Thermal conductivity, shear viscosity and specific heat of rigid water models

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ARTICLE INFO

ABSTRACT

The thermal conductivity and shear viscosity of water are evaluated for eight rigid water models with reverse non-equilibrium molecular dynamics (RNEMD). Specific heats under constant volume and constant pressure are calculated within NVT and NPT ensembles. The five-site models (TIP5P and TIP5P-Ew) can predict thermal conductivity more accurately than other rigid water models. It appears that TIP5P-Ew is the best potential to predict the trend of the thermal conductivity. Both five-site models can accurately predict shear viscosity values as well as its trends along with temperature. Three-site model (TIP3P) has better performance in calculating specific heats.

1. Introduction

In the past decades, many water models are developed along with the intensive investigation on water by large number of molecular dynamics or Monte Carlo simulations. A 2002 review indicates that there are 46 water models [1], which were classified as rigid, flexible and polarizable models [2]. Recently, researchers proposed new well-performance models which are reparameterized based on the existing ones. For instance, TIP4P/2005 [3], which is designed to be a general purpose model for condensed phase of water, has an impressive performance in predicting a variety number of thermophysical properties; TIP4P-Ew [4], which is another extend version of four-site rigid water model, has a global improvement of predicting water properties; It has been reported that TIP5P-Ew [5] has great performance in reproducing experiment data for liquid water.

However, none of the above models has the capability to perfectly reproduce all properties of water, which probably leads to confusion when researchers need to choose appropriate model in the molecular dynamics simulations of different problems. For example, different water solvent in biology molecular dynamics can lead to reasonable or unreasonable results [6]. Furthermore, although various properties are investigated and advantage and disadvantage also are reported, independent papers that report the comparison the performances on reproducing thermophysical properties from different models are seldom. González and Abascal calculated the shear viscosity with Green–Kubo model and compared the results obtained from five rigid water models, which include TIP3P [7], TIP4P [7], TIP5P [8], SPC/E [9] and TIP4P/2005, with experiment data [10]. However, evaluations of different models on predicting thermal conductivity and specific heat have not been done. There exist two main methods, equilibrium molecular dynamics (EMD) and nonequilibrium molecular dynamics (NEMD), to determine shear viscosity and thermal conductivity. Green–Kubo method [11] is based on EMD that transport properties are related to the time integral of a correlation function. It usually can predict the result with a reasonable accuracy and precision. However, it suffers from the difficulties on complications of determining the microscopic heat flux (or other required instant properties) and slow convergence of the time integral of the heat flux (or other required instant properties) autocorrelation function. To overcome these limits of Green–Kubo method, a non-equilibrium molecular dynamics approach has been developed by Florian Müller-Plathe [12,13]. An accurate and efficient reverse non-equilibrium molecular dynamics (RNEMD) method for monoatomic molecular fluids was proposed. Later, Bedrov and Smith [14] extended the RNEMD to rigid polyatomic molecular fluids while still conserve energy and momentum of the system. However, results obtained from RNEMD somehow depend on swap frequency and carefully choosing the value is required.

In this Letter, thermal conductivity will be calculated using RNEMD method for liquid water under one atmosphere and different temperatures (298 K, 318 K). The reason of choosing RNEMD is that the operations of this approach is similar to real technique when measuring thermal or dynamic properties of fluids in the laboratories; thus it can physically reflect the properties of fluids in a 'real' situation. However, it should also be pointed out that the fluxes imposed in these MD simulations are different compared to real experiments, so the convergence of the calculated results with respect to the imposed fluxes should be checked. For RNEMD, the result must be converged as long as a steady state is established in the simulation box. For shear viscosities, a similar approach [15] is used to impose momentum flux (j_z) to the system by exchanging momentum of a mount of molecules in two specific

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slabs and then calculate the stable velocity gradient in a selected direction. Heat capacities will be calculated according to the assumed linear response [16] between enthalpy (or internal energy) and temperature. Therefore, enthalpy and internal energy of the system will be recorded during a gradual cooling process of the system. The following eight rigid models, SPC [17,18], SPC/E, TIP3P, TIP4P, TIP4P/2005, TIP4P-Ew, TIP5P and TIP5-Ew, are selected to carry out these simulations in this work based on their relatively successful performance as reported in the literatures.

