Thermal Conductivity of Nano-fluids in Nano-channels

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Abstract The behaviour of an Argon-copper nano-fluid spatially restricted in a nano-channel is studied by using Molecular Dynamics simulations. Specifically, the channel size and particle loading effects on nano-fluids thermal conductivity are investigated. A direct comparison is made between the calculated results and the prediction of classical macroscopic models with the latter under-estimating the computed values by up to 20%. The thermal conductivity enhancement is correlated with the structure of Argon atoms close to the walls of the channel and around the particle, whose solid like nature enables them to propagate heat more efficiently.

Keywords: Nanofluids, Nanofluidics, Molecular Dynamics, Nanochannel, Heat transfer, Thermal Conductivity, Argon, Copper

1. Introduction

Colloidal mixtures of nanometre sized particles in some base fluid, usually referred as nano-fluids, have been a topic of interest due to their improved thermal properties compared to those of the baseline fluids. The term nano-fluid was first coined by Eastman (2001) who achieved a 40% enhancement of the thermal conductivity of ethylene glycol with the addition of a mere 0.3% volume fraction of Cu nano-particles. Such severe enhancements clash with the classical understanding that the thermal conductivity of a nano-fluid is simply an average of those of its individual constituents, taking into account their volume fractions. This model (henceforth labeled as HC model) was first developed by Hamilton & Crosser (1962) based on the work of Maxwell and is given by:

$$\lambda_{HC} = \lambda_f \left[\frac{\lambda_p + 2\lambda_f - 2\phi(\lambda_f - \lambda_p)}{\lambda_p + 2\lambda_f + \phi(\lambda_f - \lambda_p)} \right]$$

where λ_{HC} is the thermal conductivity predicted by the model; λ_f is the thermal conductivity of the fluid; λ_p is the thermal conductivity of the particle; and ϕ is the particle loading.

Mechanisms for the reconciliation of the experimental data and numerical models were proposed, including the formation of a structured layer of liquid molecules around the particle (Li, et al., 2010), aggregation of nanoparticles(Eapen, et al., 2010), diffusion modes and the Brownian motion of the particles (Evans, et al., 2006).

Molecular Dynamics (MD), has been successful in describing thermal properties of solids and liquids (Evans, 1986; Sofos, et al., 2009; McGaughey & Kaviany, 2004), elucidating how the microscopic behaviour of certain systems contribute to the macroscopic experimental observations.

Such atomistic simulations have also been used to understand the bewildering nature of nanofluids. A study on the effect of the particle size on the thermal conductivity of a Al_2O_3-water and Al_2O_3-ethynol nanofluid has shown that decreasing particle size, while keeping the volume fraction constant, results in higher heat transfer rate (Lu & Fan, 2008), concurring with previous empirical models (Chon, et al., 2005). The same empirical models however, emphasizes the importance of the Brownian motion of the particles in the enhanced thermophysical properties observed in experiments; a claim which atomistic simulations challenge (Keblinski, 2002; Sarkar & Selvam, 2007). While the random motion of the particle itself seems unimportant, there is

numerical evidence that the increased motion of the fluid particles next to it might potentially allow for a more efficient transfer of energy (Sarkar & Selvam, 2007).The structured layer of liquid atoms surrounding the particle has also been found by some studies (Li, et al., 2010) to increase the thermal conductivity of the system while others claim that the small thickness of this layer ($\approx 1nm$) cannot possibly produce the enhancements presented by experimental data (Keblinski, 2002; Eapen, et al., 2010).

Under spatial restrictions, even conventional fluids behave differently. MD studies successfully investigated the flow of fluids through nanochannels and found inconsistencies between the observed behaviour with that predicted by classical continuum mechanics (Asproulis & Drikakis, 2011; Asproulis & Drikakis, 2010; Sofos, et al., 2009).Such atomistic simulations have also been used to portray the behaviour thermal behaviour of such systems. The size of the channel has been correlated with the thermal conductivity of the liquid residing in it (Sofos, et al., 2009) while other studies even managed to observe a flux of heat even in the absence of a temperature gradient, thus challenging the fundumentals of continuum fluid dynamics (Todd & Evans, 2800; Baranyai, et al., 1992). The Kapitza (thermal interface) resistance has been found to be largely affected by the wetting of the liquid on the solid surface (Barrat & Chiaruttini, 2003) as well as the liquid density and bonding stiffness of the wall particles (Kim, et al., 2008).

