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LIQUID LAYERING AND THE ENHANCED THERMAL CONDUCTIVITY OF Ar-Cu NANOFLUIDS: A MOLECULAR DYNAMICS STUDY

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ABSTRACT

Nanofluids – colloidal suspensions of nanoparticles in base fluids – are known to possess superior thermal properties compared to the base fluids. Various theoretical models have been suggested to explain the often anomalous enhancement of these properties. Liquid layering around the nanoparticle is one of such reasons. The effect of the particle size on the extent of liquid layering around the nanoparticle has been investigated in the present study. Classical molecular dynamics simulations have been performed in the investigation, considering the case of a copper nanoparticle suspended in liquid argon. The results show a strong dependence of thickness of the liquid layer on the particle size, below a particle diameter of 4nm. To establish the role of liquid layering in the enhancement of thermal conductivity, simulations have been performed at constant volume fraction for different particle sizes using Green Kubo formalism. The thermal conductivity results show 100% enhancement at 3.34% volume fraction for particle size of 2nm. The results establish the dominant role played by liquid layering in the enhanced thermal conductivity of nanofluids at the low particle sizes used. Contrary to the previous findings, the molecular dynamics simulations also predict a strong dependence of the liquid layer thickness on the particle size in the case of small particles.

Nomenclature

U	Interatomic potential
K	Thermal conductivity
V	Volume
T	Temperature
k_B	Boltzmann constant
J	Heat current vector
E_i	Total energy of atom i
h	Partial enthalpy of the system
N	Total number of atoms
$g(r)$	Radial distribution function
r_{ij}	Distance between atoms i and j
F_{ij}	Force exerted on atom i by j
v_i	Velocity of i^{th} atom
Greek letters	
ε	Depth of the potential well
σ	Finite distance at which U=0

Subscripts	
i,j	The atom's indices
Superscripts	
*	Reduced units

INTRODUCTION

Nanofluids have emerged as high performance heat transfer fluids which have the potential to substantially improve the performance and compactness of heat transfer equipment, especially miniaturized devices, dealing with high energy dissipation densities. Since the beginning of the 21st century there has been an exponential increase in research aimed at unraveling the reasons for the often anomalous enhancement of the thermal conductivity shown by nanofluids. Atomistic simulation is an effective tool that could be used to better understand thermal transport at the nanoscale. In recent times, classical molecular dynamics simulations have been used extensively to study nanofluid systems. Many theories have been proposed to explain the anomalous enhancement of the thermal conductivity of nanofluids. Keblinski et al. [1] proposed four possible mechanisms responsible for the enhanced thermal conductivity: Brownian motion, liquid layering around the nanoparticle, ballistic thermal transport inside the nanoparticle and nanoparticle clustering. Liquid layering refers to the existence of a solid-like liquid layer at the interface of nanoparticle and the base fluid, due to the strong intermolecular interaction between the solid and liquid atoms. Liquid layering around the nanoparticle might play a significant role in the enhancement of thermal conductivity of the nanofluids, as the solid-like liquid layer might exhibit a higher thermal conductivity than the base fluid.

Li et al. [2], using molecular dynamics simulation, suggested that a thin layer of liquid around the nanoparticle also moves with the Brownian motion of the particle. The experimental work of Firlar et al. [3] utilizing TEM images of alumina-water nanofluid suggested the existence of a thin layer of a solid-like region, 4 nm thick, between the solid and liquid regions.

The thermal conductivity of a nanofluid can be determined using the Green-Kubo formalism which is an equilibrium molecular dynamics (EMD) approach based on fluctuation-dissipation theorem [12]. Sarkar et al. [4] calculated the thermal conductivity of argon-copper nanofluid using Green-Kubo method incorporating a partial enthalpy term. Babaei et al. [5] calculated the thermal conductivities of several multi-component systems using the same method. Eapen et al. [7] modeled the enhancement in thermal conductivity by the strong attraction through the self correlation of the potential flux between the nanoparticle and the fluid, in the autocorrelation function for thermal conductivity calculation. Wang et al. [6] reported the strong dependence of thermal conductivity on the particle size. The model proposed by them predicted a significant increase in the thermal conductivity of the nanofluid at very low particle sizes.

In the present work, molecular dynamics simulation is utilized to explore the effect of the particle size on the extent of liquid layering around the nanoparticle, and to predict the thermal conductivity of the nanofluid.

