プロパンベースアルコールの熱伝導率に及ぼす水酸基の影響：
分子動力学シミュレーションによる検討

Investigation into influence of hydroxyl group placement on the thermal conductivity of propane-base alcohols using molecular dynamics simulation

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Alcohols play an important role in coolants and other applications in industry, and a detailed understanding of the mechanisms of their thermal conductivity would be useful in the design of new liquids. In this study, the influence on thermal conductivity of the placement and number of hydroxyl groups situated on a 3-carbon (propane) chain is investigated using equilibrium molecular dynamics simulation. The study shows that short-range pairwise interaction plays a significant role in thermal conduction. This pairwise interaction is shown to be dominated by the presence of the hydroxyl groups. While increasing the number of groups is shown to increase their influence on the pairwise thermal conductivity, the choice of location of two groups on the carbon chain is not observed to change their importance for pairwise thermal conductivity.

Key Words: Thermal Conductivity, Molecular Dynamics Simulation, Alcohol, Green-Kubo Method

1. Introduction

Molecular simulation provides useful insight into the details of thermal transport, and much focus has recently been on alcohols. For example, Matsubara et. al. [1] recently demonstrated that hydroxyl groups play an important role in providing heat paths for heat flux. It has also been shown that such groups may hinder thermal conductivity due to formation of unfavourable conformations [2]. Thus the structure of the alcohol and corresponding placement of hydroxyl groups has a significant influence on the resulting thermal conductivity, however the effect of the quantity and placement on the carbon chain is still unclear. In this work we consider placement of hydroxyl groups on a propane molecule and investigate the influence of quantity and position on the thermal conductivity.

2. Method

In order to gain a molecular perspective of thermal conductivity, molecular dynamics simulations are employed. The OPLS-AA [3] model is used to model the alcohols. The length of bonds featuring one hydrogen atom were frozen using SHAKE [4], as were angles involving two hydrogen atoms. Other motion internal to the alcohols (other bonds, other angles and dihedral motion) is allowed to vibrate freely, albeit under a reduced time-step compared to the rest of the simulation, using the Respa algorithm [5]. Thus while the simulation itself is conducted with a time-step of 2 fs, the aforementioned internal alcohol forces are computed with a time-step of 0.2 fs, which was found sufficient to realise atomic motion without aliasing of vibration frequencies. Following initial random placement of the molecules, each simulation was initially given 150 ps to equilibrate under constant temperature (300 K) and pressure (1 atm) conditions, and then calculation of thermal conductivity occurred over a period of 2 ns with fixed volume. For each simulation, the number of molecules were added based on the density of each liquid in a cubic simulation box size of around 40 Å. Molecular dynamics simulations were conducted using LAMMPS [6] while in-house software was utilised for post-processing.

The Green-Kubo relations [7,8] are used to calculate the thermal conductivity. The advantage of employing this method is that it gives ready access to the nanoscopic details of conduction. The Green-Kubo equation is based upon linear response theory and uses the time-correlation of heat flux to calculate total thermal conductivity (Eq. 1 and 2).

$$\kappa = \frac{V}{3k_B T^2} \int_0^\infty \langle J(t).J(0) \rangle \; dt \tag{1}$$

$$J(t) = J_{diffusive} + J_{virial} \tag{2}$$

The virial term is made up of a linear combination of mode contributions (Eq. 3) and the pair-interaction term (J_{pair} in Eq. 3) can further be broken down into contributions from every pair interaction (eg, the flux of oxygen atoms due to interaction with carbon atoms, J_{OC}, and so on) (Eq. 4), permitting a detailed insight into the terms leading to the calculation of the flux (Eq. 2).

$$J_{virial} = J_{pair} + J_{dihedral} + J_{bond} + J_{angle} + ... \tag{3}$$

$$J_{pair} = J_{OO} + J_{OH} + J_{CC} + J_{CO} + J_{CH} + ... \tag{4}$$
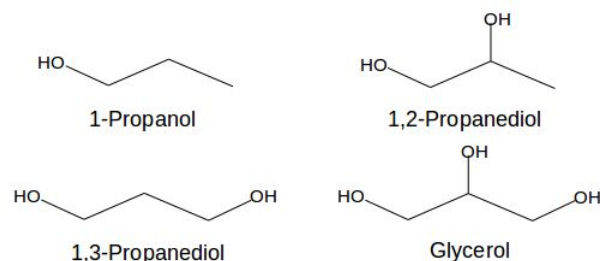

Fig. 1 Representative images of the molecules used in this study.

Four alcohol molecules are chosen as the basis for this study. All molecules are similar in that they have three carbon atoms as a base chain, but differ distinctly in the arrangement of the hydroxyl groups connected to the base carbon chain (Fig. 1). The four molecules were chosen to give variation to the number of hydroxyl groups and their placement within the alcohol.

