# EFFECTS OF NANOPARTICLES CONCENTRATION TO TRANSPORT PROPERTIES OF NANOFLUIDS USING MOLECULAR DYNAMICS SIMULATION

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# DECLARATION

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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Date……..

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This thesis is the result of my own investigations, except where otherwise stated.
Other sources are acknowledged by giving explicit references.
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# LIST OF ABBREVIATIONS AND SYMBOL

| Abbreviations | Explanation |
|---|---|
| LAMMPS | Large-scale Atomic/Molecular Massively Parallel Simulator |
| MD | Molecular Dynamic |
| EMD | Equilibrium Molecular Dynamic |
| NEMD | Non-equilibrium Molecular Dynamic |
| SPH | Smoothed particle hydrodynamics |
| PBC | Periodic boundary condition |
| NP | Nanoparticle |
| K | Degree Kelvin |
| Pa.s | Pascal second |
| Å | Angstrom |
| V | Volume |
| $K_B$ | Boltzmann constant |
| $\mu$ | Viscosity |
| L-J | Lennard-Jones |
| g(r) | Radial distribution function |
| m | Mass |
| n | Molarity |
| $\rho$ | Density |
| N | Total number of particles |
| Φ | L-J potential |
| $P_{xy}$ | Stress tensor |
| $B_v$ | Bulk modulus |
| $A$ | Avogadro constant |
| O-H | Oxygen-Hydrogen linkage |
| $k$ | Thermal conductivity |
| $\emptyset$ | Volume concentration |

# ABSTRAK

Bendalir nano adalah bendalir pemindah haba yang berpotensi besar dalam menggantikan bendalir pemindah haba konvensional. Bendalir nano terdiri daripada zarah yang bersaiz nano dengan saiz lingkungan 1-100nm yang berlegar di dalam bendalir asas. Kehadiran bendalir nano adalah untuk meningkatkatkan sifat perpindahan bendalir asas. Namun begitu, cabaran utama utama untuk merealisasikan hasrat ini ialah kelemahan dalam memahami sifat fizik zarah. Halangan yang sering terjadi adalah peningkatan kelikatan dalam usaha meningkatkan konduksian haba bagi bendalir nano. Bagi mengisi jurang penylidikan, tesis ini menetapkan objektif untuk melihat kesan bilangan zarah-zarah nano dalam mempengaruhi kelikatan dan kekonduksian haba di dalam suhu tertentu. Simulasi dinamik molekul dengan kaedah Green Kubo telah digunapakai untuk menjalankan eksperimen penyerakan zarah nano di dalam bendalir nano. Zarah nano yg digunakan dalam simulasi ini ialah zarah nano kuprum yang diselerakkan di dalam air. Di akhir simulasi didapati, ketumpatan asal air bertambah apabila zarah nano diselerakkan di dalam air. Ketumpatan air bertambah dengan bertambahnya bilangan zarah kuprum yang diselerakkan di dalam sistem. Kelikatan dan kekonduksian haba juga bertambah selari dengan peningkatan zarah kuprum di dalam bendalir nano. Kelikatan bendalir didapati meningkat dengan kadar yang banyak disebabkan berlaku penggumpalan antara zarah-zarah kuprum. Kekondukisan haba juga menunjukkan peningkatan yang sangat ketara.

# ABSTRACT

Nanofluid has a big potential to replace conventional fluid as heat transfer medium. Nanofluid consists of nanoparticles with size range 1-100nm and been dispersed in a base fluid. The existence of nanofluid is to improve the transport properties of base fluid. However, the main challenge to accomplish this is the lack of knowledge related to atomic physics. The common problem faced is the increases of viscosity in order to attain a higher thermal conductivity. To fill the research gap, the objectives of this thesis are to study the effect of nanoparticles towards viscosity and thermal conductivity at a desired temperature. Molecular dynamic simulation using Green Kubo method was implemented to conduct the simulation of dispersion of nanoparticles in nanofluid. Copper nanoparticles have been chosen to simulate with water. In the end of simulation, it is found out that density of water increased when the nanoparticles are dispersed into the water. The density of water increased with the addition number of copper atoms in the system. The viscosity and thermal conductivity also increased respected to the increase of nanoparticles concentration. There was a big increasing in viscosity value that might cause by composition of copper to copper atoms. There also showed an obvious increasing in thermal conductivity which is too significant.

# CHAPTER 1: INTRODUCTION

The biggest challenge in industries like electronics, manufacturing, transportation and nuclear reactor application is cooling. Cooling has become the major technical challenge since centuries ago. When talk about cooling system, we cannot run from fluid where all cooling systems are used various types of fluid. However, single-phase heat transfer fluids such as water, engine oil, ethylene glycol, propylene glycol and transformer oil are very poor in performance in industry due to low values of their thermal conductivity. The heat transfer intensification is very important to achieve significant energy and cost savings. In order to achieve better cooling performance, many efforts have been made in enhancing these fluids properties. From Table 1.1 shows that water possesses the highest thermal conductivity amongst those heat transfer fluids. Interestingly, water is only two to three orders of magnitude lower than metals and metal oxides. It is therefore proposed that a potential heat transfer fluid produced by dispersing nanometer size solid particles into liquid to elevate its inherent poor thermal conductivity, namely nanofluids be explored. The exploitation of nanofluids with enhanced thermal conductivity requires understanding the properties at the fundamental level. This thesis addresses the thermal transport of nanofluids at nanoscale level. This chapter presents an introduction to nanofluids and states the problem statement of the recent research. Towards the end of this chapter, the objectives of this thesis are spelt out and the scope of this research is highlighted.

