



Heat transport in liquid water at extreme pressures: A non equilibrium molecular dynamics study

Fernando Bresme^{a,b,*}, Frank Römer^a

^a Chemical Physics Section, Department of Chemistry, Imperial College London, SW7 2AZ, London, UK

^b Department of Chemistry, Norwegian University of Science and Technology, Trondheim, Norway

ARTICLE INFO

Available online 22 October 2012

Keywords:

Computer simulations
Water
Thermal conductivity
Equation of state
Non equilibrium computer simulations

ABSTRACT

We investigate the structure and heat transport of liquid water at high pressures and temperatures, 1–50 kbar and 300–600 K, *i.e.*, in a region of the phase diagram that is challenging for experimental investigations. Using equilibrium and non equilibrium molecular dynamics simulations and the TIP4P/2005 water model, we compute the structure and thermal conductivity of liquid water. At extreme pressures, 20–50 kbar the tetrahedral order characteristic of the hydrogen bonded network is severely disrupted, and the liquid radial distribution function becomes very similar to that of simple liquids. At these extreme conditions the thermal conductivity does not feature an anomalous behavior, and decreases with temperature as observed in a wide range of simple liquids. The dependence of the thermal conductivity with temperature and pressure follows experimental observations, and we find that it can be accurately predicted in terms of the liquid isothermal compressibility, by using a modified Leibfried–Schlömman equation. We also analyze whether the thermal conductivity follows the \sqrt{T} scaling behavior characteristic of hard sphere fluids, a behavior that has been suggested following the analysis of high pressure and high temperature experimental data. Upon close inspection we find clear deviations from this scaling behavior both in simulation and experimental data.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Water is no doubt the most important liquid on Earth. It has been extensively investigated both through experiments and computer simulations. The polar character of the liquid and the three dimensional hydrogen bond network structure confer water unique properties, either as a medium that efficiently screens ionic interactions, or by promoting hydrophobic interactions. The explanation of the latter has motivated a considerable amount of studies [1–7]. Moreover, water is an anomalous liquid, featuring a wide range of thermodynamic and dynamic anomalies, which have been well characterized experimentally and theoretically [8]. The desire to find a sound microscopic explanation to these anomalies has motivated a huge amount of theoretical and simulation work. Different interpretations have been put forward to explain the water anomalies. One of these assumes that the anomalies follow from the neighborhood of the thermodynamic states to a hypothesized critical point [9], whereas in other interpretations it has been suggested that they are the result of a competition between two distinctive structures featuring different degree of short range order [10].

Liquid water also features important dynamic anomalies, such as the maximum in the diffusion coefficient. Recent work has suggested

that the anomalous diffusion region is linked to the structurally anomalous region of the phase diagram, which is characterized by a decrease of order upon compression [11], unlike what happens in more simple liquids. Transport properties such as the thermal conductivity do also feature an anomalous behavior. The thermal conductivity increases with temperature and reaches a maximum at temperatures of the order of 400 K at the saturation pressure. Although this dynamic behavior must be connected to the peculiar hydrogen bond structure of water, there is not as yet a full microscopic theory that explains the dependence of the thermal conductivity of the liquid with temperature and pressure. Such microscopic understanding is desirable, as water features the highest thermal conductivity of any molecular liquid, a property that is important in heat management applications.

In order to advance the understanding of the thermal transport mechanism of water, we investigate in this work its properties at extreme conditions, 1–50 kbar and 300–600 K. Such conditions are relevant to explain physicochemical processes in the interior of the Earth, to understand the behavior of (heavy)-water in atomic plants, where it is used as coolant and moderator, or to construct models to explain the dynamics of planetary interiors [12]. Extreme pressures can also be generated in experiments with femtosecond laser pulses [13,14], and experimental set ups employed in ophthalmic laser applications [15]. The study of water at these extreme conditions provides a route to indirectly analyze the relevance of hydrogen bonding on heat transport, as the hydrogen bonding structure of liquid water is expected to be severely disrupted at extreme pressures. Indeed, several

* Corresponding author at: Chemical Physics Section, Department of Chemistry, Imperial College London, SW7 2AZ, London, UK.

E-mail address: fbresme@imperial.ac.uk (F. Bresme).

experimental studies have shown that these high pressures have a considerable impact on the structure of water [16,17]. X-ray and neutron scattering analysis show that the water structure is distorted, although it has also been suggested in some works that the degree of deformation of the hydrogen bond network might be small [17]. At high pressures excluded volume effects become significant. The characteristic double peak in the structure factor, indicative of the open network structure disappears at ~52 kbar at 800 K [16], and the structure becomes remarkably similar to that of simple liquids [18]. Similar conclusions have been reported on the basis of *ab initio* simulations of water using density functional theory [19]. Current density functional theories are inaccurate and fail to reproduce structural and dynamic properties of water [20], hence this agreement at extreme conditions is encouraging.

The impact of pressure on the thermal conductivity was also addressed in early investigations by Lawson et al. [21]. It was suggested that the increase in thermal conductivity with temperature could be connected to the transport of energy of diffusing molecular groups, in particular H^+ and OH^- . However, recent computer simulation studies have shown that the anomalous increase of the thermal conductivity with temperature can be reproduced using water models [22–24] that do not allow dissociation. These models accurately reproduce the hydrogen bonding network, and hence highlight the relevance of this structure in determining the anomalous behavior mentioned above. More recent experiments have employed the diamond-anvil cell to extend the measurements to much higher pressures, ~35 kbar, and temperatures, 673 K. [25]. In that work it was suggested that the thermal diffusivities and thermal conductivities scale with the square root of the temperature at higher temperatures, whereas the scaling is not fulfilled at ambient conditions. This observation suggests that the transport mechanism for high temperature/pressure is different from that operating at near ambient conditions. We will re-examine in this paper this scaling behavior using both simulation and experimental data.