For classical molecular dynamics, potential function plays a key role in driving atoms' evolutions in space. All potential functions of rigid water molecules share the same form, which consist of the contributions from electrostatic, dispersion and repulsive forces:

$$E_{ab} = \sum_i^{on\ a} \sum_j^{on\ b} \frac{k_C q_{a_i} q_{b_j}}{r_{a_i b_i}} + \sum_i^{on\ a} \sum_j^{on\ b} 4\varepsilon_{a_i b_j} \left[\left(\frac{\sigma_{a_i b_j}}{r_{a_i b_j}} \right)^{12} - \left(\frac{\sigma_{a_i b_j}}{r_{a_i b_j}} \right)^6 \right] \quad (1)$$

where, a and b denotes two different molecules, subscript i and $\underline{j}$ represent atom i in one individual molecule for all three-site rigid water molecule, k_c is electrostatic constant. For four- and five-site rigid water models, i and j represent massless but charged site in the first summation, still denotes atom in the second summation. Short range force is neglected when the distance of two atoms exceeds the cutoff distance, while long range force is evaluated with PPPM method [19] which splits long range effect into short range and long range parts. For four- and five-site models, Coulomb forces on virtual sites are redistributed to real atoms [20]. All parameters for different potentials are given in Table 1.

For rigid polyatomic molecule, the degree of freedom of each atom should be carefully treated through equation below when calculating the atomic temperature,

$$\left(\frac{3-c}{2} \right) k_B T = \frac{1}{2} m v^2 \quad (2)$$

where c is the number of constrains due to geometry constrain algorithm (here SHAKE [21] is employed), and k_b is Boltzmann constant. Since the shapes of all water molecules are geometrically fixed, c can be calculated easily for each atom. Here c is 1 if the degree of freedom counting method in reference [13] is applied, i.e., one constraint of one atom contribute to 1/2 constrain. The temperature in each slab can be estimated by averaging all atomic temperature within, while heat flux (q) can be calculated by accumulating exchanged molecular kinetic energies. After heat flux (q) and temperature gradient are obtained, Fourier's Law can be employed to calculate thermal conductivity.

$$k = -q/\nabla T \quad (3)$$

For shear viscosity calculation, degree of freedom estimation will not be a concern, and all procedures are similar. Velocity in each slab is calculated locally by averaging all atoms' velocity [22]. Simulation is done until symmetric temperature or velocity profile is stably established.

The enthalpy of the system, which will be used for specific heat calculation, is calculated by summing up internal energy and the product of pressure and volume of the system, while internal energy accounts for potential energy (Van der Waals, Coulomb pairwise energy, etc.) and kinetic energy.

$$H = E_e + PV = K_e + P_e + PV \quad (4)$$

where P and V are pressure and the volume of the simulation box, K_e is kinetic energy, P_e is potential energy, and E_e is internal energy. Specific heats at constant pressure and constant volume will be calculated through the following formulas:

$$c_p = \frac{1}{M} \left(\frac{\partial H}{\partial T} \right) \bigg|_p \quad (5)$$

and

$$c_v = \frac{1}{M} \left(\frac{\partial E_e}{\partial T} \right) \bigg|_v \quad (6)$$

where, M is the total mass of the simulation box.