The present study employs MD models to investigate the nature of a nanofluid restricted in a channel of nano-metre characteristic dimensions. The thermal conductivity of the colloid is observed as a function of the wall separation distance. The results from the simulations are compared to those predicted by the classical HC model.

2. Simulation Method

The simulations are carried out using the software LAMMPS (Plimpton, et al., 2007). The computational model comprises of a nano-channel filled with argon atoms with one or more Copper particles suspended in it. The walls of the channel are fixed perpendicular to the ydirection (parallel to the xz plane). The channel height considered ranges from 10σ to 38σ.

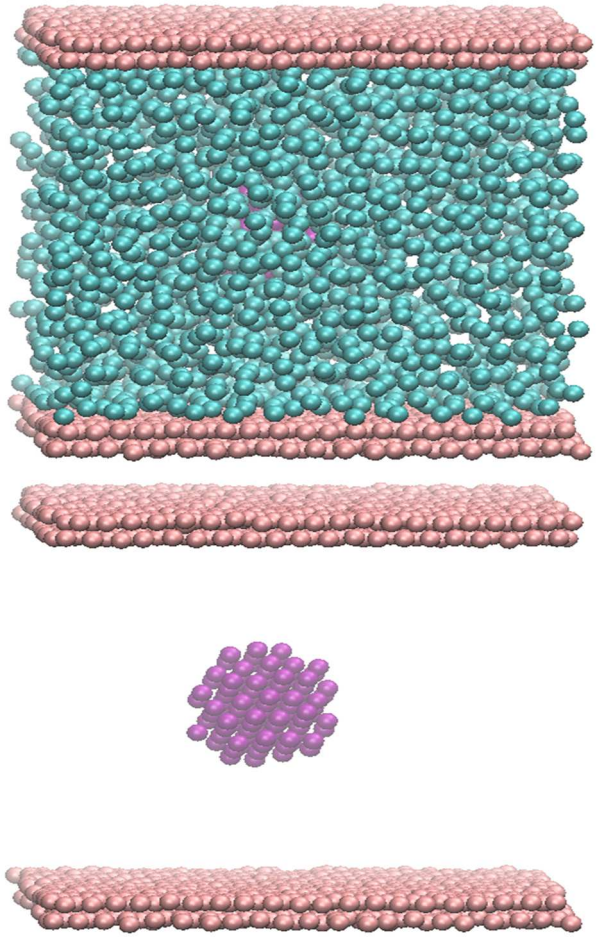

Figure 1 Molecular Dynamics model visualised in VMD. The top image depicts the whole model, while the bottom one makes the Argon atoms transparent

Periodic boundary conditions are employed parallel to the walls of the channel emulating its perpetual continuation. All atoms are placed on a Face Cubic Center (fcc) lattice. Each wall consists of two (1 1 1) fcc planes. The nano-particle is then placed in the centre of the channel by scooping out a sphere of Argon atoms and replacing them with the correct number of Copper atoms. The particle used inthe present study is of radius 2.12σ. Figure 1shows the atomistic scale model (Humphrey,

et al., 1996).

The interatomic interactions between the argon atoms are modelled through a Lennard-Jones (LJ) potential:

$$V_{ij}^{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

where i, j are the indices for two arbitrary particles in the system, $r_{ij}$is their inter-atomic distance and $\epsilon$and $\sigma$are the energy and length scales, respectively. The LJ parameters between the atoms of the system are shown in Table 1. The interactions between solids and liquids are calculated using the Lorentz-Berthelot mixing rule. For computational efficiency, inter-atomic interactions beyond a cut-off distance $r_c = 2.2\sigma$ are disregarded. The LJ parameters for the potentials between the atoms in the simulation are given in the Table below:

Atoms	$\boldsymbol{\epsilon}$	$\boldsymbol{\sigma}$
Liquid - Liquid	1.0	1.0
Wall - Liquid	0.6	0.75
Wall - Particle	39	0.85
Particle – Liquid	6.3	0.8693
Particle - Particle	39.676	0.738

Table 1 Lennard Jones parameters forthe atoms used in the simulation

The equations of motion for the particle i are given by

$$m\ddot{r}_{ij} = \sum_{i\neq j} \nabla V_{ij}$$

The wall particles are fixed onto their initial lattice sites by spring potentials which urge them to return to their equilibrium positions $r_0$via a restoring force given by

$$F = -\kappa(r_i - r_0)$$

where κ is the wall stiffness, a parameter vital to the realistic manifestation of the wall (Kim, et al., 2008).

Furthermore, in order to control the temperature of a system, each of the fcc planes of the walls is assigned a thermostat, whose function is to rescale the velocities of the atoms about their mean positions in such a way as to match the desired temperature. The temperature in which the simulations are run is $0.71\,k_B/\epsilon$ in which Argon is in its liquid form. The Argon atoms collide and interact naturally with the walls exchanging energy. Any excess viscous heat is transferred onto the walls through these interactions and is then dissipated into the environment via the thermostats.

The thermal conductivity is calculated using the Green-Kubo relations (Kim, et al., 2008) given by

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

where λ is the thermal conductivity, k_B is the Boltzmann constant, V is the volume of the system, T is the temperature of the system and J is the microscopic heat flux of the system given by

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

where F_{ij} is the force on atom i due to the neighbouring atom j, $\boldsymbol{v}_i$ is the velocity of particle i and h is the microscopic enthalpy of the system.

The angular brackets in the thermal conductivity equation denote the heat flux auto-correlation function (HFACF) which describes how long it takes for microscopic heat fluctuations (which oscillate about zero) to dissipate. In an equilibrium system this function must eventually decay to zero and its integral is proportional to the thermal conductivity.

Finally, as part of the analysis of the results, the Mean Square Displacement (MSD) of the liquid atoms is considered. The quantity is calculated from the definition:

$$MSD(t) = \frac{1}{N}\langle\sum_{i=1}^{N}\left[r_i(t) - r_j(0)\right]^2\rangle$$

MSD provides the average distance travelled by a group of atoms due to Brownian motion. It is very useful in providing insight in the behaviour of liquids.

The time step for the simulation is $2fs$ and each case was run for a total of 5×10^6 time steps through the micro-canonical ensemble

(NVE). The correlation length used for the HFACF simulations is 2000 time steps.

3. Results

In the cases considered, the height of the channel varies, while keeping the particle size constant.

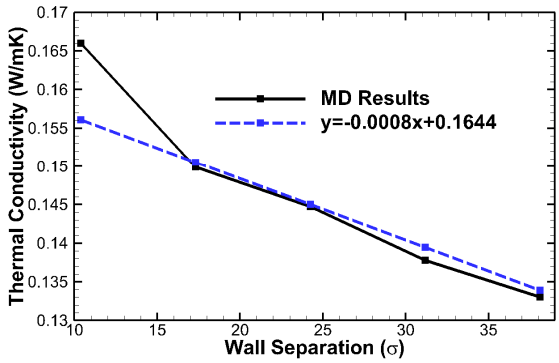

Figure 2 Thermal conductivity of nano-fluid as a function of the wall separation. The yellow line plots the results from the MD simulations, while the pink line plots a linear fit to all but the first point.

Figure 2 shows the calculated thermal conductivities as a function of the wall separation. As the channel size increases, the volume fraction of particles in the system decreases. With the exception of the first point (in which the particle is less than 3σ away from the walls of the channel), there exists a linear relationship

$$y = -0.0008x + 0.1644$$

which correlates with the predictions a coefficient of determination $R^2 = 0.9952$

Figure 3 plots the same thermal conductivities as a function of the particle loading. In addition, the values predicted by the classical HC model are also plotted.It is obvious that as the volume fraction increases, the MD results predict much higher thermal conductivities while, as the particle loading approaches zero, the two converge close to $\approx 0.132 W/mK$; the thermal conductivity of liquid argon at temperature $0.71\, k_B/\epsilon$(Muller-Plathe, 1997). In order to get a better understanding of this enhancement, the radial distribution (rdf) functions for the particle was plotted (Figure 4) for all channel heights to illuminate the nature of the liquid atoms around it.