## 1.1 Nanofluids

A nanofluid is a fluid that contain nanoparticles. It is engineered by suspending solid nanoparticles or nanofibers with size of 1-100nm into conventional heat transfer fluids (Choi, S. U. S., 1995). Nanoparticles are useful in enhancing fluid properties. Nanoparticles enrich thermo-physical, chemical and physiochemical fluid properties that are related to most biomedical and engineering fluids. A significant characteristic property of nanoparticle diffusion is related to nanoparticle surface area to volume ratio; this property gives nanoparticle an advanced feature over its counter-sized particles, i.e. micro-particles (Iijima M, Kamiya H, 2009). The suspension of

nanoparticles (nanofluid) is favorable than suspension of micro or millimeter sized particles because it is more stable due to their high surface to volume ratio which is capable of minimizing erosion and clogging. In addition, nanofluids have better stability because of the larger surface-area-to-volume ratio of nanoparticles which overcome differences in density. Therefore, the utilization of nanofluids opens the potentialities to improve the efficiency of thermal system while maintaining the existing footprint. On the other hand, nanofluids can deliver the same efficiency of the cooling system at smaller and lighter footprint as reduced inventory of heat transfer fluids. In time, improved cooling performance and lower manufacturing or operating cost in thermal system are the major advantage gained from the application of nanofluids. This evolvement of heat transfer fluid can be used in various applications such as automotive cooling system, solar collector, heat exchanger etc. Typical types of nanoparticles used in nanofluids' related researches are titanium oxide (Jia L, Peng L, Chen Y, Mo S, Li X, 2014) (Said Z, 2014), aluminium oxide (Ariana MA, Vaferi B, Karimi G., 2015) (Mallick SS, 2013) and copper (Muthtamilselvan M, 2010) (Wei X, 2010). Water, ethylene glycol and oil are often used as a base fluid in nanofluids.

**Table 1.1 Room-temperature thermal conductivity for solids and liquids (Eastman, J. A., Phillpot, S. R., Choi, S. U. S., & Keblinski, P., 2004)**

| Material | | Thermal conductivity at room temperature (W/m.K) |
|---|---|---|
| Metallic solids | Silver | 429 |
| | Copper | 401 |
| | Aluminium | 237 |
| Nonmetallic solids | Diamond | 3300 |
| | Carbon nanotubes | 3000 |
| | Silicon | 148 |
| | Alumina ($Al_2O_3$) | 40 |
| Metallic liquids | Sodium at 644K | 72.3 |
| Nonmetallic liquids | Water | 0.613 |
| | Ethylene glycol | 0.253 |
| | Engine oil | 0.145 |

For the sake of this stimulating benefit, many researches in the scientific community are being carried out with the goal of realizing various applications of nanofluids. Earlier, research concentrated mostly on thermal conductivity, only recently afterwards researchers investigated into other area of interest such as

viscosity, specific heat, density, critical heat flux, heat transfer coefficient, entropy and wear resistance. From the researchers works, nanofluids can be produced by two methods which are called as the two-step process and the one-step process. In a regular two-step process, the nanoparticles are first produced in dry powder form and then mixed with the heat transfer fluids. Yet, these nanofluids are not stable even though the stability could be upgraded by pH control and surfactant addition. In the one-step process, the synthesis and dispersion of nanoparticles are done at the same time. These nanofluids have better stability due to the weakened Van der Waals force between nanoparticles. However, the two-step process is always preferred by most researchers because of its low setup cost.

## 1.2 Problem Statement

The applications of nanofluids appear promising in heat transfer industry but the development of this field is inhibited by:

a) Thermal conductivity enhancement cannot be explained by classical theories.
b) Lack of agreement between results obtained in different laboratories.
c) Thermal conductivity enhancement is always accompanied by higher viscosity.

Experimental studies have higher expenses of material and equipment. High costs to produce nanofluids and difficulties in preparing stable nanofluids are the main barriers to perform experiments with nanofluids. To conduct the experiment such as the flowing of nanofluids inside the microtube is quite hard and consume much time. Many equipment and apparatus are required especially when the experiment required a different concentration level of fluids. Experimental studies also have high chance in expose to error in results. Experimental research can create artificial situations that do not always represent real-life situations. This is largely due to fact that all other variables are tightly controlled which may not create a fully realistic situation. Therefore, numerical modeling of nanofluids, where a suitable approach is selected to simulate the flow, could be the best solution for problems involved with nanoparticle suspensions.

## 1.3 Objectives of Project

The following objective is investigated by using LAMMP simulation:

a) Effect of thermal conductivity and viscosity to the number of nanoparticles (concentration) being suspend into the host fluid.

## 1.4 Scope of Work

This project focuses on simulate the flow nanofluid inside the microtube by using molecular dynamic simulation. In this project, LAMMPS is being used. LAMMPS is a classical molecular dynamics code with a focus on materials modelling. It's an acronym for Large-scale Atomic/Molecular Massively Parallel Simulator. LAMMPS makes use of Message Passing Interface (MPI) for parallel communication and is free and open-source software, distributed under the terms of the GNU General Public License.

