The Comparison Between Water Models In Predicting Water Thermal And Dynamic Properties From Molecular Dynamics

Abdusalam Alkhwaji, Salem Elbahloul, Khairil Fadzli Bin Abu Bakar, Mohd Zulkifly Abdullah

Abstract: This molecular dynamic simulation study is made using Lammps software to compare outcome results of thermal properties of most known five rigid water models. The water has received special attention because it is commonly used base-fluid in heat transfer application. This study focuses on computing water thermal conductivity, dynamic viscosity, density, specific isobaric heat capacity, specific isochoric heat capacity. A significant outcome of this study is to compare results and suggest an optimal model which can be used to evaluate water thermal properties. Lammps, a powerful molecular dynamics software, is used to do the molecular dynamics calculation in this study. Atomic initial position, intermolecular forces, etc., are prepared using Moltemplate. Atomistic model types of water used in this study are the simple point charge (SPC) model, The extended simple point charge (SPC/E) model, The TIP-type models (TIP3PEW, TIP4PEW andTIP4-2005). This study investigates efficiency of five water types in predicting thermal properties at four temperatures. A comparison between these five models is made by calculating thermal conductivity, viscosity, density, specific isochoric heat capacity, and specific isobaric heat capacity. Results were verified against reference thermal properties at 288, 300, 312 and 324 K. Results of this research indicate that values of thermal properties were very accurate and close to known values, that could make this study very useful in helping researchers to pick up the right water model when calculating any of the studied properties.

Index Terms: Molecular dynamics; water thermal properties; Specific thermal capacity; thermal conductivity; Water models; SPC, SPC/E, TIP3PEW, TIP4PEW, TIP4-2005; Lammps.

1. INTRODUCTION

In this investigation, water thermal and dynamic properties calculated from Molecular dynamics using five water models. The simple point charge (SPC) [1], the extended simple point charge (SPCE) [2], the three-site transferable intermolecular potential water molecules (TIP3PEW) [11], and two models of the four-site transferable intermolecular potential water molecules (TIP4PEW and TIP4-2005) [3,4]. In the literature, there is still noticeable documented discrepancy between experimental and Molecular Dynamic water thermal and dynamic properties. It has been documented that water properties from Molecular Dynamic can be very accurately depending on the used water model. That bring the focus of this study to compare between most known five water models. Some of the attempts which made by other authors are summarized in this introductory as following: Meguel Angel et al. [5] published his results from Molecular Dynamics simulation using GROMACS package to evaluate dynamic viscosity of four water types using 500 water molecules. His results showed difference in performance between all models. Pekka Mark et al. [6] used CHARMM software to determine self-diffusion coefficients and radial distribution functions, for the TIP3P, SPC, and SPC/E water models. His simulations indicated that the SPC/E water model has produced the best bulk water dynamics and structure.

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Water thermal conductivity is calculated with either the equilibrium molecular dynamics (EMD) or the nonequilibrium molecular dynamics (NEMD) methods. The EMD uses the Green-Kubo formula, which requires a direct calculation of the heat flux, while the NEMD method, a known heat flux is imposed and the temperature gradient is computed [7]. Roemer et al. [8] reported thermal conductivity results using nonequilibrium molecular dynamic investigation of SPC/E and TIP4-2005 water models, where both models showed good agreement with the reference data from National Institute of Standards and Technology database. Previously, Yijin et al. [9] published their results of thermal conductivity, shear viscosity of eight rigid water models using reverse non-equilibrium molecular dynamics, their results showed that only five-site water models were able to predict accurate thermal properties. In our study, The Green Kubo method (G-K) is employed. The G-K method is reported to be able to predict well thermal properties for various site models in a wide range of temperatures.

In this study, the EMD method for liquid water are used to calculate the water thermal conductivity and dynamic viscosity at one atmosphere and temperature of 288, 300, 312, and 324 K. Results converge very well to the properties of water. Isobaric specific heat capacities are calculated for temperature gradient of 12 K. Isochore specific heat capacity evaluated using the mean square deviation of the energy. Molecular Dynamics (MD) simulation is a powerful method to study water liquid, which allows for the direct simulation of the atomic motion, energy exchanges and interaction forces between particles (either atoms or molecules). Lammps [10-11[has been used to simulate many water models, nanofluids and nano heat-transfer studies. In this study, Lammps is employed to evaluate water thermal and dynamic properties. Moltemplate [12-13] is another software which helps in building atomic interaction, initial positions, and bond types of water molecules inside the simulation box. Water thermal properties are calculated when equilibrium is reached. That

