\beta}.
\] 
(12)

where \( \Delta_{\text{HH}} = u_{\text{HH}} - T S_{\text{HH}} \) is the change in free energy due to the formation of one H-bond. Any volume change accompanying formation of H-bonds is neglected in the present treatment. The first term on the right side of Eq. (12) represents the equilibrium constant for the donor-acceptor reaction shown in Eq. (11). The second term accounts for the probability for the donor and acceptor sites to be in close proximity for bonding to be possible. The third term, \( P_{\beta} \), accounts for the probability that the \( e_1 - O \) axis of the first molecule and \( O - d_2 \) axis of the second molecule are collinear for bonding to be possible. Note that these two axes need not necessarily be collinear although they both lie at an angle \( \beta \) with respect to the field axis. This is because either of these axes can lie anywhere on the surface of a cone of half angle \( \beta \), caused by the independent rotation of each of them about the \( \mathbf{E} \)-field axis. If we then fix the position of one of the axis, say, \( e_1 - O \) axis, \( P_{\beta} \) can be expressed as the ratio of the num-
ber of molecules whose O-d$_2$ axis is collinear with the fixed $e_1$-O axis to that of the number of molecules whose O-d$_2$ axis can lie anywhere on the surface of the cone. This can be easily seen to be given by the expression

$$P_\beta = \frac{2\pi}{N_\beta} \int_{\omega=0}^{2\pi} \frac{n_\beta(\theta, \omega)}{2\pi \sin \theta} d\omega.$$

where $\omega$ represents the degree of rotation of the molecule about the O-d$_2$ axis (refer to Fig. 1). The molecular orientation ($\theta', \Phi'$) is fixed by the angles ($\beta, \omega$) and the tetrahedral geometry of the molecule. Combining Eqs. (9), (10), (12), and (13), along with the criteria for mass balance ($N_\beta = N_\beta - 2m_\beta$), we derive the following expression for the non-bonding probability of donor sites whose $e_1$-O axis makes an angle $\beta$ with respect to the E-field axis,

$$Y_\beta = \frac{N_\beta}{N_\beta} = \frac{1}{1 + 2C\rho^2 e^{-\hat{EB}2kT} \int_{\omega=0}^{2\pi} \left(\frac{d\theta}{Y}\right) \frac{d\theta}{Y} d\omega},$$

where $\rho'=n'/V$ is the bulk density of the liquid at temperature $T$, and

$$\chi = \cos^{-1}(\sin(\beta)\sin(\omega - 30^\circ)\sin(109.47^\circ))$$
$$+ \cos(\beta)\cos(180^\circ - 109.47^\circ),$$

(15a)

$$\lambda = \cos^{-1}(-\sin(\beta)\sin(\omega + 30^\circ)\sin(109.47^\circ))$$
$$+ \cos(\beta)\cos(180^\circ - 109.47^\circ),$$

(15b)

$$\gamma = \cos^{-1}(-\sin(\beta)\sin(109.47^\circ)\cos(\omega))$$
$$+ \cos(\beta)\cos(109.47^\circ),$$

(15c)

$$\theta = \cos^{-1}(-\sin(\beta)\sin(54.73^\circ)\cos(\omega))$$
$$+ \cos(\beta)\cos(54.73^\circ),$$

(15d)

are the angles made by O-d$_1$, O-d$_2$, $e_2$-O, and the dipole moment axes of the molecule with respect to the field axis. One can easily show that Eq. (14) is valid for representing the fraction of unbonded sites of other types ($d_1$, $d_2$, and $e_2$) as well due to the symmetry of tetrahedral geometry.

Knowing $\{Y\}$ and $\chi$, we can use the following equations to calculate two properties that can be considered to represent the “average structure” of the liquid: the average number of H-bonds formed per molecule ($\langle n^{HB}\rangle$), and the average dipolar alignment of a molecule represented by $\langle \cos(\theta) \rangle$.

$$\langle n^{HB}\rangle = \int_{\theta=0}^{\pi} \int_{\Phi=0}^{2\pi} [Y_1 - Y_2 + Y_3 - Y_4] \sin(\theta) d\theta d\Phi,$$

(16)

$$\langle \cos(\theta) \rangle = \int_{\theta=0}^{\pi} \int_{\Phi=0}^{2\pi} \chi_1 \sin(\theta) d\theta d\Phi.$$

(17)