This study aims to analyze the efficiency and performance of nanofluid with different concentration number of nanoparticles. From this molecular dynamic simulator, thermal conductivity and viscosity value of nanofluid can be obtained.

The problems involved for the implementation of the parallel solver only include the steady-state cases, for instance, a 3D steady-state thermal conduction problem. Hence, the efficiency of the simulation of the typical 3D conduction problem will provide a platform to analyst and evaluate the performance and effectiveness of parallel solver implementation for other similar finite element modelling cases.

# CHAPTER 2: LITERATURE REVIEW

This chapter focuses on presenting a review of experimental, application, analytical and numerical works that related to the nanofluids in order to expose the structure for this thesis.

## 2.1 Molecular Dynamic Simulation of Nanofluids

Molecular dynamic simulation can be divided into types, conventional and computerize types. Both conventional and computerize approach on the nanofluids problems became popular among researcher past few years. (M.Nasiri-Lohesara, M.Gorji-Bandpy, 2014) investigated numerically using two-phase approach on turbulent forced convection of different nanofluids consisting of $\gamma$-Al2O3/water and CuO/water in a concentric double tube heat exchanger. Another researcher (M. M. Ghosh and R. K. Rai, 2013), have modelled the thermal evolution during Brownian motion of nanoparticles by stochastic analysis. Review of numerical investigation on nanofluids by conventional and novel methods have been made. It includes the studies on conducted using methods such as Lattice Boltzmann, Eulerian–Lagrangian, thermal dispersion and Eulerian–Eulerian (Bahiraei, 2014). Contemporary nanofluids simulation with thermal dynamic program has been simulated by using LAMMPS (Adil Loya, Jacqueline L. Stair & Guogang Ren, 2014). Cerium oxide, $CeO_2$ nanoparticles was added in the water and simulated to determine the dispersion percentage and viscosity. The rheological values of simulation were obtained and agreed within 5 % of the experimental values.

## 2.2 Mono and Hybrid nanofluids

Mono-type of nanofluid use single type of nanoparticles whether metal, metal oxide, metal carbides, metal nitrides or carbon material while hybrid nanofluids are nanofluids that have two or more types of nanoparticles being disperse in the base fluid. There are three types of hybrid nanofluid which are metal matrix nanocomposites, ceramic matrix nanocomposites and polymer matrix

nanocomposites. Research studies on nanofluid that contain hybrid nanoparticle showed better improvement in thermal and rheological characteristics of base heat transfer fluid compared to mono nanoparticle based nanofluids. The comparisons between mono nanofluid and hybrid nanofluid have been reviewed in term of preparation, characterization properties, application, stability and cost (D. Dhinesh Kumar & A. Valan Arasu, 2018). Figure 2.1 shows the comparison of mono and hybrid nanofluid on thermal conductivity respected to temperature.

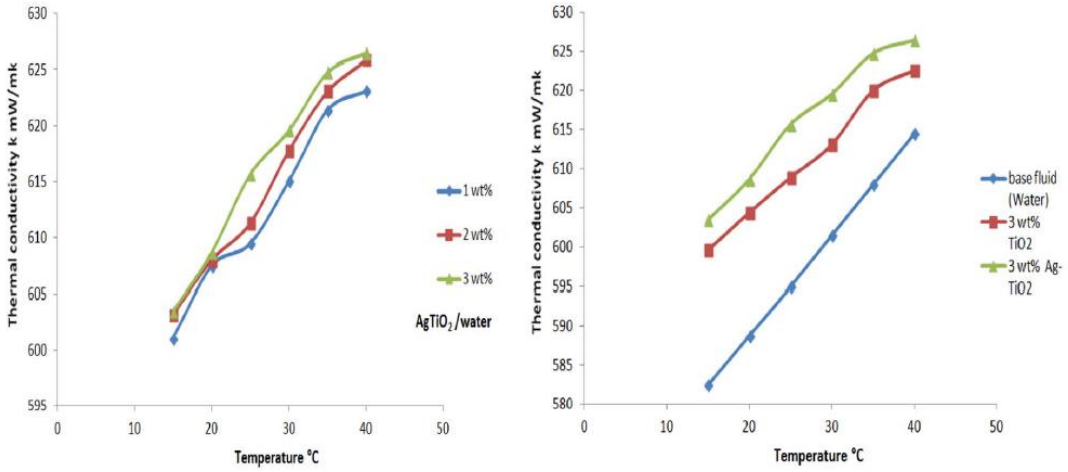



**Figure 2.1 The comparison of hybrid and mono nanofluid on thermal conductivity respected to temperature. (D. Dhinesh Kumar & A. Valan Arasu, 2018)**

3D modelled is employed over stretching sheet in the presence of rotation to examine the impact of thermal radiation, heat generation and chemical reaction (Tanzila Hayat, S. Nadeem, 2017). The results concluded that in the presence of radiation, heat generation and chemical reaction the heat transfer rate of hybrid nanofluid is higher than single nanofluid.

