Lammps as Nano-scale Lab to Estimate Fluid Thermal Properties from Molecular Dynamics

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ABSTRACT

On the one hand the complexity of nano-scale thermofluid system considered as an expensive to investigate experimentally, on the other there are available discrete models such as Molecular Dynamics model offers an affordable and accurate choice for researchers to perform nano-scale investigation to look at different fluid aspects. In this paper we demonstrate how engineers can benefit from the Molecular Dynamics simulation to estimate water thermal properties. Lammps software was used in this study to calculate water thermal properties. The atomistic model type of water which has been used is the four-site transferable intermolecular potential water molecules (TIP4PEW). The thermal properties of water to be estimated are thermal conductivity, viscosity, density, specific isochoric and isobaric heat capacities, Prandtl Number, and Volumetric thermal expansion coefficient. Results compared to experimental data, and showed very good agreement. That prove the usefulness of molecular dynamics simulation as an engineering research tools to investigate thermal properties of any fluid. This study suggests Lammps as an excellent simulation tools to perform computational studies of Thermofluid properties and consider Lammps as a cost affordable nanoscale lab, since it is an opensource software. The accuracy of Lammps depends on the quality of the force field. The results of these study were compared to experimental published water properties at temperatures of 288, 300, 312 and 324 K and pressure 1 atm.

Keywords: Molecular dynamics; water thermal properties; specific isochoric & isobaric thermal capacities; dynamic viscosity, thermal conductivity; Prandtl Number; Volumetric thermal expansion coefficient; Lammps.

1. Introduction

Literatures published on modelling fluid flow in nanochannels/nanopores at nano-scale level indicate how important is nanoscale studies to both biomedical, thermofluid and energy-related fields. Nano-channels and nanofluids are two examples of the ongoing worldwide nanoscale thermofluid studies which have tremendous improvement in the field of heat exchanger design, solar thermal energy and other thermal management fields [1-4]. Water is another topic which have been studied by many researchers at the nanoscale size. Molecular Dynamics approach is an effective tool to study fluids at nanoscale level. The most commonly used Molecular Dynamics softwares are Lammps, Gromacs, Amber, Charmm and Namd. Each one has some good features such as being an open source software (Lammps and Gromacs). Gromacs software is used commonly for biological studies. Lammps is a great MD-simulation tools for material and fluids. Using GROMACS package, Meguel Angel [5] evaluated shear viscosity of 500 water molecules of four water types, results indicate variant performances of tested models. Pekka Mark [6] performed MD-simulation using CHARMM simulation software, to determine self-diffusion coefficients and radial distribution functions, g(O-O), g(O-H), and g(H-H) for the TIP3P, SPC, and SPC/E water models. The results of this MD-simulation compared versus experimental data, where the SPC/E water model showed best bulk water dynamics and structure. Water thermal conductivity is typically calculated utilizing either with equilibrium molecular dynamics simulations (EMD) or the nonequilibrium molecular dynamics (NEMD) methods. The EMD method apply the Green-Kubo formula and requires a direct calculation of the heat flux while in the NEMD method a known heat flux is imposed and the temperature gradient is calculated [7]. The goal of the present research is to perform a nanoscale study to evaluate thermal properties of the TIP4PEW water model using Lammps [8-9], and Moltemplate [10-11]. The water was taken as a case study for using Lammps to perform a discrete fluid model simulation instead of the macroscopic continuum model. In this paper, thermal conductivity, dynamic viscosity, density, specific isochoric and isobaric heat capacities, Prandtl Number, and volumetric thermal expansion coefficient were determined using EMD method for liquid water under one atmosphere and temperatures of 288, 300, 312 and 324 K. The EMD is the most common used method and it is known as an accurate technique to calculate thermal properties of fluids. The MD-results compared to the experimental published water properties from reference [12] and showed good agreement. This study demonstrates the usefulness of using Lammps to study many thermofluid phenomena at nanoscale dimension.