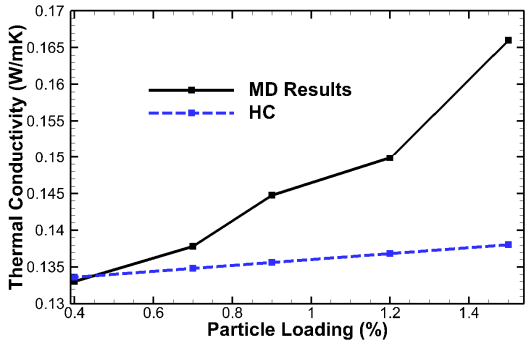

Figure 3 Thermal conductivity of the nano-fluid against the particle loading in the system. The green line plots the results from the MD simulations while the red line plots the results predicted by the HC model

Again, with the exception of the point with the highest volume fraction, which corresponds) to the case where the channel is narrowest, the shape and values of the curve resemble those of similar studies on nanofluids, which are unrestricted in space (Sarkar & Selvam, 2007).

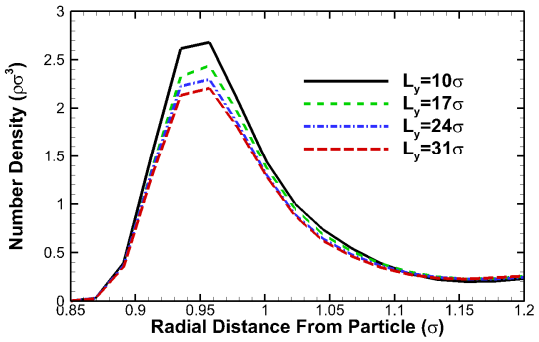

Figure 4 RDF diagrams between the particle and liquid atoms show the increasing density in the nanolayer as the channel gets narrower

Figure 4 clearly shows that as the wall separation increases, the density of the nanolayer around the particle decreases. As mentioned in the introductory section, this layer is believed to improve the thermal conductivity of the nano-fluid. The difference in the jump between the densities of the first two layers (10σ and 17σ) is significantly bigger than those observed between the other consecutive cases, shedding light on the deviation of the first point in Figure 2.

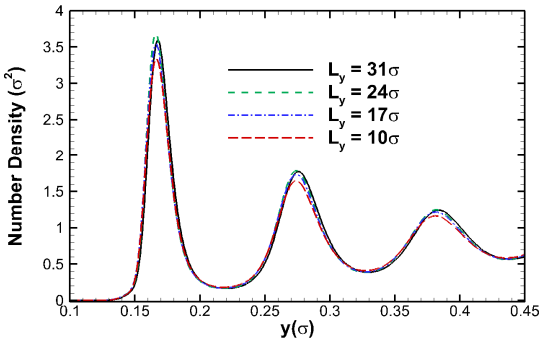

Figure 5 Density profiles normal to the channel walls

In addition to the RDF diagram, Figure 5 shows the density profiles of the argon atoms close to the channel walls. In contrast to the particle's nano-layer which decreases with increasing channel size, the layers close to the wall seem to increase. The two phenomena are not independent. At small wall separations, the particle "steels" argon atoms from the layers of the wall, lowering their density.