## 2.3 Nanofluids Properties

Nanofluid properties generally are upgraded from the base fluid properties. It is more reliable to perform in industry and certain application due to its new properties and performance. The properties that usually being study by researchers are;

### 2.3.1 Density

Density of nanofluid is proportional to the volume ratio of nanoparticles and base fluid in the system. As the density of solids is always higher than that of the liquids, normally the density of nanofluid is found to increase with addition of nanoparticles to the fluid. The density of the $Al_2O_3$/propanol nanofluid has been measured at room temperature by using hydrometer and high precision balance (Sommers AD,Yerkes KL, 2010). The result showed nearly linear the relationship between density and particle concentration. There are a few limited works and consequence correlations for density of nanofluids. So, further experimental works should be conducted to develop a diverse model including the dependence of density on nanoparticle size, shape, temperature and surfactant.

### 2.3.2 Viscosity

Viscosity is the quantity that describes a fluid's resistance to flow. Officially, viscosity is the ratio of shear stress to velocity gradient. Generally, viscosity decreases with the increasing in temperature and increases with the increasing of concentration solution. In nanofluid, the viscosity increases with the increase number of nanoparticles being dispersed in the fluid. The simulation of cerium oxide, $CeO_2$ dispersed into the water found that the viscosity of nanofluid increased as the volumetric concentration increase. The simulation results then are compared with experiment results as shown Figure 2.2 (Adil Loya, Jacqueline L. Stair & Guogang Ren, 2014).

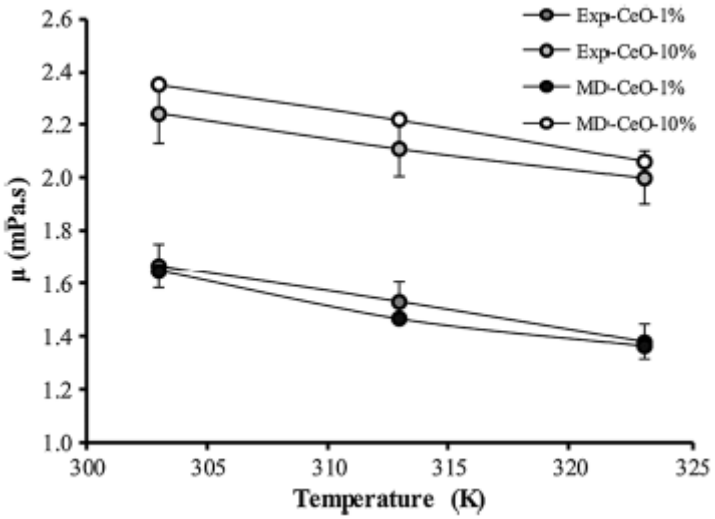



**Figure 2.2 Measured viscosities of CeO2 nanoparticles in water from temperatures 300-325 K**

The viscosity values have been determined experimentally where the viscosity of MWCNT-$Fe_3O_4$ nanocomposite nanofluids and observed increases of 1.27-times and 1.5-times for 0.3% vol at temperatures of 20 °C to 60 °C, respectively, as compared to water (Sundar LS, Singh MK, Sousa ACM, 2014). The viscosity of single nanoparticle (Fe3O4/water)-based nanofluid has been observed that it increases with increasing particle volume concentration but it decreases with increasing temperature (Sundar LS, Singh MK, Sousa ACM, 2014).

### 2.3.3 Thermal Conductivity

Thermal conductivity is the most important in transport properties because heat transfer coefficient is depending on thermal conductivity of fluid. The thermal conductivity of nanofluids was proved will be increased linearly with the concentration of nanoparticles and temperature as shown in Figure 2.3. Si/MWCNT/water hybrid nanofluids was prepared and then the thermal conductivity was measured in the particle concentrations of 0.1%, 0.5% and 1.0% wt in the temperatures range from 27 °C to 40 °C (Baghbanzadeha M, Rashidib A, Rashtchiana D, Lotfib R, Amrollahib A., 2012). Preparation of 95% of Al2O3/5% of MWCNT and 90% of Al2O3/10% of MWCNT water based hybrid nanofluids have been made and the thermal conductivity was estimated at different particle concentrations (Nine MJ, Batmunkh M, Kim JH, Chung HS, Jeong HM, 2014).