TABLE 1
PARAMETERS OF WATER MODELS

Model	σ	ε	q_H	q_O	θ
SPC	3.16600	0.15535	0.41000	-0.82000	109.47
SPC/E	3.16600	0.15535	0.42380	-0.84760	109.47
TIP3PEW	3.15061	0.15210	0.41700	-0,83400	104.52
TIP4PEW	3.16435	0.16275	0.52422	-1.04844	104.52
TIP4-2005	3.15890	0.18521	0.55640	-1.11280	104.52

is by collecting global and per-atom quantities each femtosecond, and then averaging energy each picosecond, in order to calculate thermal and dynamic properties.

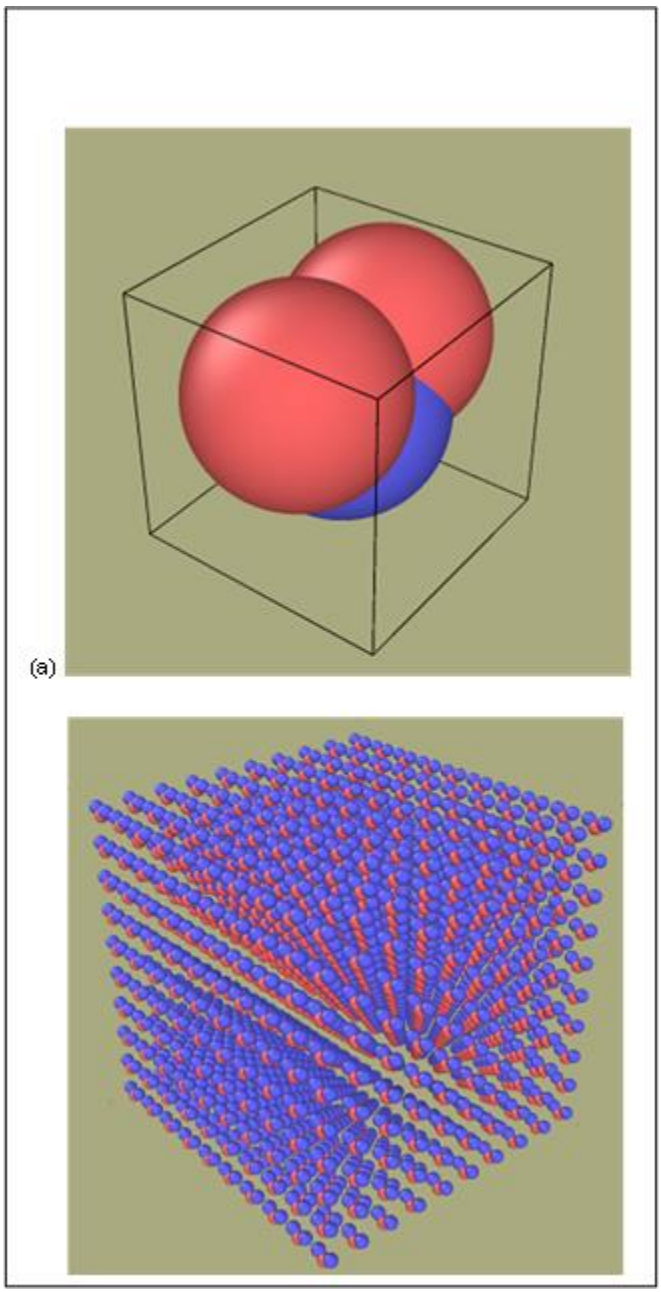
Thermal conductivity and dynamic viscosity are calculated using the Green-Kubo method which is the most popular MD-technique for this calculation. The significant usage of calculating water thermal and dynamic properties is to find an optimal water model which produces best water thermal and dynamic properties. The reference values of thermal and dynamics properties at 288, 300, 312 and 324 K are collected from an online water property calculator [14], so that an optimal water model will be capable of reproducing these values at each of the mentioned four temperatures.