2. Basics of Molecular Dynamics

Provided that there is a sufficient number of molecules within the simulated liquid box, the liquid properties can be computed from the discrete particle information by averaging the fluid quantities. The present section discusses molecular-based models. Molecular dynamics is about solving the Newton second law by integration to determine molecules positions, velocity and interaction force [13].

$$\boldsymbol{m_i \frac{d^2\vec{r}}{dt^2} = \sum_{j\neq i, j=1}^{N} \vec{F}_{ij} + \sum_{j_w \neq i, j=1}^{N_w} \vec{F}_{ij_w} + \vec{F}_{sou}\,\vec{\imath}} \tag{1}$$

The first term of the right-hand side states the molecular force derived by the Lennard-Jones potential, followed by the second term which illustrates the molecular force between particle i and other solid nanochannel wall particles denoted as j when water molecules interact with the nanochannel wall. The external force represented by the last term in Eq. 1, which can be gravity, or electric force, or pressure. The force can be derived from the derivative of potential energy with respect to atomic distance:

$$\boldsymbol{F_{ij} = -\frac{\partial \varphi_{ij}}{\partial r_{ij}}} \tag{2}$$

Forces can be computed from a variety of interatomic energy models such pair potentials (e.g. LJ, Morse, Buckingham), multi-body potentials (e.g. EAM, CHARMM, UFF, DREIDING), reactive potentials (e.g. ReaxFF) and others. The LJ potential represented by the function $\boldsymbol{\varphi_{ij}}$ which is given by:

$$\boldsymbol{\varphi_{ij} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]} \tag{3}$$

Where r is the distance between two molecules, σ is a molecular length scale, and ε is an interaction strength parameter. Eq. 1 can be integrated using the Verlet algorithm, or the finite difference methods, or velocity Verlet algorithm or any other available methods. Thermostats are algorithms which used to rescale the velocities of molecules to the simulated liquid box temperature, such as the Berendsen thermostat and the Langevin dynamics. The process of preparing Molecular Dynamics simulation starts with building the molecule initial position (x, y, z) of all atoms. The second step is to create the force field. Thus, two steps can be easily generated using Moltemplate software. Then it might be required to do energy minimization to find an optimal structure of the system. The final step is to calculate the trajectory by solving Newton's second law Eq.1 for all atoms in the force field at each timestep [13-14].

3. The Fluid Simulation Sitting – (TIP4PEW water model)

The simulation system contains 1000 water molecules in a cubic region as in figure 1. The periodic type of boundary condition was adopted for this Molecular Dynamics simulation. The constant temperature, number of atoms and pressure (NPT) conditions were applied when calculating dynamic viscosities and Isobaric specific thermal capacities. While NVT was applied to determine isochoric specific heat capacities. During calculation of thermal conductivities, the NPT-, NVT- and NVE-ensembles were applied to the water box. Duration of each ensembles was 1 ns (1000000 femtoseconds).

