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Research paper

A reliable approach for calculating thermophysical properties of liquid using molecular dynamics simulations

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HIGHLIGHTS

- Thermophysical properties of water are evaluated with equilibrium molecular dynamics.
- Deficiency in the conventional data processing method is investigated.
- New data processing method is developed to ensure the reliability of the obtained properties.
- Criterion is introduced to determine the minimum domain size under given conditions.

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ABSTRACT

This paper presents a new data processing method for calculating more reliable thermophysical properties of liquid using Green-Kubo Method based molecular dynamics (MD) simulation. In this study, MD simulations of water are first performed using three common water models. A new approach for analysing the simulation data is then developed to obtain statistically meaningful thermophysical properties such as thermal conductivity and viscosity. It is demonstrated that for a given desired standard deviation for a specific simulation, a suitable simulation box size can be determined. The proposed approach can assure the repeatability and reliability of the calculated thermophysical properties of liquid.

1. Introduction

During the past few decades, the transport phenomena of liquids have been of great interest in a wide variety of applications. For example, miniaturized systems such as nano-electromechanical systems (NEMS) technology [1] and nanofluids [2–5] have received considerable attentions more recently. Transport properties, such as thermal conductivity and viscosity, serve as the most significant characteristics of materials in thermal studies [6–8]. Hence, accurate measurement of thermophysical properties of liquid plays a critical role in the functionality of NEMS and nanofluids.

Water is the most investigated liquid in the literature due to its widespread use and ubiquity in our environment. Several experimental and numerical methods have been developed to estimate its thermophysical properties. For example, Duangthongsuk and Wongwises applied transient hot-wire apparatus and Bohlin rotational rheometer to measure thermal conductivity and viscosity of water-based nanofluid, respectively [9]. In their study, before the thermophysical properties of nanofluid were measured, the thermophysical properties of the base fluid (pure water) were measured to validate the experimental apparatuses. However, in many cases, experimental measurement can only provide limited insight into the mechanism of thermophysical properties change as a function of certain parameters. As a result, computer simulations have been carried out in order to better understand the properties of mixed molecules and the microscopic interactions between them. A variety of modelling techniques have been developed for calculating the thermophysical properties over the years [10–12]. Among them, molecular dynamics (MD) approach can provide detailed atomic-level information and has been widely employed in many numerical simulation studies on the thermophysical properties of liquids [13–15].

MD simulations for calculating thermophysical properties of liquids could be categorized into two types namely non-equilibrium molecular dynamics (NEMD) [16,17] and equilibrium molecular dynamics (EMD) [18]. In EMD, the system is in equilibrium when the properties are evaluated whereas an external field drives the system away from thermodynamic equilibrium in NEMD. In order to calculate thermophysical properties in EMD simulation, fluctuation-dissipation and

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linear response theorem are usually applied. In contrast, In the NEMD simulations, an external field such as shear force or heat flux needs to be applied to create shear flow or temperature gradient, respectively. Then, the desired properties are monitored and calculated. In a comparative study by Schelling et al. [19], it has been concluded that the EMD approach has considerable advantages over the NEMD approach. Firstly, although both EMD and NEMD approaches show finite size effects, these effects are more severe in NEMD. Secondly, EMD is more appropriate for geometries where periodic boundary conditions are applied in all three directions. On the contrary, NEMD could only accomplish the calculations in one direction. Hence, EMD simulation is applied in this study.

In EMD simulation, Green-Kubo (GK) method, introduced by Green [20] and Kubo [21], has been well-established and widely used for calculating thermophysical properties of liquids. This method is based on Green-Kubo formalism where thermal conductivity or viscosity is calculated by integrating over time of the ensemble average of the autocorrelation of the external field [22].

On the other hand, the most critical part of a molecular dynamics simulation is the potential models. So far, many water models have been developed in order to study the structure and properties of water at the atomic scale. According to a report by Guillot [23], water models are classified into four main types, namely rigid, flexible, dissociable, and polarizable. It has been a matter of discussion that which model may reproduce the most accurate and reliable results in MD simulation of thermophysical properties. However, the answer to this question is not very clear so far as each water potential model was developed to reproduce certain properties under given conditions. In this regard, there are scarcely published studies that compare the performance of different models on reproducing thermophysical properties. For example, González and Abascal [24] calculated the shear viscosity using Green–Kubo method in order to compare five rigid water models including TIP3P [25], TIP4P [25], TIP5P [26], SPC/E[27] and TIP4P/2005 [28]. In a broader study, thermal conductivity, viscosity and specific heat of various rigid water models were calculated and compared with each other using MD simulation [29]. The authors showed that recent developed models, such as TIP5P, are capable of illustrating more accurate values compared with conventional ones.

