Chemical Physics Letters 687 (2017) 270–275

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Thermal characterization assessment of rigid and flexible water models in a nanogap using molecular dynamics

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ARTICLE INFO

Article history:
Received 24 May 2017
In final form 5 September 2017
Available online 7 September 2017

Keywords:
Molecular dynamics
Water
Thermal conductivity

ABSTRACT

The thermal properties of the TIP3P and TIP5P water models are investigated using equilibrium and non-equilibrium molecular dynamics techniques in the presence of solid surfaces. The performance of the non-equilibrium technique for rigid molecules is found to depend significantly on the distribution of atomic degrees of freedom. An improved approach to distribute atomic degrees of freedom is proposed for which the thermal conductivity of the TIP5P model agrees more closely with equilibrium molecular dynamics and experimental results than the existing state of the art.

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1. Introduction

Water plays a key role in biological, chemical, and a variety of engineering systems. The estimation of water properties in the past generally relied on empirical correlations and equations of state [1], whereas the molecular dynamics (MD) approach has recently become more common with the increase in computational capabilities [2]. Gulliot [3] counted 46 water models in the literature, and this number continues to increase with recently developed models such as the Four-Site Transferrable Intermoleculer Potential (TIP4P) and Five-Site Transferrable Intermoleculer Potential (TIP5P). These models are usually classified as rigid, flexible, or polarizable [4].

Mao and Zhang [5] state that one of the major challenges with water models is to reproduce experimental data including the melting and boiling points, specific heat, viscosity, and thermal conductivity. Thermal conductivity is one of the properties most infrequently considered, and requires the use of specific techniques such as Equilibrium Molecular Dynamics (EMD) or Non-equilibrium Molecular Dynamics (NEMD). EMD relies on the Green–Kubo formalism and the calculation of the autocorrelation function. The significant computational time involved means that estimates of water thermal conductivity using the EMD technique are limited in the literature. Bresme et al. [6] estimated the thermal conductivity of the supercooled TIP4P/2005 water model [7] using EMD and found higher results than in experiments. Rosenbaum et al. [8] presented EMD results of the thermal conductivity for SPC/E [9], TIP4P-Ew [10] and TIP4P-FQ [11] potentials and achieved 10–20% relative errors with respect to the experiments. English and Tse [12] also used the EMD technique with TIP5P potential of Mahoney and Jorgensen [13] and reported good agreement with experiments for thermal conductivity. Sirk et al. [14] reported both NEMD and EMD thermal conductivity results that agreed with experiments and suggested further investigation of the thermal behaviour of water-solid interfaces. They studied several different water models, reported that the bond and angle stretching in water molecules do not significantly contribute to the heat transport, and did not find any significant difference in thermal conductivity for the rigid TIP3P, TIP4P and SPC/E models. Kumar and Stanley [15] found very high thermal conductivity using NEMD and the rigid TIP5P potential of Mahoney and Jorgensen [13], but Mao and Zhang [5] reported good agreement with experiments for the TIP5P potential re-parametrized by Rick [16].

NEMD, proposed by Muller–Plathe [17], effectively reproduces the experimental procedure by imposing a heat flux on the system and is often more computationally efficient than EMD; however, the size effect and thermal gradient dependence should be carefully considered when extrapolating to bulk properties [18]. NEMD was initially developed for simple monoatomic substances, and afterwards extended to polyatomic substances [19] and rigid molecules [20]. Bedrov and Smith [20] applied NEMD to rigid water molecules such as those in the TIP5P model, but this required that a classical MD solver be modified to include an implementation of the rigorous algorithm they describe. More generally, the calculation of the temperature of rigid molecules by means of the

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http://dx.doi.org/10.1016/j.cplett.2017.09.012
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equipartition theorem requires careful consideration of the number of degrees of freedom within the domain [21,19]. A simple and rigorous approach to calculate the temperature of rigid molecules that can intersect the domain boundary in NEMD studies would be valuable.

This study proposes a new method to calculate the temperature and thermal conductivity in MD simulations, and compares the performance of the proposed method for the rigid TIP5P and flexible TIP3P water models with that of Mao and Zhang [5]. The proposed method is found to give more reasonable temperature profiles than that of Mao and Zhang [5] when molecules are rigid and the atomic density is non-uniform due to the presence of solid-liquid interfaces. Solid blocks are introduced to apply Muller–Plathe algorithm [17] without the need to implement the algorithm of Bedrov and Smith [20]. Temperature profiles using NEMD and the thermal conductivity predictions of both NEMD and EMD are presented to compare with experimental data.

2. Methodology

2.1. Non-equilibrium molecular dynamics

Two copper blocks are separated by regions filled with water molecules in a simulation box with periodic boundary conditions in all directions, as shown in Fig. 1. The simulation box has initial dimensions of $3.2 \times 3.2 \times 6.9\ \text{nm}^3$ and contains 2592 copper atoms and 1448 water molecules. We applied the velocity swapping of the Muller–Plathe algorithm [17] to the monoatomic copper atoms to generate a thermal gradient and estimate the thermal conductivity of the intervening water regions. This obviated the need to swap the momentum and angular momentum of rigid molecules, and considerably simplified the procedure.