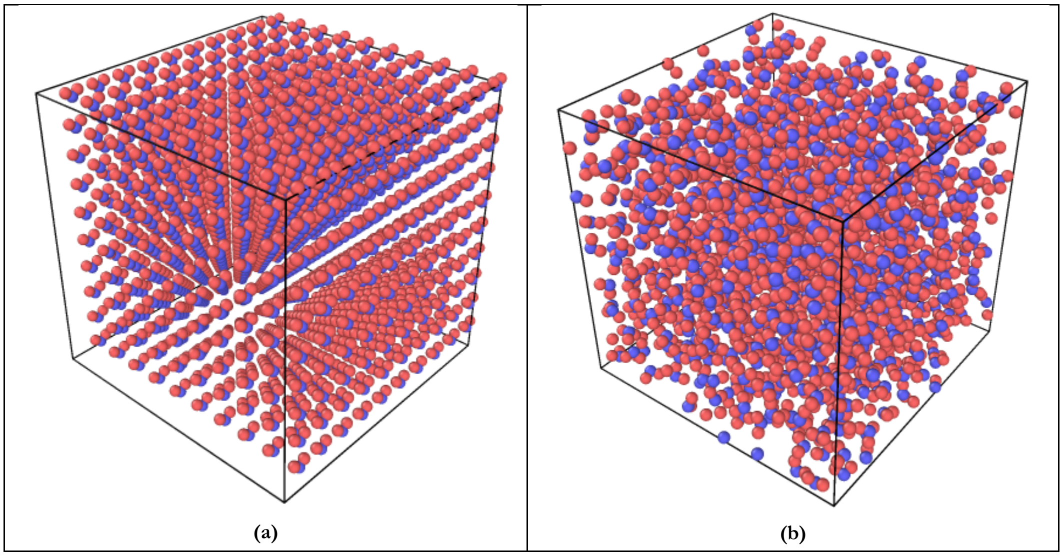

Figure 1: *System model initial sitting of 10x10x10 water molecules (a) before and (b) after pressure equilibration (NPT ensemble)*

The energy E_{ab} between molecules a and b is represented by the sum of the coulomb and Leonard-Jones potentials centred on the sites, by

$$E_{ab} = \sum_{ij} \left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{r(ij)} \right] \tag{4}$$

Where r_{ij} is the distance between atoms i and j and q_i and q_j are each site k, 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 model parameters are given in Table 1.

Table 1: *Parameters of TIP4PEW water model* [15]

Model	*σ*	*ε*	q_H	q_O	θ
TIP4PEW	3.16435	0.16275	0.52422	-1.04844	104.52

4. The Green Kubo Formula

The Green Kubo formula is a Molecular dynamic relation relates microscopic fluxes at either NPT, NVT or NVE ensembles, to thermal conductivity or dynamic viscosity. The G-K method uses a correlation function to calculate the transport coefficients during the equilibrium state. [16-17]

$$\boldsymbol{k = \frac{1}{3Vk_BT^2}\int_0^{\infty} < q_i(0)q_i(t) > dt} \tag{5}$$

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

The heat flux is defined as

$$\boldsymbol{q = \left[\sum_{j=1}^{N} v_j E_j - \sum_{\propto=1}^{N} H_{\propto}\sum_{j=1}^{N_{\propto}} v_{\propto j}\right] + \frac{1}{2}\left[\sum_{i=1}^{N}\sum_{j=1,j\neq i}^{N_{\propto}} r_{ij}(v_j.F_{ij})\right]} \tag{6}$$

Where particle velocity is v_j, total energy per atom is E_j, and the averaged partial enthalpy is H_α. Displacement and interatomic forces are r_{ij} and F_{ij} respectively, and N is number of particles. The averaged partial enthalpy is given by;

$$\boldsymbol{H_{\propto} = \frac{1}{N_{\propto}}\sum_{j=1}^{N_{\propto}}\left(E_j + r_j.F_j\right)} \tag{7}$$

5. Dynamic Viscosity

Dynamic viscosity is a measure of the momentum flux and it is defined by the gradient of velocity.

$$\tau = -\mu\frac{dv}{dy} \tag{8}$$

Where τ is the shear stress, and $\frac{dv}{dy}$ is the gradient of velocity. Dynamic viscosity has units of pressure-time and is calculated using the Green-Kubo formula using the following formula [16-17]

$$\boldsymbol{\eta_{xy} = \frac{V}{k_BT}\int_0^{\infty} < P_{xy}(0)P_{xy}(t) > dt} \tag{9}$$

Where η is the dynamic viscosity. The stress tensor P is given by

$$\boldsymbol{P_{xy}} = \sum_{j} \boldsymbol{m_j v_{xj} v_{yj}} + \frac{1}{2}\sum_{i\neq j} \boldsymbol{r_{xij} F_{yij}} \tag{10}$$

Where only the three stress tensor components of off-diagonal P_{xy}, P_{xz}, and P_{yz} are used.