2. THE SIMULATION SITTING

The simulation system is 1000 water molecules in a cubic region as indicated in figure 1. The used boundary is periodic and atom type is real. The NPT ensemble is constant temperature, number of atoms and pressure, were applied to calculate dynamic viscosities and Isobaric specific heat capacities. While NVT was applied to determine isochore specific heat capacities. To calculate thermal conductivities, NPT, NVT and NVE ensembles are required. Duration of each ensembles was 1 ns. The energy E_{ab} between molecules a and b is the sum of coulomb and Leonard-Jones potentials centred on the sites, which is given as [9],

$$E_{ab} = \sum_{ij}\left[\frac{A_{kk}}{r_{ij}^{12}} - \frac{B_{kk}}{r_{ij}^{6}} + \frac{q_i q_j}{r(ij)}\right] \quad (1)$$

Where r_{ij} is the distance between the centres of oxygen atoms in the two water molecules and qi and qj are charges Oxygen and Hydrogen atoms respectively, the parameters A_{kk} and B_{kk} were given by $A_{kk} = 4\varepsilon_k\sigma_k^{12}$ and $A_{kk} = 4\varepsilon_k\sigma_k^{6}$, where ε_k represents interaction strength, and σ_k is an interatomic length scale. Parameters of four water models are in table 1 [3].



3. THERMAL CONDUCTIVITY AND GREEN-KUBO FORMULA

The G-K relations are a well-known Molecular dynamic method which relates microscopic fluxes at either NPT, NVT or NVE ensembles (equilibrium conditions), to thermal and dynamic properties. The G-K relates the autocorrelation function (ACF) to transport coefficients during the equilibrium state [15]. Newton's second law describes atom's motion in space, where F = m a, F is the force exerted on the particle in N, mass m in kg, and its acceleration a in m/s2. Molecular Dynamic simulation uses initial condition of masses and force in order to calculate atom's position and velocity. The interatomic potential and thermostat are used to calculate total force acting on the atoms. The Green Kubo method is an EMD approach to obtain thermal conductivity from the relationship between heat flux and autocorrelation function in the equilibrium state [8]

$$\boldsymbol{k} = \frac{\mathbf{1}}{\boldsymbol{3VK_BT^2}} \int_0^\infty < \boldsymbol{J_i(0)J_i(t)} > \boldsymbol{dt} \tag{2}$$

Where k, V, T, and KB, are the thermal conductivity, volume of the simulation box, system kinetic temperature, Boltzmann constant, respectively. J is the per-atom contributions of kinetic, potential and virial from non-bond, bond, and angle interaction.

<J(0)J(t)> is the heat flux autocorrelation function. Heat flux is defined as

$$J = \left[\sum_{j=1}^{N} v_j E_j - \sum_{\propto=1}^{N} h_\propto \sum_{j=1}^{N_\propto} v_{\propto j}\right] + \frac{1}{2}\left[\sum_{i=1}^{N}\sum_{j=1,j\neq i}^{N_\propto} r_{ij}(v_j . F_{ij})\right] \tag{3}$$

where vj is the velocity of particle j, Ej is per atom energy for kinetic and potential, hα is the average partial enthalpy of species α, rij and Fij are the displacement and interacting forces between particles i and j, respectively, and N is the total number of particles. The average partial enthalpy refers to the average of the sum of kinetic energy, potential energy, and average virial per particle. The kinetic and potential terms of the heat flux, given in the above equation, express transported energy, while the virial contribution represents work done by the stress tensor [8], which is given by.

$$\boldsymbol{h_\propto} = \frac{\mathbf{1}}{\boldsymbol{N_\propto}} \sum_{\boldsymbol{j=1}}^{\boldsymbol{N_\propto}} \left(\boldsymbol{E_j} + \boldsymbol{r_j . F_j}\right) \tag{4}$$

4. DYNAMIC VISCOSITY

Dynamic viscosity measures the ability of a fluid to transmit momentum perpendicular to the stream velocity.

$$\tau = -\mu \frac{dU}{dy} \tag{5}$$

Where τ is the momentum flux in units of momentum per area per time, and gradient $\frac{dU}{dy}$ is the gradient of velocity. Viscosity has units of pressure-time. The Molecular dynamic method which has been used to calculate dynamic viscosity is based on the Green-Kubo (GK) formula which relates the ensemble average of the auto-correlation of the stress/pressure tensor to the viscosity 'μ'. This was done in a fully equilibrated simulation using the following formula [8]

$$\eta_{xy} = \frac{V}{k_B T} \int_0^\infty < P_{xy}(0) P_{xy}(t) > dt \tag{6}$$

Where η is the viscosity, and $< \boldsymbol{P_{xy}(0)P_{xy}(t)} >$ is the stress autocorrelation function. The stress tensor P is given by

$$\boldsymbol{P_{xy}} = \sum_{\boldsymbol{j}} \boldsymbol{m_j v_{xj} v_{yj}} + \frac{\mathbf{1}}{\mathbf{2}} \sum_{\boldsymbol{i\neq j}} \boldsymbol{r_{xij} F_{yij}} \tag{7}$$

Where only the three stress tensor components of off-diagonal Pxy, Pxz, and Pyz are taken into account for the autocorrelation function.

