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Investigation into the Effects of Nanoparticle Size and Channel Depth on the Thermo-physical Properties of Water Nanofluids in the Nanochannel Using Molecular Dynamics Simulation

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Abstract
In this research, an in-house code which uses the molecular dynamics method to study the flow of different nanofluids in the copper nanochannel and computes the thermo-physicals properties has been developed. The flow of nanofluids has been studied from hydro-thermally viewpoint and temperature jump at the wall has been applied. Parametric study to consider the effect of different parametric such as nanoparticle size channel and depth of them on the flow and its properties has been done. The results show that increasing the size of nanoparticles will decrease the viscosity and thermal conductivity; but it will increase the specific heats of nanofluids. Also, the thermal conductivity increases as a function of the nanochannel depth when the channel depth is increased. Although, the nanochannel dimension has no effect on the other thermo-physical properties of nanofluids. Moreover, the interaction and tendency between water and nanoparticles were studied using radial distribution function (RDF).

Keywords: Nanoparticle Size, Channel Depth, Viscosity, Thermal Conductivity Coefficient, Specific Heat.

1. Introduction

Molecular dynamics method is one of the most common numerical methods for modeling the behavior of materials in nanoscale. Many of the parameters that are costly and sometimes impossible to be investigated in empirical experiments are possible in the molecular dynamics simulation. Moreover, the molecular dynamics simulation is an appropriate tool to understand and justify the physics governing the phenomenon. Hence, it could be said that molecular dynamics simulation could have an important role in describing the experimental results of thermal conductivity of nanofluids.

Despite the studies performed, researchers have confirmed no exact mechanisms for increasing the thermal conductivity of nanofluids so far. In addition, due to the heavy volume of the calculations of molecular dynamics simulation, usually simple potential functions such as Lennard-Jones have been used in the simulations. In this study, calculating the thermo-physical and investigating the heat transfer physics in nanofluids have been examined with the help of simulating actual materials with more complex potential functions such as water fluid

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and gold and silver nanoparticles. The experimental results confirm the increase of their conductivity, and the effects of various factors such as the size and the depth of nanochannel on the nanofluids properties and the flow will be studied.

Bushehri et al. (2016) have studied the thermal conductivity of water fluid with SiO_2 and Pt nanoparticles using molecular dynamics method and Green-Kubo's relations. They have used the SPC/E model in order to consider the interaction between water molecules and have calculated the thermal conductivity coefficient of water equal to 0.63 W/(m.°K) at 293 °K, where there is an acceptable consistency between the simulation and experimental results. Their investigation indicates that the increase of nanoparticle size, lead to decrease in the thermal conductivity coefficient. They have also reported that increase of the nanoparticle size is associated with reducing of water viscosity.

Hu et al. (2016) have investigated the flow and conductivity of argon-copper nanofluid using non-equilibrium molecular dynamics method. They have used the Lennard-Jones interaction function in order to model the interaction of fluid and nanoparticle and reported that increase of the diameter of the nanoparticle coupled with the increase in the nanofluid velocity in the channel causes a significant increase in the thermal conductivity coefficient. However, if the nanofluid is stationary, increase in the size of the nanoparticle will not affect the thermal properties significantly.

By using the molecular dynamics method, Lee et al. (2016) have calculated the thermal conductivity coefficient of nanofluid in order to investigate the effect of temperature and size of nanoparticles on the thermal properties of argon-copper nanofluid using the Green-Kubo's formula. They have also used the Lennard-Jones interaction function to model the interaction between fluid and nanoparticle. Their results indicate that increasing the size of nanoparticle as well as its volumetric percentage in the fluid leads to improvement in the thermal properties of argon, so that, for a nanofluid with 8% vol. of copper nanoparticles having a size of 2 nm, which is associated with an increase of about 50% in the thermal conductivity coefficient. In the case of temperature, they have observed that increase in the temperature has not a significant effect on the thermal conductivity of the nanofluid. Their results also indicate that increase of nanoparticle size is associated with reduction of nanofluid viscosity.

Frank et al. (2015) have used molecular dynamics and Green-Kubo's relations to investigate the thermal properties of argon-copper nanofluid inside a channel. They have used the Lennard-Jones interaction function to model the interaction between fluid and nanoparticle. Their results show that increasing in the channel depth reduces the thermal conductivity of the nanofluid, whereas it has little effect on the thermal conductivity of pure argon.

Mao and Zhang (2012) have investigated the specific heat capacity of water using molecular dynamics method by different interaction models and reported that TIP3P interaction model for water molecules is of the least amount of error compared with experimental values. This means that they have calculated the specific heat capacity of water, i.e., 4.18 kj/(kg.°K), equal to 4.48 kj/(kg.°K).

Evaluation of the performed studies shows that most of these studies have been conducted on Argon fluid, there are less investigations dealing with water nanofluid. The studies also confirm that the simulation of the thermal conductivity of water or water nanofluid is highly dependent on the interaction function used for water, which results in a significant difference between the results of simulation and experimental data. From the aspect of the method of calculating the thermal conductivity coefficient, investigations show that equilibrium molecular dynamics and the Green Kubo's method have been used in most studies and the non-equilibrium molecular dynamics is less addressed. Investigation of the previous studies in the field of viscosity and thermodynamic properties of nanofluids shows that molecular dynamics simulation methods have been done less and more focused on experimental studies.

Hence, according to the investigations into the studies in the field of thermal properties of nanofluids, it could be said that studying the thermo-physical properties of water nanofluid in nanochannels would be an appropriate idea for continuing in this field, and the effects of the material, size of nanoparticles and the channel depth of nanofluid for two nanoparticles of gold and silver in the copper nanochannel can be studied.

