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A molecular dynamics study of dielectric constant of water from ambient to sub- and supercritical conditions using a fluctuating-charge potential model

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Abstract

Molecular dynamics calculations have been performed based upon a fluctuating-charge model TIP4P-FQ over a wide range of state points from ambient to sub- and supercritical conditions in order to investigate dielectric properties of water. The TIP4P-FQ could successfully reproduce the experimental dielectric constant. The dielectric constant is dominated not only by the intermolecular orientational correlation but also by the magnitude of each molecular dipole moment. Interesting behavior of these two contributions is reported as a function of temperature and density. Averaged number of hydrogen bonds has also been found to have a strong correlation with the dielectric constant. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Dielectric constant of water is one of the most important physical parameters which rules the dissolution of organic and inorganic substances in water. A striking feature of the dielectric constant of water is that an exceptionally large value at ambient condition, 78, decreases along an isochore to be a few tens, for example, at temperature slightly higher than the critical temperature and then, along the isotherm, the value becomes small rapidly as the density of the fluid decreases, approaching to unity in the dilute gas limit [1]. This presents the ions and organic substances a variety of solubility behavior in water as a function of temperature and density, which opens a way to the industrial application of sub- and supercritical water such as extraction and chemical reaction. Now, it is very interesting to clarify a molecular mechanism which determines the dielectric constant of water over a wide range of state points.

Microscopic picture for the dielectric properties of water has actively been investigated mainly by computer simulations [2,3]. In particular, a number of studies have been done for ambient water [2–13], demonstrating that the fluctuation of the total polarization comes from short-ranged strong intermolecular orientational correlation by the hydrogen bond as well as the weak but abundant long-ranged correlations. Further, the dielectric properties have been investigated, too, for water at high temperatures [14–18]. However, potential

functions adopted in these studies are mostly based upon fixed point charge model [14–16] such as TIP4P and SPC/E. Their parameters were optimized to describe ambient water, resulting in an effective fixed molecular dipole moment 2.18 and 2.35 D for TIP4P and SPC/E, respectively.

The fixed molecular dipole moment in these potential models is an essential shortage if dielectric constant is to be studied over a wide range of state points including sub- and supercritical regions. First, the dielectric constant is proportional to the mean-square fluctuation of the total dipole moment of the system which is the summation of the molecular dipole moment. Second, the dipole moment of water molecule has a distribution in its inhomogeneous environment. This distribution depends much upon the state points as demonstrated by many MD calculations based upon polarizable potential model such as RPOL [19–22], TIP4P-FQ [23,24], and PPC [18,25] and Car–Parrinello method [26,27]. Now, it is clear that the dielectric constant of the fluid is determined not only by the intermolecular orientational correlation of the dipole moment vector but also by the squared average of the fluctuating magnitude of the moment.

Thus, in the present study, dielectric properties of water have been analyzed using the polarizable potential model TIP4P-FQ over a wide range of state points from ambient to sub- and supercritical states. The model has been proved to be of high-quality in describing liquid water [24]. Based upon this calculation, two contributions to the dielectric constant, i.e., the magnitude of molecular dipole moment and the intermolecular orientational correlation, are analyzed separately.

2. Calculations

Molecular dynamics calculations have been performed for the system consisting of 256 and 10 648 TIP4P-FQ water molecules contained in a cubic cell with periodic boundary conditions. Equations of motion of the molecule and partial charge, each of which is in contact with Nosé–Hoover chain thermostat separately, were solved numerically by RESPA method with $\Delta t = 0.5$ fs.

Here, as in our previous study [23], a wall potential was added to the charge in order to avoid the numerical instability which might occur in the long-time MD calculation. Coulombic interactions between the charges were calculated by Ewald method. Details of the potential functions and the equations of motion are presented elsewhere [23,24].

3. Results and discussion

For the present MD calculations by the Ewald method, dielectric constant ϵ of the fluid may be calculated according to the standard expression [28]

$$\epsilon - 1 = \frac{\langle M^2 \rangle}{3kTV}, \tag{1}$$

where M is the total dipole moment of the system, k is the Boltzmann constant, T is the temperature, and V is the volume. Here, high-frequency dielectric constant was approximated as usual to be unity in spite of the polarizable model. For the present system, which is composed of electrically neutral molecules, M is obtained by

$$M = \sum_i \boldsymbol{\mu}_i, \tag{2}$$

where $\boldsymbol{\mu}_i$ is the dipole moment vector of molecule i. In contrast to the fixed point charge model, where only the orientation of the vector $\boldsymbol{\mu}_i$ varies with the magnitude being fixed, the present fluctuating charge model changes both the magnitude and orientation of the dipole moment vector of each molecule.

