Molecular Dynamics Simulation of the Effect of the Solid Gas Interface Nanolayer on Enhanced Thermal Conductivity of Copper-CO2 Nanofluid

Zeeshan Ahmed, Ajinkya Sarode, Pratik Basarkar, Atul Bhargav, Debjyoti Banerjee

Abstract—The use of CO_2 in oil recovery and in CO_2 capture and storage is gaining traction in recent years. These applications involve heat transfer between CO_2 and the base fluid, and hence, there arises a need to improve the thermal conductivity of CO_2 to increase the process efficiency and reduce cost. One way to improve the thermal conductivity is through nanoparticle addition in the base fluid. The nanofluid model in this study consisted of copper (Cu) nanoparticles in varying concentrations with CO_2 as a base fluid. No experimental data are available on thermal conductivity of CO_2 based nanofluid. Molecular dynamics (MD) simulations are an increasingly adopted tool to perform preliminary assessments of nanoparticle (NP) fluid interactions. In this study, the effect of the formation of a nanolayer (or molecular layering) at the gas-solid interface on thermal conductivity is investigated using equilibrium MD simulations by varying NP diameter and keeping the volume fraction (1.413%) of nanofluid constant to check the diameter effect of NP on the nanolayer and thermal conductivity. A dense semi-solid fluid layer was seen to be formed at the NP-gas interface, and the thickness increases with increase in particle diameter, which also moves with the NP Brownian motion. Density distribution has been done to see the effect of nanolayer, and its thickness around the NP. These findings are extremely beneficial, especially to industries employed in oil recovery as increased thermal conductivity of CO_2 will lead to enhanced oil recovery and thermal energy storage.

Keywords—Copper-CO_2 nanofluid, molecular interfacial layer, thermal conductivity, molecular dynamic simulation.

I. INTRODUCTION

GLOBAL warming caused by the CO_2 emission from various sources has been a serious concern these days. CO_2 has a significant percussion on the climate and is therefore extensively studied. Lots of efforts are being made to reduce carbon dioxide emission to the atmosphere different techniques such as capture and sequestration. [1], [2]. CO_2 capture and geological storage are considered to be feasible options to pacify and reduce the greenhouse gas emissions during the transition phase towards the use of renewable energy. So, the prognostication of thermal conductivity of CO_2 is considered to be prime relevance in the process of capture, transport, and injection of CO_2.

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Nanofluids defined as fluids with suspensions of NPs which are potential heat transfer fluids even at very low concentrations have exhibit an exceptional increase in thermal conductivities when compared to the base fluids. For example, thermal conductivities of Al_2O_3-water nanofluid were increased 10% [3] and 30% [4] with diameters of 13 nm and 40 nm at the same particle volume fraction of 4.3%, respectively, and up to 40% increase if the Cu particles of 10 nm at much lower concentration as 0.3% were dispersed in water [5]. More arousing results were detected in suspension of CNTs, which is up to 150% thermal conductivity enhancement in suspension of 1.0 vol.% multiwalled CNTs in oil [6]. Till the present date, numerous studies have been done on determining the thermal conductivity of nanofluids. Furthermore, Jang and Choi [7] proposed four mechanism of energy transport in nanofluids: 1) base fluid molecules interactions, 2) thermal diffusion of NPs in base fluid, 3) Brownian motion of NPs, and 4) thermal interactions of NPs with base fluid molecules. Ren et al. [8] proposed a collateral model describing the heat transfer mechanism in nanofluid by adding nanolayer effect on thermal conductivity. The NP motions enhance the overall heat transport by micro-convection in the suspended fluid. Prasher et al. [9] captured the aggregation effect in addition to Brownian induced convection for the enhancement. Such behavior and physical phenomenon make nanofluids very attractive to be used to enhance the heat transfer properties. Lee et al. [10] studied the effect of particle size on Cu-liquid argon based nanofluid with different volume fraction and found out that there is reduction in thermal conductivity enhancement with decrease in NP diameter.