6. Specific Isobaric and Isochoric Heat Capacities

During the NPT ensemble equilibrium, the isobaric specific thermal capacity between temperatures of T_1 and T_2 and the associated total energies of E_1^{tot} and E_2^{tot} respectively. The quantum contribution of intermolecular vibrational moles to the calculated isobaric specific heat capacity denoted as $\left(\frac{\partial Q}{\partial T}\right)$, which is documented in table 1 [1], includes the quantum contribution term for temperatures of 288, 300, 312, and 324 K.

$$\boldsymbol{C_P} = \frac{E_2^{tot} - E_1^{tot}}{T_2 - T_1} + \frac{\partial Q}{\partial T} \tag{11}$$

Table 2: *Quantum contributions term of equation 11*

Temperature (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 given as [18]

$$\boldsymbol{c_v} = \frac{\langle E^2\rangle - \langle E\rangle^2}{K_B T^2} \tag{12}$$

Where at the NVT equilibrium the average energy is <E>, cv is the specific isochoric thermal capacity of the entire system, and kB is Boltzmann constant = 1.3806504e-23 J/K.

7. Prandtl Number

The water Prandtl Number describes the ratio of the momentum diffusivity, $\boldsymbol{\vartheta}$, to the thermal diffusivity α. It is therefore an important thermofluid property. The Prandtl Number indicates the effect of momentum in velocity boundary layer, as well as the effect of heat transfer by diffusion in thermal boundary layer. The Prandtl Number is given by [19].

$$\boldsymbol{Pr} = \frac{c_p \mu}{k} = \frac{\vartheta}{\alpha} \tag{13}$$

8. Volumetric Thermal Expansion Coefficient

Volumetric thermal expansion coefficient β (1/°C) of water provides a measure of the density changes in response to a change in temperature at constant pressure [19].

$$\boldsymbol{\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\Delta\rho/\rho}{\Delta T}\right)_p = \frac{1}{V(p,T)}\frac{V(p.T+\varepsilon)-V(p.T-\varepsilon)}{2\varepsilon}} \tag{14}$$

9. Results and Discussion

Figure 2 shows water thermal conductivity results, Maximum absolute error (the magnitude of the difference between the experiment and the estimated values) recorded was 0.15 kW/m.K at temperature of 300 K, while at the rest of temperatures, errors were less than or equal to 0.1.

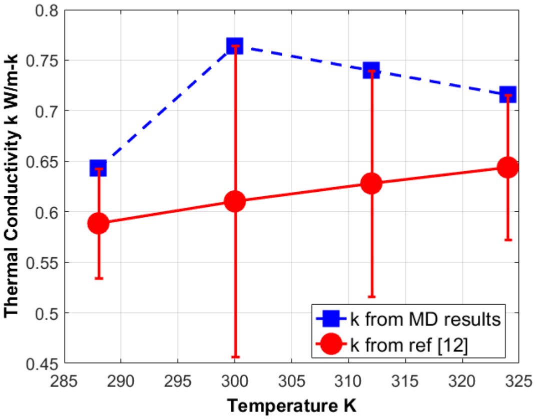

Figure 2: *Thermal conductivities from Molecular Dynamics versus experimental values*

Figure 3 illustrates dynamic viscosities from Molecular Dynamic simulation versus experimental values and error-bar. The maximum error was 0.00003 Pa. s at temperature of 288 K. At the rest of temperatures, dynamic viscosities have not showed significant errors.