METHODOLOGY

a. Numerical Procedure

The computational model consists of a spherical copper nanoparticle suspended in liquid argon filled in a cubical box. Simulations were performed using seven different particle sizes from 2 to 8 reduced units, which corresponds to 1.28nm and 5.126nm respectively (1 reduced length unit = 0.64nm). The box size was adjusted every time the particle size was changed, to keep the volume fraction of nanoparticles constant. By maintaining the volume fraction constant during the simulations, the dependence of the extent of the layering around the nanoparticle and the thermal conductivity on the particle size is obtained from the results.

In the present study the interatomic interactions between copper atoms in the nanoparticle, argon atoms in the base fluid and between copper atoms and argon atoms were all modeled using Lennard-Jones (LJ) potential with appropriate LJ parameters.

$$U\left(r_{ij}\right) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \quad \textbf{(1)}$$

where the LJ parameters ε and σ represent the energy and length scales respectively and r_{ij} is the distance between atoms *i* and *j*. The length and energy parameters for argon are taken as 3.405 Å and $1.67\times10^{-21} J$ [8] respectively, and for copper, they are 2.3377 Å and $6.625\times10^{-21} J$ respectively [9]. The Berthlot mixing rule was used to obtain the parameters representing the copper-argon interaction, as follows.

$$\sigma_{sl} = \frac{\sigma_s + \sigma_l}{2} \text{ and } \varepsilon_{sl} = \sqrt{\varepsilon_s . \varepsilon_l} \qquad \textbf{(2)}$$

The extent of liquid layering around the nanoparticle was determined by plotting the radial distribution function (RDF) of argon atoms in the spherical shell – shaped regions around the nanoparticle (Fig 1). The atoms contained in each spherical shell were identified as belonging to a specific group. The RDF of each group of atoms was calculated during the simulation. The RDF plots were then used to identify the extent of region around the nanoparticle, where the influence of the nanoparticle is felt. This was done by identifying the shell at which the RDF resembles that of liquid argon. The thermal conductivity of the nanofluid system was determined using Equilibrium Molecular Dynamics (EMD) approach.

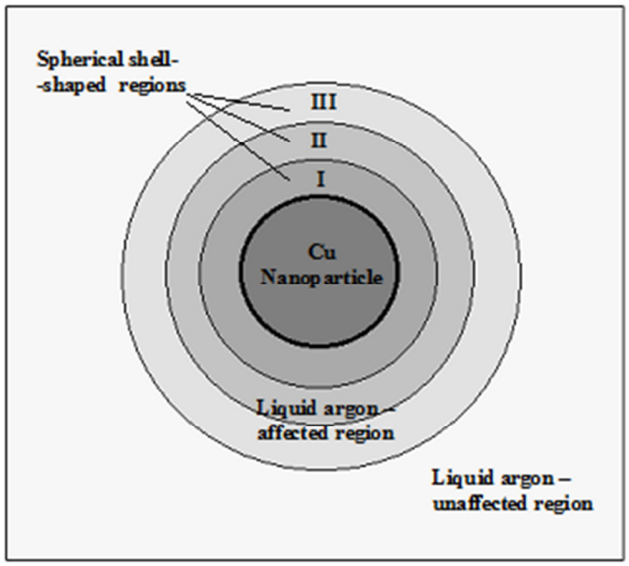


Fig 1. Schematic representation of the computational domain, showing the copper nanoparticle and the affected region around the nanoparticle. The affected region is shown divided into spherical shell-shaped regions.

The simulations were performed at a specified non dimensional temperature of T* = 1.35 and non dimensional density ρ*=0.6. The system was equilibrated at the specified temperature utilizing the NVT ensemble and was subsequently transferred to the NVE ensemble in order to collect dynamical data. To bring down the computation time, a neighbor cutoff radius [13] equal to 2.5σ was used in the force calculations. The time integration of the equations of motion was done using the LAMMPS MD code [11].

b. Green-Kubo Formalism

An Equilibrium Molecular Dynamics simulation relates the equilibrium heat current autocorrelation function to the thermal conductivity through the Green-Kubo relation.

$$k = \frac{1}{3k_B V T^2}\int_0^t \langle J(0)J(t)\rangle dt \qquad \textbf{(3)}$$

where k is the thermal conductivity, V the system volume, T the system temperature, k_B the Boltzmann constant, J the heat current vector, and the angular brackets denote the ensemble average.