To the best of author's knowledge, thermal conductivity of nanofluid in gas phase is not reported in open literature so far. In this work, an MD simulation was performed to study the effect of nanolayer on the enhancement of thermal conductivity of novel Cu-CO_2 nanofluids. The volume fraction was kept constant at 1.413% and diameter of NP taken are 1 nm, 2 nm, and 3 nm to see the diameter effect on the thermal conductivity of the nanofluid. Visual MD (VMD) has been used to see whether the above mentioned physical phenomenon exists in the gaseous phase. This study confirms the presence of nanolayer in gaseous phase and hence is the cause of enhanced thermal conductivity which may have potential to enhance oil recovery and thermal energy storage.

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II. SIMULATION SETUP AND METHODOLOGY

In the present work, gaseous CO_2 with a suspension of Cu NP is modeled. The CO_2 molecule was represented by the conventional EPM2 model [11]. The LJ potential [12], [13] was used for interatomic interaction between different atoms, which is given by:

$$\varphi(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad (1)$$

where φ is the LJ potential, r_{ij} is the distance between atoms i and j, ε_{ij} is the interaction strength, and σ_{ij} is an interatomic length scale between atoms i and j. The cutoff radius of~ 4 σ_{O-O} is chosen as thermal conductivity is almost independent after this distance. For EPM2 CO_2, the LJ potential parameters are shown in Table I.

TABLE I
LJ PARAMETERS USED FOR CARBON-CARBON AND OXYGEN-OXYGEN INTERACTION

S.No	σ_{O-O}	ε_{O-O}	σ_{C-C}	ε_{C-C}
1	3.03 Å	80.507 K	2.757 Å	28.13 K

The Lorentz Berthelot mixing rule [12] was used to compute the interaction between different types of atoms i and j, which is given by:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (2)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \times \varepsilon_j} \quad (3)$$

For interactions between Cu atoms, EAM potential was used [14]. In EAM potential, the potential energy of an atom, i, is given by:

$$E_i = F_\alpha\left(\sum_{i \neq j} \rho_\beta(r_{ij})\right) + \frac{1}{2}\sum_{i \neq j} U_{\alpha\beta}(r_{ij}) \quad (4)$$

where r_{ij} is the distance between atoms i and j, $U_{\alpha\beta}$ is a pair-wise potential function, ρ_β is the contribution to the electron charge density from atom j of type β at the location of atom i, and F is an embedding function that represents the energy required to place atom i of type α into the electron cloud.

MD simulations were performed in the canonical ensemble (NVT) using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD package [15] and visualized by Visual Molecular Dynamic (VMD) [16]. Thermal conductivity of CO_2 gas was determined through Green-Kubo formalism and compared with the available

experimental data which gave validation error of 2.8%. The Nose–Hoover thermostat was used for maintaining the constant temperature conditions. Spherical region was carved out by inserting Cu NP in three different configurations. Fig. 1 shows the simulation box of 2 nm NP with 755 molecules and the other configurations are shown in Table II.

TABLE II
DETAILS OF OTHER CONFIGURATIONS USED TO PERFORM THE SIMULATIONS

S.No	NP diameter	Box dimension	Number of molecules	Volume Fraction
1	1 nm	33.33 Å	100	1.413%
2	2 nm	66.66 Å	755	1.413%
3	3 nm	100 Å	2510	1.413%

The simulation domain size was varied so that all the configurations have the constant bulk density of gaseous CO_2 (186 kg/m^3) and constant volume fraction of 1.413%. Sufficient time steps were performed for the equilibration process to achieve equilibrium state, which was under canonical ensemble (NVT), where total number of atoms (N), system volume (V), and temperature (T) were constant for each of three different simulation systems. The temperature was fixed at 300 K. Then, fluctuation of autocorrelations was performed under the micro-canonical ensemble (NVE) where total number of atoms (N), system volume (V), and energy (E) were constant for data computation to get the correct thermal conductivities for each nanofluid system. Periodic boundary condition was applied in all three directions, and the electrostatic interactions were calculated using the Particle Mesh Ewald method [17] with a tolerance of 10^{-5}. The cutoff distance for the L-J interaction was 12.12 Å, and Cu particle was treated to be a rigid body. Newton's equations of motion were integrated using the velocity Verlet algorithm with a sufficient time step.
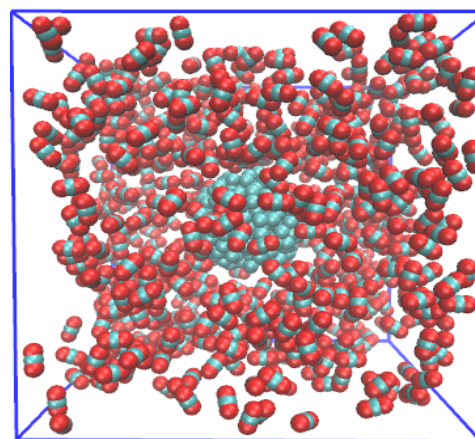

Fig. 1 Cross sectional view of the Cu-CO_2 nanofluid with 2 nm diameter under investigation.