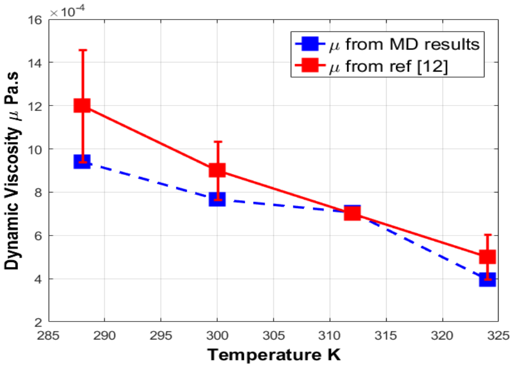

Figure 3: *Dynamic viscosities from Molecular Dynamics versus experimental values*

Figure 4 shows specific isobaric heat capacities, experimental values at the corresponding temperatures, and the error bars. Maximum error was about 0.53 kJ/kg.K at temperature of 324 K.

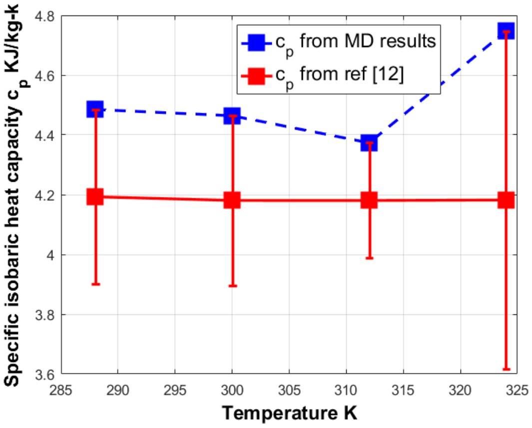

Figure 4: *Specific isobaric heat capacities from Molecular Dynamics versus experimental values*

The specific isochoric heat capacities in Figure 5 are plotted versus experimental specific isochoric heat capacities and error bars. The maximum error was recorded equal to 0.16 at temperature of 300 K.

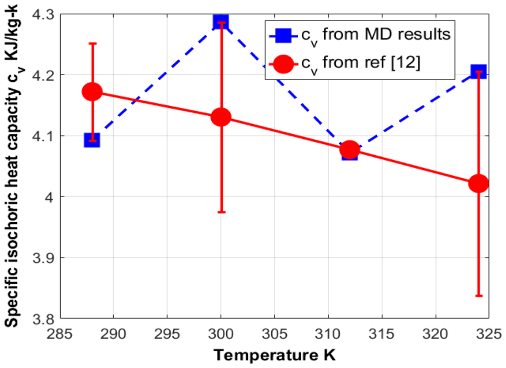

Figure 5: *Specific isochoric heat capacities from Molecular Dynamics versus experimental values*

In figure 6, Densities from MD-simulation are underestimated at temperatures of 288. 300, and 324 K. The maximum error was 10 Kg/m^3.

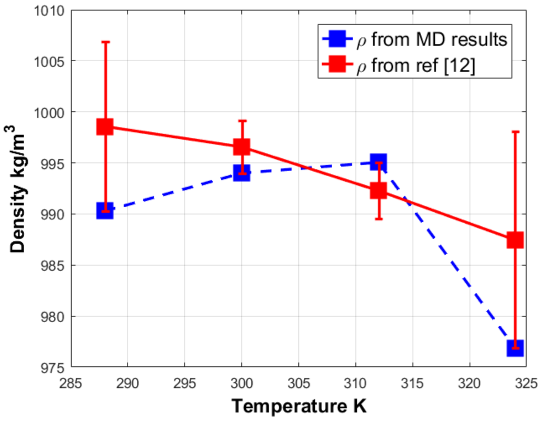

Figure 6: *Densities from Molecular Dynamics versus experimental values*

The Prandtl number results are plotted in figure 7 versus experimental Prandtl number for temperatures of 288, 300, 312 and 324 K and pressure of 1 atm. The maximum error between both quantities was 2.