5. ISOBARIC AND ISOCHORIC SPECIFIC HEAT CAPACITIES

Figure 6 illustrates the temperature (K) and total energy (Kcal/mol) of the simulated water box for two different conditions where the system initially was at 288 K and pressure of 1 bar, then temperature increased to 300 K at constant pressure 1 bar. The isobaric thermal capacitance is calculated for simulated water box during NPT ensemble equilibrium, to rise water molecule's temperature from T_1 to T_2 and the associated total energy E_1^{tot} and E_2^{tot} respectively. Figure 4 illustrates ΔT and ΔE between temperatures of 288 and 300 K.

$$\boldsymbol{C_P} = \frac{\boldsymbol{E_2^{tot} - E_1^{tot}}}{\boldsymbol{T_2 - T_1}} + \frac{\boldsymbol{\partial Q}}{\boldsymbol{\partial T}} \tag{8}$$

Where E^{tot} is the total energy per molecule and $\frac{\partial Q}{\partial T}$ is the quantum contribution of intramolecular vibrational moles to the isobaric specific heat capacity. These quantum contribution equals to -9.3 J mol^{-1} K^{-1} (- 0.5166 KJ/Kg-K) at 298 K and 1 atm [16]. Table 2 declares the quantum contributions at temperatures of 288, 300, 312 and 324 K, made by interpolation.

Table 2

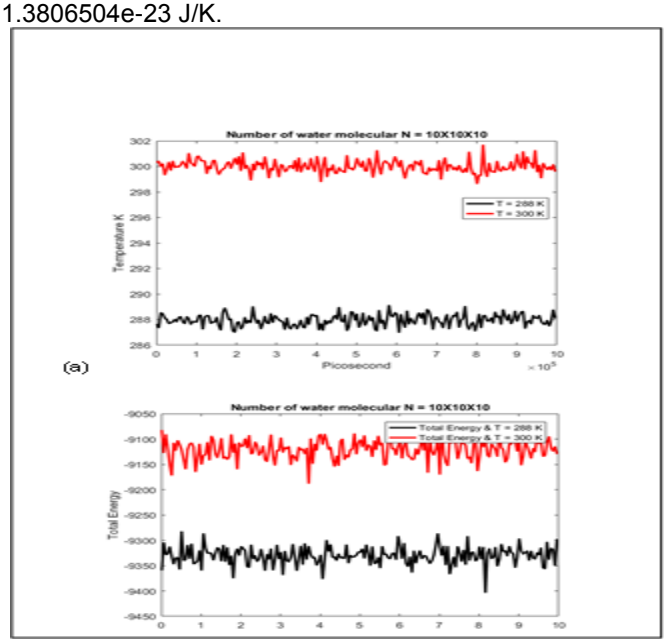
Quantum contributions term of equation 8

Temperatures K	Quantum contributions KJ/Kg-K
288	- 0.4993
298	- 0.5166
300	- 0.5201
312	- 0.5409
324	- 0.5617

The isochoric specific heat capacity is proportional with the mean square deviation of the energy [17]

