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PREDICTION OF THE TEMPERATURE-DEPENDENT THERMAL CONDUCTIVITY AND SHEAR VISCOSITY FOR RIGID WATER MODELS

Yijin Mao and Yuwen Zhang
Department of Mechanical and Aerospace Engineering
University of Missouri
Columbia MO 65211, USA
Email: zhangyu@missouri.edu

ABSTRACT

The temperature-dependent thermal conductivity and shear viscosity of liquid water between 283K and 363K are evaluated for eight rigid models with the reverse non-equilibrium molecular dynamics (RNEMD). The five-site models (TIP5P and TIP5P-Ew) have apparent advantages in estimating thermal conductivities than other rigid water models that overestimate the value by tens of percent. For shear viscosity, no single model can reproduce all experimental data; instead, five- and four-site models show their own strength in certain temperature range. Meanwhile, all of current rigid models obtain lower values than experimental data when temperature is lower than 298K, while TIP5P and TIP5P-Ew model can relatively accurately predict the values than others at temperature range from 298K to 318K. At higher temperature range, shear viscosity of liquid water can be reproduced with four-site model (TIP4P-2005, TIP4P-Ew) fairly well.

INTRODUCTION

Water properties have been intensively investigated in the past decades, at the molecular simulation level – both from quantum (AIMD) [1] and classical molecular dynamics. A 2002 literature review indicates that there are 46 water models [2], which are categorized into rigid, flexible and polarizable models [3]. Recently, new well-performance models which are reparameterized based on the existing ones are proposed through further studies. For instance, TIP4P/2005 [4] that is designed to be a general purpose model for condensed phase of water has an impressive performance in predicting a variety of thermal properties. Another extended version of four-site rigid water model, TIP4P-Ew [5], has a global improvement in predicting water properties. TIP5P-Ew [6] that was reparameterized based on TIP5P model has been reported that it 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 leads to confusion when researchers need to choose an appropriate model before conducting their molecular dynamics simulations in terms of different problems. In this work, both thermal conductivity and shear viscosity will be calculated with RNEMD method for liquid water at temperatures ranging from 283K to 363K. The following eight rigid models, SPC, 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.

PHYSICAL MODEL

The RNEMD comprise of two main steps, which including generating flux in an unphysical way [7] and measuring corresponding gradient when steady-state is reached. Figure 1 gives a 2D schematic of the RNEMD in calculating thermal conductivity. First, the box is uniformly divided into M (even number) slabs, as framed by the dashed lines. Then n hottest molecules in M/2+1 slab and coldest ones in 1st slab will be selected and paired; then the kinetic energy in each pair will be swapped. Thus, an unphysical heat flux flowing from M/2+1 slab to 1st slab is generated. As a result, two physical heat fluxes, flowing from 1st to M/2+1 and from M+1 to M/2+1, are generated in response. If the kinetic energy is swapped periodically, a stable heat flux and a corresponding temperature gradient will be established. The final heat flux can be calculated as,

$$q" = \frac{E_{ke,ex}}{2tA} \quad (1)$$

where $E_{ke,ex}$ denotes the exchanged kinetic energy between each pair, A is area that heat flux flow across, and t is the total simulation time.

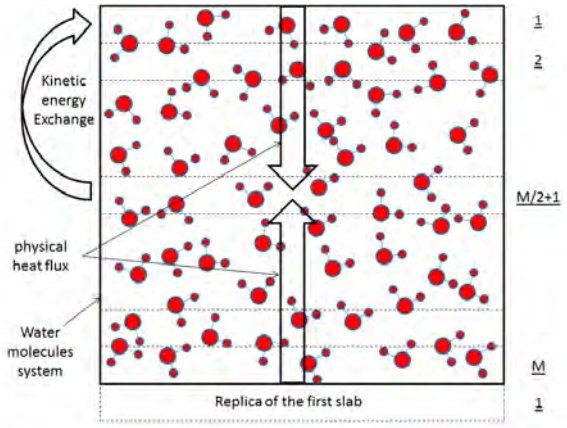

Fig. 1 Schematic of reverse non-equilibrium molecular dynamics (RNEMD)

