The effect of an external magnetic field on the structure of liquid water using molecular dynamics simulation

Kai-Tai Chang[a) and Cheng-I. Weng[b)
Department of Mechanical Engineering, National Cheng Kung University, Tainan,
70 Taiwan, Republic of China

Through a series of molecular dynamics simulations based on the flexible three-centered water model, this study analyzes the structural changes induced in liquid water by the application of a magnetic field with a strength ranging from 1 to 10 T. It is found that the number of hydrogen bonds increases slightly as the strength of the magnetic field is increased. This implies that the size of a water cluster can be controlled by the application of an external magnetic field. The structure of the water is analyzed by calculating the radial distribution function of the water molecules. The results reveal that the structure of the water is more stable and the ability of the water molecules to form hydrogen bonds is enhanced when a magnetic field is applied. In addition, the behavior of the water molecules changes under the influence of a magnetic field; for example, the self-diffusion coefficient of the water molecules decreases. © *2006 American Institute of Physics.*
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I. INTRODUCTION

The changes which occur in the structure of liquid water under the effect of an external magnetic field are important in various applications, e.g., water treatment, biological processes, and biotechnology. Since 1980, the effects of applying a magnetic field to liquid water have been intensively studied. It has been shown that the water vaporization rate, an essential process for all biological processes, is significantly affected by the application of a static magnetic field in both air and oxygen environments.[1] Studies[2,3] have found that various aspects of the liquid water structure, including the size of the water cluster, change when exposed to a magnetic field. The use of a magnetic field to generate large water clusters is of considerable interest in a number of practical applications. The influence of an external magnetic field on the internal energy and heat capacity of pure water has been investigated using Monte Carlo simulations.[4] The effect of a constant magnetic field on the electrical conductivity of water has also been studied.[5] It has been reported that the dissolution rate into water of some materials, e.g., oxygen and copper sulfate, is significantly accelerated by the presence of a magnetic field.[6,7] Applying an increasing magnetic field to water can also reduce critical supercooling and prompt equilibrium solidification when the strength of the magnetic field is higher than 0.5 T.[8] The self-diffusion coefficient of water can also be altered under a magnetic field. Applying a magnetic field to water can reduce the corrosion rate of steel.[9] Hosoda *et al.* measured the refractive index of water at atmospheric pressure under magnetic fields of up to 10 T and found an increase of approximately 0.1% as a result of a more stable hydrogen bonding.[10] Magnetic fields can also weaken the van der Waals bonding between water molecules.[11] The effect of the magnetic field in enhancing the hydrogen bonding was confirmed by Inaba *et al.*[12] The authors proposed that both the increased melting point of H_2O and D_2O under a magnetic field of 6 T and the reduced entropy in liquid water under the application of a magnetic field were the result of a strengthening of the hydrogen bonds. Several papers have investigated the viscosity of pure water under a magnetic field of 10 T.[13–15] Ishii *et al.*[15] indicated that the relative change of viscosity of pure water under a transverse magnetic field of 10 T is less than 10^{-4}.

It is difficult to investigate the changes which occur in the structure of liquid water when exposed to magnetic fields using direct experimental approaches. Therefore, numerical methods are generally employed to obtain detailed insights into the structural changes. Molecular dynamics (MD) simulations provide a powerful means of investigating the enhanced hydrogen-bonding mechanism from an atomic viewpoint. Although some recent studies have used computational simulations to examine the effect of an electrical field on the structure of liquid water,[16,17] molecular dynamics simulations of water under the influence of an external magnetic field have yet to be reported.

II. METHOD

In the present study, each simulation case considers 4096 water molecules within a cubic simulation box with sides of length 48 Å. Periodic boundary conditions are imposed in each dimension of the simulation box. The density of the water molecules is assumed to be 0.997 g/cm^3 throughout, and the scaling method[18] is used to scale the temperature of the water molecules to an equilibrium temperature of 300 K during the course of the simulations. All of the calculations are performed in the canonical *NVT* ensemble. The multiple time step method[19,20] is used to reduce the computation time, and the Verlet algorithm[19,21] is employed to calculate the

a)Electronic mail: asiki.me90g@nctu.edu.tw
b)Author to whom correspondence should be addressed: also at to Guang University, Jaoshi Shiang, Ilam, Taiwan, Republic of China; electronic mail: weng@mail.ncku.edu.tw

