Comparative Study of the Thermal Neutron Scattering Libraries for Light Water Based on the Molecular Dynamics Simulation with Various Water Models

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1. Introduction

The molecular dynamics (MD) simulation is a powerful computational tool used to describe the motions of atoms and molecules over time. This simulation helps understand physical and chemical phenomena within molecules during atomic/molecular interactions. Light water has been extensively used and researched in various scientific fields such as nuclear engineering, biological science, material science, and so on. Due to its significance in most biological activities and physical-chemical processes, the water models are progressively developed to precisely simulate systems containing the water molecules using the MD simulation codes.

The water models are the parameterized descriptions for modeling the structure and physical characteristics of the water molecules. These models are instrumental in determining the arrangement of individual atoms within water molecules and simulating their inter/intra-atomic interactions. Since each model inherently possesses specific approximations and limitations, it is essential to select an appropriate model according to the objectives of the simulation.

In this study, we performed MD simulations using GROMACS-2023 code [1] with various water models: SPC [2], flexible SPC [3], TIP4P/2005 [4], TIP4P/2005f [5], and TIP5P [6]. To verify the performance of the simulations, we calculated several physical properties of light water and compared them with experimental values. Subsequently, thermal neutron scattering libraries for light water based on these models were generated through the nuclear data processing code, NJOY2016 [7]. Each library was compared with that of ENDF/B-VIII.0 [8,9].

2. Methods and Results

In this section, we introduce the thermal neutron scattering law and the water models used to generate the scattering cross sections for light water.

2.1 Thermal Scattering Law

The thermal scattering law, $S(\alpha,\beta)$, as defined by Eq. (1), is a function of α and β.

$$s(\alpha,\beta)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\beta\hat{t}}e^{-\gamma(\hat{t})}\,d\hat{t}, \tag{1}$$

Here α represents the momentum transfer parameter, and β denotes the energy transfer parameter, which are defined by Eqs. (2) and (3), respectively.

$$\alpha=\frac{E'+E-2\mu\sqrt{E'E}}{AkT}, \tag{2}$$

$$\beta=\frac{E'-E}{kT}, \tag{3}$$

where A is the mass ratio of the scattering nuclide to the neutron and μ is the cosine of the scattering angle in the laboratory system. $\hat{t}$ is time measured in the unit of $\hbar/kT$ seconds. The intermediate scattering function $\gamma(\hat{t})$ is given by Eq. (4).

$$\gamma(\hat{t})=\alpha\int_{-\infty}^{\infty}P(\beta)\left[1-e^{-i\beta\hat{t}}\right]e^{-\beta/2}d\beta, \tag{4}$$

where

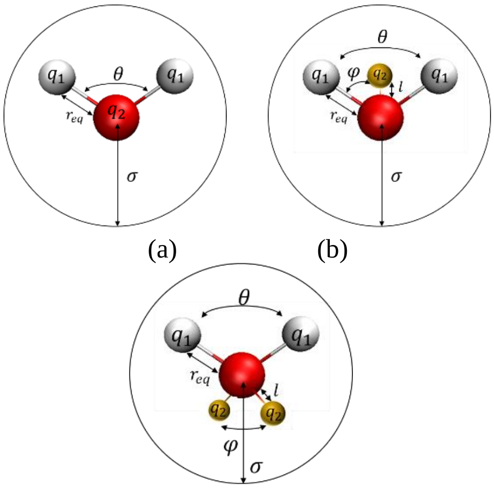
$$P(\beta)=\frac{\rho(\beta)}{2\beta\sinh(\beta/2)}, \tag{5}$$

where $\rho(\beta)$ is called as the frequency spectrum. To calculate the inelastic scattering cross section of the thermal neutron scattering libraries, the frequency spectrum is necessarily required as an input parameter of the LEAPR module of the NJOY code. In this study, the frequency spectra are obtained from Fourier transform of the velocity auto-correlation function calculated through GROMACS MD simulations.

2.2 Water Models

Water models such as SPC, flexible SPC, TIP4P/2005, TIP4P/2005f, and TIP5P were selected for MD simulations to produce thermal neutron scattering cross section of light water. In this study, it is assessed which water model results in the cross section data most similar to those of ENDF/B-VIII.0 and experiments.

Figure 1 shows the conceptual diagram of water models. The SPC and flexible SPC models are represented by a simple structure consisting of three particles: two hydrogen atoms and one oxygen atom. Unlike the SPC models, the TIP4P/2005 and TIP4P/2005f models are described by four particles including two hydrogens, one oxygen, and one imaginary charged particle. The TIP5P model is similar to the TIP4P/2005 models but it has two imaginary charged particles. These structural characteristics are related to the interatomic potential.



