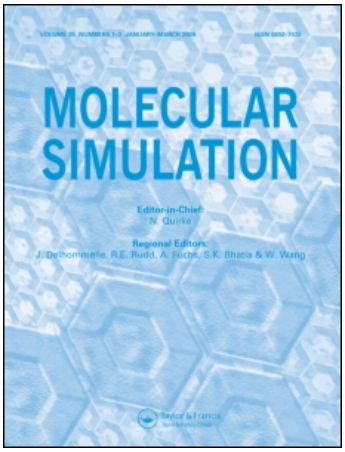

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Molecular dynamics simulation of liquid water under the influence of an external electric field

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Molecular dynamics simulations of liquid water were performed at 258K and a density of 1.0 g/cm^3 under various applied external electric field, ranging $0 \sim 10^{10}$ V/m. The influence of external field on structural and dynamical properties of water was investigated. The simple point charge (SPC) model is used for water molecules. An enhancement of the water hydrogen bond structure with increasing strength of the electric field has been deduced from the radial distribution functions and the analysis of hydrogen bonds structure. With increasing field strength, water system has a more perfect structure, which is similar to ice structure. However, the electrofreezing phenomenon of liquid water has not been detected since the self-diffusion coefficient was very large. The self-diffusion coefficient decreases remarkably with increasing strength of electric field and the self-diffusion coefficient is anisotropic.

Keywords: Molecular simulation; Molecular dynamics; Liquid water; External electric field

1 Introduction

Water is the most common liquid in nature and it is also important in numerous chemical and biological processes. With the availability of computers, Monte Carlo (MC) and Molecular dynamics (MD) simulations have been introduced and much of research effort has been devoted to examining the microscopic structure and dynamics properties of liquid water utilizing computer simulations [1–8]. It is known that liquid water is connected random tetrahedral hydrogen-bonds network [1,2]. However, many experiments indicate that this random tetrahedral network is not perfect and it contains some structural defects or inhomogeneous regions at microscopic level. Previous studies have shown that, although the majority of the molecules participate in four hydrogen bonds in liquid water, many molecules also participate in two, three or five hydrogen bonds [3–5]. Liquid water exhibits a very peculiar thermodynamical and transport behavior. These anomalies can be explained by hydrogen-bonding structural peculiarities [6,7].

The changes of structural and dynamic properties of water and aqueous solutions under the influence of an external electric field are quite important for electrochemistry and biology [9]. Some other studies of water and aqueous solutions under an external electric field by computer simulation have appeared. Rose and Benjamin [10] carried out a molecular dynamics study of adsorption of ions near charged platinum–water surface. Lee and Rasaiah [11] determined the ionic mobility from data obtained in the presence of an electric field. Zhu *et al.* [12] performed an MD simulation of pure water under the influence of an oscillating external electric field. Svishchev and Kusalik [13] investigated the electrofreezing phenomena under a high electric field. Jung, Yang, and Jhon [14] using the ring structure, analyzed the structural change of liquid water induced by an external electric field. More recently, Tang, Chan, and Szalai [15–17] investigated the effects of confinement on the structural and transport properties of an electrolyte in a nanopore with the presence of an external electric field. However, the distribution of the number and the angle of hydrogen bonds were not mentioned in these studies. Moreover, it is also not clear how the structure of hydrogen bonds and the diffusivity are related to the strength of the external electric field.

In this paper, we performed a set of molecular simulations at 258K under an external electric field varying from $0 \sim 10^{10}$ V/m. We investigated the

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relationship between structural changes and the external electric field in terms of radial distribution functions and the hydrogen-bonding structure. In addition, we also calculated the diffusivities of liquid water under the external electric field. The remainder of this manuscript is organized as follows. Section 2 contains a brief description of the molecular model and the molecular dynamics simulation methods. Section 3 presents our simulation results and section 4 summarizes our conclusions.

