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Thermal Conductivity of Ordered Molecular Water

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Abstract

We use molecular dynamics simulation to investigate thermal transport characteristics of water with various degree of orientational and translational order induced by the application of an electric field. We observe that orientational ordering of the water dipole moments has a minor effect on the thermal conductivity. However, electric-field induced crystallization and associated translational order results in approximately a 3-fold increase of thermal conductivity with respect to the base water, i.e., to values comparable with those characterizing ice crystal structures.

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Introduction

Water and ice are important materials for biological functions.[1] In many instances preserving biological viability of cellular materials over long times requires freezing. [2,3] In this context, understanding of thermal transport properties of water with various structures is critical for fundamentally understanding the cooling process. Apart from biological applications, the thermal transport properties of water are particularly important in light of the universality of water as a coolant.

There are a number of molecular-level studies of thermal transport in water. [4,5,6] These studies elucidated details of the mechanism of heat flow in water using both equilibrium and non-equilibrium simulation methods. Furthermore, for a number of empirical models describing interactions between water molecules, the calculated thermal conductivity, λ , is in very good agreement with the experimental value of 0.61 W/m-K (1atm, 300 K).[7] Molecular dynamics (MD) simulations have also proven useful in the determination of interfacial transport properties of water - organic liquid interfaces characterized by different degrees of hydrophobicity. [8]. However, we are not aware of any molecular simulations addressing the role of structural order on water thermal conductivity, as well as determination of ice thermal conductivity, which, at room temperature, is about four times larger than water thermal conductivity.

In this paper we use non-equilibrium molecular dynamics (NEMD) to study the relationship between thermal conductivity of water and the degree and type of structural order induced by the application of an electric field. In the next section we describe our models, structure preparation, and the method for determining thermal conductivity. The

third section presents the results including thermal transport and structural characterization. We end with the summary and conclusions section.

2. Model Structures and Simulation Methods

To determine thermal conductivity we use the so-called direct method where a planar heat source and sink are applied. [9] The sink and source planar regions are located at the center and at the edge of the rectangular periodic simulation box, as shown in Fig. 1. Atomic velocities were scaled up (down) in the heat source (sink) regions so that heat was added at a constant rate of $dQ/dt = 4.3 \times 10^{-4}$ eV/fs to the source and removed at the same rate from the sink. The molecules in the rest of the system evolved according to Newton's equations of motion with no coupling to any external thermostat. With this setup the total energy of the system is conserved. We monitored the temperature profile along the z direction by calculating and time averaging the total kinetic energy of the water molecules in a given 1.0 Å thick slab.

Prior to the application of the heat source and sink, all structures are heated to 600 K, cooled down to 300K and equilibrated with constant pressure (1 atm) and temperature for 200,000 MD steps (of 10^{-15} s). Then the *global* thermostat is turned off and the application of *local* heat source and sink leads to a steady state temperature profile. After about 100,000 MD steps a steady state temperature profile is established and we collect the average temperature profiles over about 300,000 MD steps. An example of such an obtained temperature profile is shown in Fig. 1 (top panel). The profile is piece-wise linear allowing us to obtain thermal conductivity, λ , using Fourier's law, $j_Q = -\lambda \partial T / \partial z$,

where $j_Q = (dQ/dt)/2A$ is the heat flux, with A being the cross-sectional area (the factor of 2 accounts for heat flow in both positive and negative z -directions in periodic systems).

A Simple Point Charge (SPC) [10] flexible water molecule is used for all simulations. A time step of 1 fs is used in all simulations which is sufficient to resolve the higher vibration modes of the flexible model and provide sufficient level of energy conservation over the entire production phase of the simulation runs.

Simulation cell cross section (x-y dimensions) size was 3x3nm, while the length of the simulation cell (in the z direction) was varied up to 50 nm, to evaluate possible finite size effects associated with proximity of the heat source and sink. [11] The finite size effects were most pronounced for crystalline structures, since the mean free path of heat carrying thermal waves (phonons) is larger than in liquid water structures. In these simulations cells of sizes 30 nm and larger exhibited size-converged results. For structures with no crystalline order sizes of 15 to 20 nm were already providing satisfactory results.

A uniform electric field was applied in the length (z direction) of the simulation cell to induce ordering through interaction of the electric field with the water dipole moments. We used electric field strengths ranging from 0 to 7 V/nm. The highest fields lead to structures with both orientational and translational order, as described in the next section, and consistent with prior studies on the effect of electric field on water structure. [12, 13]

3. Results

The calculated thermal conductivities as a function of the electric field strength are shown in Fig. 2. The solid curve corresponds to the case in which electric field strength was increased and applied to molecular structures previously equilibrated at the lower value of the field. At zero field the thermal conductivity is 0.70W/m-K, which compares well with the experimental value. At lower field strengths the application of the electric field has a minor effect on λ . However, beyond of 5.0 V/nm fields (which are very large by experimental standards), there is a very significant increase of thermal conductivity.