After the system reaches to a steady-state, a symmetric temperature profile will be established, and it will be recorded during the sampling period. The thermal conductivity can then be obtained through Fourier's Law,

$$k = \frac{q"}{dT/dx_i} \tag{3}$$

where x_i could be x, y, and z. Temperature gradient and accumulated exchanged energy will be calculated with least-square fitting. The error bar will be calculated through,

$$\Delta k = k\left(\frac{\Delta E_{ke,ex}}{E_{ke,ex}} + \frac{\Delta G_T}{G_T}\right) \tag{4}$$

where, $\Delta E_{\mathrm{ke,ex}}$ and ΔG_T are error bar from each linear fit, and G_T represents temperature gradient in this fitting.

For shear viscosity calculation, similar approach is applied to the same system, except exchanging momentum instead of kinetic energy for pairs of molecules. The corresponding velocity gradient will be calculated through,

$$j_i = \frac{P_{mo,ex,i}}{2tA} \tag{5}$$

where $P_{\mathrm{mo,ex,i}}$ represents the amount of exchanged momentum in i component (i could be x, y, z), which can be calculated as,

$$P_{mo,ex,i} = \sum_{j=1}^{n} \frac{1}{2} M_j \left(v_{posj,i} - v_{negj,i}\right) \tag{6}$$

where $v_{\mathrm{posj,i}}$ and $v_{\mathrm{negj,i}}$ represent positive and negative velocity component in the i direction (bulk velocity of the box is excluded) of j^{th} molecule pair. Similarly, shear viscosity can be calculated through newton's law for fluid,

$$\mu = \frac{j_i}{dv_i/dx_i} \tag{7}$$

where i could be x, y, z. Error bar will estimated as,

$$\Delta\mu = \mu\left(\frac{\Delta P_{mo,ex,i}}{P_{mo,ex,i}} + \frac{\Delta G_v}{G_v}\right) \tag{8}$$

where $\Delta P_{i,ex}$ and ΔG_v are error bar from each linear fit, G_v represents velocity gradient in its least-square fit.

In this work, eight different rigid water models will be studied; all potential functions of these rigid water molecules share the same form, which consist of the contributions from electrostatic, dispersion and repulsive forces:

$$E_{ab} = \sum_{i}^{on\ a}\sum_{j}^{on\ b} \frac{k_C q_{a_i} q_{b_j}}{r_{a_i b_j}} + \sum_{i}^{on\ a}\sum_{j}^{on\ b} 4\varepsilon_{a_i b_j}\left[\left(\frac{\sigma_{a_i b_j}}{r_{a_i b_j}}\right)^{12} - \left(\frac{\sigma_{a_i b_j}}{r_{a_i b_j}}\right)^{6}\right] \tag{9}$$

where, a and b denotes two different molecules, subscript i and 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, but the electrostatic force is evaluated with PPPM method [8] that splits this effect into short range and long range parts. For four- and five-site models, Coulomb forces on virtual sites are redistributed to real atoms by adopting the algorithm in [9]. Simulations were carried out within the framework of the open-source molecular dynamics software LAMMPS [10].

RESULTS AND DISCUSSIONS

In this work, the linear response of temperature distribution as a result of imposed heat flux to the system is well established. Figure 2 gives the final results of thermal conductivities for each model at various temperatures. The solid-black triangle represents the data from the experiments [11]. It can be seen both five-site models have better performances than the rest of models at all temperatures. Minor discrepancies exist between TIP5P and TIP5P-Ew when temperature is 298K, 313K, and 363K. It is interesting to notice that five-site models, either TIP5P or TIP5P-Ew, can always reproduce experimental value. Therefore, five-site models are the priority choices when thermal conductivity of the system is an essential factor determining the precision of the MD simulation. However, it should also been pointed out that the trends of thermal conductivity versus temperature from TIP5P and TIP5P-Ew are not perfectly ideal, comparing with the increasing trend that experimental values hold. Comparing with five-site, both four-site and three-site models over predict the value by tens of percent. Similar trends from results obtained from the five-site models can also be observed. For example,