MD method relates the thermal conductivity of fluid to equilibrium heat flow autocorrelation function through Green-Kubo equation [18], which is written as:

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$$\frac{1}{3Vk_BT^2}\int_0^\infty \langle J(0).J(t)\rangle \qquad (5)$$

where k is the thermal conductivity of fluid, k_B is the Boltzmann's constant, T is the thermodynamics temperature, V is the volume, J is the instantaneous microscopic heat flux vector,

$$J = \frac{1}{V}\left[\sum_j \frac{1}{2}e_j v_j + \frac{1}{2}\sum_{i\neq j}(r_{ij}.F_{ij}).v_j\right] \qquad (6)$$

where F_{ij} represents the interaction between particles i and j, which is ruled by interaction potential function, and e_j represents surplus energy of the atom j, which is calculated by:

$$e_j = \sum_j \frac{1}{2}m_j v_j^2 + \frac{1}{2}\sum_{i\neq j}\varphi_{ij} \qquad (7)$$

where m_j represents the mass of the jth particle, vj is the velocity of particle j, and φ_{ij} is the pair potential between particles i and j. During the simulation, it was found that NP moves and rotates due to Brownian motion, and most of the CO_2 molecules always move with the NP. Similar observation was also reported by Li et al. [20]. It has also been observed that the NP does not disintegrate into atoms due to the much stronger EAM potential. Through visualization from VMD, it has been seen that the number of CO_2 molecules that are attracted to NP surface is related to the size of nanoparticle. This is due to the more interactive force on the molecules due to increase in number of Cu atoms with increase in diameter. Hence, these molecules seem to form a thin layer at the Cu-gas interface which has a varying thickness and increases with increase in nanoparticle diameter. This is the reason why for three different sizes of nanoparticles, the enhancement of thermal conductivity is more significant than that with a small sized nanoparticle.

The density distribution of CO_2 has been examined from the surface of nanoparticle. The computational domain is divided into many spherical shells and the number of atoms within each spherical shell are accounted to obtain the density of bulk fluid and nanolayer density. The bin size was varied for different nanoparticle diameter to get the maximum nanolayer density which decides the nanolayer thickness of the system. Table III shows the semi-solid nanolayer thickness for different nanoparticle diameter.

TABLE III
NANOLAYER THICKNESS VALUES FOR DIFFERENT NANOPARTICLE DIAMETER

S.No	NP diameter	Nanolayer thickness
1	1 nm	0.2 nm
2	2 nm	0.4 nm
3	3 nm	0.6 nm

The density of nanolayer for 3 nm diameter is more orderly in when compared to other particle diameters. Figs. 2 (a)-(c) show the distribution of densities of CO_2 molecules around the nanoparticles at different time (t_1 = 1800 ps, t_2 = 1900 ps and t_3 = 2000 ps) with respect to the distance from the nanoparticle and it shows that density of CO_2 fluctuates a little with time, which confirms the nanoparticle Brownian motion, but the thickness of nanolayer does not affect much.
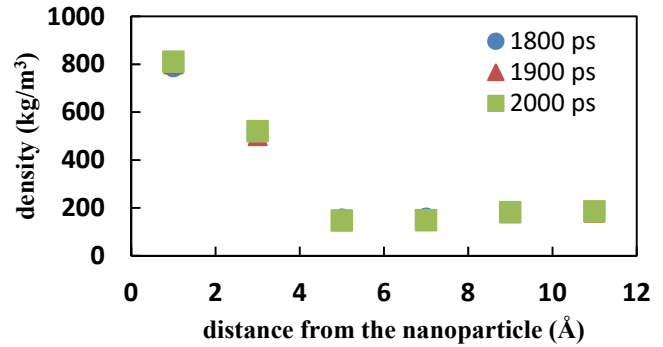