The heat current vector is calculated as follows.

$$J = \sum_i^N v_i E_i + \frac{1}{2}\sum_i^N \sum_{j\neq i}^N r_{ij}\left(F_{ij}.v_i\right) - \sum_i^N v_i h \qquad \textbf{(4)}$$

where F_{ij} is the force exerted on atom i by its neighbor j, E_i is the total energy of atom i and h is the partial enthalpy of the system. For heterogeneous systems like a nanofluid, the Green-Kubo equation should contain the partial enthalpy term. In a single component system, the partial enthalpy term can be neglected [5].

RESULTS AND DISCUSSION

a. Validation of the model

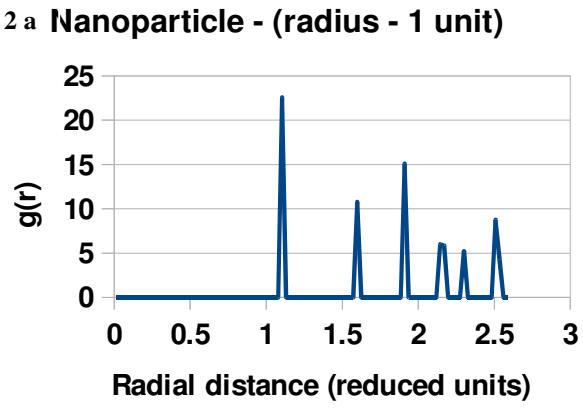
The system containing 500 argon atoms was simulated at T*= 1.35 and ρ* = 0.6 to validate the model, where T* and ρ* are the nondimensional units of temperature and density. A thermal conductivity of 3.43 (reduced units) was obtained from the simulation, which agrees well with the experimental result (3.5 units) and computational result (3.4 units) from the literature [10]. Sarkar et al [4] had simulated a system of argon atoms varying

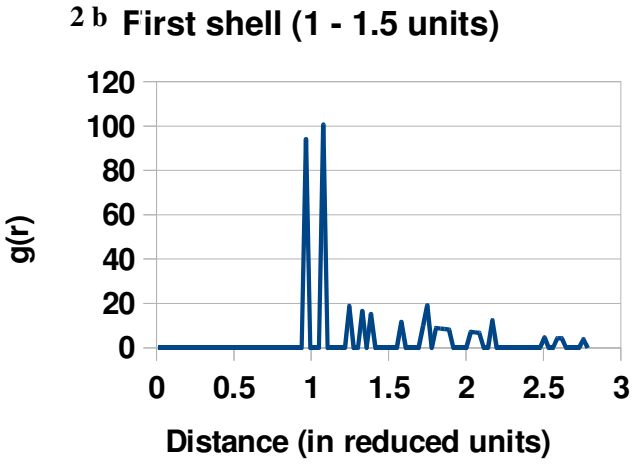
the number of atoms from 32 to 2048. They reported a steady convergence of thermal conductivity of liquid argon after 500 atoms. This explains our choice of the size of the system used for validating the model as 500 atoms. As the system under study consists of argon-copper nanofluid, experimental results are not available in literature for validating the results of the present study.

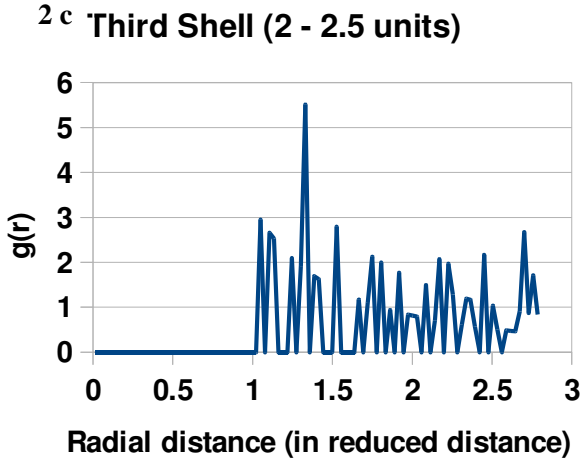
b. Characterization of the liquid layer using RDF

Simulations were performed at T*= 1.35 and ρ* = 0.6, maintaining the volume fraction of nanoparticles constant at 3.34%. Seven sets of runs were performed with 7 different particle sizes, from 2 to 8 (reduced units) in intervals of 1. The radial distribution functions of adjacent spherical shells of thickness, Δr=0.5 (in reduced units) around the nanoparticles were plotted for three different particle sizes 2, 4 and 6 (reduced units).