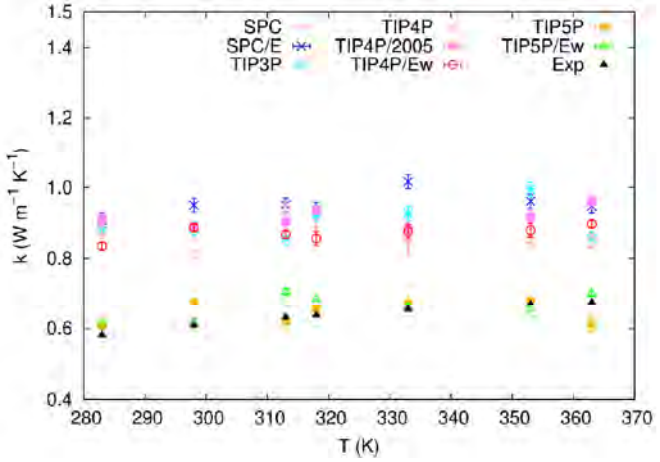

Fig. 2 Thermal conductivities predicted by eight rigid models

the thermal conductivity obtained from TIP4P model decreases when temperature increases to 298K from 283K. Therefore, it can be concluded that none of a single rigid water model can reproduce the trends of experimental data of thermal conductivity.

Table 1 summarizes the thermal conductivities, its uncertainties and relative error to experimental value of all results showed in Fig. 3. It can be seen that the uncertainties of all cases are within 3.35%, which mean that the results in this work is very reliable. As discussed above, five-site models perform best with comparatively small relative errors. For TIP5P, it reaches to the maximum error of 11.50% (overestimate) at 298K, and minimum error of 1.97% (underestimate) at 313K; for TIP5P-Ew, the maximum error of 11.99% (overestimate) happen at 313K, and minimum of 1.06% (overestimate) at 333K.

All the shear viscosities are combined in Fig. 3 where the trends of the values versus the temperature can be easily recognized. At this time, no single model can reproduce the trend of the experimental data; instead, each model shows its own strength in a certain temperature range. When temperature is in the range from 298K to 318K, five-site model could be the best choice; and if temperature is around 333K four-site model is better. In particularly, four-site models (TIP4P-2005, TIP4P-Ew) precisely predict the shear viscosity at 353K and 363K. It is interesting to notice that all of three-site model underestimate the shear viscosity by a certain relative error. However, this error is decreasing as temperature increase from 283K to 363K, which hints that three site model may have best performance for hot water. Considering the computation cost, three-site model still could be an alternative choice when study hot water related problem. In addition, for lower temperature, none of these models can precisely estimate shear viscosity at lower temperature of 283 K. Even the best one, five-site model reaches significant errors.

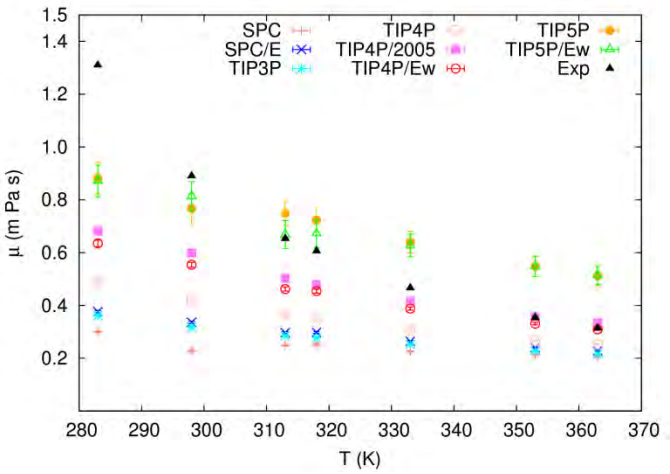

Fig. 3 Shear viscosities trends predicted by eight rigid models

Table 2 summarizes the shear viscosities, uncertainties and relative error to experimental data for all cases reported in Fig. 4. Uncertainties of each case are relatively small, and the maximum error of 7.92%, comes from TIP5P-Ew at 313K. For lower temperature case (283K), none of eight models can precisely reproduces the experiment value and the best result from TIP5P underestimate the viscosity by by 32.49%. On the other hand, all of these eight rigid models accurately predict the decreasing trend of shear viscosity versus temperature. It can also be seen that TIP5P-Ew performed the best at 298K, 313K, and 318K, with relative error of -8.61%, 2.41%, and 10.91%, respectively; TIP4P-2005 has the minimum relative error when temperature is 333K and 353K, with -10.66% and 0.94% error; TIP4P-Ew shows the best agreement with experiment value at 363K with only -1.66% error. Based on current results, TIP4P does not show any advantage of predicting shear viscosity.