As reported by many authors for the fixed point charge water [2,3], convergence of the calculated dielectric constant is very slow so that the test of the statistics of the calculation becomes important. In Fig. 1, cumulative average of the dielectric constant is plotted as a function of the length of the present MD production run for 256 water system at several state points along the isochore at 1 g/cm³ and along the isotherm at 700 K. For water at ambient condition, the present calculation of 650 ps might be slightly short compared with that required to obtain a sufficient convergence of
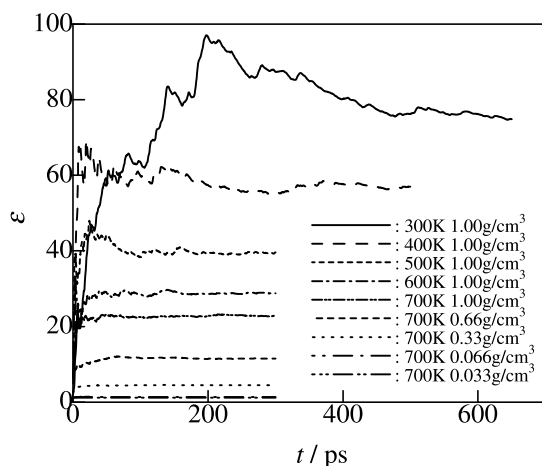
Fig. 1. Cumulative average of the calculated dielectric constant of water at various state points along an isochore at 1 g/cm^3 and along an isotherm at 700 K as a function of the length of MD run.

Table 2
Calculated dielectric properties of TIP4P-FQ water at various densities along an isotherm at 700 K

	ρ (g/cm^3)				
	1.0	0.66	0.33	0.066	0.033
ϵ	21	12	4.3	1.4	1.2
ϵ (experiment [1])	27	14	5.1	1.4	1.2
$\langle \boldsymbol{\mu}_i \rangle / \mathrm{D}$	2.30	2.15	2.02	1.89	1.87
$\langle \boldsymbol{\mu}_i^2 \rangle / \mathrm{D}^2$	5.30	4.62	4.08	3.57	3.49
G_K	2.54	2.56	1.69	1.14	1.08
ρ/ρ_c	3.0	2.0	1.0	0.2	0.1

the reduced unit. They show a good agreement between the calculation and experiment. Thus, the TIP4P-FQ model can describe the dielectric constant of water sufficiently well from ambient to sub- and supercritical water by taking account of the polarization of water molecule following the electric field on it.

The present TIP4P-FQ water reaches the critical point at temperature lower than the real water by about 70 K [23]. Then, it is interesting to compare the calculated dielectric constant of water at supercritical states with the experimental one at the same state points reduced by the critical constants. The reduced state points in the calculation are $\rho^* = \rho/\rho_c = 3.0$, 2.0, 1.0, 0.20 and 0.10 along the isotherm at $T^* = T/T_c = 1.22$ (700 K), where the experimental dielectric constant is 22 ($\rho = 0.97$ g/cm^3), 12 ($\rho = 0.64$ g/cm^3), 4.4 ($\rho = 0.32$ g/cm^3), 1.4 ($\rho = 0.064$ g/cm^3), and 1.2 ($\rho = 0.032$ g/cm^3), respectively, along the same isotherm at $T^* = 1.22$ ($T = 789$ K) [1]. It is encouraging to find that the calculated values in Table 2 show an excellent agreement with the experiment.

As stated above, in TIP4P-FQ water, magnitude of each molecular dipole moment fluctuates in response to the instantaneous electric field by all other water molecules. Then, the mean-square

Table 1
Calculated dielectric properties of TIP4P-FQ water at various temperatures along an isochore at 1.0 g/cm^3

	T (K)					
	300	300 ($N = 10\,648$)	400	500	600	700
ϵ	73	72	56	40	29	21
ϵ (experiment [1])	78	78	54	40	32	27
$\langle \boldsymbol{\mu}_i \rangle / \mathrm{D}$	2.60	2.61	2.44	2.37	2.33	2.30
$\langle \boldsymbol{\mu}_i^2 \rangle / \mathrm{D}^2$	6.80	–	6.01	5.67	5.45	5.30
G_K	3.10	3.05	3.57	3.33	2.97	2.54

fluctuation of the total dipole moment, i.e., the dielectric constant, may be divided formally into two microscopic factors, the squared average of the molecular dipole moment and the orientational correlation as