In these simulations, all water molecules systems are treated in the same manner, except applying different potential and geometrical parameters (see Table 1). For transport properties evaluation, all the simulation has been performed in canonical ensemble (NVT) using the artificial mass based Nośe–Hoover thermostat [23] for a sample size of 900 water molecules cubic system, whose boundaries is treated as periodic with dimension of 30 Å × 30 Å × 30 Å. Thus the density is 996.67 kg/m³. The simulation box is divided into 20 slabs in z direction, and 10 hottest molecules at bottom slab and coldest in middle slab will be selected to exchange kinetic energy (or momentum in the x-direction for shear viscosity calculation). The simulation time step is 1 fs and the total time is 2 ns, excluding the equilibration stage. The cut-off distance for short range force is 1.04 nm. An equilibration of 0.2 ns is carried out before RNEMD is performed. In order to achieve a reasonable linear response, swap frequencies of 200 and 50 are carefully chosen for thermal conductivity and shear viscosity calculations, respectively. The sample times of calculating gradients are 200 ps. For specific heat at constant volume simulation is performed in NVT ensemble, while specific heat at constant pressure is done in NPT ensemble. Nośe–Hoover thermostat relax the temperature every 10 fs, while for Nośe–Hoover barostat control pressure every 100 fs. The value of internal energy in NVT ensemble and enthalpy in NPT ensemble are recorded when the temperature of the system is controlled at various temperatures, namely, 283, 293, 303, 313, 323, 333 and 343 K. In order to carry out simulation within the framework of the open-source molecular dynamics software LAMMPS [24], RNEMD for thermal conductivity and shear viscosity for polyatomic molecule fluid are implemented. While five-site rigid water models are also available with PPPM/TIP5P solver to obtain long range Coulomb force, some additional function including counting degree of freedom for single atom are also added into the original codes.

Table 1
Parameters of eight rigid water models.

Model	σ (Å)	ε (kcal mole^{-1})	qH (e)	qO (e)	$\theta°$	$\varphi°$	qM/qL (Å)	LB (Å)
SPC	3.16600	0.15535	0.41000	−0.82000	109.47	N/A	N/A	1.00000
SPC/E	3.16600	0.15535	0.42380	−0.84760	109.47	N/A	N/A	1.00000
TIP3P	3.15061	0.15210	0.41700	−0.83400	104.52	N/A	N/A	0.97520
TIP4P	3.15365	0.16348	0.52000	−1.04000	104.52	N/A	0.15000	0.97520
TIP4P-Ew	3.16435	0.16275	0.52422	−1.04844	104.52	N/A	0.12500	0.97520
TIP4P/2005	3.15890	0.18521	0.55640	−1.11280	104.52	N/A	0.15460	0.97520
TIP5P	3.12000	0.15999	0.24100	−0.24100	104.52	109.47	0.70000	0.97520
TIP5P-Ew	3.09700	0.17801	0.24100	−0.24100	104.52	109.47	0.70000	0.97520

Table 2
Comparison of results from different Kspace Solver.

298 K/SPC	Ewald	PPPM	RE (%)
K (W m^{-1} K^{-1})	0.89	0.88	2.01
η (Pa s)	2.81×10^{-5}	2.72×10^{-4}	3.32
c_v (kJ kg^{-1} K^{-1})	3.82	3.45	9.54
c_p (kJ kg^{-1} K^{-1})	4.33	4.45	−2.69
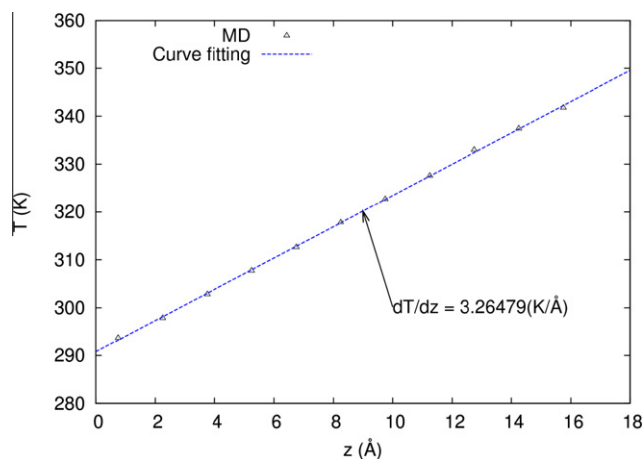
Figure 1. Established temperature gradient for TIP5P-Ew water system at 318 K.