2. Molecular Dynamics Simulation Procedure

In the molecular dynamics approach, the system variations are obtained by integrating the equations of motion. First, the initial location of particles is determined based on an initial configuration model and the equilibrium velocity distribution of the particles is defined by the Maxwell-Boltzmann distribution relation according as blow (Leach, 2001).

$$p(v_{\alpha,i}) = \left(\frac{m_i}{2\pi k_B T}\right)^{\frac{1}{2}} exp\left[-\frac{1}{2}\frac{m_i {v_{\alpha,i}}^2}{k_B T}\right] \qquad \alpha = x, y, z, \tag{1}$$

After determining the initial conditions, the intermolecular and intramolecular forces are calculated and integrated with the equations of motion and the new location and velocity of the atoms are obtained with the help of Verlet algorithm. This loop is continuously repeated until the system finally reaches balance.

2.1. Interaction Potential Function

In the present study, four potential fields including two intermolecular potential energies (Van der Waals and electrostatics), and two intramolecular potential energies (bond stretching and bond bending) are considered for the entire molecular system.

Water is considered as the base fluid and Lennard-Jones interaction potential function, Coulomb and harmonic interaction functions have been used.

Recent studies in the field of fluid simulation, especially water, show that the use of Pcff force fields (Pang et al. 2010; Chen et al. 2007; Wu et al. 2009) shows good and acceptable results with less error in predicting their properties, compared to other models of water. It is also used from this model in the present study. In the Pcff force field, interaction functions of equations (2-5) are used for modeling intermolecular and intramolecular interactions.

$$U_{LJ}^{ij}(r_{ij}) = \varepsilon_{ij}\left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^9 - 3\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right], \tag{2}$$

$$U_{Coul}^{ij} = B\frac{q_i q_j}{\varepsilon_0 r_{ij}} \qquad B = 332.0647, \tag{3}$$

$$U_{str} = \frac{1}{2}k_{str}(R - R_0)^2[1 + C(R - R_0) + D(R - R_0)^2], \tag{4}$$

$$U_{bend} = \frac{1}{2}k_{bend}(\theta - \theta_0)^2[1 + C(\theta - \theta_0) + D(\theta - \theta_0)^2], \tag{5}$$

The coefficients corresponding to the interaction functions of the Pcff force field for water, nanoparticles and wall are presented in Table 1.

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) open source code is used to perform all calculations. First, we extract the data file required by LAMMPS through writing programming code, and then by writing the LAMMPS input file, we call the required functions from the reference program.

Table 1. Values of energy functions of water, nanoparticles and wall

Atom type	σ (Å)	ε (kcal/mol)	Load (e)	Molecular mas (gr/mol)
O	3.6080	0.2740	-0.7982	15.9994
H	1.098	0.0130	0.3991	1.0079
Cu	2.6775	3.8187	-	63.5460
Ag	3.0222	4.1002	-	107.6880
Au	3.0177	6.0980	-	196.9670
bond type	Bonding length/bending angle Reference	Tension/bending constant	Constant coefficient "C"	Constant coefficient "D"
O-H	R_0=0.970	K_{str}=563.28 (kcal/mol. Å^2)	C= -1428.22	D=1902.12
H-O-H	Θ_0=103.700	K_{bend}=49.84 (kcal/mol)	C= -11.60	D= -8.00

2.2. Mixing Rules

The Lorentz–Berthlot mixing rules provide a simple tool for calculating "i,j" interference parameters in order to take into account the heterogeneity between the regions of the atomic interactions of different molecules (Lee et al. 2016; Rajabpour et al. 2013).

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}, \tag{6}$$

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_{ii} + \sigma_{jj}\right), \tag{7}$$

2.3. Material and Methods

In the section we reviewed the calculation of thermo-physical properties such as thermal conductivity, specific heats and viscosity.

In this study, we are used the non-equilibrium molecular dynamics for calculating the thermal conductivity coefficient adjusting to Fourier's law. The strategy of this method is so that, in the equilibrium state of the system, disturbance is created in the walls by establishing a thermal flux. This is done by embedding two hot and cold zones in the walls with the temperature variations relative to the location calculated and the thermal conductivity coefficient obtained according as blow (Mao and Zhang, 2012; Bresme and Romer, 2013).

$$K = \frac{Q}{A\frac{dT}{dz}}, \tag{8}$$

The following procedure is carried out to perform the simulation and calculate the thermal conductivity coefficient of the nanofluids:

1. Building the simulation box.
2. Minimizing the energy of the simulation box.
3. Equilibrium of the simulation box temperature: All calculations are performed at a temperature of 298 °K and for this purpose, the simulation box by the NVT ensemble reaches temperature equilibrium for 10 ps, where the Nose-Hoover thermostat is used for keeping it constant (Chopkar et al. 2008). This thermostat is of velocity scaling type and maintains the temperature of the system by scaling the velocities and the instantaneous temperature, which is modeled based on the kinetic energy theory. Therefore, we can obtain the system temperature from equations 9 and 10.

$$\frac{3}{2}NK_BT = KE(T), \tag{9}$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}), \tag{10}$$

4. Another NVT ensemble is used to calculate the thermal conductivity of the nanofluid for 5 ns by considering each time step equal to 1 fs.
5. Obtaining dT/dz: in order to obtain temperature distribution in z direction, the channel depth is divided and the temperature is calculated in each part.
6. Calculating the thermal conductivity of nanofluid: thermal conductivity coefficient is obtained from the temperature gradient divided by the flux applied to the walls.