The mean moment of the molecule, parallel to the field, can now be calculated from Eq. (6) to be $[\mu \langle \cos(\theta) \rangle (2e_n + 1) \times (r^2 + 2)/(2e_n + r^2)] + [\alpha^2 n \varepsilon \cos(\theta^2 - 1)/(2e_n + r^2)]$, so that polarization $P$, which is moment per unit volume, becomes

$$P = \frac{\varepsilon}{4\pi} (\varepsilon - 1) E = \frac{n_\beta}{V} \frac{\mu \langle \cos(\theta) \rangle (2e_n + 1)(r^2 + 2)}{3(2e_n + r^2)}$$
$$+ \frac{\alpha^2 \varepsilon \varepsilon \varepsilon E (r^2 - 1)}{(2e_n + r^2)}.$$

(18)

Equations (2), (9), (10), (14), (15), (17), and (18) form a complete set for predicting the influence of E-field and temperature on the orientation of dipoles and H-bonds at various molecular orientations.

### III. LIMITING FORMS OF THE PROPOSED THEORY

Two limiting forms of the theory are discussed in this section.

1. In the limit of low E-field (where $\mu E \ll kT$), Eqs. (10) and (14) reduce to

$$Y_\beta = \frac{N_\beta}{N_\beta} = \frac{1}{1 + \frac{1}{2\pi} \rho' e^{-\hat{EB}2kT} 2\pi \langle e_n \rangle}.$$

(19)

Equation (19) is similar in form to that derived earlier using a different method and compared extensively against simulation data, the only difference being in the numerical value of the factor multiplying the term $\rho' e^{-\hat{EB}2kT} 2\pi \langle e_n \rangle$ in the denominator. This difference only alters the value of $e^{HB}$ [see Eq. (12)] that is extracted by fitting the theoretical predictions for the average number of H-bonds formed per molecule $\langle n^{HB}\rangle$ to experimental data (to be discussed later in Sec. IV in the context of Fig. 3); the final results for H-bond stoichiometry remains the same. The Kirkwood’s correlation factor $(g)$ in this low-field limit is defined as follows:

$$g = \frac{9KTV\varepsilon (e_n - r^2)(2e_n + r^2)}{e_n^4 4\pi N_{AV} (r^2 + 2)^2 \mu^2}.$$

(20)

Where $N_{AV}$ is the Avagadro number. Substituting the value of $e_n$, obtained using Eqs. (2), (9), (10), (14),
FIG. 2. Dielectric constant of water at different temperatures and field strengths.

(15), (17), and (18) into Eq. (20), yields the value of $g$ as predicted by the proposed theory. At low fields, it is possible to analytically solve these equations, yielding

$$g = \frac{3(2 - Y_\beta)}{2 + Y_\beta}. \quad (21)$$

Equation (21) has been derived earlier also using a different method that takes into account the dipolar correlations between a central water and H-bonded neighbors present in infinite number of shells surrounding the water molecule.

(2) In the limit of H-bonding interactions becoming zero (nonbonding probability becoming unity), Eqs. (9) and (10) can be combined to yield the following expression for the fraction of molecules with their dipoles oriented at angle $\theta$ with respect to the $E$-field axis (averaged over all azimuthal angles),

$$\bar{x}_\theta = \frac{1}{2\pi} \int_{\phi=0}^{2\pi} x_{\alpha,\beta} d\Phi$$

$$= \frac{1}{2\pi} \int_{\theta=0}^{\pi} \frac{e^{(E_o(r^2+2)/(2r^2+2))\mu E \cos \theta kT 2\pi \sin \theta}}{\int_{\theta'=0}^{\pi} \frac{e^{(E_o(r^2+2)/(2r^2+2))\mu E \cos \theta' kT 2\pi \sin \theta' d\theta'}}}.$$ \quad (22)

Equation (22) is identical to that derived earlier by Onsager.19,36

IV. RESULTS AND DISCUSSIONS

The only two adjustable model parameters are those related to the hydrogen bond interactions [see Eq. (12)]. They were deduced by fitting the theoretical results for dielectric constant ($\varepsilon_o$) at low field strengths (where $\mu E \ll kT$) to experimental data41 over temperatures ranging from the freezing to the critical point of water. The quality of fit of results of the proposed theory, with $u_{HB}^{0} = -5.58 \text{ Kcal/mole of H-bonds}$ and $s_{HB}^{0} = -6.8 \text{ cal/deg/mole of H-bonds}$, vis a vis experimental data reported in the past is shown in Fig. 2. The magnitude of these H-bond parameters fall well within the range of reported values.42,43 The predicted value of the dielectric constant of ice-I (91.3) compares well with that reported (92.0) in the literature.44 The results of Booth’s theory,45 shown in Fig. 2, will be discussed later along with the high field results. Figure 3 compares the results for $\langle n_{\text{HB}} \rangle$ against those of reported experimental/modeling studies.46–50 For reasons given in Sec. III, the deduced value of $u_{HB}^{0}$, as well as our results for $\varepsilon_o$ and $\langle n_{\text{HB}} \rangle$, are identical to those obtained earlier using a different method.40