3. Results and analysis

The Green Kubo method (Eq. 1) is applied to the heat flux components (Eq. 2) to compute the thermal conductivity. We observe that the autocorrelation of the virial term $\langle J_{virial}(0) \bullet J_{virial}(t) \rangle$ contributes significantly more to the total thermal conductivity than the other terms. It is then of interest to understand the most significant mode of interaction contributing to the autocorrelation of the virial term, in order to elucidate the primary mechanism of heat transfer in the liquid (Eq. 3). Analysis shows that the pairwise component accounts for a significant part of the thermal conductivity (Fig. 2).

Given the importance of pair-interaction in the overall thermal conductivity, it is interesting to further break down the contributions and consider the role of individual atomic pair interactions (Eq. 4). Given the 4 different atom types in each molecule, namely C, O, H-(O), H-(C), there are 16 combinations of different atomic pair interactions; the thermal conductivity of which has a total of 256 components (16 self-correlations, and the rest being cross-correlations). The contribution to the pairwise thermal conductivity of self-correlations and cross-correlations of pairwise interactions that involve oxygen and hydrogen; ie, hydroxyl groups with their surrounding atoms; are isolated (Fig. 3). A steady increase in thermal conductivity can be observed with increase in the number of hydroxyl groups, as well as a significant increase in the relative contribution to the overall pairwise contribution across 1-Propanol (61.5%), 1,3-Propanediol (83.2%), Propylene Glycol (84.6%) and Glycerol (93.6%).

Intuitively, we would expect hydroxyl groups to contribute less to 1,2-Propanediol than its isomer since the close proximity of hydroxyl groups is likely to result in intra-molecular hydrogen-bonding [2] and thus hinder inter-molecular bonding and heat transfer between molecules. As a next step, it would be interesting to isolate inter-molecular and intra-molecular hydrogen-bonding contributions to examine this further.

4. Conclusion

Equilibrium MD simulations have been performed in order to investigate the influence of positioning and numbers of hydroxyl groups on the thermal conductivity of propane-based alcohols. Our results demonstrate that the pairwise component is a major mode of thermal conduction. Further breakdown established the predominance of hydroxyl group interactions enabling us to consider this as a favourable control factor for controlling thermal conductivity. Counter-intuitively, arrangement in the case of two hydroxyl groups was found not to alter their importance in pairwise thermal conductivity. Further detailed study of inter and intra-molecular hydrogen-bonding would give valuable information on reasons for this and the possibilities to use the effect of hydroxyl group placement to tune the thermal conductivity of a molecule.
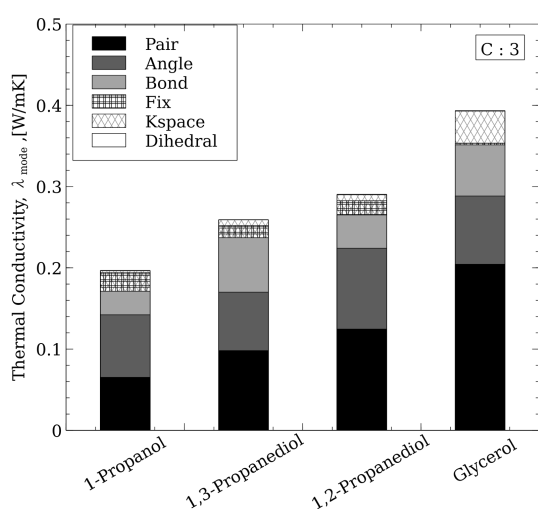

Fig. 2 Breakdown by molecule of virial contribution to different modes of interactions for propanol-based alcohols at 300 K. Here, pairwise interaction is seen to contribute significantly to the overall thermal conductivity in all the molecules.
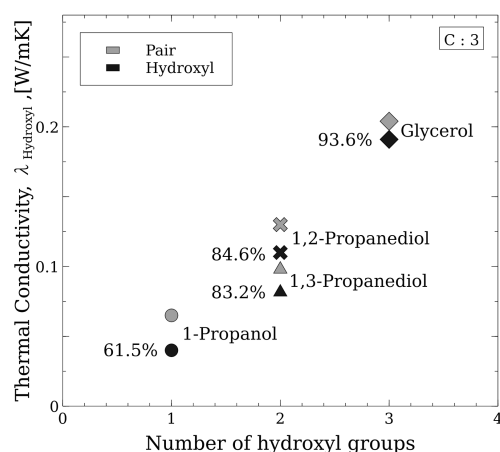

Fig. 3 Total pairwise component of thermal conductivity and the contributions from hydroxyl group interactions. A steady increase in pairwise thermal conductivity can be observed with increase in the number of hydroxyl groups, as well as significant increase in the contribution of hydroxyl groups to the overall pairwise contribution.

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