In order to reduce the computational volume, a cutoff radius of 12 Å for short-range interactions and Ewald summation method (Navas et al. 2016) is used for long-range (electrostatic) interactions by Equation 11. In the Ewald method, in order to calculate the interaction of point loads, a Gaussian distribution of the opposite load which is called real space is first considered around each point load to be shortened and converged rapidly. Then, a Gaussian load distribution which is opposite to the previous distribution and is called reciprocal space is added to the set.

$$\emptyset_{\text{elec}} = \frac{1}{2}\sum_{\text{i=1}}^{\text{N}}\sum_{\text{j=1}}^{\text{N}}\left\{\sum_{|\text{N}|=0}^{\infty}\left(\frac{\text{q}_\text{i}\text{q}_\text{j}}{4\pi\varepsilon_0}\frac{\text{erfc}(\alpha|\text{r}_\text{i}-\text{r}_\text{j}+\text{n}|)}{|\text{r}_\text{i}-\text{r}_\text{j}+\text{n}|}\right) + \right.$$
$$\left.\sum_{\text{K}\neq 0}^{\text{N}}\left(\frac{1}{\pi\text{L}^3}\frac{\text{q}_\text{i}\text{q}_\text{j}}{4\pi\varepsilon_0}\frac{4\pi^2}{\text{K}_\text{r}^{\,2}}\exp\left(-\frac{\text{K}_\text{r}^{\,2}}{4\alpha^2}\right)\cos\left(\text{K}_\text{r}(\text{r}_\text{i}-\text{r}_\text{j})\right) - \frac{\alpha}{\sqrt{\pi}}\sum_{\text{k=1}}^{\text{N}}\left(\frac{\text{q}_\text{k}^{\,2}}{4\pi\varepsilon_0} + \frac{2\pi^2}{3\text{L}^3}\left|\sum_{\text{k=1}}^{\text{N}}\frac{\text{q}_\text{K}}{4\pi\varepsilon_0}\text{r}_\text{k}\right|^2\right)\right\}, \tag{11}$$
$$\text{K}_\text{r} = \frac{2\pi\text{n}}{\text{L}}, \alpha = \frac{5}{\text{L}},$$

Radial distribution function is used to determine the distribution of distances between two types of α and β atoms, whose mathematical relation is as Equation 12 based on statistical mechanics.

$$g_{\alpha\beta}(r) = \frac{N}{\rho N_\alpha N_\beta}\sum_{i=1}^{N_\alpha}\sum_{k}^{N_\beta}\langle\delta(r-|r_k-r_i|)\rangle, \tag{12}$$

In fact, the radial distribution function specifies the tendency between atoms to stand next to each other. If the molecules approach each other, the intensity of the RDF peak value becomes greater and if separated, the peak values of the RDF diagram are reduced.

With obtaining the enthalpy of nanofluid from its kinetic and internal energy at different temperature due to the following, the slope of enthalpy-temperature shows the specific heat at constant pressure (Mao and Zhang, 2012);

$$H = E_e + PV = K_e + P_e + PV, \tag{13}$$

$$C_P = \frac{1}{M}\frac{\partial H}{\partial T}\bigg|_P, \tag{14}$$

Also, the slope of energy of the system will show the specific heat of nanofluid at constant volume as blow (Mao and Zhang, 2012);

$$C_V = \frac{1}{M}\frac{\partial E_e}{\partial T}\bigg|_v, \tag{15}$$

To calculate the viscosity, we used the equilibrium molecular dynamics methods (Bushehri et al. 2016; Lee et al. 2016). The Green-Kubo's equations has been used at equilibrium condition as blow (Hyzorek and Tretiakov, 2016);

$$\eta_{x,y} = \frac{V}{K_B T}\int_0^{\infty} < P_{x,y}(0)\, P_{x,y}(t) > dt\,, \tag{16}$$

$$P_{x,y} = \sum_{j}^{N} m_j\, v_{xj} v_{yj} + \frac{1}{2}\sum_{i\neq j}^{N} r_{xij}\, F_{yij}\,, \tag{17}$$

3. Discussion the result

In the section, the parametric studies have been conducted and the effect of some physical parameters such as nanoparticle size and dimension of nanochannel on the thermo-physical properties have been studied.

3.1.Validation

For calculating the thermal conductivity coefficient of the nanofluid, it is required to first validate the accuracy of the results. For this purpose, the thermal conductivity coefficients of pure water and then water nanofluid inside nanochannel with copper wall have been calculated using the non-equilibrium molecular dynamics simulation method and the NVT ensemble.

To calculate the thermal conductivity coefficient of water, a simulation box having dimensions of 30×30×30 Å and a number of 900 molecules of water has been used (Mao and Zhang, 2012), in which the water density in this case is equal to 996.67 kg/m^3. In the Z direction, the 30-angstrom length is divided into 20 equal parts. Since the simulation box is symmetric, the behavior of temperature changes is exactly inverted from the middle of the simulation box and thus, the temperature distribution in the range of 0-15 angstroms can be investigated. The results obtained from the simulation of non-equilibrium molecular dynamics related to the distribution of water temperature in z direction of the simulation box subjected to a thermal flux of 7.02×10^{-5} kcal/(mole.fs.Å^2) are illustrated in Figure 1.

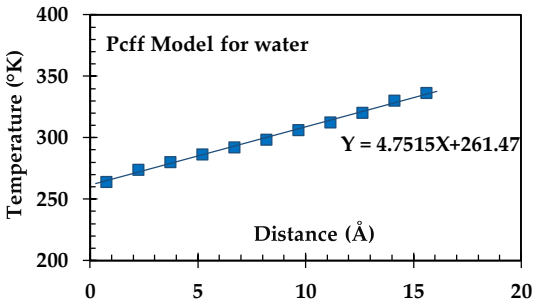


Figure 1. Diagram of water temperature distribution in nanochannel with Pcff force fields

As is shown in Figure 1, the temperature distribution has got completely linear, which indicates that the number of molecules and the calculation time considered have been very appropriate for calculating the thermal conductivity of the fluid. The value of the thermal conductivity coefficient calculated for pure water is 0.53 W/(m.°K), which is of approximately 13% difference with the experimental value provided by Ramires et al. (1995) at the temperature of 298 °K that is equal to 0.61 W/(m.°K). Using the TIP3P model, the obtained thermal conductivity coefficient for pure water for the same simulation equal to 0.745

W/(m.°K), which is of approximately 22% difference with the provided experimental value. Concerning less error rate compared to other models, the Pcff force field provides more acceptable results for calculating the thermal conductivity coefficient of water; therefore, force field is used in order to calculate the molecular interactions of nanofluid inside nanochannel.