$$\epsilon - 1 = \frac{1}{3kTV}\left\langle \sum_i \boldsymbol{\mu}_i \sum_j \boldsymbol{\mu}_j \right\rangle = \frac{N}{3kTV}\langle \boldsymbol{\mu}_i^2 \rangle G_K, \tag{3}$$

where

$$G_K = \frac{\sum_i \sum_j \langle \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \rangle}{N\langle \boldsymbol{\mu}_i^2 \rangle} \tag{4}$$

is defined such that it has a value of unity if no orientational correlation is found. Now, we may attain a deeper understanding of the dielectric constant at a molecular level than that reached from the fixed point charge model, although these two contributions might have a correlation with each other. In Tables 1 and 2, G_K and $\langle \boldsymbol{\mu}_i^2 \rangle$ as well as $\langle \boldsymbol{\mu}_i \rangle$ are listed, too.

Averaged molecular dipole moment $\langle \boldsymbol{\mu}_i \rangle$ changes its value from 2.60 D at ambient condition to 1.87 D in the high-temperature and low-density supercritical fluid. This is in good correspondence to the values reported for ice 2.6–3.1 D [29,30] and gas 1.85 D [31]. Fig. 2 shows the distribution of $|\boldsymbol{\mu}_i|$
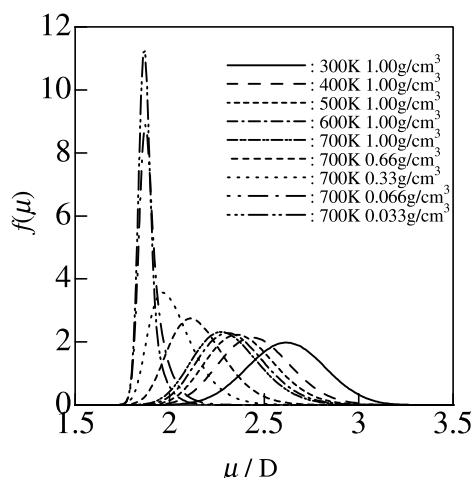

Fig. 2. Distribution of the magnitude of the molecular dipole moment vector of water at various state points along an isochore at 1 g/cm³ and along an isotherm at 700 K.

for the fluid at several temperatures along the isochore at 1 g/cm³ and at several densities along the isotherm at 700 K. As clearly shown in the figure, ambient water has a wide distribution of the instantaneous molecular dipole moment ranging from 2.1 to 3.2 D with the peak at 2.6 D, which is in good agreement with that reported originally by Rick et al. [24]. With increasing temperature, along the isochore, the averaged value of the dipole moment becomes small from 2.60 to 2.30 D and, at the same time, the distribution becomes narrow although the degree of the narrowing is rather small. On the other hand, with decreasing density along the isotherm, the peak shifts from 2.3 to 1.9 D in this density range, approaching the value found in vacuum. However, in this case, the width of the distribution becomes narrow rapidly. This must reflect the annihilation of hydrogen bonding network in the low-density fluid [21]. According to these changes, the squared average of the dipole moment which appears in the expression of the dielectric constant becomes small rapidly from 6.8 to 3.5 D². It is noticeable that the value is about a half in the low-density supercritical water compared with that in the ambient water. On the other hand, the G_K factor becomes small, too, with increasing temperature along the isochore to be 2.54 at 700 K. At the supercritical states along the isotherm at 700 K, G_K changes the value from 2.54 to 1.08. The value of the G_K factor of nearly unity found for the fluid at densities lower than 0.066 g/cm³ indicates that the intermolecular orientational correlation has almost disappeared.