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trajectories of the atoms. A smaller time step of 0.1 fs is used when simulating the rapid motions associated with the bonding and bending of the water molecules, while a larger time step of 1 fs is adopted to simulate the other motions. The simulations consider various atomic interactions, namely, those between the water molecules themselves, and the O–H bonding and H–O–H bending intramolecular interactions which take place within the individual water molecules. The inter- and intramolecular interactions of the H_2O molecules are modeled using the flexible three-centered (F3C) water model.[22]

A good model must reproduce the structure of liquid water identified by experimental x-ray and neutron diffraction methods. The results of the F3C water model are in good agreement with the experimental results.[22] This model employs a short-range truncation which significantly improves the efficiency of the computational process. The F3C water model is an interatomic potential model in which the conformational energy (U) of a molecular system comprises bonded and nonbonded terms, i.e.,

$$U = U_{bonded} + U_{nonbonded},$$

where U_{bonded} represents the bonded interactions which arise from bond stretching and bending, i.e.,

$$U_{bonded} = U_{bond} + U_{bend}$$
$$= \sum K_b(b_i - b_0)^2 + \sum K_\theta(\theta_i - \theta_0)^2,$$

where b_i, θ_i, b_0, and θ_0 are the ith O–H bond length, the ith H–O–H bond angle, the equilibrium length of the O–H bond length in a water molecule, and the equilibrium angle of the H–O–H bond angle in a water molecule, respectively.

The nonbonded interaction ($U_{nonbonded}$) is expressed as

$$U_{nonbonded} = U_{vdW} + U_{Coulomb},$$

where U_{vdW} and $U_{Coulomb}$ are the van der Waals potential and the Coulomb potential, respectively. The complete form of the van der Waals potential is given by

$$U_{vdW}(r_{ij}) = \sum [A_{SC}\varepsilon(r_0/r_{ij})^{12} - 2\varepsilon(r_0/r_{ij})^6 - S_{vdW}(r_{ij})],$$

where the parameter A_{SC} is determined by the cutoff distance specified in the F3C water model.[22] A_{SC} reduces the repulsive van der Waals energy to compensate for the loss of attractive interactions at smaller cutoff distances. In the present simulations, the cutoff distance is specified as 10 Å and the value of A_{SC} is set to 1. The general form of the truncation shift function $S_f(r)$ is given by

$$S_f(r) = \begin{cases} [f(r_c) + (r - r_c)(df(r_c)/dr)], & r < r_c, \\ 0, & r > r_c \end{cases},$$

where $f(r_c)$ and r_c are the potential function and the cutoff distance, respectively. The complete form of $S_{vdW}(r_{ij})$ is

$$S_{vdW}(r_{ij}) = [A_{SC}\varepsilon(r_0/r_c)^{12} - 2\varepsilon(r_0/r_c)^6] - 12(r - r_c)$$
$$\times [A_{SC}\varepsilon(r_0/r_c)^{12} - \varepsilon(r_0/r_c)^6]/r_c.$$

The Coulomb potential $U_{Coulomb}$ has the following form:

TABLE I. Parameters of F3C water model.

Parameters and units	H_2O-H_2O
r_0^{OO} (Å)	3.5532
ε^{OO} (kcal mol^{-1})	0.1848
r_0^{HH} (Å)	0.9000
ε^{HH} (kcal mol^{-1})	0.01
r_0^{OH} (Å)	1.7883
ε^{OH} (kcal mol^{-1})	0.0423
q^O (e.u.)	−0.820
q^H (e.u.)	0.41
b_0^{OH} (Å)	1.0000
θ_0^{HOH} (deg)	109.47
K_b^{OH} (kcal mol^{-1} Å^{-2})	250
K_θ^{HOH} (kcal mol^{-1} rad^{-2})	60

$$U_{Coulomb}(r_{ij}) = \sum \left[\frac{q^i q^j}{r_{ij}} - S_{Coulomb}(r_{ij}) \right],$$

where the potential function $S_{Coulomb}(r_{ij})$ is expressed as

$$S_{Coulomb}(r_{ij}) = [q^i q^j/r_c] - (r - r_c)[q^i q^j/r_c^2],$$

where q^i and q^j represent the partial charges of the hydrogen or oxygen atoms of two different water molecules within the cutoff distance. The parameters used in the F3C water model are given in Table I.[22]