2 Model and simulation methods

In all the simulations, the water molecules are characterized by the simple point charge (SPC) [18] potential. The MD simulations were carried out in the canonical ensemble (NVT) at an average temperature of 258K with a weak coupling to an external temperature bath [19], and the density was 1.0 g/cm^3. The simulations were performed with seven different strengths of the external electric field ranging from 0 to 10^{10} V/m. The external electric field induced an additional force, $F_i = q_i \cdot E$, where F_i is the force induced by the electric field, q_i is charge of each atom, and E is the applied electric field. The static electric field was always applied along the Z-axis of the simulation cell.

A cubic box of 216 molecules and periodic boundary conditions with the minimum image convention were employed. A spherical truncation of the Lennard-Jones interaction potential at $0.5L$ was employed, where L is the edge length of the simulation box. The long-range electrostatic interactions were treated with the Ewald method. The equations of motion were solved using the leap-frog algorithm with a SHAKE subroutine [20]. The systems were equilibrated for about 100 ps with a time step of 2 fs and then various equilibrium and dynamical properties were calculated over a period of 300 ps.

3 Results and discussions

3.1 Radial distribution functions

Radial distribution functions can be considered to reflect the structural changes of pure water caused by external field electric fields of different strengths. The oxygen–oxygen and oxygen–hydrogen radial distribution functions $g_{oo}(r)$ and $g_{oh}(r)$ for different external field strengths at 258K and a density of 1.0 g/cm^3 were shown in figure 1. As can be seen from figure 1, the height of the first peak increases and that of the first minimum decreases with increasing field strength, the positions of the first peaks are not affected by the strength of applied field, which is the same result as the observation by Kiselev and Heinzinger [21]. This result indicates that the first neighbor structure of water is enhanced significantly by applying an external field.

The second neighbor shell is strongly affected by the applied field. The height of the second peak increases with increasing field strength, and the positions of the second peaks are shifted to distances smaller by 0.2 Å when the field strengths are larger than 0.5×10^{10} V/m. This fact means that the reorientation of the water molecules caused by the applied field changes the hydrogen bond structure, which will be discussed below.

The structural change of water can be seen from figure 2, where we present snapshots of equilibrium configuration of water at 258K and a density of 1.0 g/cm^3 without and with an electric field of 0.8×10^{10} V/m. By applying an external electric field, a more ordered structure of water can be obtained. This structural change of water by the external electric field is mainly due to the permanent electric dipole moment of a water molecule. Because of the dipole moment, the external electric field aligns the dipole of water molecules in the direction of the electric field.

3.2 Hydrogen bond structure

In this section the influence of the applied field on the hydrogen bond structure will be investigated by calculating the average number of hydrogen bonds and the distributions of hydrogen bond angles. Following previous work [3,4], we have used a geometric criterion where two water molecules are taken to be hydrogen bonded if the oxygen–oxygen distance is less than 3.5 Å and simultaneously the hydrogen–oxygen distance is less than 2.45 Å and oxygen–oxygen–hydrogen angle θ is less than 30°. The quantities of interest are the percentages f_n of water molecules that engage in n hydrogen-bonds and the average number of hydrogen-bonds per water molecule n_{HB}. The values of f_n ($n = 1, \ldots, 6$) and n_{HB} are included in table 1 for various field strengths.

As shown in table 1, the fractions of molecules having four hydrogen bonds and the average number of hydrogen bonds per water molecule increase with the strength of external electric field. And the fractions of molecules having other number of hydrogen bonds decrease with increasing electric field strength. Although the separation of the oxygen atoms are not influenced by

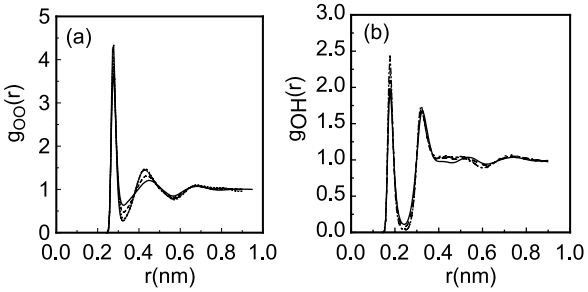

Figure 1. Oxygen–oxygen and oxygen–hydrogen radial distribution functions without external field (solid) and for field strength of 0.2 (dashed), 0.5 (dotted), and 1.0 (dash-dotted) $\times 10^{10}$ V/m at 258 K and a density of 1.0 g/cm^3.