For determining the method of calculating viscosity, the viscosity of water is obtained from two methods of equilibrium and non-equilibrium molecular dynamics and then, the method with less error percentage is used in the calculations of thermo-physical properties of nanofluids.

To calculate water viscosity, equilibrium molecular dynamics is used along NVT ensemble at a temperature of 298 °K and Pcff force field, considering alternative boundary conditions, cutoff radius of 12.5 Å, and Ewald summation method for long-range (electrostatic) interactions (Bushehri et al. 2016; Lee et al. 2016; Mao and Zhang, 2012; Muller-Plathe, 1999). Using this method, the water viscosity is obtained equal to 1.37×10^{-4} Pa.s that is of about 8.90×10^{-4} Pa.s difference with the experimental values (Mao and Zhang, 2012). There are also reported errors up to 70% in the previous studies (Mao and Zhang, 2012).

In order to validate the method of calculating specific heat of water, we obtain the specific heat in constant pressure and volume and compare it with experimental values. The specific heat in constant pressure for water at a temperature of 298 °K and a pressure of 1 atm is calculated in the NPT ensemble equal to 5.143 $kj.kg^{-1}.°K^{-1}$, which there is about 23% error in comparison to the experimental value of 4.18 $kj.kg^{-1}.°K^{-1}$ (Mao and Zhang, 2012).

The specific heat in constant volume for water at a temperature of 298 °K and a pressure of 1 atm is calculated in the NVT ensemble equal to 4.545 $kj.kg^{-1}.°K^{-1}$, where there is about 9% error in comparison to the experimental value of 4.18 $kj.kg^{-1}.°K^{-1}$ (Mao and Zhang, 2012).

3.2. Effects of Nanoparticle Size

By increasing nanoparticle size, in fact, their contact surface is reduced relative to their mass and this can influence their physical and thermal properties. Therefore, the effect of nanoparticle size on the nanofluid functional properties is investigated for two nanoparticles of gold and silver in the copper nanochannel. First, the equilibrium density of different nanofluids with 5 nanoparticle sizes is investigated using equilibrium molecular dynamics method and NPT ensemble at a temperature of 298 °K. The simulation box is manufactured containing a nanoparticle along with water molecules with initial density of 1 g/cm^3, where the number of water molecules is determined considering 5% vol. of nanoparticle, and by increasing of the nanoparticle diameter; the number of the used water molecules is increased. As is shown in Table 2, the density of gold nanofluid is greater than silver; since the gold and silver nanoparticles are of the same size, the only determining factor of density values is their molecular mass. Since gold is of greater molecular mass relative to silver (196.96 g/mol and 107.86 g/mol, respectively), it is expected that it has a greater density, as well.

Table 2. Equilibrium properties and viscosity of silver and gold nanofluids for 5 different anoparticle sizes

Nanoparticle size (Å)	Container size at x and y directions		The number of water molecules		Density (g/cm^3)		viscosity ($\times10^{-4}$ Pa.s)		μ_{NF}/μ_w	
	Ag	Au	Ag	Au	Ag	Au	Ag	Au	Ag	Au
6	16.38	16.31	595	592	1.472	1.919	3.45	3.27	1.45	1.42
7	21.21	21.12	995	991	1.469	1.913	3.08	2.54	1.30	1.10
8	25.01	25.61	1462	1456	1.466	1.909	2.82	1.27	1.19	0.98
9	28.45	29.30	2035	2025	1.469	1.908	2.49	1.15	1.08	0.93
10	33.98	34.81	2555	2680	1.468	1.905	2.28	1.85	0.99	0.80

As the results show, the increase in nanoparticle size made no significant changes in the nanofluid density and there will be a relatively low loss of density. Since the nanofluids are based on 5 volume percentages of nanoparticles and the volume is the same for all nanofluids, the volume increases with increasing particle size and the volume of water increases equally, which does not make much change in the density.

3.2.1. Viscosity

Using the equilibrium molecular dynamics and Green-Kubo's relations, the viscosity of silver and gold nanofluids with different sizes of nanoparticles was calculated at 298 °K and summarized in Table 2. The results obtained from molecular dynamics simulation show that the increase of nanoparticle size, the viscosity of nanofluids decreases, which has been observed in previous studies as well (Meyer et al. 2016; Kang et al. 2006;). The recent study was conducted on the viscosity of nanofluid with various nanoparticles, such as carbon nanotubes, SiO_2, Al_2O_3, TiO_2, ZrO_2, shows that increase in the nanoparticle diameter leads to reduce viscosity (Vakili-Nezhaad et al. 2017; Rudyak et al. 2016). In fact, by increase of nanoparticle size, the nanoparticle surface relative to its mass is recused, and it causes less interactions with water molecules and the nanochannel walls and makes the nanofluid require less force for displacement and fluidization. The results also show that the decrease in viscosity with the increase of gold nanoparticles is higher than that of silver nanoparticles, which can be due to the higher hydrophilicity of gold nanoparticles relative to silver nanoparticles. The hydrophobic and hydrophilic behaviors of the nanoparticles are investigated in the following.