Table 1 Thermal conductivities of different model at various temperatures (W m^{-1} K^{-1})

k	SPC	SPC/E	TIP3P	TIP4P	TIP4P-2005	TIP4P-Ew	TIP5P	TIP5P-Ew	Exp
283K	0.876±0.022	0.908±0.016	0.878±0.014	0.879±0.013	0.912±0.016	0.835±0.014	0.607±0.005	0.616±0.005	0.581
Err	50.95%	56.44%	51.25%	51.44%	57.04%	43.76%	4.53%	6.13%	
298 K	0.874±0.020	0.951±0.017	0.883±0.019	0.811±0.015	0.889±0.014	0.887±0.013	0.677±0.007	0.619±0.007	0.607
Err	44.01%	56.55%	45.48%	33.49%	46.44%	46.06%	11.50%	1.87%	
313 K	0.877±0.021	0.951±0.019	0.857±0.016	0.935±0.016	0.903±0.016	0.868±0.010	0.618±0.019	0.706±0.007	0.631
Err	39.02%	50.81%	35.86%	48.33%	43.23%	37.56%	-1.97%	11.99%	
318 K	0.888±0.020	0.938±0.016	0.924±0.023	0.854±0.015	0.937±0.014	0.856±0.015	0.656±0.006	0.685±0.004	0.637
Err	39.51%	47.43%	45.11%	34.15%	47.15%	34.50%	3.09%	7.59%	
333 K	0.828±0.025	1.016±0.019	0.9η±0.020	0.863±0.018	0.882±0.017	0.876±0.017	0.674±0.021	0.661±0.006	0.654
Err	26.53%	55.29%	41.72%	31.84%	34.85%	33.92%	3.02%	1.06%	
353 K	0.863±0.021	0.962±0.017	0.995±0.024	0.847±0.019	0.916±0.018	0.880±0.017	0.681±0.009	0.656±0.011	0.670
Err	28.78%	43.53%	48.49%	26.43%	36.79%	31.27%	1.71%	-2.14%	
363 K	0.852±0.019	0.948±0.023	0.855±0.019	0.847±0.018	0.961±0.021	0.897±0.014	0.612±0.020	0.702±0.006	0.675
Err	26.10%	40.41%	26.65%	25.41%	42.30%	32.90%	-9.44%	3.94%	

Table 2 Shear viscosities of different model at various temperatures (mPa·s)

μ	SPC	SPC/E	TIP3P	TIP4P	TIP4P-2005	TIP4P-Ew	TIP5P	TIP5P-Ew	Exp
283	0.300±0.003	0.376±0.005	0.362±0.005	0.490±0.010	0.681±0.013	0.635±0.012	0.882±0.059	0.872±0.060	1.306
Err	-77.01%	-71.21%	-72.25%	-62.50%	-47.85%	-51.37%	-32.49%	-33.24%	
298	0.272±0.005	0.336±0.004	0.318±0.004	0.417±0.007	0.599±0.009	0.554±0.009	0.767±0.058	0.813±0.055	0.890
Err	-69.44%	-62.27%	-64.23%	-53.15%	-32.68%	-37.74%	-13.81%	-8.61%	
313	0.249±0.002	0.297±0.003	0.285±0.003	0.366±0.006	0.503±0.008	0.462±0.008	0.749±0.047	0.668±0.053	0.653
Err	-61.80%	-54.52%	-56.33%	-43.94%	-22.98%	-29.16%	14.81%	2.41%	
318	0.253±0.005	0.298±0.003	0.278±0.003	0.348±0.005	0.480±0.007	0.454±0.007	0.724±0.045	0.672±0.052	0.606
Err	-58.25%	-50.91%	-54.22%	-42.59%	-20.85%	-25.18%	19.46%	10.91%	
333	0.226±0.002	0.264±0.003	0.253±0.003	0.308±0.004	0.416±0.006	0.388±0.006	0.640±0.041	0.627±0.043	0.466
Err	-51.54%	-43.39%	-45.81%	-33.85%	-10.66%	-16.68%	37.36%	34.62%	
353	0.212±0.002	0.239±0.002	0.228±0.002	0.267±0.003	0.357±0.005	0.331±0.005	0.548±0.039	0.548±0.039	0.354
Err	-40.01%	-32.54%	-35.60%	-24.69%	0.94%	-6.47%	54.66%	54.65%	
363	0.205±0.002	0.228±0.002	0.217±0.002	0.253±0.003	0.334±0.005	0.309±0.004	0.512±0.037	0.514±0.035	0.314
Err	-34.78%	-27.42%	-30.98%	-19.45%	6.30%	-1.66%	62.91%	63.70%	