We now proceed to study the influence of $E$-field on the internal structure of water at a fixed temperature of 289 K; effects of temperature variations will be considered later. At low field strengths, at which the dipolar interactions with field are not appreciable when compared to the H-bond interactions, the molecular distribution $\{x_{\alpha,\beta}\}$ goes through a maxima at $\theta = 90^\circ$ [Fig. 4(a)]. This maxima, hereafter referred to as the “primary” maxima, occurs due to most number of molecules being present within the cone of half angle $90^\circ$ (as compared to that present within cones of any other half angle) caused by the rotation of dipole axis at the fixed $\theta$ about the $E$-field axis. As the field strength is increased, the dipolar angle $\theta$ corresponding to this primary maxima shifts towards smaller angles, as seen in Figs. 4(a)–4(c). Interestingly, within a narrow interval of $E = 8.2 \times 10^8 – 2.2 \times 10^9 \text{ V/m}$, the molecular distribution goes through an additional “secondary” maxima. The inset of Fig. 4(c) shows this secondary maxima at $E = 10^9 \text{ V/m}$. As the field strength is increased within this interval, the molecular orientation corresponding to the secondary maxima changes from ($\theta = 84^\circ; \Phi = 45^\circ$) to ($\theta = 90^\circ; \Phi = 45^\circ$). Figure 5 shows a plot of the dipolar distribution averaged over all azimuthal angles $\{x_{\alpha,\beta}\}$. It is clear that the secondary maxima still persists.

Figure 6 shows the corresponding results for the bonding probabilities. At very low fields, the bonding probability is ~0.95, independent of the bonding angle. As the field is increased, the bonding probability goes through a primary maxima with the corresponding bonding angle approaching 54.73°. Concurrently, the distribution of the bonding probability about this maxima becomes more narrow, and the height of the primary maxima increases. Interestingly, within the same interval of field strength at which the molecular
distribution goes through a secondary maxima, the bonding probability also goes through a secondary, but a weaker, maxima. As the field strength is increased within this interval, the bonding angle corresponding to this secondary maxima is seen to change from $122^\circ$ to $125^\circ$. At the highest studied field strength of $4 \times 10^9$ V/m in Fig. 6, we note the appearance of another weak symmetric shoulder. The above-described results can be understood as follows. The primary maxima in the molecular distribution and bonding probabilities correspond to the same molecular orientation, which we hereafter refer to as orientation (a). As the field is increased, orientation (a) approaches that shown in Fig. 7(b), wherein $\theta=90^\circ$, $\Phi=45^\circ$. Two association sites $[d_1$ and $e_2$ in Fig. 7(b)], out of the total of four association sites belonging to each molecule in this orientation, are located such that their bonding angle is $54.73^\circ$. The bonding probability at these sites is high ($0.98$) for reasons as explained above (also see Fig. 6), primarily to molecules in orientation (a). Molecules in orientation (b) can thus be thought to be stabilized by strong H-bonding interactions at sites $d_1$ and $e_2$, despite the fact that their dipole moments are not favorably aligned with the $E$-field axis. The remaining two sites, $d_2$ and $e_1$, of the molecule shown in Fig. 7(b) are oriented such that their bonding angle is $125.27^\circ$. Bonding between these sites leads to the presence of the secondary maxima in the bonding probability in Fig. 6. Finally, at the highest studied field strength of $4 \times 10^{10}$ V/m, we can neglect any effects arising out of thermal energy ($\mu E \gg kT$). The presence of the weak shoulder can hence be attributed primarily to the interaction between H-bonding and dipole energy.

FIG. 4. Fraction of molecules in various molecular orientations $(\theta, \Phi)$ at $T=289$ K and different field strengths. a) $E=10^8$ V/m; b) $E=5 \times 10^8$ V/m; c) $E=10^9$ V/m. The inset is a magnified view of the marked region in Fig. 4(c), showing the secondary maxima in more detail.