3.2.2. Radial Distribution Function

To determine the hydrophilic behavior of nanoparticles with increase of size, the diagram of the radial distribution function (RDF) of water molecules with gold and silver nanoparticles in water fluid is plotted in Figure 2. As the results show, the first peak for silver nanofluid is at a distance of 3.25 Å, representing that water molecules tend to be placed at 3.25 Å from the silver nanoparticle surface, which is 3.15 Å for gold nanofluid. In fact, one can state that the gold nanoparticle possesses a greater hydrophilic property than silver nanoparticles and maintains them close to itself. The results also show that by increase in the size of the nanoparticle, the tendency of water molecules to be present next to it diminished. In fact, by increasing the size of the nanoparticle, the number of atoms deposited on the surface becomes lower than the total atoms forming the nanoparticle. Comparison of RDF diagram for silver and gold nanofluids shows that gold nanoparticles are of greater tendency to water relative to silver nanoparticles, because they are of a closer distance to each other and a higher peak intensity than silver nanoparticles.

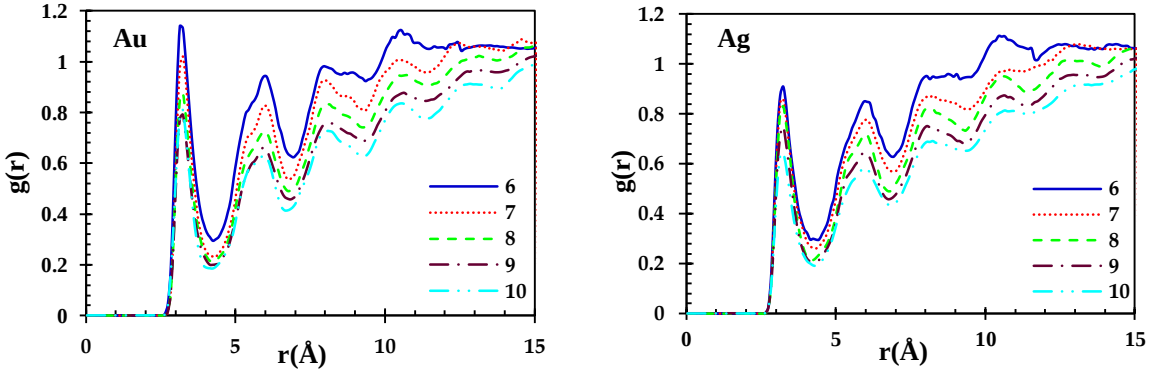


Figure 2. Diagram of radial distribution function (RDF) of silver and gold nanoparticles in water fluid having 5 nanoparticle sizes

3.2.3. Thermal Conductivity Coefficient of nanofluids

The thermal conductivity coefficient of gold and silver nanofluids with different nanoparticle sizes at the temperature of 298 °K, was calculated with the help of non-equilibrium molecular dynamics method that is presented in Table 3. The results show that the thermal conductivity coefficient of the nanofluid is reduced with increase in the nanoparticle size, it should be noted that since the volume percentage of nanoparticles in water is constant in all sizes, the increase in the diameter of the nanoparticle increases the number of water molecules. However, the contact surface of the nanoparticle with water molecules decreases; therefore, the heat transfer from nanoparticle to water decreases and the nanofluid thermal conductivity decreases, accordingly. The results of the RDF related to nanoparticle-water also confirm that the tendency of water molecules to be placed next to nanoparticles becomes lower with increasing the size of the nanoparticle. It should be kept in mind that in the heat transfer of nanofluids, the number of water molecules, placed on the surface of the nanoparticle, plays a major role in transferring heat from the fluid to the nanoparticle and vice versa. Investigation of the studies performed on aluminum oxide-water nanofluid shows that increase of nanoparticle size causes the thermal conductivity coefficient reduce (Teng et al. 2010; Chon et al. 2005). Moreover, for other nanoparticles such as ZnO and TiO_2 metal oxides, experimental results indicate that increase of the nanoparticle size is associated with a decrease in the thermal conductivity coefficient of the nanofluid (Tawfik, 2017; Chopkar et al. 2008).

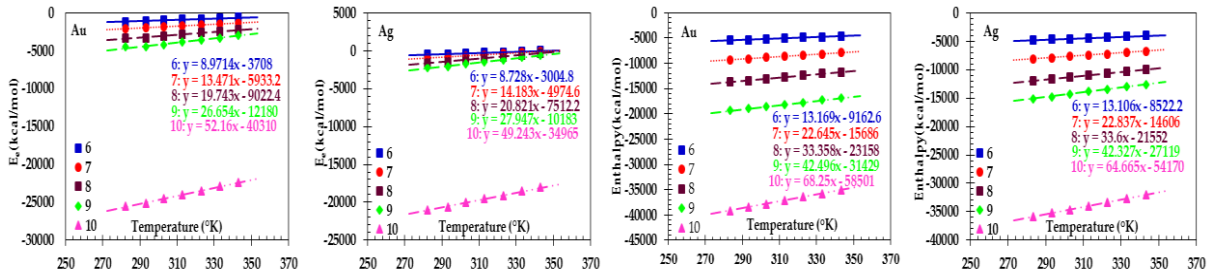
Table 3. Values of thermal conductivity of nanofluids with different nanoparticle sizes

Nanoparticle size (Å)	Thermal flux ($\times 10^{-5}$ kcal /mole.fs.Å^2)		dT/dz (°K/Å)		Thermal conductivity (W/m.°K)	
	Au	Ag	Au	Ag	Au	Ag
6	5.737	7.198	4.259	5.796	0.936	0.863
7	5.857	5.397	4.583	3.995	0.888	0.939
8	4.801	4.815	3.863	3.857	0.863	0.867
9	3.558	2.009	2.919	2.556	0.847	0.846
10	2.918	3.185	2.369	2.823	0.756	0.784

As the results show, increasing the size of nanoparticle results in a decrease in the thermal conductivity coefficient, so that this variation is linear for gold nanofluid, but for the silver nanofluid, first an increase and then a decrease in the thermal conductivity coefficient is observed with increase in the particle size.