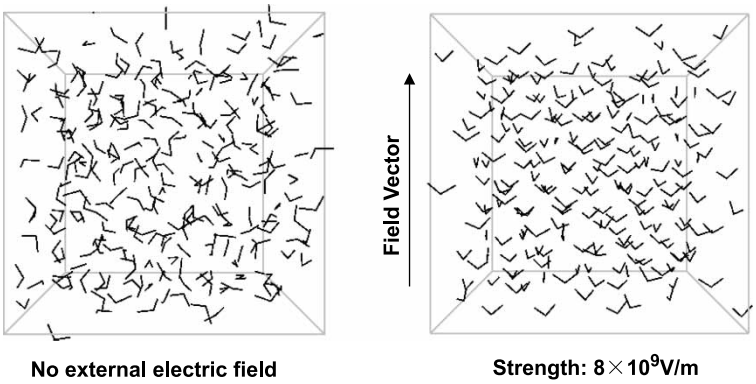

Figure 2. Snapshots of water at 258K and a density of 1.0 g/cm^3 without and with an electric field of 0.8×10^{10} V/m

the external field (see figure 1), the hydrogen bond structure is found to be more perfect with about 88% of the water molecules participating in four hydrogen bonds at the strength of 1.0×10^{10} V/m. The structure of water is more and more similar to ice-like structure with increasing strength of the electric fields. This suggests that the spatial orientation of water molecule be influenced by the external electric field, and the rotation of the water molecules caused by the external field change the position of the hydrogen atoms.

Since the position of the oxygen atoms are not influenced by the external field, these structural changes must be caused by a change in hydrogen bond angles through the reorientation of dipole moments in the electric field. In order to understand this changes, we calculated the distributions of the oxygen–oxygen–hydrogen angle θ. The distributions of the hydrogen-bond angle θ under different strengths of electric field are presented in figure 3. As can be seen from figure 3, the height of the peak increases and the distribution curve narrows with the strength of the applied field. The position of the peak shifts to smaller angle with increasing field strength. This fact indicates that with increasing strength of electric field, the bonding H atoms are progressively turning to the line joining the two oxygen atoms, thus forming in average a smaller angle θ. Consequently, the average number of hydrogen bonds per water molecule increases with the strength of external electric field, and the water system has a well-organized structure, which is similar to the structure of ice. Previous study [15] by Tang *et al.* showed little effect of electric field on hydrogen bonding of SPC/E water in a nanopore. This difference may be due to the confinement and concavity of a narrow channel which prevents extension of the H-bonding network in the radial direction, and some H atoms are closer to the pore wall and free from any H-bonding.

For the analysis of the pair dynamics of hydrogen bonded water molecules, we have calculated the following hydrogen bond correlation function:

$$C_{\mathrm{HB}}(t) = < h_{\mathrm{HB}}(0) h_{\mathrm{HB}}(t) > / < h_{\mathrm{HB}} >$$

