

Molecular Dynamics Simulation Study for Self-diffusion Coefficients of the Scaled OSS2 Water

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Received July 20, 2009, Accepted August 17, 2009

Key Words: Molecular dynamics simulation, Scaled OSS2 potential, Self-diffusion coefficient

Several attempts at developing dissociable water potentials in classical simulations to study proton hydration and H⁺/OH⁻ neutralization reactions in small clusters have been made previously beginning with pioneering work on central force models by Stillinger, Lemberg, David and Weber.¹⁻⁵ In their model the water molecules consist of H⁺ and polarizable O²⁻ ions whose bare Coulomb interactions are modified at short range. Halley *et al.*⁶ devised a new potential of the Stillinger-David-Weber form which was optimized to reproduce the experimental static correlation functions of bulk water by reducing the mean squared error between experiment and simulation by simulated annealing optimization of the potential parameters.

Ojamäe, Shavitt and Singer⁷ designed a family of potentials describing both intramolecular and intermolecular interactions, and allowing dissociation and formation of solvated proton (H₂O)_nH⁺ complexes in water called the OSS n potentials where $n = 1$ to 3 are fitted to *ab initio* Møller Plesset (MP2) calculations. The potentials are parametrized in the form of interactions between H⁺ and O²⁻ ions, with additional three-body (H-O-H) interaction terms and self-consistent treatment of the polarizability of the oxygen ions.

In the present note, we report the result of molecular dynamics (MD) simulation for the self-diffusion of bulk water at several different temperatures using the OSS2 model potential of Ojamäe *et al.*⁷ Although more accurate results could possibly be obtained with the OSS3 potential, the OSS2 model also gives good results judging by simulations of neat water except exhibiting too large bond angles for water molecules. When that deficiency is not a serious problem, it is our preferred choice because of faster and less elaborate computer code implementation compared to the OSS3 model which contains three body dipole coupling terms.

However, it is found by us that the OSS2 model could behave like a glass or an ice under ambient conditions, as discussed with L. Ojamäe⁸ and as suggested by N. Agmon,⁹ but a glass formation is absent at higher temperature (~500 K) or lower density (~0.5 g/cm³).¹⁰ Our main goal is to seek any relevant way in order to eliminate the glass formation of the OSS2 water at ambient conditions.

Molecular Models and MD Simulation Methods. In the OSS2 potential model, the total energy is given by

$$V_{\text{tot}}(r_1, r_2, \dots, r_{n_o-n_H}) \quad (1)$$

$$= V_{\text{el}}(r_1, r_2, \dots, r_{n_o-n_H}) + \sum_i \sum_j V_{\text{OH}}(r_{ij})$$

$$+ \sum_i \sum_{j,j>i}^{n_o-1} V_{\text{OO}}(r_{ij}) + \sum_i \sum_{k,k>i}^{n_H-1} \sum_j V_{\text{HOH}}(r_{ij}, r_{kj}, \theta_{ijk}).$$

The first term represents the total electrostatic energy.

$$V_{\text{tot}}(r_1, r_2, \dots, r_{n_o-n_H}) \quad (2)$$

$$= \min_{\{\mu_1, \dots, \mu_{n_o}\}} \left[\sum_i \sum_{j,j>i}^{n_o-1} \frac{q_i q_j}{r_{ij}} + \sum_i \sum_{j,j>i}^{n_H-1} \frac{q_i q_j}{r_{ij}} \right.$$

$$+ \sum_i \sum_j \frac{q_i q_j}{r_{ij}} - \sum_i \sum_{j,j>i}^{n_o-1} (\mu_i \cdot T_{ij} \cdot \mu_j) S_{ij}^{\text{dd}}(r_{ij})$$

$$\left. + \sum_i \sum_{j,j>i}^{n_o-n_H} q_i \frac{\mu_i \cdot r_{ij}}{r_{ij}^3} S_{ij}^{\text{cd}}(r_{ij}) + \frac{1}{2\alpha} \sum_j \mu_j^2 \right]$$

where $r_{ij} = r_i - r_j$, and T_{ij} is the dipole tensor. Here n_o and n_H are the number of oxygen and hydrogen atoms, respectively, q_i is the charge on particle i (+e for hydrogen and -2e for oxygen), μ_i is the induced dipole on oxygen i and α is its polarizability, and $S_{ij}^{\text{cd}}(r_{ij})$ and $S_{ij}^{\text{dd}}(r_{ij})$ are the electric field cutoff functions for charge-dipole and dipole-dipole interactions, respectively. The induced dipole moment at each oxygen site can be obtained self-consistently by imposing the conditions $dV_{\text{el}}/d\mu_k = 0$, $k = 1, 2, \dots, n_o$:

$$\mu_i = \alpha \left[\sum_{j,j \neq i}^{n_o+n_H} \frac{r_{ij} q_j}{r_{ij}^3} S_{ij}^{\text{cd}}(r_{ij}) + \sum_{j,j \neq i} \frac{T_{ij} \cdot \mu_j}{r_{ij}^3} S_{ij}^{\text{dd}}(r_{ij}) \right] \quad (3)$$

The second and third terms of Eq.(1) represent pairwise additive potential-energies between the H and O atoms and between the O and O atoms, respectively. In addition to the electrostatic and pairwise additive terms, the last term of Eq.(1) represents a three-body term. This term is short range and describes the interaction within H-O-H triplets.