FIG. 5. Fraction of molecules in various dipolar orientations $\theta$ at $T=289$ K and $E=1 \times 10^9$ V/m. The inset is a magnified view of the marked region, showing the secondary maxima in more detail.

other hand, the secondary maxima in the molecular distribution and bonding probabilities correspond to another molecular orientation, which we hereafter refer to as orientation (b). As the field is increased within the interval of $8.2 \times 10^8$–$2.2 \times 10^9$ V/m, orientation (b) approaches that shown in Fig. 7(a), wherein $\theta=0^\circ$ and the bonding angle at all four association sites is $54.73^\circ$. The resulting structure is similar to that of polarized ice, with each water molecule H bonded to four neighbors, and the dipoles pointing in the direction of $E$-field. Molecules corresponding to the orientation shown in Fig. 7(a) are thus stabilized by strong dipolar interactions with field as well as strong H-bonding interactions. On the

FIG. 6. Probability of H-bonds to be formed at different bonding angles with respect to the field axis at different field strengths and $T=289$ K. The regions marked within squares and circles show the location of the primary and the secondary maxima, respectively.

FIG. 4. Fraction of molecules in various dipolar orientations $\theta$ at $T=289$ K and different field strengths. a) $E=10^8$ V/m; b) $E=5 \times 10^8$ V/m; c) $E=10^9$ V/m. The inset is a magnified view of the marked region in Fig. 4(c), showing the secondary maxima in more detail.

FIG. 5. Fraction of molecules in various dipolar orientations $\theta$ at $T=289$ K and $E=1 \times 10^9$ V/m. The inset is a magnified view of the marked region, showing the secondary maxima in more detail.
It is clear from the above arguments that two conditions must be satisfied for molecules to be stabilized in orientation (b), and hence for the secondary maxima in the molecular distribution and bonding probability to be present. First, a sufficient number of molecules in orientation (a) must be present in the system for stabilizing those in orientation (b) through H-bonding interactions; hence, the dipolar interactions with field strength ($\mu E$) must be able to overcome the disruptive influence of thermal energy ($kT$). This minimum threshold field, in our study, turns out to be $\approx 8.2 \times 10^8$ V/m, at which point $\mu E \approx 2.4 kT$. Second, the unfavorable dipolar interactions of molecules in orientation (b) with field must not dominate over the stabilizing H-bonding interactions; hence, the strength of $E$-field must be below an upper threshold value, which in our study, turns out to be $\approx 2.2 \times 10^9$ V/m. This value of $E$ corresponds to that calculated by equating $f^{\text{HB}}$ to $\mu E$.

We now turn our attention to two properties of the system, the dielectric constant ($\varepsilon_\infty$) which is a measure of the average dipolar angle of a molecule ($\langle \theta \rangle$), and the average number of H-bonds per molecule ($n^{\text{HB}}$) [Eq. (16)]. They can, in some sense, be considered to represent the so-called “average structure” of water.

The onset of appreciable nonlinear dielectric response at a temperature of 289 K is predicted in our theory to occur at a threshold field strength of $\approx 5 \times 10^7$ V/m, in agreement with the experimentally reported value of $\approx 1-5 \times 10^7$ V/m. Past simulation studies, employing different molecular models, have yielded higher threshold values: $\approx 4 \times 10^8$ V/m (Ref. 14) and $\approx 1 \times 10^9$ V/m.6 Despite this discrepancy at low fields, the predictions for $\varepsilon_\infty$, at higher field strengths obtained using the different approaches, including ours, compare well (Fig. 8). These results probably suggest that the dielectric constant, at a given temperature, is not a very sensitive measure of the internal structure of water. The weak kink at $E \approx 10^8$ V/m in Fig. 8 occurs due to the appearance of the H-bonded stabilized orientation (b), shown in Fig. 7(b) and explained previously. Figure 8 also shows the results of Booth’s theory.45 The results obtained using the experimentally determined value of $\mu$ [=1.854 D (Ref. 38)] clearly are not in good agreement with the simulation results, especially at low fields. It is also clear from Fig. 8 that the agreement between simulation data and Booth’s theory can be substantially improved upon adjusting the value of the dipole moment of water to 2.049 D. However, then, the temperature variation of the low-field dielectric constant using this single value of $\mu$ is not well predicted (see Fig. 2). These discrepancies in Booth’s theory are not surprising, considering that Booth does not explicitly account for the H-bond interactions. The discrepancies between the predictions of Booth’s theory versus our theory for the temperature variation of dielectric constant decreases with increasing field strength (see Fig. 2) due to diminished role of H-bond interactions, when compared to that of dipole interactions. Our results for the temperature variation of dielectric constant can be understood as follows. Increasing the temperature of the fluid causes two opposing effects on the dielectric constant. First, the dipolar interactions with electric field in relation to the thermal energy ($\mu E / kT$) decreases, causing the dielectric constant to increase. Second, the H-bond interactions in relation to the thermal energy ($F_{\text{HB}} / kT$) decreases, causing the dielectric constant to decrease. The net result, shown in Fig. 2, is that the dielectric constant decreases with increasing temperature at both high and low field strengths; however, the temperature dependence at high fields is lower than at low fields.