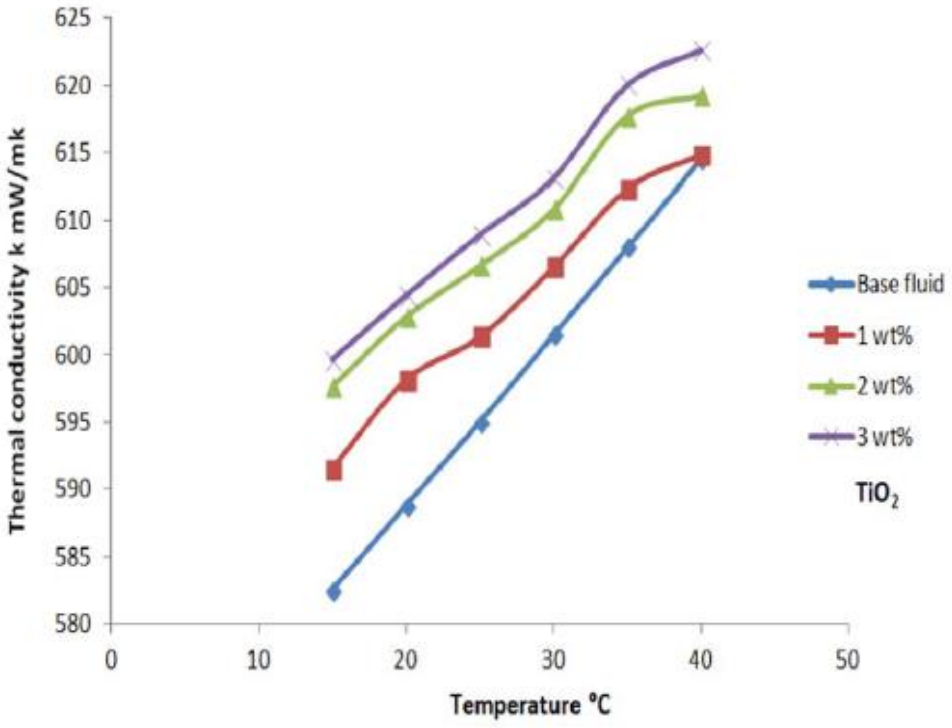



**Figure 2.3 Variation of thermal conductivity values with temperature at different weight of $TiO_2$-water (Batmunkh M, Tanshen MR, Nine MJ, Myekhlai M, Choi H, Chung H, Jeong H., 2014)**

# CHAPTER 3: METHODOLOGY

In this chapter, the methodology of molecular dynamic simulation that been used in this project is presented. This chapter starts with an introduction on molecular dynamic simulation. Then, the focus on process of equilibrium molecular dynamic simulation merged with Green Kubo is explained in detail.

## 3.1 Molecular Dynamic Simulation

Molecular dynamic (MD) simulation is a computer simulation where the atomic positions are obtained numerically from the solving of differential equation of motion which the position is related to time and provide information of individual atoms as in a motion picture (Allen, M. P., & Tildesley, D. J., 1987). The basic working principle of MD is purely based on classical mechanics without relying on any underlying assumptions. In MD simulation, the force acting on a particle can be determined from the knowledge of inter-atomic potential between atoms, which is given by:

$$\boldsymbol{F}_i = \nabla_i U \tag{3.1}$$

Where $\boldsymbol{F}_i$ is the force exerted on the particle *i*; *U* is the inter-atomic potential between atoms. Based on the information of force, acceleration of atom of particle *i* also can be calculated from Newton's second law of motion, given by:

$$\boldsymbol{F}_i = ma_i \tag{3.2}$$

Where *m* is the mass of particle *i* and $\boldsymbol{a}_i$ is its acceleration. Therefore, the velocity and position of particle *i* can be updated from the information on acceleration, they are given by:

$$v_i = \overset{\circ}{v_i} + a_i t \tag{3.3}$$

$$r_i = r_i^{\circ} + v_i t + \frac{1}{2} a_i t^{2`} \qquad (3.4)$$

Where $v_i$ and $r_i$ are velocity and position of particle $i$ at time $t$ respectively; superscript '°' is the initial value of particle $i$. After the updates on atomic velocity and position are done, Equation 3.1 to Equation 3.4 is repeated for time $t + \Delta t$ for N particles in the system. The working principle of MD is shown in Figure 3.1. based on trajectories of large collection of particles in the system, the average values of properties such as structural and thermal transport properties can be determined via statistical mechanics.

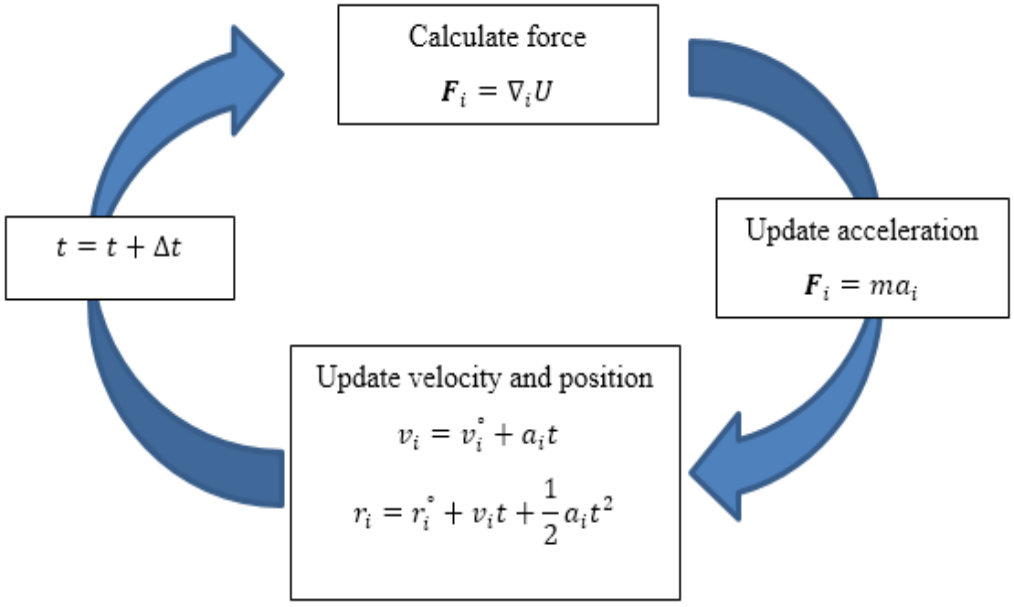



**Figure 3.1 Working principle of MD**

MD simulation can be used either for dynamic phenomena in equilibrium (EMD) or non-equilibrium (NEMD) state. To measure the response of macroscopic properties to the gradient of external fields such as force, temperature or chemical potential, NEMD method is more suitable. For instance, if temperature gradient is applied, the response is heat flow and thermal conductivity can be discovered from the amount of heat flow. However, in EMD method, no gradient of external fields is applied. This method only describes the reaction of an equilibrium system to small external fluster via linear response theory (Hansen, J., & McDonald, I., 1986). For the Green Kubo formulas, these formulas are the results of linear response theory in

statistical mechanics which transport coefficient can be expressed as time integral of appropriate time autocorrelation functions (Kubo, R., Yokota, M., & Nakajima, S., 1957).