Figure 2. Established velocity gradient for TIP4P/2005 water system at 318 K.
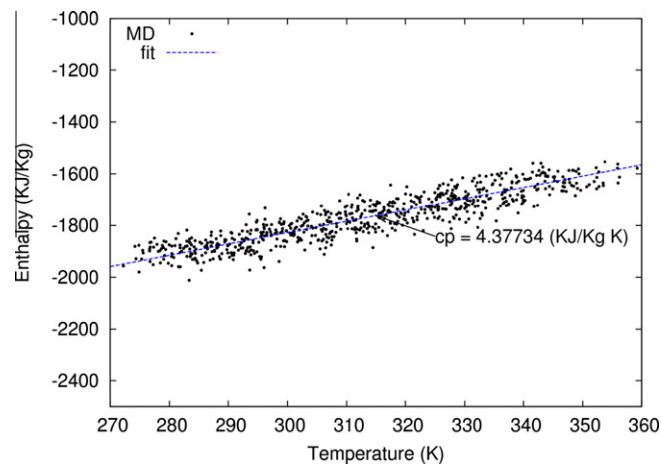
Figure 3. Relation between enthalpy and temperature for SPC/E water system.

It is worth to notice that though TIP4P-Ew and TIP5P-Ew are designed to model with Ewald summation technique, since PPPM has can well approach the same precision of Ewald summation when mesh grids increased, and considering of it is high efficiency, all these long range Coulomb interaction are solved with PPPM method. In order to get a reasonable mesh number for PPPM solver, shear viscosity, thermal conductivity, and specific heats are calculated with both standard Ewald summation and PPPM solver. The relative errors for each value are listed in Table 2, when mesh grids number is 30 in each direction. The results indicate that $30 \times 30 \times 30$ is sufficient to approximate the precision of standard Ewald summation.

Figure 1, as a sample of generated temperature gradient, shows a linear temperature profile established at domain range from the top slab to the middle in TIP5P-Ew molecule composed system at 318 K. The linear response is very good. The thermal conductivities

Table 3
Thermal conductivities at 298 K and 318 K.

298 K	Heat flux (kcal mole^{-1} Å^{-2} fs^{-1})	Temperature gradient (K Å^{-1})	Thermal conductivity (W m^{-1} K^{-1})	Relative error %
SPC	6.54×10^{-5}	2.59	0.88 ± 0.020	44.39
SPC/E	6.28×10^{-5}	2.34	0.93 ± 0.016	53.17
TIP3P	6.39×10^{-5}	2.51	0.88 ± 0.019	45.59
TIP4P	6.33×10^{-5}	2.68	0.82 ± 0.015	35.02
TIP4P-Ew	6.26×10^{-5}	2.43	0.90 ± 0.013	47.48
TIP4P-2005	6.33×10^{-5}	2.43	0.91 ± 0.014	49.11
TIP5P	6.07×10^{-5}	3.12	0.68 ± 0.007	11.32
TIP5P-Ew	5.95×10^{-5}	3.34	0.62 ± 0.007	1.87
Exp [25]			0.61	
318 K				
SPC	6.91×10^{-5}	2.75	0.87 ± 0.019	36.96
SPC/E	6.92×10^{-5}	2.56	0.94 ± 0.016	47.53
TIP3P	7.02×10^{-5}	2.57	0.95 ± 0.023	49.08
TIP4P	6.83×10^{-5}	2.76	0.86 ± 0.015	34.87
TIP4P-Ew	6.79×10^{-5}	2.50	0.94 ± 0.017	48.42
TIP4P-2005	6.79×10^{-5}	2.73	0.86 ± 0.013	35.81
TIP5P	6.54×10^{-5}	3.43	0.66 ± 0.006	4.08
TIP5P-Ew	6.44×10^{-5}	3.26	0.68 ± 0.004	7.59
Exp [25]			0.63	

Table 4
Shear viscosities at 298 K and 318 K.