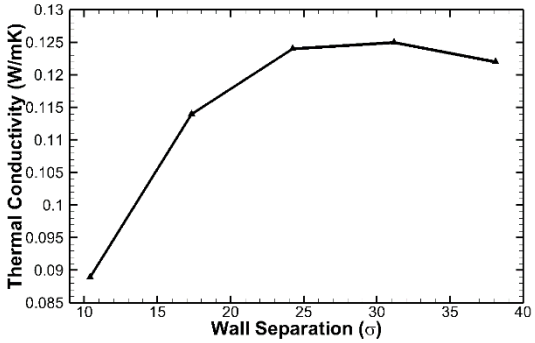

Figure 6 Thermal conductivity in the y-direction against the channel width

As a final remark, it is worth noting the anisotropy of the thermal conductivity of the nano-fluid in the directions parallel to the channel walls (x and z directions) and the normal direction (y direction). Figure 6 shows that in the latter case, the thermal conductivity increases with increasing wall separation and gradually reaches a plateau. This result requires further investigation since it contradicts the results in the x and z directions. A close look at the Mean Square Displacement (MSD) of the liquid in the y axis, shown in the bottom plot of Figure 7, sheds light on this observation. The results show that as the channel becomes narrower, the motion of the atoms becomes more restricted causing the MSD in the y direction to converge; a behaviour in contrast with the MSD of free fluids which should form a straight line extending perpetually with time (as shown in the top plot of Figure 7). Similar observations have been made in previous studies (Murad, et al., 1993; Liu, et al., 2005), which show that the diffusion coefficient is impaired when fluids are confined.

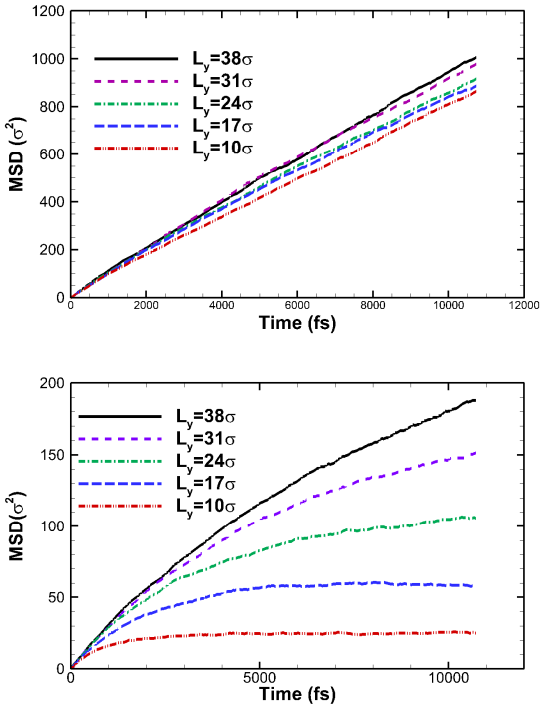

Figure 7 MSD plots of the liquid atoms. The top figure plots the MSD averaged over all dimensions while the bottom one is restricted only in the direction normal to the walls

This is a form seen in solids where the motion of the atoms is restricted to vibrations about their mean position. This restricted motion in the normal direction results in a less efficient energy flow across the width of the channel, impairing the thermal conductivity.

4. Conclusions

Equilibrium Molecular Dynamics were used to study the thermal behaviour of nano-fluids in channels of nano-metre characteristic dimensions. The thermal conductivity of the system was calculated using the Green-Kubo relations. The results show that the classical model (HC) underestimates the thermal conductivity by up to 20% compared to those predicted by the MD model of the present study. Furthermore, the thermal conductivity linearly correlates and increases with

decreasing wall distance with the exception of when the wall separation is only 10σ (where the particle is no more than 3σ away from the channel walls) in which the thermal conductivity experiences a sudden jump. This enhancement is attributed to the structured layering of Argon atoms around the particle, whose density also increases with decreasing wall separation and similarly experiences a sudden jump in the case where the channel is narrowest. In contrast, the layering of liquid atoms next to and parallel to the walls decrease in density as the channel gets smaller. This is reciprocal to the increasing densities of the particle's nano-layer since the narrower the channel is the more atoms the particle "steels" leaving a smaller number available for the layers close to the walls. Finally, the anisotropy of the thermal conductivity in the direction normal to the channel was justified by the Mean Square Displacements in the direction which shows that as the channel walls get closer to each other, the movement of the atoms becomes restricted rendering the transfer of heat across the width of the channel less efficient.

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