In this thesis, Green Kubo method type of MD simulation was used to examine the thermal transport of nanofluids. This type of simulation is called Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD software. In this software, the nanofluids were modelled by diffusing copper nanoparticles into the pure water. Then, this will be visualized by 3D visualization software, OVITO-Open Visualization Tool (Stukowsk, 2009). EMD method was chosen in this project because the main objective of this project is to determine the transport coefficients such as thermal conductivity and shear viscosity that can be calculated from a single simulation while different sets of simulation are required for NEMD method to create different gradient of interest. Moreover, EMD method evaluates the transport coefficient in smaller system compared to NEMD method, as a result will reducing computational time and amount (Jones, 2012).

## 3.2 Methodology of Equilibrium Molecular Dynamic Simulation

This method of MD simulation is integrated by Green Kubo method. Here is the sequence of step need to be set up before the simulation can be run. All this process is done by using CPUs.

### 3.2.1 Geometry Setup

Pure water system was modelled before it was suspended with copper nanoparticles to form nanofluids system. The water was modelled with two hydrogen atoms and one oxygen atom bond together with tetrahedron of O-H bonding with 104.5° angle to form a molecule. Then, thousand of molecules water were occupied in a box to make a first system. After that, some of copper particles were dispersed into the system to make nanofluids system. The atomic mass of hydrogen, oxygen and copper are 1.008 g/mol, 16.0 g/mol and 63.55 g/mol respectively. To allow a large modelling system, periodic boundary condition (PBC) was applied. This condition will overcome differences between molecular microscale and macroscale. The impact of PBC where the actual simulation takes place only for the atoms inside the primary

box at the center, and all image boxes just copy the primary box. For example, if the atom k moves out of the primary box to the upper image box, its image atom in the bottom image box (the atom with the upper arrow) moves in to replace it and keeps the number of atoms constant in the primary box (Lee, 2017) as illustrated in Figure 3.2.

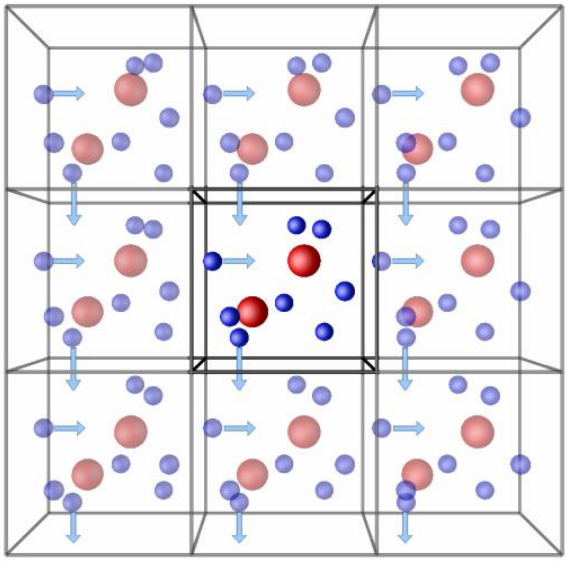


**Figure 3.2 Schematic representation of the idea of periodic boundary conditions (Petkov, Dr. Sébastien Le Roux & Pr. Valeri, 2019)**

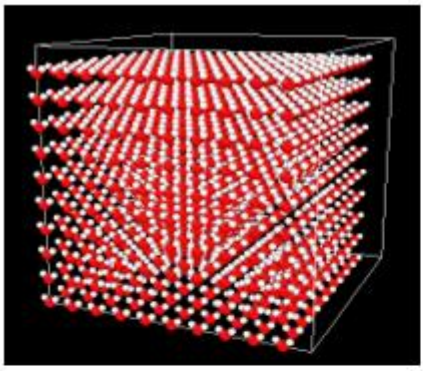
In this thesis, four different systems were modelled to achieve different objectives. The system #1 is a system with water only. In the system, the simulation box will be changed proportionally to the number of particles being added into the system. Inversely, in system #2, #3 and #4 the copper nanoparticles were added into the system to form nanofluids. The system #2 has 8-nanoparticles, system #3 has 16-nanoparticles and system #4 has 24-nanoparticles. In this case, effects of interaction between nanoparticles are considered and the volume of each system are different because the are addition in particle inside the box. The suspension of nanoparticles can be modelled in well-dispersed state or aggregated state as the effect of interaction between nanoparticles. Well-dispersed state can be modelled by positioning the nanoparticles apart from each other so that it has insufficient time to aggregate with in the time domain while the aggregated state can be modelled by positioning the nanoparticles close to each other in the beginning of simulation. In this thesis well-

dispersed state is chosen and being run at temperature 300K. The detail of system #1, #2, #3 and #4 are presented in Table 3.1.