298 K				
	Momentum flux (g mole^{-1} Å^{-1} fs^{-2})	Velocity gradient (Å fs^{-1})	Shear viscosity (Pa s)	Relative error %
SPC	1.25×10^{-5}	3.81×10^{-4}	$(2.72 \pm 0.026) \times 10^{-4}$	69.49
SPC/E	1.45×10^{-5}	3.61×10^{-4}	$(3.34 \pm 0.038) \times 10^{-4}(7.29 \times 10^{-4})$	62.53
TIP3P	1.41×10^{-5}	3.67×10^{-4}	$(3.18 \pm 0.041) \times 10^{-4}$ $(3.21 \times 10-4)$	64.23
TIP4P	1.72×10^{-5}	3.42×10^{-4}	$(4.17 \pm 0.072) \times 10^{-4}$ $(4.94 \times 10-4)$	53.15
TIP4P-Ew	1.99×10^{-5}	2.89×10^{-4}	$(5.73 \pm 0.096) \times 10^{-4}$ $(8.55 \times 10-4)$	35.61
TIP4P-2005	2.09×10^{-5}	3.01×10^{-4}	$(5.75 \pm 0.085) \times 10^{-4}$	35.37
TIP5P	2.68×10^{-5}	2.84×10^{-4}	$(7.83 \pm 0.504) \times 10^{-4}$ $(6.99 \times 10-4)$	12.03
TIP5P-Ew	2.66×10^{-5}	2.71×10^{-4}	$(8.13 \pm 0.512) \times 10^{-4}$	8.61
Exp [25]			8.90×10^{-4}	
318 K				
SPC	1.18×10^{-5}	4.04×10^{-4}	$(2.42 \pm 0.022) \times 10^{-4}$	60.04
SPC/E	1.36×10^{-5}	3.86×10^{-4}	$(2.91 \pm 0.030) \times 10^{-4}$	51.93
TIP3P	1.31×10^{-5}	3.93×10^{-4}	$(2.78 \pm 0.030) \times 10^{-4}$	54.22
TIP4P	1.57×10^{-5}	3.74×10^{-4}	$(3.48 \pm 0.052) \times 10^{-4}$	42.59
TIP4P-Ew	1.84×10^{-5}	3.34×10^{-4}	$(4.58 \pm 0.073) \times 10^{-4}$	24.51
TIP4P-2005	1.93×10^{-5}	3.37×10^{-4}	$(4.76 \pm 0.071) \times 10^{-4}$	21.56
TIP5P	2.60×10^{-5}	3.15×10^{-4}	$(6.84 \pm 0.461) \times 10^{-4}$	12.81
TIP5P-Ew	2.59×10^{-5}	3.20×10^{-4}	$(6.72 \pm 0.486) \times 10^{-4}$	10.91
Exp [25]			6.06×10^{-4}	
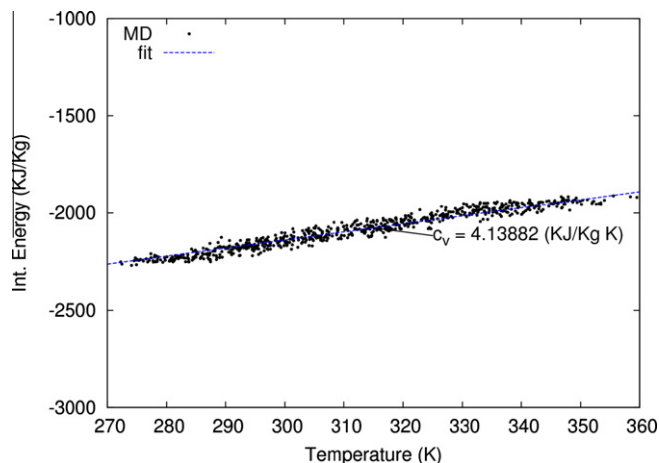
Figure 4. Relation between internal energy and temperature for TIP4P-Ew water system.

Table 5
Specific heats.

	c_p (kJ kg^{-1} K^{-1})	Relative error %	c_v (kJ kg^{-1} K^{-1})	Relative error %
SPC	4.25591	1.82	3.46096	17.20
SPC/E	4.51339	7.98	4.12349	1.35
TIP3P	4.48039	7.19	4.14095	0.93
TIP4P	4.93893	18.16	4.55668	9.01
TIP4P-Ew	4.79089	14.61	4.91585	17.60
TIP4P-2005	4.99979	19.61	5.14207	23.02
TIP5P	5.02839	20.30	6.56332	57.02
TIP5P-Ew	5.90856	41.35	5.65392	35.26
Exp [25]	4.18		4.18	