where $h_{\mathrm{HB}}(t)$ is a time-dependent hydrogen bond variable which is equal to 1 if a pair of water molecules is hydrogen bonded at time t and zero otherwise. The correlation function $C_{\mathrm{HB}}(t)$ describes the probability that a hydrogen bond is intact at time t, given it was intact at time zero with the bonding state. Thus, the dynamics of $C_{\mathrm{HB}}(t)$ describes the structural relaxation of hydrogen bonds and the associated relaxation time τ_{HB} can be interpreted as the time scale of reorganization of hydrogen bonds. The time dependence of $C_{\mathrm{HB}}(t)$ under different strengths of an electric field is shown in figure 4 and the corresponding relaxation times are included in table 1. It is found that the rates of hydrogen bond structural relaxation depend significantly on the strengths of the electric field. Again, the relaxation is found to decay at a slower rate with increasing strength of the external field. We can conclude that the hydrogen-bond structure of water depends considerably on the strength of electric field, and the hydrogen bond structure is enhanced with increasing applied electric field.

Table 1. The percentage of water molecules having n number of hydrogen bonds (f_i), average number of hydrogen bonds per water molecule (n_{HB}) and relaxation time of hydrogen bonds (τ_{HB}) at various field strengths.

Field strength (10^{10} V/m)	f_1	f_2	f_3	f_4	f_5	f_6	n_{HB}	τ_{HB}(ps)
0	0.217	3.621	23.417	66.854	5.853	0.0367	3.746	10.3
0.1	0.154	2.968	21.972	69.196	5.676	0.0345	3.773	11.5
0.2	0.092	2.086	18.322	74.782	4.704	0.0168	3.821	14.6
0.3	0.065	1.572	15.420	79.000	3.933	0.0138	3.852	17.8
0.5	0.044	1.093	13.143	82.835	2.879	0.0059	3.874	21.1
0.8	0.020	0.817	12.490	83.961	2.706	0.0039	3.885	24.8
1.0	0.015	0.587	10.401	87.429	1.519	0.0022	3.900	27.1

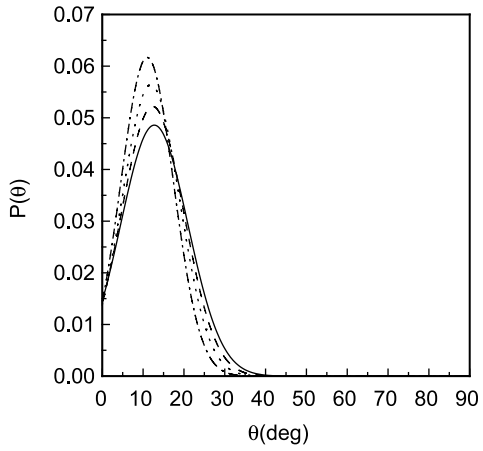

Figure 3. Distribution of the hydrogen-bond angle θ under different strengths of electric field. The denotations are the same as in figure 1.

3.3 Self-diffusion coefficients of liquid water

The translational diffusion coefficient D can be obtained from the integral of the velocity autocorrelation function or from the mean-square displacement (MSD). In this study, the latter was used to determine D. The expression is

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{\mathrm{d}}{\mathrm{d}t}|r_i(t) - r(0)|^2$$

where r_i is the positional vector. The time dependences of the MSDs at different electric fields are shown in figure 5.

The self-diffusion coefficients of water at 258K and density of $1.0\,\mathrm{g/m^3}$ under various strengths of electric fields are presented in table 2. The self-diffusion coefficient of water without an external field is calculated as $7.56\times10^{-10}\,\mathrm{m^2/s}$, which agrees with previous result obtained by Chandra and Chowdhuri [3]. The self-diffusion coefficient decreases remarkably with the increasing strength of electric field as a consequence of the increased hydrogen bond structure. The self-diffusion coefficient under the electric filed of $1.0\times10^{10}\,\mathrm{V/m}$ is about one-eleventh of the value obtained without an electric field. We note that even under the electric filed of $1.0\times10^{10}\,\mathrm{V/m}$, the self-diffusion coefficient is about twenty thousand times as large as is ice (the self-diffusion coefficient of ice at 263K without electric field is $2.8\times10^{-15}\,\mathrm{m^2/s}$ [14]). This means that under an external electric field water system has a more perfect structure, which is similar to ice structure but still in liquid state. We also calculated the self-diffusion coefficients for the motion along x, y and z directions, which were included in table 2. The self-diffusion coefficient of the z direction is less than that of the x and y directions. The anisotropy is enhanced with increasing field strength, the self-diffusion coefficient of the x and y directions are about double that of the z direction at the strength of $1.0\times10^{10}\,\mathrm{V/m}$. This can be explained that the translational motion of the water molecules are hindered by the additional force induced by the external electric field.