In this paper we investigate the heat conduction of water at high pressures using non equilibrium molecular dynamics simulations in combination with the most accurate empirical non polarizable/rigid model of water, the TIP4P/2005 [26]. This model has been extensively investigated, including the phase diagram in the high pressure region [27], which is of particular interest to us. It was shown that the TIP4P/2005 model features a plastic phase at very high pressures, 80 kbar, in agreement with the observations reported by Takii et al. using the TIP4P and TIP5P models [28]. For the non equilibrium simulations we have employed boundary driven molecular dynamic simulations. This is a well established method that has been successfully employed to investigate a wide range of fluids, simple, polar, non polar and ionic fluids [22,23,29–33]. The thermal conductivity of water has been computed before using empirical rigid and flexible models [22,23,34–37], although most of these studies have focused on specific thermodynamic states near the standard pressure and temperature ~300 K. Very recently we have performed an extensive investigation of the thermal conductivity of water at subcritical and supercritical conditions. We find that the TIP4P/2005 model successfully reproduces the anomalous increase of the thermal conductivity with temperature as well as the thermal conductivity maximum [24]. To the best of our knowledge, there are no previous simulation studies aimed to quantify the thermal transport of water in the 10's of kbar pressure range. We attempt this study in the present paper.

The article is structured as follows. We first describe the non equilibrium simulation method and justify the rigid models employed in this work. A discussion of the main results, water structure, thermal conductivities, including the analysis of the dependence of the thermal conductivity with pressure and temperature follows. We also propose an equation that connects the thermal conductivity to the isothermal compressibility of water. The main conclusion and final comments close the paper.

2. Computer simulation details

All the simulations were performed using the TIP4P/2005 model introduced by Abascal and Vega [26,38]. In a recent review by these authors the performance of a wide range of empirical models was critically discussed [39]. The main conclusion from this analysis is that the TIP4P/2005 model is the most accurate empirical rigid/non-polarizable model available. The extensive investigation reported for this model [27], including the high pressure region of the phase diagram, makes it an ideal starting point for our investigation. Previous experimental studies on ice at very high pressures, ~20 GPa have shown that the OH bond length does not change significantly with pressure [28]. Recent experiments of water covering pressures in the GPa range have also reported good agreement between the experimental pair correlation functions and the corresponding function obtained using the SPC/E model [16]. Similarly *ab initio* density functional computations of water, again in the GPa range and 600 K, did not show appreciable dissociation nor significant changes in the O–H intramolecular distance [19]. Hence the use of a rigid model seems justified as a first approximation to investigate the thermal conductivity at extreme pressures.

In this paper we report equilibrium and non equilibrium simulation of the TIP4P/2005 model. The equilibrium simulations were performed in the *NPT* ensemble, in order to obtain the equation of state and structural properties for specific thermodynamic states. A typical simulation consisted of 500 molecules and 2 ns equilibration and a further 2 ns were employed to obtain ensemble averages. The trajectories were generated by using the leap-frog algorithm with a time step of 2 fs. A cutoff of 1 nm, was employed to truncate the dispersion interactions. No long range dispersive corrections were included in the computations. The coulombic interaction were computed in full with the Particle-Mesh [40] (PME) variant of the Ewald method. All the molecules were kept rigid by using the SETTLE algorithm [41].

The non equilibrium simulations were performed using prismatic boxes with cell dimensions, $\{L_x, L_y, L_z\}/L_x = \{1, 1, 3\}$, with $2.0 < L_x < 2.4$ nm, which were constructed by replicating a pre-equilibrated cubic box of water at the desired pressure and temperature. The non equilibrium simulations were performed using boundary driven non equilibrium molecular dynamics [29,30]. Hot and cold thermostats were defined at the edges and in the middle of the simulations, hence rendering a box that is fully periodic. The thickness of the thermostatting layers was between 0.09 and 0.16 nm. Following our previous work [24], for the initial configuration we select those molecules in the hot and cold regions, and the position of the oxygen atoms is restrained with a harmonic potential, with a force constant of $1 \text{ MJ mol}^{-1} \text{ nm}^{-2}$. Hence the molecules are free to rotate but they remain in the hot and cold regions for the whole duration of the simulation. These “hot” and “cold” molecules are thermostatted using the velocity re-scale algorithm [42] at the desired temperatures. This algorithm samples the canonical ensemble by rescaling the velocities using an appropriate scaling factor. We have chosen for this study $\tau = 0$ as coupling constant. The rest of the molecules, *i.e.*, those that are not restrained in the thermostat regions, are not coupled to a thermostat and follow Newtonian dynamics. These “free” molecules can exchange momentum with the “hot” and “cold” ones and in this way a temperature gradient and heat flux is set along the simulation box. Fig. 1 shows the temperature probability distributions for the “hot”, “cold” and “free” molecules. The probability distribution conforms to a Gaussian distribution, whose width is larger for the thermostatted molecules, as the number of molecules, 40, is much less than for “free” molecules, 4239. Similarly, as expected the width of the distribution for the thermostatted molecules at higher average temperature (550 K) is larger than for the lower temperature, a result that follows again from the dependence of the fluctuations of the temperature in the canonical ensemble. For the system analyzed in Fig. 1 the temperature fluctuations of the free molecules also conform to a Gaussian distribution, and again the

Download English Version:

<https://daneshyari.com/en/article/5411867>

Download Persian Version:

<https://daneshyari.com/article/5411867>

[Daneshyari.com](https://daneshyari.com)