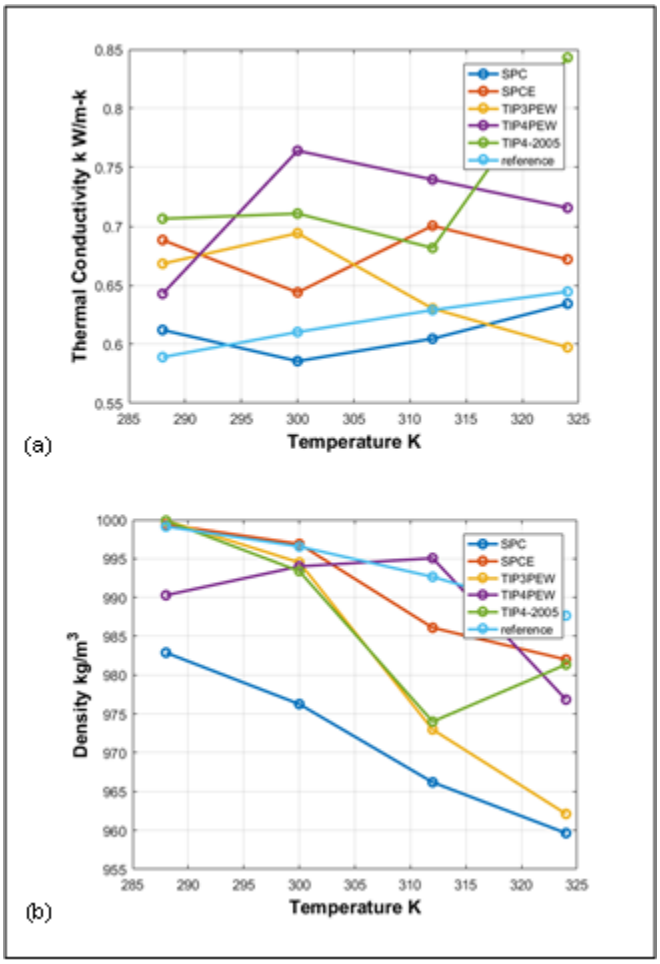
$$C_v = \frac{< E^2 > - < E >^2}{K_B T^2} \quad (9)$$

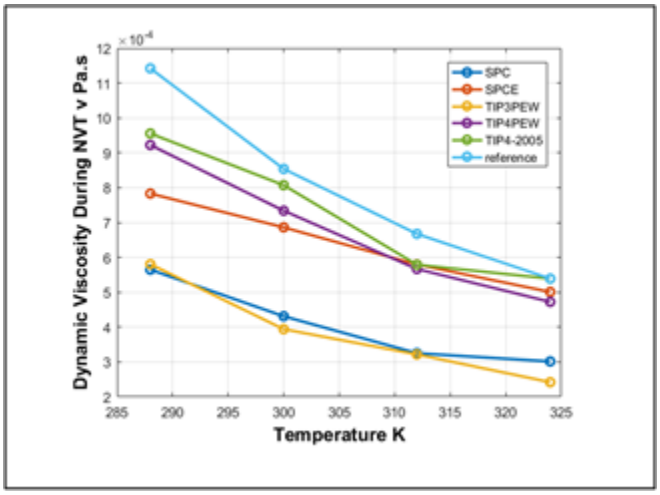
Where the average energy of a system in thermal NVT equilibrium is <E>, and k_B is Boltzmann constant = 1.3806504e-23 J/K.