(a) (b)

(c)

Fig. 1. Conceptual diagram of water models (a) SPC and flexible SPC models, (b) TIP4P/2005 and TIP4P/2005f models, (c) TIP5P model

The potential parameters for each water model are shown in Table I. q_1 and q_2 are the charges of each atom which are used to calculate the Coulomb potential as defined by Eq. (6). The Coulomb potential represents the electrostatic interaction between the charged particles.

$$V_{Coul}(r_{ij}) = \frac{k \cdot q_i \cdot q_j}{r_{ij}} \tag{6}$$

where k is the electrostatic constant. r_{ij} is the distance between the ith and jth atoms.

To represent the attractive and repulsive interactions between molecules, the Lennard-Jones potential is also used.

$$V_{LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \tag{7}$$

where σ denotes the minimum distance between particles and ε represents the average depth of the intermolecular interactions.

The flexible SPC and TIP4P/2005f models are distinguished from other rigid models (SPC, TIP4P/2005, and TIP5P) by their capacity to describe the intramolecular interactions of the water molecule. These flexible water models effectively depict the motions involved in bond stretching and angle bending. To account for changes in bond length, r and angle, θ of the water molecules, intramolecular potentials are employed. In case of the flexible SPC model, both the bond stretching and angle bending are represented by the harmonic functions as defined by Eqs. (8) and (9).

$$V_{bond}(r) = \frac{1}{2}K_b(r - r_{eq})^2 \tag{8}$$

$$V_{angle}(\theta) = \frac{1}{2}K_\theta(\theta - \theta_{\mathrm{eq}})^2 \tag{9}$$

where $V_{bond}(r)$ and $V_{angle}(\theta)$ are the intramolecular potential for describing the bond stretching and angle bending, respectively. K_b and K_θ are the strength constants. r_{eq} and θ_{eq} are the equilibrated bond length and angle, respectively.

The TIP4P/2005f model employs a more intricate intramolecular potential known as the Morse potential for the bond stretching motion, which is given by Eq. (10).

$$V_{\mathrm{bond}}(r) = D_r\{1 - \exp[-\beta\,(r - r_{eq})]\}^2 \tag{10}$$

where D_r and β are the parameters that determine the bond strength and width, respectively.

2.3 GROMACS Simulation Results

The GROMACS simulations are performed in the following order: creating the water system, energy minimization, system equilibrium, and production run. We constructed water systems consisting of approximately 2000 water molecules at 293.6 K and 1 bar for each individual water model. To minimize the energy of the systems, the steep algorithm was used. The equilibrium process was performed for 250 ps under NVT and NPT conditions. Subsequently, the production run was performed for 1 ns under NPT condition.

Consequently, several physical properties and frequency spectra were calculated using the GROMACS code for all water models presented previously. The dipole moments, diffusion coefficients, heat capacities, thermal expansion coefficients, and dielectric constants for water models are shown in Table II.

The calculated dipole moment values show comparable results with the experimental data, showing relative errors of around 20%. Regarding the diffusion coefficients, the TIP4P/2005 and TIP4P/2005f models tend to produce smaller values compared to other models. In the case of heat capacities, the two flexible water models and TIP5P model tend to produce considerably larger values than those calculated for other rigid models. The rigid and flexible SPC models are shown to result in much larger thermal expansion coefficients than other models. Additionally, the dielectric constants calculated with the TIP4P/2005 and TIP4P/2005f models are substantially smaller than the values obtained with other models. Consequently, it was confirmed that MD simulations using various water models predict the physical properties of water with relatively different trends.

Figure 2 shows the frequency spectra calculated with water models. As previously mentioned, these spectra can be used as the input parameters for the NJOY code to generate the thermal neutron scattering cross sections for light water. In this study, the frequency spectrum from the ENDF/B-VIII.0 was used as reference data for comparison. As shown in Fig. 2, the reference spectrum exhibits two peaks at energies of 20.5 and 41.5 meV, which are attributed to intramolecular bending and stretching motions of water molecules, respectively.

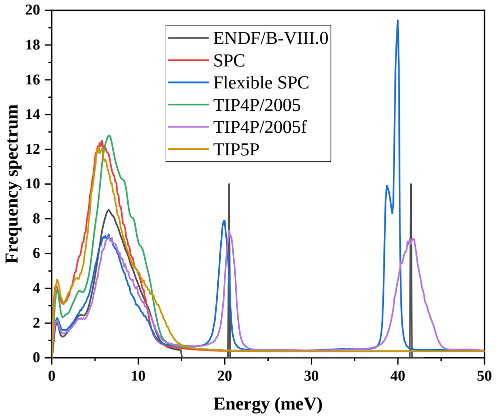


Fig. 2. Comparison of frequency spectra calculated with water models

Since the two peaks occur due to intramolecular interactions, they appear only in the frequency spectra calculated using the flexible water models. The peak positions of the bending and stretching motions calculated using the TIP4P/2005f model match the reference data very closely, because the reference data was also calculated with GROMACS, the same code as in this study. For the flexible SPC model, slight shifts in the peak positions were observed at lower energies of 20.0 and 40.0 meV. The positions of these peaks were served as input parameters for the NJOY code.