This study employs the algorithm proposed in Ref. 23, in which the Lorentz forces acting on the charged particles are considered, to simulate the movement of the charged particles in the homogeneous external magnetic field. A charged particle performs Larmor oscillations of Larmor frequency when the magnetic field is applied. The algorithm[23] describes a charged particle exposed to a static homogeneous external magnetic field which moves spirally with Larmor frequency. In a strong magnetic field, the algorithm can be derived using a Taylor expansion of the second-order velocity Verlet algorithm or from a velocity transformation. Since the time step in the present simulations is sufficiently small, this study adopts the simpler form of the algorithm presented in Ref. 23, in which the strength of the magnetic field is dependent on the value of the time step. The magnetic field is assumed to act in the z direction in the simulation boxes, and the velocities of the oxygen and hydrogen atoms change in both the x and the y directions. The present simulations are based on the following:

$$r_x(t + \Delta t) = r_x(t) + \Delta t v_x(t) + \frac{1}{2}(\Delta t)^2[a_x^C(t) + \Omega v_y(t)],$$

$$r_y(t + \Delta t) = r_y(t) + \Delta t v_y(t) + \frac{1}{2}(\Delta t)^2[a_y^C(t) - \Omega v_x(t)],$$

$$r_z(t + \Delta t) = r_z(t) + \Delta t v_z(t) + \frac{1}{2}(\Delta t)^2 a_z^C(t),$$
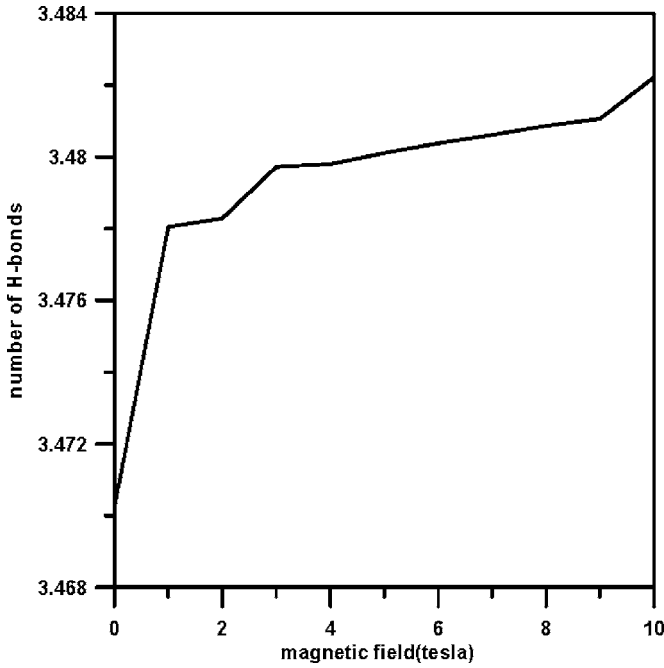
FIG. 1. Variation of number of hydrogen bonds under magnetic fields with magnitudes ranging from 0 to 10 T at 300 K.

$$v_x(t + \Delta t) = v_x(t) + \frac{1}{2}\Delta t[a_x^C(t) + a_x^C(t + \Delta t) + 2\Omega v_y(t)]$$
$$+ \frac{1}{4}(\Delta t)^2\Omega[a_y^C(t) + a_y^C(t + \Delta t) - 2\Omega v_x(t)],$$

$$v_y(t + \Delta t) = v_y(t) + \frac{1}{2}\Delta t[a_y^C(t) + a_y^C(t + \Delta t) + 2\Omega v_x(t)]$$
$$- \frac{1}{4}(\Delta t)^2\Omega[a_x^C(t) + a_x^C(t + \Delta t) + 2\Omega v_y(t)],$$

$$v_z(t + \Delta t) = v_z(t) + \frac{1}{2}\Delta t[a_z^C(t) + a_z^C(t + \Delta t)],$$

where a^C represents the accelerations which are independent of the velocities of the atoms and the Larmor frequency and $\Omega = qB/m$ is determined by the magnetic field B.

In the present simulations, the strength of the magnetic field ranges from 1 to 10 T. Initially, the computational procedure assumes a zero magnetic field effect and is run for 40 ps to obtain an equilibrium temperature of 300 K. The magnetic field is then applied from 40 to 140 ps simulation time.

