



Microscopic picture of heat conduction in liquid ethylene glycol by molecular dynamics simulation: Difference from the monohydric case

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ABSTRACT

The present study investigates the molecular-scale heat transfer in the liquid of ethylene glycol, which is widely used as heat transfer media. First, by combining existing molecular models, we developed a new united atom model of ethylene glycol, and showed that this model reasonably reproduces the experimental thermal conductivity. Using the non-equilibrium molecular dynamics simulations with this model, we characterized the heat transfers due to different kinds of inter- and intramolecular interactions on the basis of a picture that a single pair interaction is a path of heat transfer. These characteristics were compared with those of ethanol (Matsubara et al., 2017) to elucidate the molecular mechanism which realizes an enhanced thermal conductivity because of an additional hydroxylation on ethanol. The results indicate that the thermal conductivity enhancement occurs because the additional heat paths provided by the second hydroxyl group increases the amount of heat conduction owing to all of the van der Waals, Coulomb, and covalent interactions. In particular, the increase in the number of the paths associated with the intermolecular Coulomb interaction between the non-hydrogen bonding hydroxyl groups is prominent and consequently the Coulomb interaction, which is an efficient heat carrier, performs the largest amount of heat conduction in ethylene glycol. Although the second hydroxyl group also increases the number of hydrogen bonds, the direct heat transfer via the hydrogen bonds accounts for only a small portion of the total heat conduction. On the other hand, this augmentation of hydrogen bond, since it keeps a dense molecular packing against the increase in molecular volume, is indispensable in increasing the density of heat paths.

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1. Introduction

Ethylene glycol (EG), as well as its mixture with water, is a heat-transfer fluid particularly used as antifreeze because of high thermal conductivity and wide temperature range of liquid phase. Such liquid based on EG also is a base fluid to which nano-additives are added to make nanofluids of an enhanced thermal conductivity [1,2]. Insights into the molecular picture of heat conduction in the liquid state of EG lead to a deeper understanding of the properties of the EG-based heat-transfer fluids. The structures of liquid EG have been extensively studied by molecular simulations, and most of these studies focus on the development of the realistic molecular models for EG [3–10]. EG has approximately four hydrogen bonds per molecule and forms a three-dimensional network as water does [11,12]. As for the molecular conformation, a recent ab-initio molecular dynamics (MD) study suggested that an EG molecule in the liquid can take both trans and gauche forms and the

trans fraction at room temperature is ~20% [13]. The MD study of Lin et al. [14] investigated the effect of different conformations of EG molecule on the thermal conductivity, using various molecular models.

The molecular expression of the heat flux indicates that heat conduction in a molecular system is composed of two major modes of microscopic heat transfer [15,16]. One is the heat transfer associated with the transport of molecules, and the other is the heat transfer via the inter- and intramolecular interactions. In a liquid phase, the latter mode accounts for the most part of the total heat conduction. Therefore, in order to comprehensively understand the molecular mechanisms of heat conduction therein, it is a good start point to clarify the properties of heat transfer due to a specific interaction and its dependence on the structural and chemical characteristics of the constituent molecules. Using MD simulation, we have investigated how each type of interaction contributes to the heat conduction in typical liquids, including simple liquids [17] and their mixtures [18], linear and branched alkanes [19,20], and monohydric linear alcohols [21,22]. In recent studies [18,20–22], we introduced the atomistic heat path (AHP) analysis. In the

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AHP analysis, within the framework of non-equilibrium molecular dynamics (NEMD) simulation, a single pair interaction is considered as an atomistic path for heat transfer and then the heat transfer associated with a specific interaction is characterized by the path density and efficiency per path. Since the configuration of the paths is corresponding to the neighboring structures of molecules, the analysis allows us to connect the heat transfer characteristics with microscopic structures.

In the present study, we apply the AHP analysis to liquid EG. The results are compared with those of the same analysis in the previous study for ethanol [21], a monohydric alcohol having the same number of carbon atoms. The comparison is made for their saturated liquids at the same reduced temperature $T/T_c = 0.7$, where T_c is the critical temperature, so that the thermodynamic conditions for the two liquids are equivalent under the law of corresponding states. Thus, we aim to elucidate the molecular mechanisms of the efficient heat conduction in EG with a focus on the difference in the number of hydroxyl groups in molecule. In Section 2, we develop a new molecular model for EG by combining existing models so that the model is consistent with the one employed in our ethanol simulations. The validation of the model against the experimental data is also given there. Section 3 explains our NEMD simulation and AHP analysis. In Section 4, the results for the saturated liquid of EG at $T/T_c = 0.7$ are discussed in comparison with those of ethanol. Finally, Section 5 concludes the paper.