Moreover, we have noticed that the common data collection method of predicting thermal conductivity and viscosity of liquids using MD simulation is questionable. Take the method used in [18,30,31] for example, when the values of thermal conductivity or viscosity somehow converged after a certain period of production run time, the MD simulation stopped. Then, the values of the thermal conductivity or viscosity in the three directions were recorded. The average value of the properties in the three directions was worked out and presented as the calculated thermal conductivity or viscosity. There were some similar studies, such as the water model comparative study carried out by Mao and Zhang [29], in which the standard deviations of certain thermophysical properties were reported in Tables 3 and 4 of their paper. However, it was not clearly explained how these statistical values were calculated. Also, thermal conductivity of the supercooled water is estimated using GK equation by English and Tse [32]. They did not describe their data collection approach in detail. However, their MD simulation resulted in an uncertainty. In particular, the standard deviation of their calculated thermophysical properties was three times greater than that from the experimental measurement. Similarly, in many other available studies in the literature, data collection procedure has not been clearly described, as the focus of those studies such as [17,33,34] was more on the results reporting and discussion. In addition, Kumar et al. [34] stated that the applied data collection and processing method in their study suffers from poor convergence even for extremely long simulations.

It appears that the common data collection method does not consider the effects of simulation box size, initial conditions, thermostat effectiveness, data sampling frequency, etc., on the simulated thermophysical properties. However, it has been known that these parameters could have significant effects on the results of MD simulations. For example, the MD simulation box size affected the simulated mechanical properties of the nano-material [35]. The simulations were also dependent on the initial conditions that could be changed by using different random number seed. As a result, sufficient number of independent simulations must be carried out and average values of the simulated results should be used in order to obtain reliable results [36]. Hence, a new approach that can produce reliable and repeatable results with controllable standard deviations should be developed.

An intrinsic problem associated with the GK calculation is the artificial correlations. The common method of mitigating the problem is to choose a system size large enough to minimize these correlations. Recently, Muraleedharan et al. [37] tried to mitigate the problem for multicomponent systems (Solid particles immersed in a base fluid) by increasing the number of particles. They observed that adding more particles is likely to hamper the development of the artificial self-correlations. In either method, researchers normally find the proper size or number of particles by trial and error and there are no clear quantified criteria to select an appropriate simulation domain size or particle numbers. Thus, we believe it is important to find a quantifiable data processing method to ensure the reliability and accuracy of the simulated properties.

In the present study, a common problem of MD simulation is considered and a new reliable data-processing approach is developed. In addition, by using the new approach, a criterion in accordance with the standard deviation of the simulation results is introduced. This criterion can be used to select the appropriate size of the system based on the level of the accuracy that is desired for a given simulation. Without the loss of generality, three common rigid water models including SPCE, TIP3P, and TIP4P-2005 will be used at different temperatures and the data collection procedure on the reliability of the simulated thermal conductivity and viscosity of water will be investigated. It is shown that the proposed data collection and processing method is able to effectively control the standard deviation of the simulated values and thus produce reliable and repeatable thermophysical properties from MD simulations.

2. Methodology

In this section, the method of calculating thermal conductivity and viscosity by employing Green-Kubo method based EMD simulation will be first described. Then, a new data collection and processing method will be introduced for calculating thermophysical properties of water using MD simulations.

2.1. Thermal conductivity

When a liquid system is in equilibrium, it has a constant average temperature and an average heat flux of zero over a finite time period. However, the temperature fluctuates instantaneously, and as a result, a finite heat flux exists at each instant of time [38]. This phenomenon is the base of the Green-Kubo method to calculate thermal conductivity and viscosity in EMD simulation.

In macroscopic scale study, thermal conductivity k is a coefficient that relates the macroscopic heat current vector (**J**) to the temperature (T) gradient in the form of Fourier's law [39]:

$$\vec{j} = -k\hat{A}\cdot\vec{\Delta T} \quad (1)$$

However, in microscopic scale study, in order to calculate the thermal conductivity k using EMD simulation, Green-Kubo (GK) method relates the lattice thermal conductivity of the system to the integral of the average of the time correlation function of the heat current through the following relation [21,40]: