Prediction of Thermal Conductivity of Liquid Methane/Ethane-Cu Nanofluids via Molecular Dynamics Simulations

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ABSTRACT

The improvement of thermal conductivity by suspending nanoparticles in two hydrocarbon-based nanofluids is investigated by means of molecular dynamics simulations. Base fluids are methane and ethane and nanoparticles are pure copper. Two temperatures for which the experimental values for the thermal conductivity of the pure fluid exist are chosen. The Green-Kubo relation is utilized to calculate the thermal conductivity of colliodal systems. The effect of mass fraction of nanoparticles is investigated for each nanofluid and at each temperature.

Keywords: nanofluid, thermal coductivity, molecular dynamics

1 INTRODUCTION

Due to the enhancement effect of nanoparticles suspended in a base fluid (the combination usually refered to as nanofluids) on thermal properties, investigations on nanofluids have been gaining pace experimentally, theoretically and numerically. Nanofluids have great potential for adoption as superior heat transfer fluids and energy storage applications utilizing phase change materials (PCM) [1]. Among the thermophysical properties of nanofluids, the thermal conductivity of most nanofluids is highly improved with respect to the thermal conductivity of the base fluids (e.g. [2]). Cosequently, computational tools such as molecular dynamics (MD) and Brownian dynamics simulations have been utilized to predict the change in the thermal conductivity by suspending nanoparticles in the base fluid. Bhattacharya et al. [3] utilized Brownian dynamics simulation and the Green-Kubo relation to predict the thermal conductivity of Aluminum oxide-ethylene glycol and Copper-ethylene glycol nanofluids. The calculated thermal conductivities were in agreement with experimental data. Keblinski et al. [4] suggested four possible major mechanisms for the observed enhancement of thermal conductivity. They showed that the effect of the Brownian motion does not adequately explain the observed enhancement. Nearly-identical heat current autocorrelation functions extracted from MD simulation for two cases with and without constraint center of mass verified the previous finding that the Brownian motion has a minor influence on thermal conductivity enhancement. Eapen et al. [5] investigated the thermal conduction enhancement of a model nanofluid containing platinum particles in xenon base fluid by MD simulations and the Green-Kubo method. Their results showed an increase of thermal conductivity upon increasing the concentration of nanoparticles. They indicated that the enhancement of thermal conductivity is mainly due to the strong inter-atomic interactions between fluid and the nanoparticle. Sarkar and Selvan [6] also performed MD simulations and used the Green-Kubo relation to obtain thermal conductivity and diffusion coefficient of the Ar-Cu nanofluid containing a single particle inside the base fluid. Their calculations also indicated enhancement of thermal conductivity due to increase of particle loading.

All MD simulations on thermal conductivity of nanofluids so far have been performed on model systems. In this paper, two more practical nanofluids containing hydrocarbons as base fluids, methane/ethane-copper nanofluids, will be investigated by performing MD simulations. The Green-Kubo relation is utilized to obtain the thermal conductivity of nanofluids from the outcome data of MD simulations. The effect of mass fraction of nanoparticles on the thermal conductivity of nanofluids will be investgated. For each nanofluid, two different temperatures is considered and the rate of enhancement of thermal conductivity for different temperatures are compared.

2 PROBLEM FORMULATION

2.1 Methodology

In this paper, MD simulations were performed for predicting thermal conductivity of liquid methane and ethane-Cu nanofluids. The Green-Kubo relation [7] which is an equilibrium method was used to obtain the thermal conductivity of nanofluids. The Green-Kubo relation reads as:

$$k = \frac{V}{3k_B T^2}\int_0^\infty < \mathbf{J}(t)\mathbf{J}(0) > dt. \quad (1)$$

In equation (1), k is the thermal conductivity, $< \mathbf{J}(t)\mathbf{J}(0) >$ is the heat flux autocorrelation function (HFACF) that is obtained from equilibrium molecular dynamics in time, V is the volume of the system of particles, k_B is the Boltzmann's constant and **J**(t) is the microscopic heat flux,

$$\mathbf{J}(t) = \frac{1}{V}\left[\sum_j \mathbf{v}_j E_j + \frac{1}{2}\sum_{i\neq j}\mathbf{r}_{ij}\left(\mathbf{v}_j.\mathbf{F}_{ij}\right)\right], \quad (2)$$

where $\mathbf{v}_j$ and E_j are the velocity and instantaneous excess energy of particle *j*, respectively and $\mathbf{r}_{ij}$ and $\mathbf{F}_{ij}$ are the displacement vector and interacting force between particles *i* and *j*, respectively.

The Lennard-Jones (LJ) potential was chosen for intermolecular interactions between all particles. The LJ parameters, σ and ε, for copper atoms are 2.3377 Å and 9.4512 kcal/mol, respectively [8]. For both methane and ethane molecules the OPLS united-atom force field was used [9]. In this force field, for methane, CH_4 is taken as a single interaction site for LJ interactions, whereas for ethane, CH_3 is taken as the single interaction site for LJ interactions and therefore each ethane molecule includes two sites of LJ interacions which are connected with a fix bond length of 1.53 **Å**. The force field parameters for methane and ethane molecules are given in Table 1. The Lorentz-Berthelot mixing rule [10] was used for obtaining the LJ parameters among the methane/ethane molecules and copper atoms,

$$\sigma_{CH_4/CH_3-Cu} = \frac{\sigma_{CH_4/CH_3} + \sigma_{Cu}}{2}, \quad (3)$$

and

$$\varepsilon_{CH_4/CH_3-Cu} = \left(\varepsilon_{CH_4/CH_3}\varepsilon_{Cu}\right)^{1/2}. \quad (4)$$

pseudoatom	σ (Å)	ε (kcal/mol)
CH_4	3.73	0.294
CH_3	3.775	0.207

Table 1 OPLS Lennard-Jones parameters [9] for methane and ethane.

2.2 Computational Details

The LAMMPS [11] software package was used for simulations. For the nanofluid with methane as the base fluid, first a box of 512 fcc unit cells ($8\times8\times8$ lattice constant) was made with a lattice constant of 6.35. Then, for each mass fraction, a sphere was carved at the center of simulation box and copper atoms were located on a 3.61 **Å** fcc lattice crystal inside the sphere. For nanofluids with ethane as the base fluid, PACKMOL software package [12] was used to generate the initial configurations of all particle postions. For each mass fraction, a box containing 1000 ethane molecules and a specific number of copper atoms for each case was created (for mass fraction of 14.3%, an instantaneous snapshot of the atoms is shown in Fig. 1). The periodic boundary condition was considered on all boundaries and the adopted integration time step was 1 fs. The cutoff value for pair-wise interactions was 10 **Å**. In order to equilibrate the system, simulations were initially run for 200,000 time steps under the NPT (isothermal-isobaric) condition. Then, for 1,200,000 time steps, systems were run under the NVE condition and calculations of heat current were performed for the last 1,000,000 time steps.

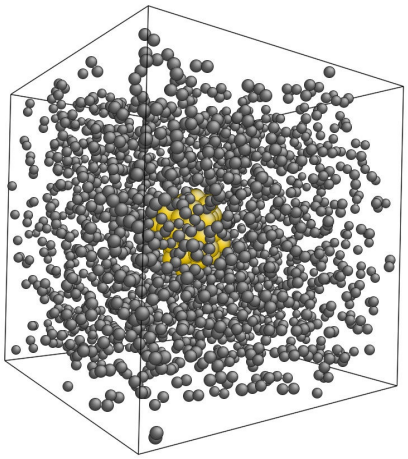

Figure 1: A sample of simulation box.

3 RESULTS AND DISCUSSION

Before presenting the nanofluid-related information and in order to validate the MD predictions, thermal

conductivities of pure methane and ethane are compared with the experimental data [13]. In Table 2, the predicted values for thermal conductivity of pure methane and ethane at T=100K and 110K and T=100K and 150K, respectively are given and compared with experimental values. Results indicate that for pure methane and ethane, the MD predictions are generally in good agreement with experimental values.

Fluid	T(K)	MD	Experiment [13]	Error(%)
Methane	100	0.199	0.208	-4.3
	110	0.181	0.191	-5.4
Ethane	100	0.296	0.248	+19.6
	150	0.221	0.202	+9.7

Table 2 Thermal conductivity (W/mK) of pure liquid methane and ethane.

Then the effect of mass fraction on thermal conductivity was investigated by increasing the particle size located at the center of simulation box in both mehane and ethane base fluid. For methane, for both applied temperatures on the system, simulations were performed for three mass fractions of 2.45%, 14.52% and 58.66%, which correspond to particle diameters of 6.35 $\dot{A}$, 12.70 $\dot{A}$ and 25.4 $\dot{A}$, respectively. Results of MD simulations are given in Table 3. For both temperatures, MD calculations show that by increasing the mass fraction of particles, the thermal conductivity of the colloidal system increases. Comparison of the predicted values of thermal conductivities between two temperatures indicates that the increase rate of thermal conductivity at the higher temperature is greater than the increase rate of thermal conductivity at the lower temperature. For both temperatures, for the highest value of concentration, thermal conductivity is markedly affected by the thermal conductivity of copper suspensions.

T(K)	Mass Fraction(%)	Particle Diameter ($\dot{A}$)	Thermal Conductivity
100	2.45	6.35	0.464
	14.52	12.70	0.601
	58.66	25.4	37.58
110	2.45	6.35	0.394
	14.52	12.70	2.67
	58.66	25.4	63.38

Table 3 Thermal conductivity of methane-Cu nanofluids for various mass fractions.

Finally, the effect of mass fraction was investigated on the thermal conductivity of ethane-copper nanofluid which contains a hydrocarbon with higher number of carbon atoms and consequently more complexities in simulations. For both temperatures, simulations were performed for three mass fractions of 2.7%, 14.3% and 53.98%, which correspond to particle diameters of 5.72 $\dot{A}$, 11.44 $\dot{A}$ and 22.88 $\dot{A}$, respectively (Table 4). Similar to what was observed previously for methane-copper nanofluids, for both temperatures, MD calculations indicate that by increasing the mass fraction of particles, the thermal conductivity of the colloidal system increases. Here, also, comparison of predicted values of thermal conductivities between two temperatures suggests that the increase rate of the thermal conductivity with mass fraction at the higher temperature is greater than the increase rate of thermal conductivity at the lower temperature. For both temperatures, for the highest value of concentration, thermal conductivity is markedly affected by the thermal conductivity of copper suspensions.

T(K)	Mass Fraction(%)	Particle Diameter ($\dot{A}$)	Thermal Conductivity
100	2.7	5.72	0.651
	14.3	11.44	4.37
	53.98	22.88	15.80
150	2.7	5.72	2.55
	14.3	11.44	6.52
	53.98	22.88	35.00

Table 4 Thermal conductivity of ethane-Cu nanofluids for various mass fractions.

4 CONCLUSIONS

In this paper, MD simulations in conjunction with Green-Kubo relation were utilized to predict the thermal conductivity of two hydrocarbon nanofluids: methane-copper and ethane-copper. The OPLS united-atom force field was chosen for the interaction potential between hydrocarbon's molecules. For each nanofluid, simulations were run at two temperatures for which the experimental value of thermal conductivity for pure fluids exist. The effect of mass fraction was investigated by changing the size of the single copper particle at the center of a box of hydrocarbon molecules. Results of MD simulations showed that the thermal conductivity increases by increasing the mass fraction and particularly for a very big value of mass fraction the thermal coductivity of susupension is highly affected by the thermal conductivity of particles. The rate of increase of thermal conductivity with mass fraction was higher at the higher temperature for both hydrocarbon nanofluids.

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