In Fig. 3, in order to obtain an overview of the phase behavior of these two contributions to the dielectric constant, the ratios of the values $\langle \boldsymbol{\mu}_i^2 \rangle$ and G_K at various state points to those of ambient water (300 K, 1 g/cm³) are plotted along the isochore and the isotherm as a function of temperature and density, respectively. Both ratios $\langle \boldsymbol{\mu}_i^2 \rangle / \langle \boldsymbol{\mu}_i^2 \rangle_{\text{ambient}}$ and $G_K/G_{K\text{ambient}}$ decrease to be about 0.8 as the temperature increases to 700 K along the isochore. It should be noted here that the decrease in $\langle \boldsymbol{\mu}_i^2 \rangle$ is responsible for the decrease of the dielectric constant to the extent which is of the same order of magnitude as the decrease in G_K. The two contributions reduce the value of the
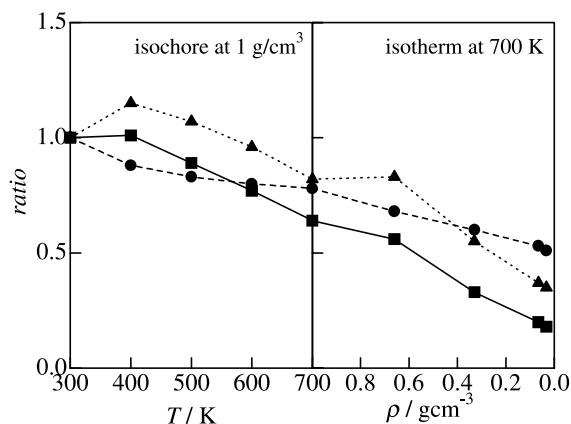
Fig. 3. Ratios of the averaged squared molecular dipole moment and the G_K factor of water at various state points along an isochore at 1 g/cm^3 and along an isotherm at 700 K to those at ambient condition. Product of these two factors is also plotted. ($\bullet$): $\langle \boldsymbol{\mu}_i^2 \rangle / \langle \boldsymbol{\mu}_i^2 \rangle_{\text{ambient}}$, ($\blacktriangle$): $G_K / G_{K\text{ambient}}$, and ($\blacksquare$): $(\langle \boldsymbol{\mu}_i^2 \rangle G_K) / (\langle \boldsymbol{\mu}_i^2 \rangle G_K)_{\text{ambient}}$.

dielectric constant together to be about 0.6 of that at ambient condition. The decline of the orientational correlation and the decrease in the electric field may be related to the structural change of water from the ice-Ih-like structured one to the simple-liquid-like less structured one, which is found for water as the temperature increases [20]. Further, with decreasing density along the isotherm at 700 K, two factors become small further. Now, the G_K factor shows the ratio as small as about 0.35, while $\langle \boldsymbol{\mu}_i^2 \rangle$ has the ratio of about 0.5. This implies that the orientational correlation is more sensitive to the variation of density than the magnitude of the molecular dipole moment. These two factors reduce the dielectric constant together to be about 0.2 of the value at ambient circumstance. In particular, it is very interesting to find that the decrease in $\langle \boldsymbol{\mu}_i^2 \rangle$ reduces the dielectric constant to about a half, which has entirely been neglected in the previous calculations based upon the fixed point charge model such as TIP4P and SPC/E.

The induced dipole moment may also have a close connection with the hydrogen bond. This leads to an interesting examination of the correlation between the dielectric constant and the averaged number of hydrogen bonds. Here, a pair of water molecules are defined to form a hydrogen bond when one of the hydrogen–oxygen distances is less than 2.5 Å and, at the same time, interaction between them is more negative than −17.4 kJ/mol, at which the hydrogen–oxygen radial distribution function and the pair interaction distribution function, respectively, show their minima. The averaged number of hydrogen bonds was calculated following these geometrical and energetical criteria for water at state points studied in our previous Letter [23]. Fig. 4 shows the calculated dielectric constant ϵ and the averaged number of hydrogen bonds n_{HB} as a function of temperature along several isochores. The ordinate of n_{HB} was scaled such that the two plots overlap with each other. In the figure, the experimental dielectric constant is also presented. The figure clearly shows an excellent overlap of the dielectric constant and the averaged number of hydrogen bonds. This indicates that these two have a conformal behavior as a function of temperature and density. Inset of the figure also shows a very strong linear correlation between the calculated dielectric constant and the number of hydrogen bonds.
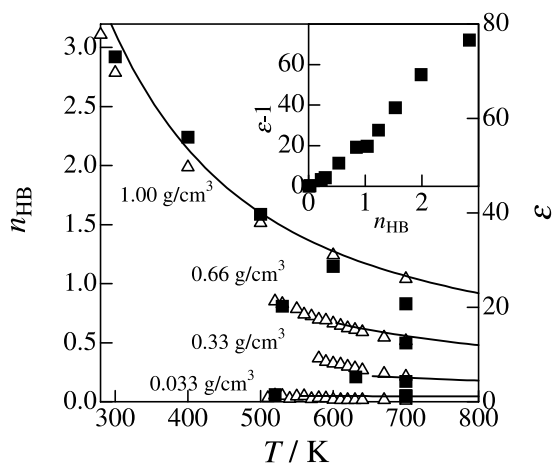

Fig. 4. Correlation between dielectric constant and averaged number of hydrogen bonds of water at various state points along isochores. ($\blacksquare$): calculated dielectric constant, ($\triangle$): calculated number of hydrogen bonds, and (—): experimental dielectric constant. The inset also presents a correlation between the calculated dielectric constant and the number of hydrogen bonds.

Acknowledgements

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