2. Molecular model and validation

Our new potential model for EG is mostly based on TraPPE-UA force field for glycols [3]. This model is a united-atom (UA) model, where the hydroxyl H and O atoms and a methylene group ($-\text{CH}_2-$) are considered as the interaction sites. The modification was made only in the bond stretching potential. That is, we adopted the same bond stretching potential as that of NERD force field for alcohols [4] whereas in TraPPE-UA, the bond length is not allowed to change. With this treatment, the representation of inter- and intramolecular interactions in the model is close to those in our previous simulation of monohydric alcohols [21]. Specifically, the present EG model differs only slightly from those of monohydric alcohols in the points that there is no van der Waals interactions between H atom and other atoms and that a repulsive interaction acts between the two OH groups in the same molecule as described below. This point is advantageous in making comparison between the results for different molecules. Furthermore, as we will see later, the introduction of bond stretching motions lead to a good reproduction of the experimental thermal conductivity at the standard state. Other existing molecular models for EG [5–10] were less preferred. Earlier models [6,9,10] are minor modifications of the OPLS-UA model [8] and the intramolecular motions are limited to the torsional ones only whereas recent models [5,7] include more complicated treatments than the present model. The explicit potential form of the present EG model is shown in Table 1. The intramolecular sites have the bond stretching, angle bending, and torsion interactions. The non-bonded interaction is expressed by the van der Waals (vdW) + Coulomb interactions, and is defined for the intermolecular site pair and the intramolecular site pair separated by three or more covalent bonds, but these interactions for the site pair separated by three bonds (i.e., 1–4 pairs) are scaled by 1/2. In addition, the intramolecular non-bonded O...H pair has a short-range repulsive interaction in order to avoid too strong association of two hydroxyl groups in a molecule [3].

MD simulations were performed to examine the present EG model by comparing the MD results with literature data. We employed our in-house MD program for all the MD simulations

Table 1

United-atom force field for ethylene glycol. The bond stretching potentials and their parameters were those of NERD [4]. All other potentials are those of TraPPE-UA [3,23]. Here, r_{ij} is the distance between atoms i and j , θ the bond angle, ϕ the dihedral angle, ϵ_0 the vacuum permittivity, and q_i the partial charge of atom i .

Bond stretching: $U_{\text{str}}(r_{ij}) = k_r(r_{ij} - r_{\text{eq}})^2/2$				
	k_r kJ/(mol·Å ²)	r_{eq} Å		
CH ₂ –CH ₂	2800	1.540		
CH ₂ –O	3300	1.428		
O–H	5200	0.961		
Angle bending: $U_{\text{ang}}(\theta) = k_\theta(\theta - \theta_{\text{eq}})^2/2$.				
	k_θ/k_B K	θ_{eq} degree		
CH ₂ –CH ₂ –O	50,400	109.47		
CH ₂ –O–H	55,400	108.5		
Torsion: $U_{\text{tor}}(\varphi) = c_0 + c_1(1 + \cos \varphi) + c_2(1 - \cos 2\varphi) + c_3(1 + \cos 3\varphi)$.				
	c_0/k_B K	c_1/k_B K	c_2/k_B K	c_3/k_B K
O–CH ₂ –CH ₂ –O	503.24	0	–251.62	1006.47
CH ₂ –CH ₂ –O–H	0.000	209.82	–29.17	187.93
Non-bonded: $U_{\text{nb}}(r_{ij}) = 4e_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] + q_i q_j / (4\pi\epsilon_0 r_{ij})$.				
For heterogeneous pair, $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ and $e_{ij} = \sqrt{e_{ii}e_{jj}}$.				
	e_{ii}/k_B K	σ_{ii} Å	q_i a.u.	
H	–	–	0.435	
O	93	3.02	–0.700	
CH ₂	46	3.95	0.265	

O...H Repulsive: $U_{\text{rep}}(r_{ij}) = a/r_{ij}^{12}$, $a/k_B = 7.5 \times 10^7$ KÅ¹², only for the intramolecular non-bonded O...H pair.

in the present study. First, we calculated the vapor–liquid coexistence curve for the present model by equilibrium MD simulations in a vapor–liquid coexistence system with a $60 \times 60 \times 180$ Å³ rectangular MD box containing 1792 molecules. The cutoff distance of 25 Å was used for the vdW interaction while the Coulomb interaction was evaluated with the smooth particle mesh Ewald (SPME) [24]. We obtained the liquid and vapor densities ρ_{liq} and ρ_{vap} , respectively, at five values of temperature T . The coexistence curve was determined by fit with the scaling law $\rho_{\text{liq}}(T) - \rho_{\text{vap}}(T) = A(T_c - T)^{0.32}$ and the law of rectilinear diameters $[\rho_{\text{liq}}(T) + \rho_{\text{vap}}(T)]/2 = \rho_c + B(T_c - T)$ [19,25], where A , B , the critical temperature T_c , and the critical density ρ_c are the fitting parameters. The vapor–liquid coexistence curve obtained by the present simulation is plotted in Fig. 1 in comparison with the results of TraPPE-UA. The results of the two models agree well, which indicates that the present model inherits the predictive performance of the vapor–liquid equilibria from TraPPE-UA. Thus, the present

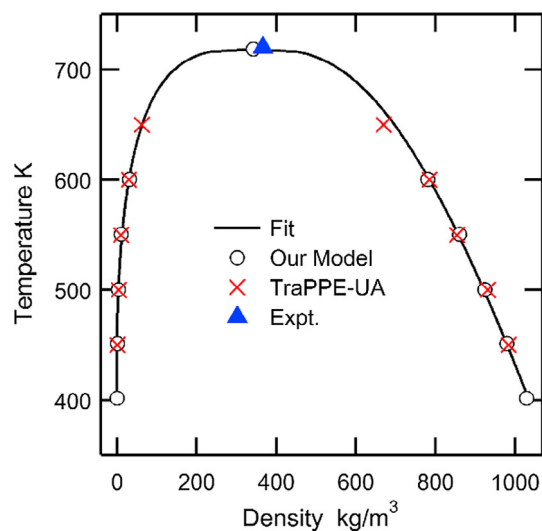


Fig. 1. Vapor–liquid coexistence curve obtained from the MD simulations with our model. The results of TraPPE-UA [3] and the experimental critical point [7] are also included.

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