We used Gaussian isokinetics¹¹⁻¹⁴ to keep the temperature of the system constant. Ewald summations were used in our simulations with the parameter for $\kappa = 5.0/L$ and the real-space cut distance r_{cut} and K_{max} chosen as 0.5 L and 7, respectively, where L is the length of the box. (L = 0.987 nm for 32 water molecules of this study) The double summations in reciprocal space, which cannot be reduced to a single summation due to the cutoff functions, were ignored. This is reasonable as the distances in reciprocal space are larger than the length L of the box. The equations of motion were solved using velocity Verlet algorithm¹⁵ with a time step of 10⁻¹⁵ second (1 fs).

The simulations were first validated by checking our results against Ojamäe's work for pure water using the same OSS2 model. The calculated oxygen-hydrogen (O-H) radial distribution function $g(r)$ and the hydration number $n(r)$ for hydrogen in the 216 molecule pure water system are nearly identical,¹⁶ even though Ojamäe *et al.* used a different method³ for the Ewald summations in the calculation of the induced dipole moment. The equilibrium properties at each temperature are averaged over five blocks of 2,000,000 time steps, for a total of 10,000,000 time steps (10 ns) after for 2,000,000 time steps to reach an equilibrium state. The configuration of each ion is stored every 10 time steps for further analyses.

Results and Discussion

Preliminary molecular dynamics (MD) simulations of the OSS2 water have been carried out at the ambient condition of 298 K and 0.998 g/cm³ and the result of the local structure was reported elsewhere.¹⁶ It is essential to calculate the mean square displacement (MSD) in order to obtain the self-diffusion coefficient of the OSS2 water. However, the calculated MSD at the ambient condition does not show the behaviour of a usual liquid as seen in Fig. 1 (the solid line) and we were unable to get the self-diffusion coefficient from the MSD of the OSS2 water at the ambient condition.

An alternate way for the OSS2 water to move vividly is to decrease the density of the system gradually at 298 K and the calculated MSD of the OSS2 water at the density of 0.542 g/cm³ shown in Fig. 1 (the dotted line) is a smooth well-behaved straight line. The self-diffusion coefficient of the OSS2 water from the MSD is estimated as approximately 2.037×10^{-5} cm²/sec, obtained from the slope between 2 ~ 10 ps, and is increased as the density of the system is further

decreased. This result is comparable with the experimental results of 2.26,¹⁷ 2.299,¹⁸ or 2.296¹⁹ in the unit of 10^{-5} cm²/sec at the ambient condition of 298 K and 0.998 g/cm³.

When the temperature of the system is increased gradually at 0.998 g/cm³, the OSS2 water also moves vividly and the calculated MSD at 380 K shows also a smooth well-behaved straight line as seen in Fig. 1 (the dashed line). The obtained self-diffusion coefficient of the OSS2 water from the MSD is approximately 1.837×10^{-5} cm²/sec and is increased as the temperature of the system is further increased. The self-diffusion coefficient of the OSS2 water at 500 K is a very close value to the experimental ones.

As a result we found that decreasing the density or increasing the temperature of the system invokes the vivid mobility of the OSS2 water molecules. This might indicate that the total potential energy V_{tot} given in Eq. (1) is too strong and the system of the OSS2 water behaves like a glass or an ice under ambient conditions. From this we deduce that reducing the total potential energy V_{tot} of the system might cause the same effect as decreasing the density or increasing the temperature of the system. By choosing the scaling factor λ as $V'_{\text{tot}} = \lambda V_{\text{tot}}$ in Eq. (1), the charge of particle i is simply scaled by $q'_i = \lambda^{1/2} q_i$ for the electrostatic energy of Eq. (2) and the induced dipole moment at each oxygen site can be obtained self-consistently by the same way as before scaling. The other three potential energies (V_{OH} , V_{OO} , and V_{HOH}) are also simply scaled by λ likewise.