In order to understand this behavior of λ as a function of the electric field strength, we calculated the oxygen-oxygen (O-O) radial distribution functions (RDF) for the structures at each of the field strengths; 0, 3, 5, and 7 V/nm, as shown in Fig. 3. The RDFs at zero and 3 V/nm fields are similar, and characteristic of the liquid water. At 5 V/nm the RDF becomes modulated indicating the onset of crystallization [13]; however, a dramatic increase in number and sharpness of features is apparent in the RDF corresponding to the 7 V/nm field. In fact, a snapshot of the 7 V/nm field structure (Fig. 4) shows the presence of evident crystalline order.

Figure 2 also shows the thermal conductivity for structures that were obtained by step-wise decreasing of the field strength from the 7 V/nm value. The thermal conductivity for these structures remains high, well above that characterizing water. Only at zero electric field does the thermal conductivity return to the original value. The fact that the thermal conductivity is high upon decreasing of the electric field is due to translational order present in corresponding structures. As shown in Fig. 3, the RDF of the 2 V/nm structure has signatures of crystalline order, unlike that characterizing liquid

water. Upon returning to the zero field value, the crystalline order is lost and the conductivity returns to the original value. The hysteresis observed in Fig. 2 is likely due to small system size and relatively short time scales amenable to MD simulations, which suppress transitions to equilibrium structures at given field values.

To analyze the role of orientational order on thermal conductivity, we monitored the mean dipole moment of the simulation box (per water molecule), normalized to the dipole moment of a water molecule (2.273 Debye). Figure 5 illustrates the change in dipole moment with increasing and decreasing electric field strength. The orientational order increases very rapidly with the electric field, well before the crystallization [13] and is almost the same for increasing and decreasing field strengths. This compared against the data in Fig. 2 demonstrates that orientational order has very little effect on thermal conductivity, and it is the translation order that matters.

We also determined thermal conductivity of the perfect crystal ice Ic structure prepared by periodic repetition of the cubic unit cell structure [14,15]. The thermal conductivity of the model ice Ic structure is 2.24 W/m-K which is close to the experimental value of 2.4 W/m-K for hexagonal ice, and is about 20% larger than thermal conductivity of the ordered structure prepared with 7 V/nm electric field. To understand the structural origin for this difference, we show in Fig. 6 the O-O RDF for ice Ic structure. Comparison of Fig. 6 to the 7 V/nm case in Fig. 3 shows clearly that the ice Ic structure is more and longer range ordered. In fact, a detailed analysis of the 7 V/nm structure reveals a number of structural defects, such as grain boundaries. These defects provide additional scattering sites to the thermal mechanism of phonon scattering which lowers the phonon mean free path and thus thermal conductivity. It is also possible that

the high external electric field might scatter phonons, or affect the phonon spectra in a way detrimental to thermal transport.

4. Summary and Conclusions

Non-equilibrium MD simulations has been used to predict the effect of translational and orientational ordering on thermal conductivity in water. Translational order has been shown to have a significant effect on thermal conductivity. By contrast orientational order plays a minor effect in determining the rate of heat flow through water structures.

The results of our studies might be relevant to the on-going discussion about the origins of large thermal conductivity enhancements exhibited by nanofluids, i.e., fluid suspensions of nanosized solid particles. [16] A few investigators [17, 18] have proposed that the enhancement is due to the ordered layer of liquid molecules near the solid particle. Our study suggests that significant enhancement is possible only in the presence of crystalline order. Such order is unlikely to be induced by charged nanoparticle surfaces, as the electric fields required to achieve crystallinity at room temperature are very high.

Figure 1: Top panel: A snapshot of atomic positions of the model structure comprised of 27036 water molecules. Bottom panel: Temperature profiles obtained from the heat source-sink simulations. The slope of the temperature profile allows determining thermal conductivity. The arrows indicate positions of the 5 Å wide heat source and sink.

Figure 2: Thermal conductivity as a function of electric field strength. Solid squares; values for increasing field strength; Open squares; decreasing field strength.

Figure 3: Oxygen-Oxygen Radial Distribution Functions, $g(r)$, for different electric field strength. Results for 3 V/nm, 5 V/nm and, 7 V/nm are for structures obtained by step wise increasing of the electric field from the zero value. Data for 2 V/nm structure correspond to decreasing electric field. Note that for display purposes each curve's y-axis has been progressively shifted by 5 units starting with the 2nd curve from the bottom.

Figure 4: Portion of simulation cell after application of 7V/nm electric field showing crystalline arrangement of water molecules.

Figure 5: Mean dipole moments for simulation box of water molecules for various applied electric field strengths. Solid squares – increasing field, open squares – decreasing field.

Figure 6: Oxygen-oxygen radial distribution function for ice I-c structure at room temperature.

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