Concurrent to the above-explained decrease in the average dipolar angle of a molecule ($\langle \theta \rangle$) with increasing field strength, the average number of H-bonds per molecule, $\langle n^{\text{HB}} \rangle$, is found to increase (see Fig. 9). Similar trends have been observed earlier also in related simulation studies, although the absolute magnitudes differ. Sutmann,16 for example, showed that $\langle n^{\text{HB}} \rangle$ increases from $\approx 2.03$ at zero field to $\approx 2.73$ at $4 \times 10^{10}$ V/m. Similarly, Kiselev and Heinzinger15 showed that $\langle n^{\text{HB}} \rangle$ increases from $\approx 2.7$ at zero field to $\approx 3.1$ at $2 \times 10^{10}$ V/m. It may be noted that the zero-field value of $\langle n^{\text{HB}} \rangle$ predicted by both these simulation approaches are not in agreement with those reported elsewhere (see Fig. 3). The cooperativity between the H bonding and dipolar interactions, experienced by a molecule on an average, can be understood based on the following arguments. Formation of H-bonds decreases the thermal motion of molecules, thereby reducing the relative role of thermal energy in disrupting dipolar alignment. Dipolar alignment in $E$-field, on the other hand, facilitates enhanced H-bonding interactions through two related effects. First, it reduces the ability...
of molecules to undergo thermal motion, thus facilitating H bonding. Second, it enhances the probability of complementary association sites to satisfy the orientational criteria for bonding to be possible. At higher temperatures, the zero-field value of \( \langle n^{HB} \rangle \) decreases for reasons explained earlier based on Fig. 3. The effect of temperature on \( \langle n^{HB} \rangle \) is diminished at higher field strengths due to the decreased influence of the disruptive thermal energy in relation to cooperative dipole energy.

V. CONCLUSIONS

We have developed a comprehensive theoretical framework for understanding the behavior of water in external E-fields. The attractiveness of the theory lies in the use of fairly simple physical concepts to account for H-bonded clusters of all possible shapes and sizes. The relevance of the predicted results broadly falls under three categories. The first category of results served more to ascertain the robustness of the theory through comparison with those reported earlier in the literature based on both simulation and experimental techniques. Examples of such properties include the temperature variation of the low-field dielectric constant and average number of H-bonds per molecule of water, low-field dielectric constant of ice-I, and the high field dielectric response. We have also demonstrated that the theory reduces to correct known forms in limiting conditions of either the field strength or the H-bond energy reducing to zero. The second category of results served to provide insights into the inherent response of water to E-fields in terms of the H-bond stoichiometry and molecular orientations. Such results are useful in deconvoluting the effects of E-field and surface in many practically encountered situations, such as that near an ion, near a charged electrode, or within a biological nanopore. This problem attains special significance in the light of the reported structural changes in water being induced by the presence of a surface also.\(^{31-34}\) In this context, an important conclusion of the present study is that E-fields can only enhance the H-bond structure of water, not disrupt it at any of the practically attainable field strengths. Past suggestions of the weakening of H-bond structure near the so-called “structure breaking” ions\(^{5,6}\) or near charged electrodes\(^{10,11}\) cannot be hence attributed to effect of E-field alone. The third category of results relates to the somewhat surprising finding that, within a certain window of field strength, H-bonds can stabilize molecules with their dipoles lying perpendicular to that of field. The fraction of such molecules is relatively small; for every thousand molecules with their dipoles aligned in the direction of field, roughly one is aligned perpendicular to that of the field. One can hence think of them as defects in an otherwise highly ordered arrangement of molecules. The role of these defects, if any, on the transport or solvation properties of water in E-fields remains to be seen.

ACKNOWLEDGMENTS

The authors are grateful to Professor M. L. Berkowitz for helpful discussions.