Figures 2, 3 and 4 show the plots of radial distribution functions of the affected region around copper nanoparticles of three different radii. The plots clearly indicate that the structure of argon in the layer adjacent to the particle exhibits a certain level of ordering which in turn establishes the presence of a liquid layer around the nanoparticle. Subsequent simulations with different particle sizes show an interesting result, that the thickness of the layering increases with a decrease in particle size. This trend is seen below a particle size of 6 (reduced units). This is contrary to the general finding that the layer thickness is not influenced by the particle size [1], and shows that it is affected by the size in the case of small particles.







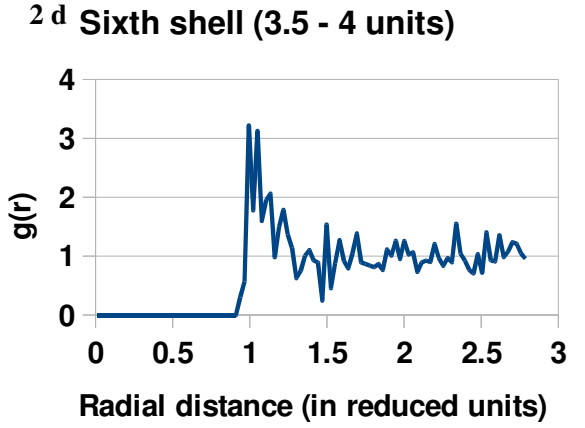
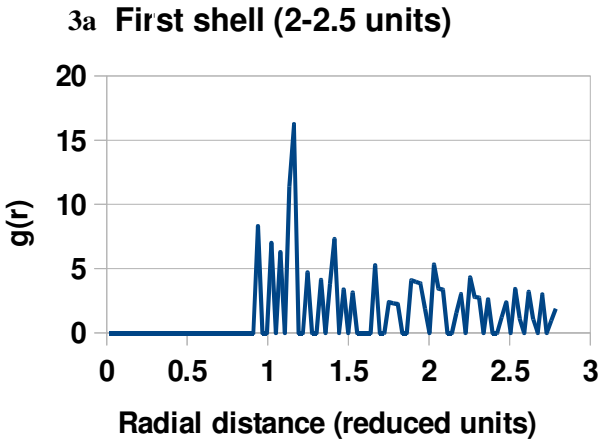
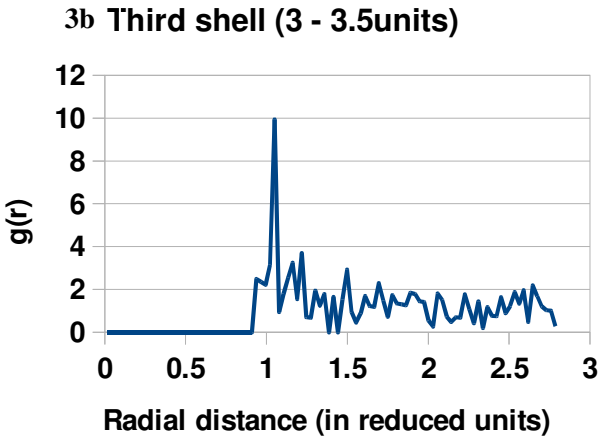


Fig 2 a-d. Radial distribution function versus radial distance (in reduced units) for nanoparticle of radius 1 unit and for the 1st 3rd and 6th spherical shells of liquid argon of thickness 0.5 units around the nanoparticle.





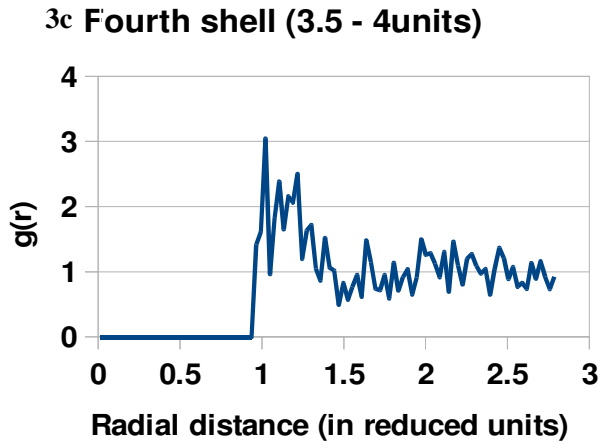
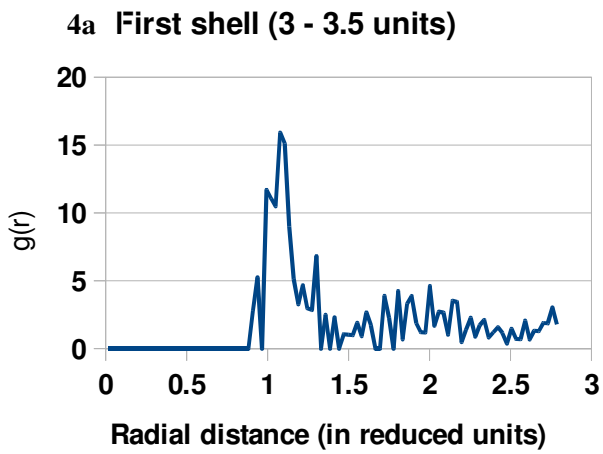