3.2.4. Specific Heats of nanofluids

Their energy values must be used to determine the thermal properties of nanofluids, so that the changes of enthalpy with temperature are used to calculate Cp, and the changes of energy potential be used with temperature to calculate Cv. Thereupon, the diagrams of potential energy and enthalpy versus temperature are depicted in Figure 3 for silver and gold nanofluids with different nanoparticle sizes. The results showed a completely linear relationship between the potential energies and the temperature, which indicates the equilibrium of the system. The results show that potential energy decreases with increasing of the size of nanoparticle, so that this reduction is negligible for nanoparticles of less than 9 Å, but it decreases intensively for nanoparticles with a diameter of 1 nm. The results also show that the process of potential energy variations with the temperature increases by increasing the nanoparticle size.



a- potential energy for gold b-potential energy for silver c-Enthalpy for gold d-Enthalpy for silver

Figure 3. Diagram of potential energy and enthalpy versus temperature for gold and silver nanofluids with different nanoparticle sizes

Also, the results showed a completely linear relationship between the enthalpies and temperature and the nanofluid enthalpy decreases with increase in the nanoparticle size, where an almost linear trend is observed for them. The results also show that the variations of enthalpy versus temperature increase by increasing the nanoparticle size, which is almost the same for both nanofluids. By using potential energy and enthalpy, Cv and Cp values for nanofluids are calculated as summarized in Table 4.

Table 4. Values of specific heat of nanofluids in nanochannel with different nanoparticle sizes

Nanoparticle size	Enthalpy ($kj.kg^{-1}$)		Cp ($kj.kg^{-1}.°K^{-1}$)		Cv ($kj.kg^{-1}.°K^{-1}$)	
(Å)	Ag	Au	Ag	Au	Ag	Au
6	-270.19	-225.24	0.77	0.57	2.19	1.74
7	-574.16	-508.54	1.68	1.29	2.13	1.57
8	-1181.07	-1046.59	3.43	2.64	2.13	1.56
9	-2181.39	-2182.57	6.35	4.94	2.05	1.52
10	-8767.55	-7423.21	16.23	13.27	2.88	2.24

As the results show, by increase in the nanoparticle size, the nanofluid enthalpy decreases, which is of less value for silver nanofluid. The results also show that by increase in the nanoparticle size, Cp value of the nanofluid increases, where the values of specific heat capacity calculated at the constant pressure for silver nanofluid are greater than that for gold nanofluid. In fact, by increasing of the nanoparticle size, its volume is increased and more heat is needed to be consumed for changing the nanofluid temperature, so that in addition to the fluid, the nanoparticle temperature is also raised up to one degree, and since silver has a higher thermal conductivity than gold, it requires more heat for increasing the temperature. In the case of Cv, the calculated results indicate that in the nanofluid having nanoparticle size of less than 9 Å, increasing of the nanoparticle size leads to a small reduction in the Cv value, however for the nanofluid with 1 nm of nanoparticle size, the Cv increase, suddenly.

3.3. Investigation of the Effects of Channel Size

Since the properties of the nanofluid inside nanochannel are also the case of discussion, the channel size can be of a great effect on the nanofluid properties due to its nanoscale dimensions. Therefore, the thermal conductivity and viscosity properties of gold and silver nanofluids with nanoparticle size of 0.5 nm and 2% vol. nanoparticle at the temperature of 298 °K are investigated using equilibrium and non-equilibrium molecular dynamics method to survey the size of different copper nanochannels.

3.3.1. Viscosity

The viscosity of silver and gold nanofluids is calculated at various depths, which is presented in Table 5. The results obtained from the simulation show that the depth of the copper channel does not have much effect on the viscosity of water and silver and gold nanofluids. In fact, there is an interaction between the water-water, water-channel walls, water-nanoparticles, and nanoparticles-channel walls during the passage of fluid from the nanochannel, where no changes occur in them with increase of the channel size. This is because the channel size begins from 2.5 nm and the nanoparticles are actually located in the center of the channel and thus, the increase in the channel depth does not change the interaction between the nanoparticle and the channel wall. Given that the surface of the nanoparticle and the channel wall have not changed, their interaction with water molecules will not accordingly not change changed, and no change is practically occurred in the calculation of viscosity.

Table 5. Equilibrium properties and viscosity of silver and gold nanofluids with different channel depths

Channel depth (nm)	The number of nanoparticle	Container size at x and y directions		The number of water molecules		viscosity ($\times 10^{-4}$ Pa.s)		μ_{NF}/μ_w	
		Ag	Au	Ag	Au	Ag	Au	Ag	Au
2.5	1	29.44	30.88	700	788	2.78	2.40	0.94	0.81
5	2	29.44	30.88	1400	1576	2.75	2.36	0.95	0.81
7.5	3	29.44	30.88	2100	2364	2.81	2.49	0.96	0.85
10	4	29.44	30.88	2800	3152	2.78	2.38	0.95	0.81