at 298 and 318 K are given in Table 3. It can be seen that both five-site rigid model have the better performance among all the reported cases: the relative errors at 298 and 318 K are 11.32% and 4.08% (TIP5P), 1.87% and 7.59% (TIIP5P-Ew), respectively. For 298 K, TIP5P-Ew has better performance than TIP5P model, while TIP5P performs better than TIP5P-Ew at 318 K. In contrast, SPC model overestimate the thermal conductivity by 44.39% and 36.96%; SPC/E has over predicted by 53.17% and 47.53%; TIP3P has relative error at 45.59% and 49.08%. Four-site models also yield large relative error range from 34.87% to 49.11%. In addition, the experiment data shows the trends that thermal conductivity for liquid water increase with increasing temperature at one atmosphere pressure. The results in this work indicate that five models (SPC/E, TIP3P, TIP4P, TIP4P-Ew, and TIP5P-Ew) could predict this trend. Therefore, take the trends prediction factor, TIP5P-Ew still can be considered to be the best.

The velocity gradient of TIP4P/2005 at 318 K is shown in Figure 2, where the linear relation between v_x and z can be observed. Table 4 summarizes the shear viscosity of each model at 298 K and 318 K, respectively. It can be seen that TIP5P and TIP5P-Ew still showed the best performances, with relative error ranging from

8.61% to 12.03% (relatively larger than thermal conductivity results), in comparison with other models, at 298 K. For the cases at 318 K, the performances are even better with small and stable relative error, 10.91% and 12.81%, respectively. The results indicate that all of eight rigid models can predict decreasing trends of shear viscosity with increasing temperature. It is worthwhile to mention that shear viscosity obtained from RNEMD is close to that from Green–Kubo method for some models, compare to the value in reference [10]. The values from reference [10] is also listed in Table 4 (column 4, in the parenthesis). For examples, the value of TIP3P from RNEMD is 0.318 ± 0.0041 m Pa s, while the result from Green–Kubo method is 0.321 m Pa s. Meanwhile, the viscosity obtained using TIP4P is 0.417 ± 0.0072 m Pa s, while the value obtained from Green–Kubo method is 0.494 m Pa s. When TIP5P model is used in the RNEMD simulation, the viscosity is 0.783 ± 0.0504 m Pa s whereas Green–Kubo method yields 0.699 m Pa s. For SPC model and TIP4P-2005 model, the differences, which are relatively larger, are −54.2% and −32.7%, respectively. Moreover the result based on Green–Kubo method shows that TIP4P/2005 is the best model for shear viscosity prediction at 298 K, which is different from the conclusion obtained from RNEMD. Since RNEMD is an approach close to the real experiment technique; the obtained results are still meaningful that can be a guide for other non-equilibrium molecular dynamics simulations treating with those systems composed with rigid-water molecules.

Specific heat simulations are also performed in NVT and NPT ensemble within the same simulation boxes. The internal energy and enthalpy are obtained during the gradual cooling process in

the simulation boxes from 343 to 283 K. The relationship between enthalpy (internal energy) and temperature for SPC/E (TIP4P-Ew) model is shown in Figures 3 and 4. Figure 3 indicates the linear relationship between enthalpy and temperature, while Figure 4 shows the similar relation between internal energy and temperature. The values of specific heats are corresponding to the slopes of Figures 3 and 4, since the assumed linear relationship is applied. The obtained specific heats are given in Table 5. It is interesting to note that three-site models (SPC, SPC/E, TIP3P) come out to be the best models to predict the specific heat at constant volume, while TIP5P and TIP5P-Ew overestimated the values much more than others. The value of specific heat at constant pressure predicted by SPC/E, TIP3P and TIP4P agree well with experimental results. However, the consistency between two specific heats is not well. If taking all these results together, it can be found that three-site model, TIP3P, turns to be the best in prediction both specific heats.

In conclusion, if molecular dynamics method is used to simulate heat transfer for a rigid water molecular system, the five-site models (TIP5P-Ew) are better choices. For dynamic problem that involves water flow in micro and nanosystems, the five-site models (TIP5P, TIP5P-Ew) are also appropriate choices. If a problem emphasizing dynamic response of the temperature to a heating or cooling process, the three-site models are good candidates, especially TIP3P model.

Acknowledgment

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