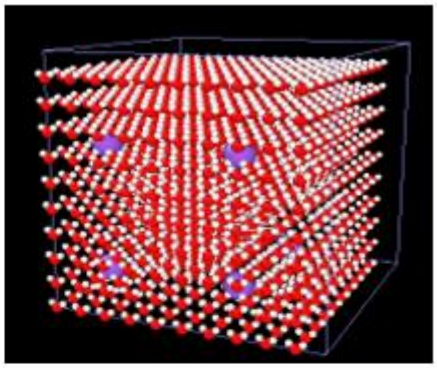
.

**Table 3.1 Number of atoms of each element.**

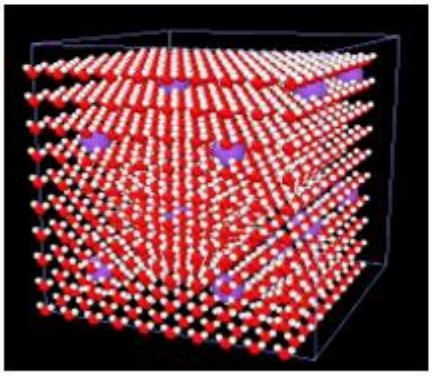
| System | No. of copper atom | No. of oxygen atom | No. hydrogen atom | Total no. of atom in system |
|---|---|---|---|---|
| #1 | 0 | 1000 | 2000 | 3000 |
| #2 | 8 | 1000 | 2000 | 3008 |
| #3 | 16 | 1000 | 2000 | 3016 |
| #4 | 24 | 1000 | 2000 | 3024 |



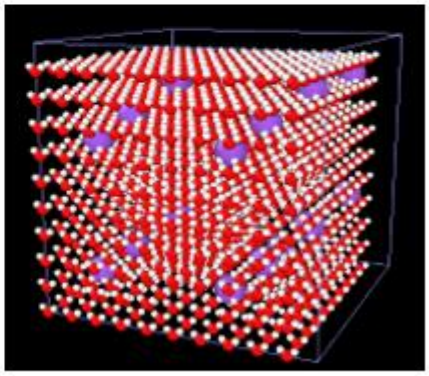
System #1: molecules of pure water only



System #2: 8-nanoparticles in well-dispersed state inside the water



System #3: 16-nanoparticles in well-dispersed state inside the water



System #4: 24-nanoparticles in well-dispersed state inside the water

**Figure 3.3 Snapshot of four different systems from the OVITO.**

From the modelling of the system above, the system will present the real-life situation. The thermal transport properties of water in the simulation box will be compared to real properties of water in term of thermal transport properties at certain temperature. These properties can be determined after the end of simulation of system #1. The simulation box of liquid water (base fluid) has a volume of 30,497.83 $Å^3$ and contain 3,000 atoms. Based on finite study reported by (Sarkar, S & Selvam, R. P. , 2007), the result of simulation of water was in good agreement with real life data when the number of water molecules is more than 500. Therefore, the properties of water from the simulation should be not too far from the real data.

### 3.2.2 Inter-atomic Potential Definition

Inter-atomic potential or pair potential is the real input in MD simulation. For this nanofluid system, there will be two interaction, namely O-H and O-Cu. Figure 3.4 showed geometry of a copper atom interacting with a molecule of water. For this phenomenon, Lennard-Jones (L-J) potential (Lennard-Jones, J. E., 1924) was used to describe these two inter-atomic interactions. The L-J potential, $U_{LJ}(r)$, is defined by:

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \quad (3.5)$$

Where $r$ is inter-atomic distance, $\varepsilon$ is the lowest energy of the potential curve (≡well depth, cohesive energy) and $\sigma$ is the interatomic distance at which the potential is zero as shown in Figure 3.5.

Then, its force form of repulsive and attractive term is,

$$F_{LJ} = \frac{24\varepsilon}{\sigma}\left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7}\right] \quad (3.6)$$

When two Lennard−Jones atoms approach each other from a long distance, several features are noted here.