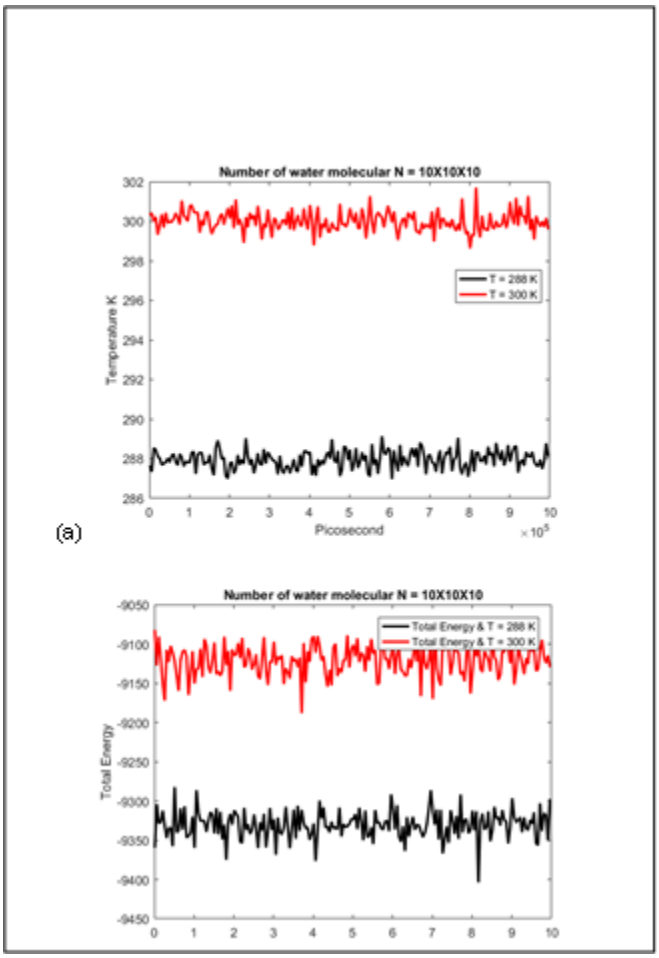


RESULTS

The results show that the dynamic viscosity of water decreases with an increase in temperature. As indicated in Figure 4, which represents dynamic viscosity profiles at 1 atmospheric pressure and temperatures of 288, 300, 312 and 324 K using Green Kubo formula where the minimum error was reported for TIP4-2005, followed by TIP4PEW and SPC/E. While SPC and TIP3PEW water models have largest errors. These dynamic viscosity results agreed with a published result, in which the RNEMD method [9] was used to calculate viscosity and thermal conductivity. Another study was conducted by Miguel [6] where Green Kubo method was used to determine only dynamic viscosities of SPC/E, TIP3PEW, TIP4PEW and TIP4-2005 water models, where his results of dynamic viscosity were 0.000321, 0.000494, 0.000699, 0.000729 Pa.s, respectively, and they verified their results versus an experimental value of 0.000855 Pa.s. Frank Römer [8] reported that thermal conductivity at 324 K was equal to 0.85 ± 0.03 W/K-m which confirms result of this work from figure 3-a, where at temperature of 324 K conductivity was 0.8432 W/K-m. Results from Migual et al. shows good agreement with results of this work, even though their reference temperature was 289 K while the closest used reference temperature in this paper is 300 K, but that has negligible effect. Both TIP4-2005 and TIP4PEW models have an excellent convergency toward the online water property calculator values at 288, 300, 312, and 324 K and 1 atmospheric pressure. The SPC/E water model has acceptable behavior throughout the observed temperatures. Whoever SPC and TIP3PEW have slightly divergency from the online calculator values. Throughout observation of Figure 3-a, it is clear that the trend of thermal conductivities versus temperatures curves were developed in an opposite to that of dynamic viscosities of each water model. Since best fit was for SPC model, worst for TIP4PEW and TIP4-2005 models, while SPC/E model developed an acceptable dynamic viscosity values at each temperature. Water thermal conductivity result of SPC converged very well to the online water property calculated values, while SPC/E gave an acceptable fit. Figure 3-b shows density curves of five water models at four temperatures, it is clear that SPC/E model presents the best curve fit to the web-generated densities at almost all temperatures. It is noticeable, that a worst convergency in predicting densities belong to SPC model. The TIP3PEW model diverges toward the SPC model but densities of TIP4PEW and TIP4-2005 models suffered from divergency at temperature of 312 K and came back toward the online water property calculator values of densities. In figure 5-a, the isobaric specific heat capacities of five models at four temperature plotted versus the standard online calculated values. The TIP4-2005 TIP3PEW water models show an overestimation of isobaric specific heat capacities by 0.45 and 0.65 Pa. s respectively. The SPC/E represents the best fit where error was only 0.1 Pa. s. However isochoric specific heat capacities of the SPC and SPC/E water models were underestimated. The maximum errors were 0.1 and 0.2 Pa. s respectively. This result show different performance of five water models in determine water thermal and dynamic viscosity. Water thermal and dynamic properties have been evaluated computationally which save the cost of using experimental equipment that add more powerful to the Molecular Dynamics approach.







CONCLUSIONS

These MD-simulation results prove consistency and stability of calculated thermal and dynamic water properties of the five investigated water models. It is noticeable that dynamic viscosities follow real physical behaviors of water liquid where temperature increase causes viscosity decrease for each of the five water models. Thermal conductivities showed also slightly deviation around the standard online calculated values at the studied range of temperatures, but this little deviation was documented previously in other published work for these five models and others as well. During monitoring temperature, pressure and energy of each water model, a perfect water thermal and dynamic behaviors were documented which reflect very close values of real water thermal and dynamic properties and in minimum computational cost. Thermal conductivities and dynamic viscosities of SPC/E converged very well to the standard online water property calculator values. Thermal conductivities of the TIP4PEW and TIP4-2005 water models were overestimated slightly while the SPC and SPC/E have better results. It is clear that increasing simulation time results in more converged results. Specific isobaric and isochoric heat capacities have acceptable results with low errors.

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