III. RESULTS AND DISCUSSION

Electric fields break or distort the hydrogen-bond angle by causing a reorientation of the water molecules, and hence weaken or destroy the hydrogen-bond network.[24] This effect is the reverse of that which occurs under a magnetic field; i.e., the hydrogen bonding is enhanced. The influence of the magnetic field on hydrogen bonding is shown in Fig. 1. As described previously, the structure of the water molecules is more ordered and stable under an applied magnetic field. In

determining the average number of H bonds, the present study adopts the geometric criterion[25] that a hydrogen bond will be formed if the distance between the oxygen and hydrogen atoms of a pair of water molecules is less than the first minimum of the F3C O–H radial distribution (2.4 Å).[22] The simulation results presented in Fig. 1 indicate that the number of hydrogen bonds increases when a magnetic field is applied. Specifically, as the strength of the magnetic field increases from 1 to 10 T, the number of hydrogen bonds increases by approximately 0.34%. This slight increase in the number of hydrogen bonds indicates that the magnetic field enhances the water networking ability. Water clusters (even with random arrangements) have equal hydrogen bonding in all directions. The higher number of hydrogen bonds implies that the size of the water cluster increases under a magnetic field, and hence the structure of the water molecules becomes more compact. The present results showing an increased number of hydrogen bonds are consistent with the findings presented by Hosoda *et al.*[10] who suggested that the enhancement of the hydrogen-bond strength under a high magnetic field is caused by the increased electron delocalization of the hydrogen-bonded molecules. Furthermore, the effect of the magnetic field in increasing the number of hydrogen bonds is consistent with a weakening van der Waals bonding force between the water molecules under a magnetic field[11] and the suppression of thermal motions as a result of the tighter hydrogen bonding induced by the Lorentz forces.[12] Additionally, the increased number of hydrogen bonds implies that there are more water molecules forming hydrogen bonds. However, the structure of the liquid water is still unclear.