CONCLUSION

In this work, thermal conductivities and shear viscosity of liquid water are computed with RNEMD approach and the results are compared among all results obtained from eight water rigid models. Linear temperature profiles can be well established for all rigid models and it is shown that five-site models can very precisely reproduce experimental value of thermal conductivities, while other models overestimate by tens of percent. For shear viscosity, none of all eight rigid models can reproduces all experiment values, but trends from each model accurately match that from the experiment. Five-site model can relatively accurately predict the real value of liquid water at lower temperature. Four-site model is a better choice of estimating shear viscosity at higher temperature. Therefore, the five-site models (TIP5P, TIP5P-Ew) are better choices if molecular dynamics simulation is used to study thermal emphasized problem for a water molecular system, like bubble nucleation in liquid water. For dynamic problem that involves water flow in micro- and nano- size systems, the five-site models (TIP5P, TIP5P-Ew) are also appropriate choices(in particular, for liquid water with lower temperature). When temperature is higher, TIP4P-2005 or TIP4P will be the best choice.

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REFERENCES

[1] Lee, H. S., Tuckerman, M. E., 2007, "Dynamical Properties of Liquid Water from Ab initio Molecular Dynamics Performed in the Complete Basis Set Limit," Journal of Chemical Physics, 126, 164501.

[2] Guillot, B., 2002, "A Reappraisal of What We Have Learnt During Three Decades of Computer Simulations on Water," Journal of Molecular Liquids, **101**, pp. 219-260.

[3] Caleman, C., 2007, "Water models in computer simulations," Journal of Chemical Physics, **221**, 709.

[4] Abascal, J. L. F., Vega, C., 2005, "A General Purpose Model for the Condensed Phases of Water: TIP4P/2005," Journal of Chemical Physics, **123**, 234505.

[5] Horn, H. W., Swope, W. C., and Pitera, J. W., 2004, "Development of An Improved Four-Site Water Model for Biomolecular Simulations: TIP4P-Ew," Journal of Chemical Physics, **120** (20), pp. 9665-9678.

[6] Rick, S. W., 2004, "A Reoptimization of the Five-Site Water Potential (TIP5P) for Use with Ewald Sums," Journal of Chemical Physics, **120** (13), pp. 6085-6093.

[7] Müller-Plathe, F., 1999, Reversing the Perturbation in Nonequilibrium Molecular Dynamics: An Easy Way to Calculate the Shear Viscosity of Fluids, Physicals Review E, **59** (5), pp. 4894-4898.

[8] Hockney, R. W., 1998, Eastwood, J. W., Computer simulation using particles, Taylor & Francis, New York, NY.

[9] Berendesen, H. J. C., van Gunsteren, W. F., 1984, *NATO ASI C 135*, D. Reidel, Dordrecht.

[10] Plimpton, S. J., 1995, Fast Parallel Algorithms for Short-Range Molecular Dynamics, Journal of Computation Physics, **117**, pp. 1-19.

[11] Haynes, W. M., *Handbook of Chemistry and Physics*, 91st ed., Taylor & Francis, New York, NY, Chap. 6.