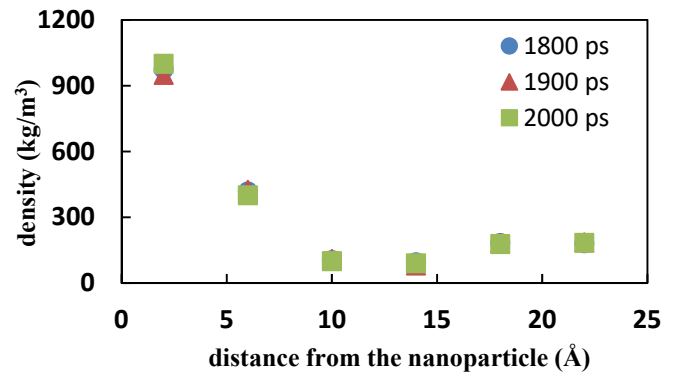Fig. 2 (a) Density distribution around 1 nm particle

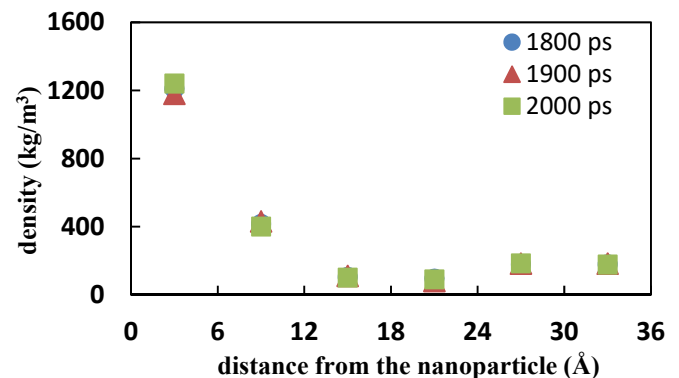Fig. 2 (b) Density distribution around 2 nm particle

Fig. 2 (c) Density distribution around 3 nm particle

The thermal conductivities of the nanofluid were also calculated via GK theory with different nanoparticle loadings by keeping the constant volume fraction as 1.413% (shown in Fig. 3). From Fig. 3, it is obvious that the thermal conductivity of liquid in nanofluid is higher than that of base fluid and it

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has an increasing trend with the increase in NP diameter. The modification in gas improves with increasing nanoparticle loadings. The solid's contribution to nanofluid's thermal conductivity is negligible, no matter how high is the thermal conductivity of solid nanoparticle [19]. It is the lattice thermal conductivity, not the electronic thermal conductivity, which enhances the nanofluid thermal conductivity as there is vibrational transportation of heat between nanoparticle and base fluid. The thicker the dense layer, enhancement in the thermal conductivity is more significant.
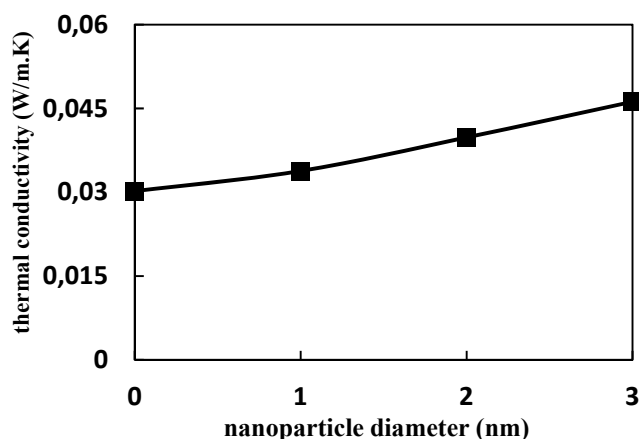