First we scale the value of λ gradually at the ambient condition of 298 K and 0.998 g/cm³, and calculate the MSD of the scaled OSS2 water to obtain the self-diffusion coefficient. The final value of λ is determined as 0.801 and the calculated MSD shows also a smooth well-behaved straight line shown in Fig. 1 (the long-dashed line). The self-diffusion coefficient

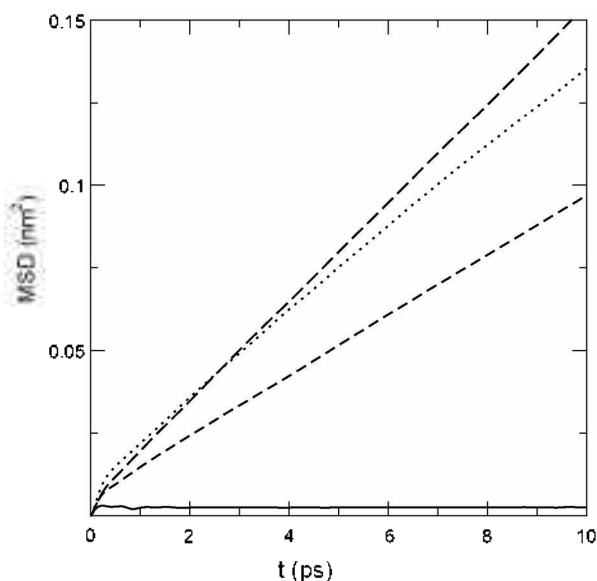


Figure 1. Mean square displacements (MSD) of the OSS2 water at several different states. Solid line : at the ambient condition of 298 K and 0.998 g/cm³, dotted line : at 298 K and 0.542 g/cm³, dashed line : at 380 K and 0.998 g/cm³, and long-dashed line : at 298 K and 0.998 g/cm³ with the scaling factor $\lambda = 0.801$.

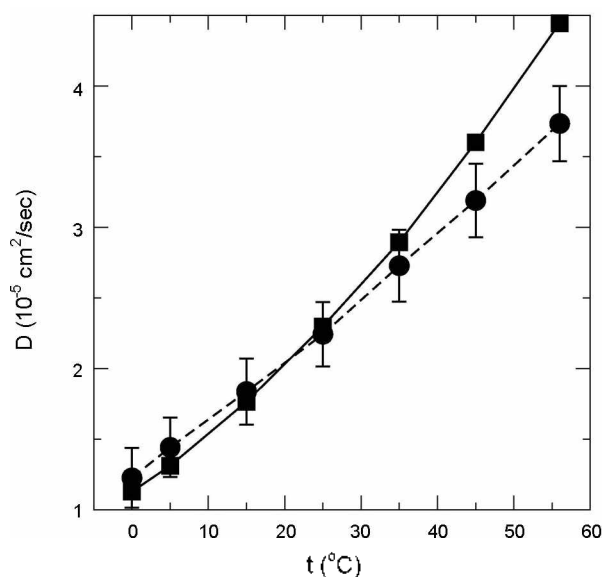


Figure 2. Self-diffusion coefficients of the scaled OSS2 water at several different temperatures. ■ : experimental values¹⁸ and ● : calculated values. The error bar represents a standard derivative.

of the scaled OSS2 water at the ambient condition from the MSD is estimated as approximately $(2.243 \pm 0.227) \times 10^{-5}$ cm²/sec. obtained from the slope between 2 ~ 10 ps. The MD simulation result is in an excellent agreement with the experimental results.¹⁷⁻¹⁹

In order to verify the scaling process of the total potential energy of the original OSS2 water, we calculate the self-diffusion coefficients at several different temperatures using the scaling factor of $\lambda = 0.801$. The calculated MSD at each temperature shows a smooth well-defined straight line (not shown) and Fig. 2 shows comparison of self-diffusion coefficients of the scaled OSS2 water at several different temperatures at 0.998 g/cm³. The agreement between experimental and MD simulation results is within a standard deviation except higher temperatures.

It is interesting to note that the MD simulations at low temperatures of 263 K and 268 K using the scaling factor of $\lambda = 0.801$ after a short simulation period recover the behavior like a glass or an ice even though the MD simulations were carried out from the initial vivid configuration of the scaled OSS2 water at 273 K. This might indicate the freezing point of the scaled OSS2 water lies between 268 K and 273 K. The study of the freezing process of the scaled OSS2 water might be fairly interesting but beyond the scope of this study.

In summary classical MD simulations using the original OSS2 model potential derived from *ab initio* calculations can be used to understand the self-diffusion behavior of the scaled OSS2 water at several different states. We found that reducing the total potential energy as well as decreasing the density or increasing the temperature of the system invokes the vivid mobility of the original OSS2 water molecules. By choosing the scaling factor λ of the total potential energy as 0.801 (equivalently scaling the charge of particle by $\lambda^{1/2} = 0.895$), the

obtained MD results for the self-diffusion coefficients of the scaled OSS2 water at several different temperatures are in general agreement with the experimental results, which indicates the original OSS2 model potential energy is too strong resulting in the behavior like a glass or an ice. The extension of this study to large systems ($N \sim 216$) and the freezing process of the scaled OSS2 water are presently under study.

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