Additionally, the spectra in the energy range of 0 to 15 meV result from intermolecular interactions. Three peaks appear at energies of approximately 0.5, 3.0, and 7.0 meV, respectively, due to the three types of vibrational motions in water molecules: interatomic bending, stretching, and libration. The spectra calculated with TIP4P/2005, TIP4P/2005f, and TIP5P models effectively describe the three intermolecular vibrational motions, but the SPC and flexible SPC models do not seem to accurately reproduce the intermolecular stretching motion.

Table I: Potential parameters for each water model

	SPC	Flexible SPC	TIP4P/2005	TIP4P/2005f	TIP5P
σ (Å)	3.166	3.166	3.1589	3.1644	3.1200
ε $(\mathrm{kJ\cdot mol^{-1}})$	0.650	0.650	0.7749	0.7749	0.6694
r_{eq}(Å)	1.0000	1.0000	0.9572	0.9419	0.9572
l(Å)	-	-	0.1546	0.1546	0.7
$q_1(e)$	+0.410	+0.410	+0.5564	+0.5564	+0.2410
$q_2(e)$	-0.820	-0.820	-1.1128	-1.1128	-0.2410
$\theta_{eq}{}^{\circ}$	109.47	109.47	104.52	107.4	104.52
φ°	-	-	52.26	52.26	109.47
D_r $(\mathrm{kJ\cdot mol^{-1}})$	-	-	-	432.581	-
$K\theta$ $(\mathrm{kJ\cdot mol^{-1}\cdot Å^{-2}})$	-	3450	-	-	-
β (Å)	-	-	-	2.287	-
$K\theta$ $(\mathrm{kJ\cdot mol^{-1}}\cdot rad^{-2})$	-	383.0	-	367.81	-

Table II: Calculated physical properties for water models

	Dipole moment (e)	Diffusion coefficient $(10^{-5} cm^2/s)$	Heat capacity $(\mathrm{J\cdot mol^{-1}}\cdot K^{-1})$	Thermal expansion $(10^{-4}/K)$	Dielectric constant
SPC	2.27	4.00	86.87	8.32	68.78
Flexible SPC	2.46	2.11	118	6.63	81.54
TIP4P/2005	2.25	1.68	78.93	1.03	49.52
TIP4P/2005f	2.33	1.63	110.2	0.66	52.56
TIP5P	2.29	2.44	140.14	3.72	99.34
Experimental data	2.95[a]	2.3[b]	75.39[c]	2.53[c]	78.4[e]

[a, b, c, d, e] The experimental values were referenced from References 10, 11, 12, 13, and 14.

2.4 Scattering Cross Sections for Light Water

The scattering cross sections for light water were produced with the NJOY2016 code using the frequency spectra calculated through MD simulations. The scattering cross sections are compared in Fig. 3.

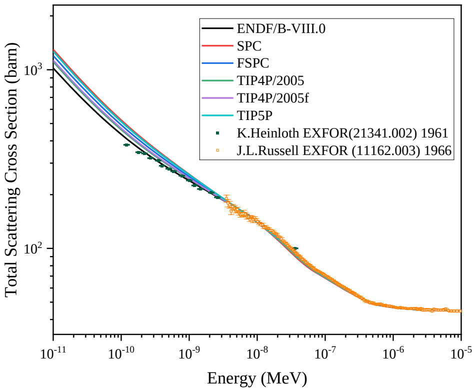


Fig. 3. Comparison of scattering cross sections of light water according to water models

The scattering cross sections calculated using the TIP4P/2005 and TIP4P/2005f models showed the highest similarity to that of ENDF/B-VIII.0. In the case of SPC models, the rigid model caused the largest differences with the ENDF/B-VIII.0, while the flexible model resulted in better agreement with the ENDF/B-VIII.0. For the TIP5P model, the calculated frequency spectra effectively described the three types of intermolecular motions, but the resulting scattering cross sections showed relatively poor agreement with the ENDF/B-VIII.0.

3. Conclusions

In this study, we employed the MD simulations using GROMACS-2023 code to investigate the influence of various water models such as SPC, flexible SPC, TIP4P/2005, TIP4P/2005f, and TIP5P. These water models were evaluated through the comparison of the calculated physical properties with experimental data. Subsequently, NJOY2016 code was used to generate the thermal neutron scattering cross sections of light water based on frequency spectra calculated through MD simulations. As a result, the scattering cross sections calculated using the TIP4P/2005 and TIP4P/2005f models demonstrated better agreements with the ENDF/B-VIII.0.

In conclusion, the choice of water models in MD simulations has a substantial impact on predicting the motions of water molecules. We have concluded that the TIP4P/2005 and TIP4P/2005f models are the most promising candidates for generating the scattering cross sections of light water.

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