3.3.2. Thermal Conductivity Coefficient

In order to investigate the effect of the copper nanochannel depth on the thermal conductivity coefficient, it has been calculated using non-equilibrium molecular dynamics method at the temperature of 298 °K and channel depth of 2.5 nm to 10 nm for water and silver and gold nanofluids. Since the thermal conductivity coefficient obtained in the non-equilibrium molecular dynamic method by establishing thermal flux in the walls, the cross sections of the nanochannel wall for water, silver nanofluid, and gold nanofluid are considered equal to 3.16×3.16 nm^2, 2.94×2.94 nm^2, and 3.10×3.10 nm^2, respectively. To make a better comparison between water and the nanofluids, it is attempted to consider all the conditions as identical. Because the densities of the nanofluids are different and the nanochannel depths are considered the same for all the nanofluids, the considered surfaces are slightly different from each other. The diagram of temperature distribution along the nanochannel depth is plotted in Figure 4. As can be seen from the results, the temperature distribution diagrams for water and the other nanofluids in different nanochannel depths are linear and uniform, representing that the number of the simulation stages and details are selected properly and there are not temperature fluctuations in the system. The results show that by changing the channel depth, the temperature distribution diagrams are actually changing, so that the temperature of the fluid in the channel center is strongly dependent on the nanochannel depth and the nanofluid material. For water, the distribution of temperature in the center of the nanochannel starts at a temperature of 327 °K and ends at 383 °K at a depth of 10 nm, where the trend for silver nanofluid is also similar to water, except that the temperature ranges between 332-380 °K. However, there is also a different behavior for the gold nanofluid, so that the temperature of the channel center reaches its maximum value (i.e., 396°K) at a channel depth of 5 nm, and it changes slightly within the range with more increase in the depth of the channel.

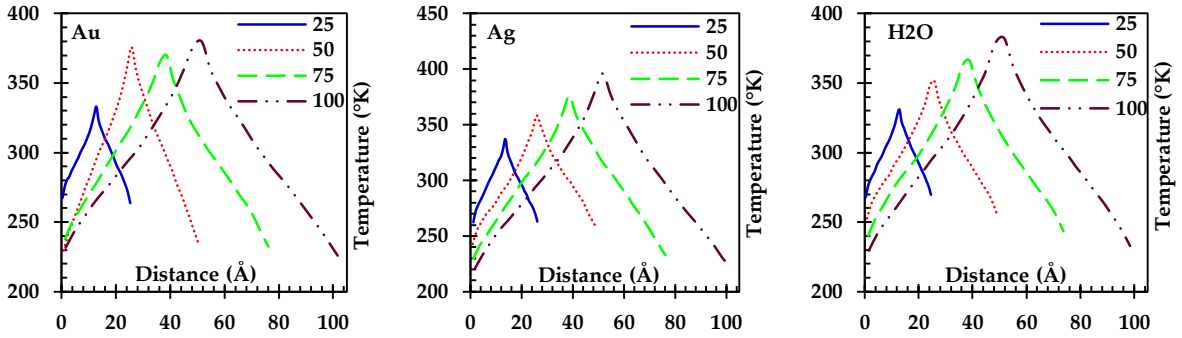


Figure 4. Diagram of temperature distribution in different nanochannel depths for water, silver and gold nanofluids

The values of thermal conductivity coefficient for water and silver and gold nanofluids are calculated using the slope of the diagram of temperature distribution and the thermal flux applied on the walls that are presented in Table 6. The results indicate that the thermal conductivity coefficient is a function of the nanochannel depth, which increases with increase of the nanochannel depth. The results also show that at a depth of 2.5 nm of the nanochannel, the thermal conductivity coefficient is almost identical for water and the other nanofluids, so that this behavior is approximately continued to depth 7.5 nm and no significant difference is observed in the thermal conductivity coefficient of water with gold and silver nanofluids. Therefore, it can be stated that the calculation of thermal conductivity coefficient by using non-equilibrium molecular dynamics method is strongly dependent on the channel size, and it increases with increase of the depth (the size of the simulating channel in *z* direction). This very important point has not yet been taken into consideration and its effect has not been studied so far.

Table 6. Values of thermal conductivity coefficient of water, silver and gold nanofluids for different channel sizes

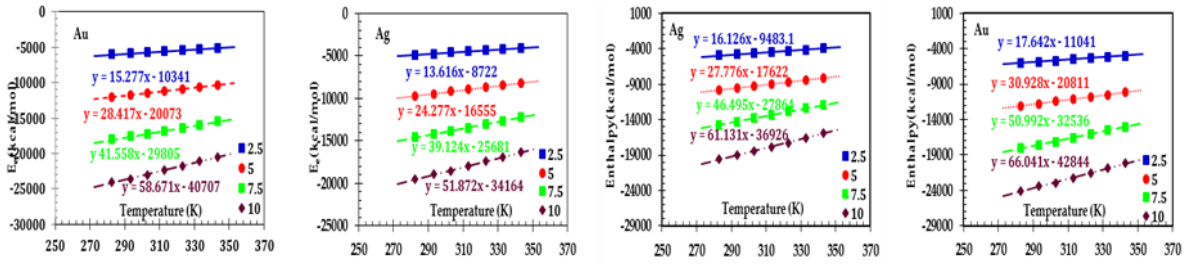
Channel size (nm)	Thermal flux ($\times 10^{-5}$ kcal /mole.fs.Å^2)			dT/dz (°K/Å)			Thermal conductivity (W/m.°K)		
	water	Au	Ag	water	Au	Ag	water	Au	Ag
2.5	3.202	3.167	3.479	4.185	4.195	4.978	0.53	0.55	0.52
5	3.636	3.865	3.878	3.502	3.881	3.978	0.72	0.74	0.71
7.5	3.849	3.965	4.197	3.072	3.277	3.352	0.87	0.89	0.88
10	3.903	4.242	4.329	2.815	2.667	2.896	0.96	1.17	1.09

The results showed a linear relationship between thermal conductivity coefficient and the nanochannel depth, and with increase in the nanochannel depth, the thermal conductivity coefficient increased. Investigation of the previous studies show that for argon and liquid argon nanofluids, the thermal conductivity calculated by equilibrium molecular dynamics and the Green-kubo method, as well as the non-equilibrium molecular dynamics method, increases with the depth of the channel. Moreover, by increasing the channel depth by more than 10 nm, the thermal conductivity of the argon fluid becomes constant (Frank et al. 2015; Hyzork et al. 2016).