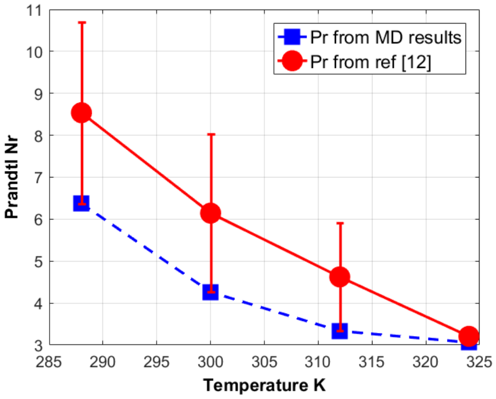

Figure 7: *Prandtl numbers from Molecular Dynamics versus experimental values*

Figure 8 shows thermal expansivities from MD-simulation versus experimental results. The maximum error between the two quantities was about 0.000125 K^{-1}.

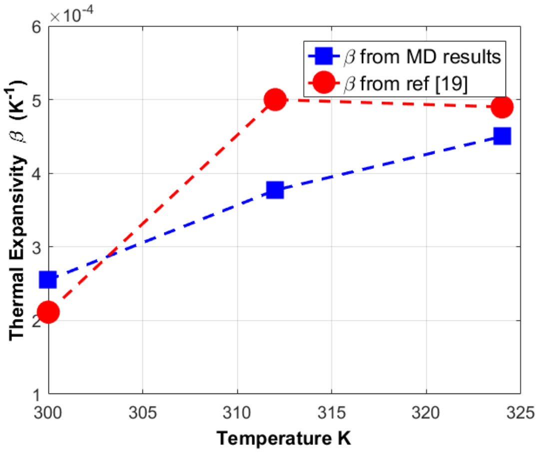

Figure 8: *Thermal expansivities from Molecular Dynamics versus experimental values*

Figure 9 illustrates absolute relative errors between MD-simulation results and experimental available values at four temperatures, were x-axis indicates all five properties while y-axis is absolute relative errors. The maximum absolute relative error of thermal conductivities was 25 % at temperature of 300 K. For dynamic viscosities, maximum absolute relative error was 23 % at temperature of 288 K. Specific isobaric heat capacities have maximum error at temperature of 324 K equal to 14 %. The maximum absolute relative error of specific isochoric heat capacities was 4.6 % at temperature 324 K. The absolute relative error of densities was negligible.

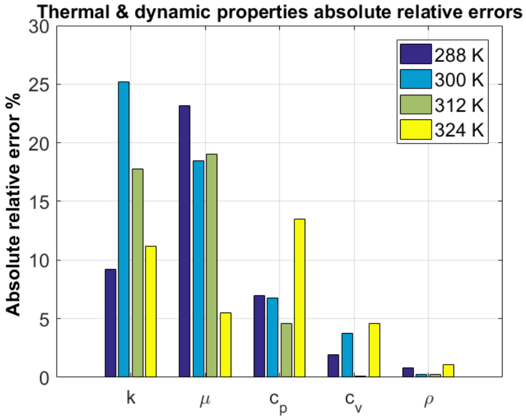

Figure 9: *Absolute relative errors between Molecular Dynamics properties and experimental values*

Thermal properties of water determined using the TIP4PEW water model and Lammps, This Molecular Dynamic approach saves the cost associated to an experimental approach.

10. Conclusions

The Molecular Dynamics results provide good argument to support Lammps as a nano-scale laboratory to investigate fluid thermal properties. In this study, we have used the TIP4PEW water model as an example of how Lammps can be used to calculate fluid thermal properties. Lammps software can be used as a Thermofluid lab to study behaviours of most fluids in nano-scale and femtoseconds- or picoseconds-scales to capture more details of interactions between molecules, and avoid approximating most of physical phenomena. From the generated MD-simulation results, it is clear that thermal properties converged to the experimental properties and that the MD thermal properties were mostly agreed with the published water thermal properties. A main cause of the errors in these Molecular Dynamics calculations is that when integration performed the noise associated with the autocorrelation function changes the physically properties slightly as for the conductivities. To minimize this noise, it is possible to search for an optimal damping factor to reduce noise from the autocorrelation function.

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