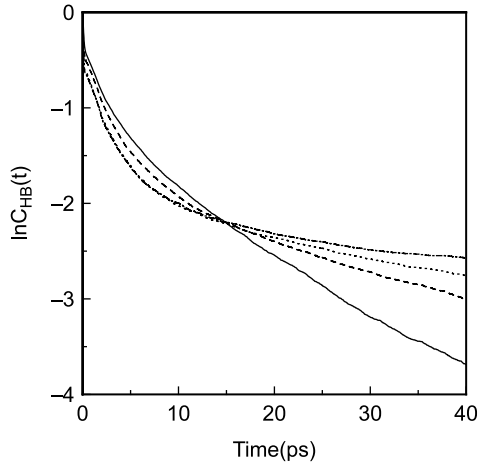

Figure 4. Time dependence of hydrogen-bond correlation functions under different strengths of electric field. The denotations are the same as in figure 1.

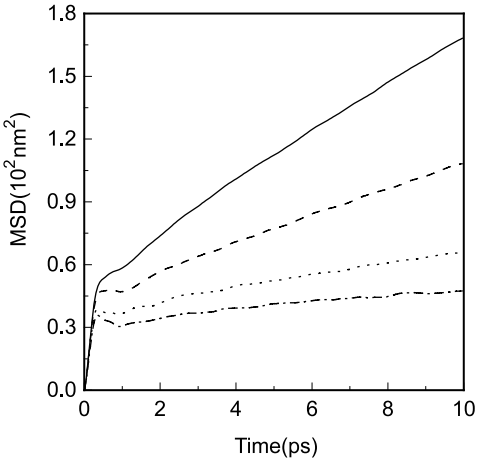

Figure 5. Mean-square displacement of water under different field strengths of 0.2 (solid), 0.3 (dashed), 0.5 (dotted), and 0.8 (dash-dotted) $\times\,10^{10}\,\mathrm{V/m}$ at 258K and a density of $1.0\,\mathrm{g/cm^3}$.

4 Conclusions

We have carried out molecular dynamics studies of the structural and dynamic properties of water at 258K and density of $1.0\,\mathrm{g/cm^3}$ under the influence of an external electric field. An enhancement of the water hydrogen bond structure with increasing strength of the electric field has been deduced from the radial distribution functions, the

Table 2. Self-diffusion coefficient of different directions calculated at various strengths of external fields. Diffusion coefficient and electric field strength are expressed in units of $10^{10}\,\mathrm{m^2/s}$ and $10^{10}\,\mathrm{V/m}$, respectively.

Field strength	D_{av}	$\boldsymbol{D_x}$	D_y	D_z
0.1	5.28	5.79	5.93	4.11
0.2	2.83	3.07	3.13	2.27
0.3	1.82	2.01	2.02	1.44
0.5	1.12	1.23	1.29	0.84
0.8	0.80	0.90	0.93	0.59
1.0	0.66	0.78	0.75	0.44

average number of hydrogen bonds and the distributions of hydrogen bond angles. With increasing field strength, water system has a more perfect structure, which is similar to ice structure. However, the electrofreezing phenomenon of liquid water has not been detected, as the self-diffusion coefficient observed was too large to be in the solid state. The self-diffusion coefficient decreases remarkably with increasing strength of electric field, and the self-diffusion coefficient is anisotropic.

Acknowledgements

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