3.3.3. Nanofluid Specific Heat

In Figures 5, the potential energy and the enthalpy of nanofluid in a channel with different depths are plotted as a function of temperature for the gold and silver nanofluids. The results show that by increasing of the channel depth, the nanofluid enthalpy decreases, which a linear trend is seen for this behavior that is similar in both nanofluids. For potential energy, a

completely similar behavior is observed. In fact, enthalpy and potential energy are of the intensity properties of each substance that are not dependent on the amount and volume of the system. Therefore, by increasing of the channel depth, it is expected that the enthalpy and potential energy will not change; however, it is observed in the following diagrams that the enthalpy and potential energy change with increasing channel depth (increasing of the nanofluid volume). It must be noted that here, the unit of energy is kcal/mol, in which the mol means a mole of the simulation box, which its value changes by increasing of the channel depth. Therefore, it is logical to observe these changes and it can be seen that by increasing of the channel depth, since the amount of the nanofluid is increased, the energy values become more negative, the absolute value of which indicates increasing of energy by increasing of the channel depth.



a- potential energy for gold b-potential energy for silver c-Enthalpy for gold d-Enthalpy for silver

Figure 5. Diagram of potential energy and enthalpy versus temperature for gold and silver nanofluids with different depths

The values of Cv and Cp for the silver and gold nanofluids are calculated using the potential energy and enthalpy, which are presented in table 7. The results indicate that no change occurred in the enthalpy of the nanofluids with increase of the channel depth and its values are almost constant. Hence, it can be said that the nanofluid enthalpy is independent of the channel depth. Since the enthalpy, and values of Cv and Cp are of the intensity properties of any material and depend on the quality of the nanofluid not the size of the container in which it is calculated, they should not be dependent on the material volume, meaning that their values must not change by increasing the channel depth. Moreover, the entire operational conditions such as temperature, volume percentage, and the size of the nanoparticles are constant in all the channels. Therefore, the values of enthalpy, Cp, and Cv calculated from molecular dynamics simulation must also be identical.

Table 7. Values of specific heat of nanofluids in nanochannel with different depths

Channel depth (nm)	Enthalpy (kj.kg^{-1})		C_p (kj.kg^{-1}.°K^{-1})		C_v(kj.kg^{-1}.°K^{-1})	
	Ag	Au	Ag	Au	Ag	Au
2.5	-1171.98	-1066.91	4.03	3.25	3.41	2.82
5	-1166.77	-1067.94	3.47	2.85	3.04	2.62
7.5	-1170.23	-1069.14	3.88	3.13	3.26	2.55
10	-1169.25	-1069.61	3.82	3.04	3.24	2.71

4. Conclusions

In this study, with the help of molecular dynamics method the effects of the size and the channel depth on the functional properties of water nanofluid containing silver and gold particles in copper nanochannel has investigated.

The results indicated that viscosity of the nanofluids decreases with increasing of the sizes of nanoparticles and this reduction for gold nanoparticle is greater than silver. This behavior

can be interpreted due to the higher hydrophilic feature of gold nanoparticle as compared to silver nanoparticle. Moreover, the channel depth does not affect the viscosity of water and other nanofluids.

Non-equilibrium molecular dynamics method for calculating thermal conductivity coefficient has been used. The results showed that since the volume percentage of nanoparticle in water is constant for all sizes, the number of water molecules increases with increase in the nanoparticle size. Consequently, the contact surface of nanoparticles with water molecules as well as the heat transfer from nanoparticle to water is reduced and as a result, the thermal conductivity coefficient of nanofluid reduces. On the other hand, the results show that the thermal conductivity increases as a function of the nanochannel depth when the channel depth is increased. The results also show that for a nanochannel depth of 2.5 nm, the thermal conductivity confident for water is almost the same as that for other nanofluids. Thus, this behavior is also true up to a depth equal to 7.5 nm, and the thermal conductivity of water does not differ much with the gold and silver nanofluids to this depth. This is a very important point and its effect have not been considered yet.

To assess the interactions and tendency between water and nanoparticle, radial distribution function (RDF) analysis was used. The results showed that the tendency of water molecules to be next to gold nanoparticles is higher than silver that causes the contact surface of water with the nanoparticle to become higher.

Specific heat has been surveyed with the help of equilibrium molecular dynamics method. The results show that, the increase of the nanoparticle size reduces the nanofluid enthalpy and increases the specific heat; however, change of the nanochannel depth does not affect the values of specific heat capacity and enthalpy, significantly.

5. Nomenclature

Ag	Silver nanoparticle	k_{bend}	Bending constant ($kcal.mol^{-1}$)
Au	Gold nanoparticle	M	Total mass
DI	Diffusion coefficient (m^2s^{-1})	m	Molecular mass ($g.mol^{-1}$)
E_i	Total of Kinetic and Potential energies ($kcal.mol^{-1}$)	$N_{\alpha,\beta}$	The number of α and β atoms
J_q	Thermal flux ($kcal.mol^{-1}fs^{-1}Å^{-2}$)	$q_{i,j}$	Minor load (e)
K	Therml conductivity coefficient ($Wm^{-1}K^{-1}$)	r	Distance between atoms (Å)
k_B	Boltzman's constant	T	Temperature (^oK)
KE	Kinetic energy ($kcal.mol^{-1}$)	U	Potential energy ($kcal.mol^{-1}$)
K_r	Mutual vector	V	volume
k_{str}	Tension constant ($kcal.mol^{-1}Å^{-2}$)		

Greek signs

ε_0	Vacuum permittivity
ε_{ij}	potential energy well ($kcal.mol^{-1}$)
σ_{ij}	r value in u(r)=0 of Leonard-Jones potential (Å)
$\eta_{x,y}$	Viscosity

Subscripts

Intra	Intramolecular
Inter	Intermolecular
nf	Nanofluid
W	Water

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