The radial distribution functions, g_{O-H}, g_{O-O} and g_{H-H}, are commonly used to examine the structure of liquid water. The structural differences of pure liquid water with and without the application of an external magnetic field of 10 T are shown in Fig. 2. Figure 2(a) presents the radial distribution function (g_{O-O}), i.e., the distribution of the interoxygen distances in any direction from a central water molecule, at 300 K under a magnetic field of 10 T. The first peak (A) occurs at 2.8 Å, which corresponds to the oxygen-oxygen distance between the two hydrogen-bonding water molecules. The second peak indicates the tetrahedral structure of the near neighbors and corresponds to the distance between two oxygen atoms belonging to two water molecules which are both hydrogen bonded to a third water molecule. When the strength of the magnetic field is increased to 10 T, the insets in Fig. 2(a) show that the height of the first peak (A) decreases slightly, while the heights of the first and second valleys (i.e., B and C) increase. However, the positions of the first peak (A) and the first valley (B), i.e., 2.8 and 3.2 Å, respectively, are unchanged, indicating that the average tetrahedral hydrogen-bonding length and the distance between two oxygen atoms belonging to two next-nearest neighbors are not influenced by the increased magnetic field. The increased heights of the first and second valleys under the external magnetic field indicate that more water molecules exist between the water shells. This enhanced connectivity between the water shells is also evident in Fig. 2(b), which illustrates the O–H radial distribution function (RDF) at 300 K under a magnetic field of 10 T. Under this magnitude
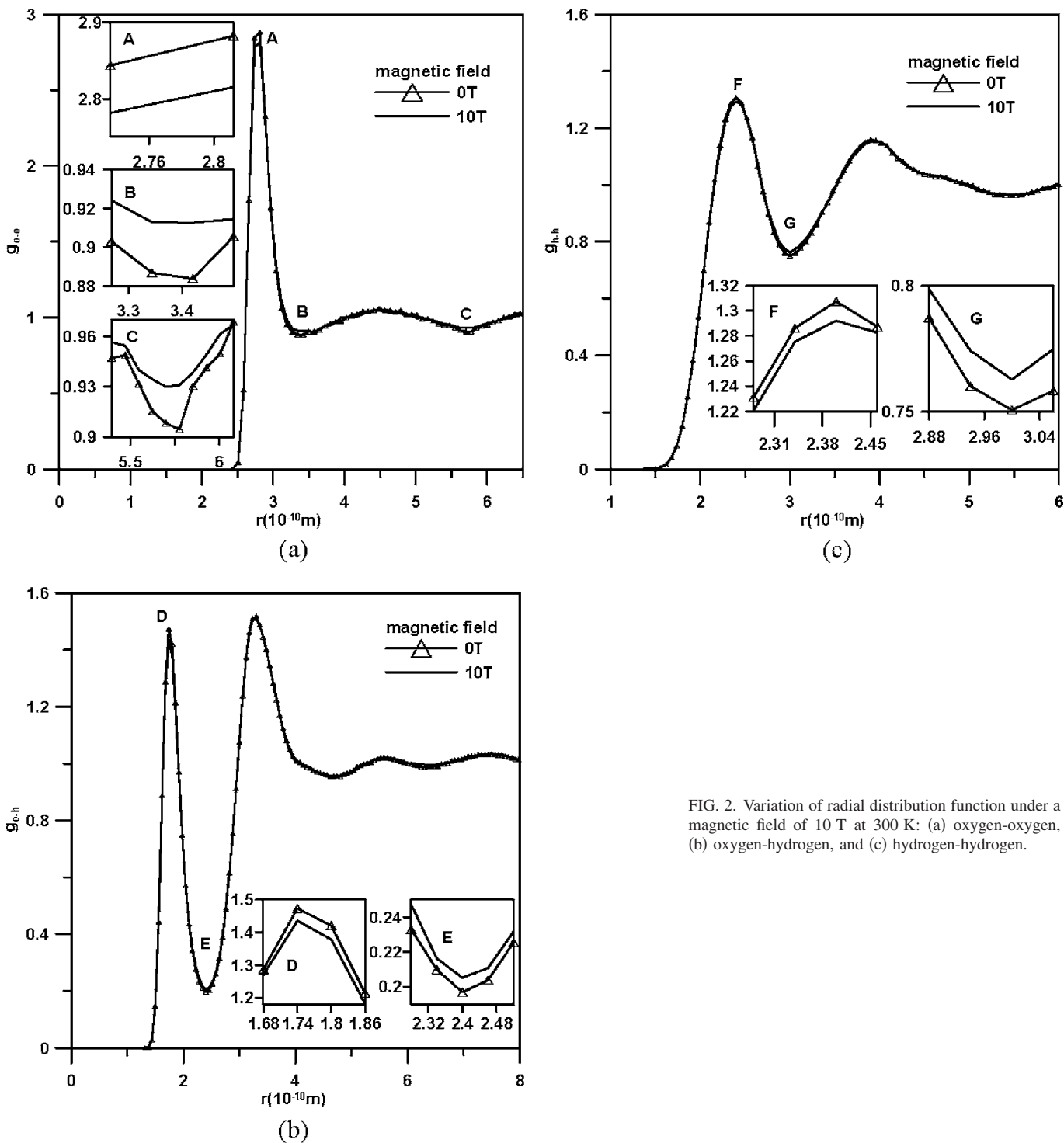
FIG. 2. Variation of radial distribution function under a magnetic field of 10 T at 300 K: (a) oxygen-oxygen, (b) oxygen-hydrogen, and (c) hydrogen-hydrogen.

of magnetic field, the first peak (D) at approximately 1.8 Å decreases, while the first valley (E) at 2.4 Å increases. The slight increase in the height of the first valley (E) indicates that more water molecules are located between the water shells. This implies that the magnetic field reforms the structure of the liquid water and forces more water molecules between the water shells, hence enhancing the connectivity between them and improving the stability of the water-water network. Consequently, a small increase in the number of hydrogen bonds is apparent under a magnetic field of 10 T. According to the results presented in Figs. 2(a) and 2(b), the water molecules tend to form more stable connections with

other water molecules in all directions. Figure 2(c) illustrates the H–H RDF at 300 K under a magnetic field of 10 T. It can be seen that the value of the first peak (F) decreases and the value of the first valley (G) increases under the effect of the magnetic field. In summary, the results presented in Fig. 2 demonstrate that magnetic fields enhance the bonding between water molecules and stabilize the structure of liquid water.