A TIP5P model with the parameters of Rick [16], or a TIP3P model with the parameters of Jorgensen et al. [22], was used for the water molecules, and a Lennard-Jones pair potential was used for the copper atoms [23]. The water-copper interactions followed the Lorentz–Berthelot rule. The net z-momentum of each copper block was set to zero every 10 fs to avoid transaction through the simulation cell. The system was equilibrated in the NPT ensemble for 100 ps at 300 K and 1 atm with a timestep of 1 fs, after which the NVE ensemble was used for a 1 ns production run. As described above, the velocities of atoms in the copper blocks were swapped rather than applying the velocity swapping algorithm of Bedrov and Smith [20] directly to the rigid TIP5P molecules. The velocities of three copper atoms were swapped every 200 fs, and LAMMPS [24] was used for MD calculations.

The system was divided into 20 bins along the z-direction (perpendicular to the water-copper interface) and the temperature in each bin was calculated by two different approaches. The first defined an atomic temperature for each atom as proposed by Mao and Zhang [5]:

$$T_i = \frac{2KE_i}{k_B M_i^I} \tag{1}$$

where KE_i is the kinetic energy of the atom, k_B is Boltzmann's constant and M_i^I is the number of degrees of freedom (DOF) for that atom. The DOF is calculated as:

$$M_i^I = 3 - \frac{C_i}{2} \tag{2}$$

where C_i is the number of distance constraints that involve atom i, and angle constraints are viewed as distance constraints on non-adjacent atoms. Note that C_i is not always an integer, e.g., there is no way to equitably distribute five angle constraints on four hydrogens in rigid methane without allowing fractional constraints. Once the atomic temperatures are calculated using Eq. (1), they are averaged over the atoms in a bin to find the temperature of that bin. This is denoted as Method 1 in this study.

We propose a new method to calculate the temperature of a domain containing rigid molecules, and denote this as Method 2. The temperature is defined by means of the equipartition theorem:

$$T = \frac{2\sum_i KE_i}{k_B \sum_i M_i^{II}} \tag{3}$$

where the sums are performed over all atoms in the domain. The number of degrees of freedom M_i^{II} of atom i is given by:

$$M_i^{II} = 3(m_i + I_i) \tag{4}$$

where m_i and I_i are the fractional contribution of atom i to the mass and to the moment of inertia of the rigid molecule. An atom without constraints is considered to be a rigid molecule of one atom and has no moment of inertia. This is believed to more equitably distribute the degrees of freedom of the rigid molecule among the constituent atoms, and is particularly important when a rigid molecule is only partly contained in the domain. The resulting DOF for atoms in the TIP5P model are summarized in Table 1.

Temperatures of the bins were calculated using Eqs. (1) or (3) and time averaged over 1000 data points taken for each of 10 equal intervals during the 1 ns production run. Theil–Sen regression [26] was used for the temperature gradient calculation to minimize the effect of outliers. The mean and standard deviation of the temperature gradient were calculated using bootstraping with 10,000 resampled temperature data [27]. Once the temperature gradient was estimated for a given heat flux, the thermal conductivity was calculated by Fourier's law [17] for both water regions as seen in Figs. 2 and 3, and they were averaged for the overall result. The temperature gradient was estimated by ignoring the outlier points for Method 1 with TIP5P as seen by the regression lines in Fig. 2a.

2.2. Equilibrium molecular dynamics

The EMD technique was performed using cubic simulation boxes with 1331 water molecules. The edge length of the simulation box converged to 3.38 nm for TIP3P and 3.42 nm for TIP5P after a 100 ps NPT equilibration at 300 K and 1 atm, giving respec-

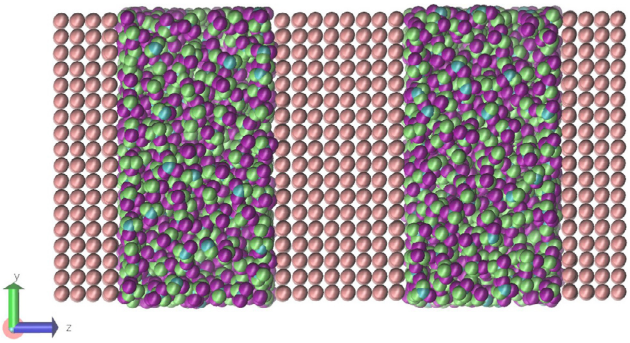

Fig. 1. TIP5P-copper model, obtained using VMD [25].

Table 1
DOF for the atoms in the TIP5P model as calculated by two different methods. M_O is for oxygen, M_H is for hydrogen, and M_L is for the ghost atoms of the TIP5P model.

	M_O	M_H	M_L
Method 1	1	1.25	1.25
Method 2	2.782	1.609	0

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