Fig. 3 Thermal conductivity variation with nanoparticle diameter

III. Conclusion

MD simulations were performed with constant volume fraction of 1.413%, and diameter effect has been observed on the thermal conductivity of the nanofluid using Green Kubo formalism. Semi solid like thin layer was visualized by VMD, and nanolayer thickness in three different cases has been calculated. Density distribution around the nanoparticle was done to determine the nanolayer thickness. The layer thickness for 1 nm, 2 nm, and 3 nm particle diameter systems are 0.2 nm, 0.4 nm, and 0.6 nm. The thermal conductivity enhancement of the nanofluid is 12%, 32%, and 53% for 1 nm, 2 nm, and 3nm diameter. It has also been seen that the nanoparticle effect is very low at the distance far away from it and density of the system is same as bulk density of gaseous CO_2 (186 kg/m^3). Also, it can be said that the presence of Cu particle leads to an increased motion of the gas molecules, which results in increased thermal conductivity. It is not the high conductivity of Cu that leads to the enhancement. It is the vibration, not the electrons that transport heat between Cu and gas. It can be concluded from this study that increase in diameter of nanoparticle in gaseous CO_2 increases the nanolayer thickness and hence increases the nanofluid thermal conductivity.

References

[1] P. Bernardo, E. Drioli, and G. Golemme, Ind. Eng. Chem. Res. 48, 4638 (2009).
[2] H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland, and I. Wright, J. Environ. Sci. 20, 14 (2008).
[3] H. Masuda, A. Ebata, K. Teramae, and N. Hishinuma, *Alternation of Thermal Conductivity and Viscosity of Liquid by Dispersing Ultra Fine Particles (Dispersion of Al2O3 , SiO2 and TiO2 Ultra Fine Particles)*, Netsu Bussei, (Japan) (1993), Vol. 7, p. 227.
[4] S. Lee, S. U. S. Choi, S. Li, and J. A. Eastman, ASME J. of HeatTransfer 121, 280 (1999).
[5] J.A.Eastman, S.U.S.Choi, S.Li, W.Yu, and L.J. Thompson, Appl. Phys. Lett. 78, 718 (2001)
[6] .S.U.S.Choi, Z.G.Zhang, W.Yu, F.E.Lockwood, and E.A.Grulke, *Anomalous Thermal Conductivity Enhancement in Nanotube Suspensions*, Appl. Phys. Lett., vol. 79, pp. 2252–2254, 2001.
[7] S. Jang and S. U. S. Choi, Appl. Phys. Lett. 84, 4316 (2004).
[8] Y. Ren, H. Xie, and A. Cai, J. Phys. D: Appl. Phys. 38, 3958 (2005).
[9] R. Prasher, P. Phelan, and P. Bhattacharya, Nano Lett. 6, 1529 (2006).
[10] S. L. Lee, R. Saidur, M. F. M. Sabri & T. K. Min. *Effects of the particle size and temperature on the efficiency of nanofluids using molecular dynamic simulation, Numerical Heat Transfer, Part A: Applications* Vol. 69 (2016) , Iss. 9,2016.
[11] J.G. Harris, K.H. Yung, J. Phys. Chem. 99 (1995) 12021.
[12] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, 1989).
[13] Supplementary material for cutoff conditions at *http://dx.doi.org/10.1063/1.4896965*, structures of CO_2, tabulated data of thermal conductivities, and equation of state.
[14] M. P. Allen and D. J. Tildesley, *Computer simulation of liquids*, Clarendon Press, U.K., 1987.
[15] S. Plimpton Lammps-Large-Scale Atomic/Molecular Massively Parallel Simulator, 2007. Available from: http:// lammps.sandia.gov/.
[16] W. Humphrey, A. Dalke, and K. Schulten, Vmd: *Visual Molecular Dynamics*, J. Mol. Graphics, vol. 14, pp. 33–38, 1996.
[17] T. Darden, D. York, L. Pedersen, J. Chem. Phys. 98 (1993) 10089.
[18] D.C.Rapaport *The Art of Molecular Dynamics Simulation*, Cambridge University Press, Cambridge, 2004.
[19] Nan Wang, Lin Shi, Jun Chen and Haifeng Jiang. Nanofluid's *Thermal Conductivity Enhancement Investigation by Equilibrium Molecular Dynamics Simulation*. vol.33 (2012). IACSIT Press
[20] Ling Li, Yuwen Zhang, Hongbin Ma and Mo Yang. *Molecular Dynamics simulation of effect of liquid layering around the nanoparticle on the enhanced thermal conductivity of nanofluids*, J Nanopart Res, vol. 12 (2010), Issue 3, pp 811–821.