Fig 3 a-c. Radial distribution function versus radial distance (in reduced units) for the 1st 3rd and 4th spherical shells of liquid argon of thickness 0.5 units around the nanoparticle of radius 2 units.



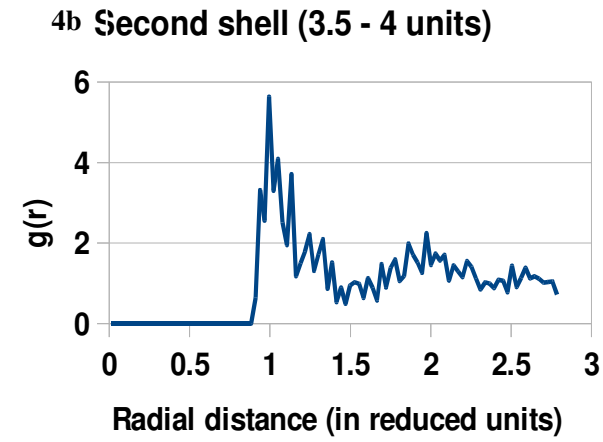


Fig 4 a-b. Radial distribution function versus radial distance (in reduced units) for the 1st and 2nd shells of liquid argon of thickness 0.5 units around the nanoparticle of radius 3 units.

Figure 5 shows the thermal conductivity enhancement and the thickness of liquid layering, as functions of the particle radius. The results are obtained from simulations for a constant volume fraction of 3.34%, by varying the particle sizes from 2 to 8 reduced units. The thermal conductivity enhancement and liquid layer thickness follow the same trend when plotted against the particle size. This result further demonstrates the presence of a strong layering at low particle sizes which in turn results in more significant thermal conductivity enhancement, up to 100% (at a particle size of 3 reduced units, which corresponds to 1.92 nm). The results also indicates that above a particle size of 6

reduced units, which corresponds to 3.84 nm, the thickness of layering remains constant and consequently the thermal conductivity enhancement reaches moderate levels reported in the literature.

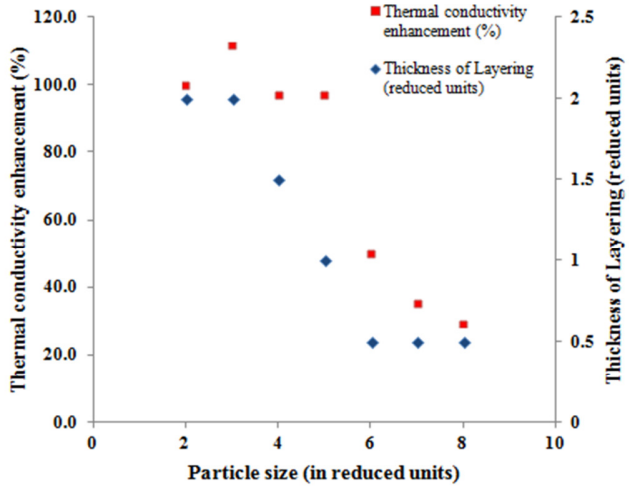


Fig 5 – Thermal conductivity enhancement and thickness of liquid layering versus Particle radius at a constant particle volume fraction of 3.34%.

CONCLUSIONS

In this paper we report the effect of the particle size on possible liquid layering around a nanoparticle, the extent of the liquid layer, and the thermal conductivity enhancement. The results of the molecular dynamics simulations indicate the presence of strong layering around a nanoparticle. The results also show that the extent of layering is strongly dependent on particle size at particle size below 3.84nm. The thickness of the layer decreases with an increase in the particle size. The thermal conductivity measurement establishes the earlier mentioned results on the significant extent of layering for small particles. The results show 100% enhancement at a particle size of 3 reduced units, which corresponds to 1.92 nm at a volume fraction of 3.34%. Studies are being undertaken to understand the reasons for the enhancement in the thermal conductivity at particle sizes larger than 5nm, where layering may not be a significant reason for enhancement.

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