This study also examines the self-diffusion coefficients of water molecules under a magnetic field. Studying the transport properties of liquid water is an important topic, both in fundamental science and in its applications. The mo-
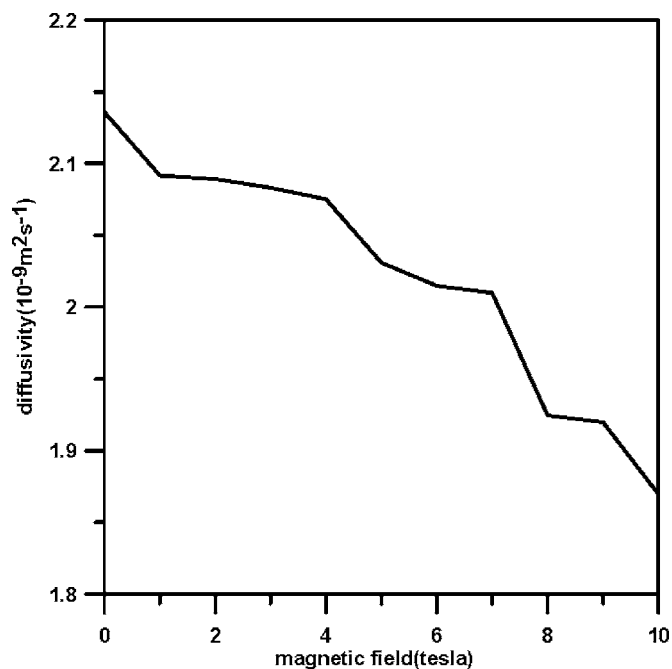
FIG. 3. Variation of self-diffusion coefficient as magnetic field increases from 0 to 10 T at 300 K.

bility of water molecules is indicated by the value of the self-diffusion coefficient, which depends on the temperature,[22] pressure, structure, and so on. Recently, several studies have investigated the self-diffusion coefficient of water molecules in different environments, including water molecules confined in a carbon nanotube,[26] between parallel plates,[27] and in sodium chloride solutions.[28] The value of the self-diffusion coefficients can be obtained from the Einstein relation based on the mean-square displacement function. The results of Figs. 1 and 2 have shown that a static magnetic field enhances the stability of water molecules, and hence influences their mobility. Calculating the self-diffusion coefficient of the water molecules provides a clearer understanding of this change in mobility. Figure 3 presents the profiles of the self-diffusion coefficient under various magnetic strengths. It is clear that the self-diffusion coefficient reduces as the strength of the magnetic field increases. The decreasing self-diffusion coefficient indicates that the mobility of the water molecules decreases when a magnetic field is applied. If the mobility of the water molecules changes, the physical properties of the water molecules, e.g., the viscosity, thermal conductivity, and melting point, also change. Even in a high magnetic field (10 T), the value of the self-diffusion coefficient of liquid water is approximately 1.9×10^{-9} m^2 s^{-1}, whereas that of liquid water at 273 K without an applied magnetic field is 1.6×10^{-9} m^2 s^{-1}. Although the reduction of the self-diffusion coefficient caused by the magnetic field is not large, it nevertheless indicates a change in the properties of the liquid water.

From the results presented in Figs. 1 and 3 which show an increasing number of hydrogen bonds and a decreasing self-diffusion coefficient as the magnetic field strength is increased, it can be surmised that a static magnetic field restricts the movement of water molecules and changes the

viscosity of liquid water. These conclusions are consistent with the assumptions reported by Ishii *et al.*[15]

IV. CONCLUSION

This study has examined the effect of a static magnetic field on liquid water at an equilibrium temperature of 300 K. It has been shown that an external magnetic field influences the number of hydrogen bonds, the structure of liquid water, and the self-diffusion coefficient of water molecules. In this study, the strength of the external magnetic field was increased from 0 to 10 T. The corresponding number of hydrogen bonds was found to increase by approximately 0.34%, indicating the formation of larger water molecule clusters. In other words, it is apparent that an applied electric field and an external magnetic field exert opposite effects on the number of hydrogen bonds. Specifically, an electric field breaks the hydrogen-bond network, while a magnetic field enhances the hydrogen-bonding ability. The magnetic field induces a tighter bonding between the water molecules and improves the stability of liquid water. Under the effect of the magnetic field, the structure of the liquid water changes and more water molecules are forced between the water shells. These molecules connect the shells and hence create a more stable water-water network. The transport properties of the water molecules, as indicated by the self-diffusion coefficient, are of considerable interest in many applications. The current simulation results have shown that the self-diffusion coefficient reduces when a magnetic field is applied. In other words, the magnetic field constrains the movement of the water molecules, and hence changes both the thermal conduction and the viscosity in the liquid state.

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