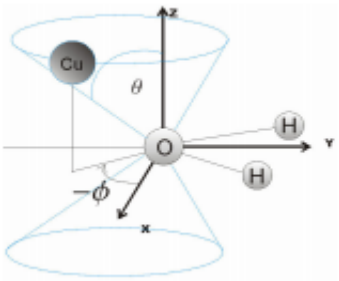



**Figure 3.4 Geometry of a copper atom interacting with a molecule of water**

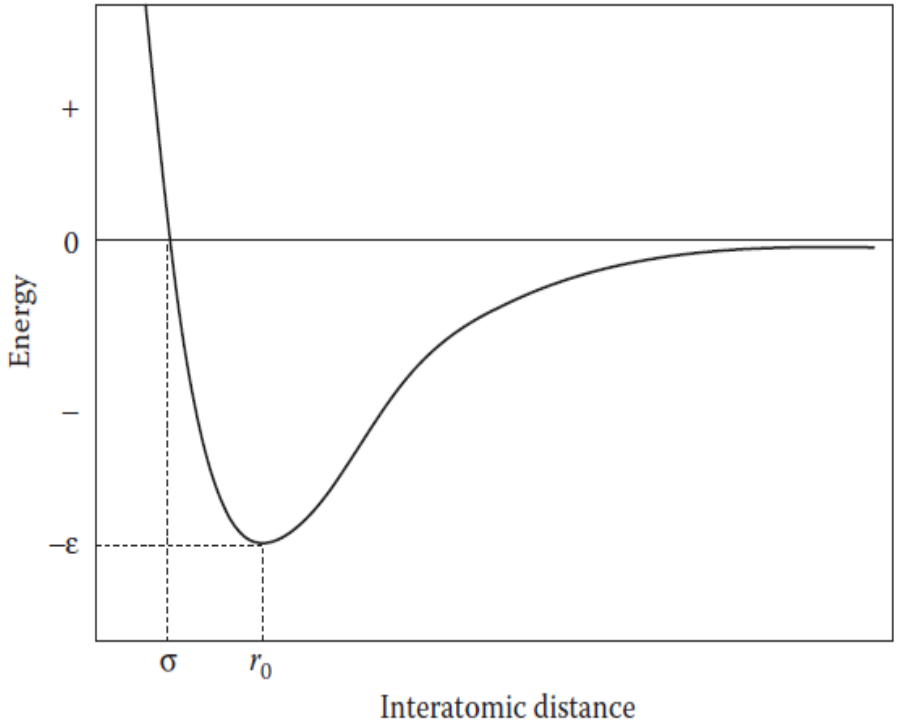



**Figure 3.5 Schematic representation of the Lennard−Jones pair potential**

**(Lee, 2017)**

At equilibrium interatomic distance, $r_o(= 2^{1/6}\sigma = 1.122\sigma)$, two forces are balanced to a net force of zero and the corresponding energy become minimum $(dU_{LJ}/dr) = 0$.

The energy passes through 0 at $r = \sigma$ and increases steeply as $r$ decreases further due to the Pauli repulsion.

### 3.2.3 Energy Minimisation

The initial geometry setup may cause bad contact that contain higher energy. When two atoms are to near to each other, it may cause high repulsive energy. Consequently, the process of energy minimization is necessary in optimizing the geometry setup with minimum energy arrangements to prevent the simulation from 'destroyed'. Energy minimization is functioning in adjusting the positions of the atoms to the nearby local energy minimum. In this work, Polak-Ribiere of conjugate gradient algorithm was used. The force gradient is integrated with previous iteration data in every iteration in order to determine the best direction for a new search which is perpendicular to the previous search direction. This is efficient for solving large scale problem as the algorithm requires modest computational amount and time. This process will be break off if any criterions below is fulfilled:

a) the global force vector is less than a certain defined threshold
b) the number of iterations exceeds defined threshold
c) the line search fails to reduce the energy during the last iteration
d) the change in energy between iteration is less than a certain defined threshold
e) the number of total force evaluation exceeds defined threshold

In this thesis, the threshold for the change in energy and global force vector were set zero while the maximum number of iteration and total force evaluation were set 100 000, 200 000, 300 000, 400 000 and 500 000 timesteps. The outcome was a zero line search act as the stopping criterion in this work. The optimized geometry then serves as a starting geometry for the MD simulation run after the energy minimisation is terminated.

### 3.2.4 Velocity Initialisation

The next step is initializing the atomic velocities by assigning random initial velocities. An appropriate numerical method is required as the trajectories prediction for all the particles in the system by solving the differential equation of motion from Equation 3.1 and Equation 3.4. The numerical method for this work is formulated by Velocity Varlet algorithm (Allen, M. P., & Tildesley, D. J., 1987) which is given by:

$$\boldsymbol{r}(t+\Delta t) = \boldsymbol{r}(t) + \boldsymbol{v}(t)\Delta t + \frac{1}{2}\boldsymbol{a}(t)\Delta t^2 \qquad (3.7)$$

$$\boldsymbol{v}(t+\Delta t) = \boldsymbol{v}(t) + \frac{1}{2}[\boldsymbol{a}(t) + \boldsymbol{a}(t+\Delta t)]\Delta t \quad (3.8)$$

Initially, Equation 3.7 was used to calculate the new positions at time $t + \Delta t$. Then, the velocities are calculated at half step using,

$$\boldsymbol{v}\left(t + \frac{1}{2}\Delta t\right) = \boldsymbol{v}(t) + \frac{1}{2}\boldsymbol{a}(t)\Delta t \quad (3.9)$$

Next, the forces and acceleration are calculated at time $t + \Delta t$, and the velocities are calculated at full step,

$$\boldsymbol{v}(t+\Delta t) = \boldsymbol{v}\left(t + \frac{1}{2}\Delta t\right) + \frac{1}{2}\boldsymbol{a}(t+\Delta t)\Delta t \quad (3.10)$$

The positions and velocities at time $t + \Delta t$ are completed at this point, and the system will be advanced to the next time step and repeated. The Velocity Varlet algorithm requires less computational amount because only one set of positions, velocities and forces need to be carried out at one time.

### 3.2.5 Equilibration

The MD simulation started with initial atomic positions and velocities, despite that, the initial configurations are not representing the state of equilibrium. Thus, the equilibration process should be performed for a certain amount of time to rest the initial configurations to equilibrium state earlier to data production. In this work, the system was equilibrated for 500,000 time steps under isobaric-isothermal ensemble (NPT), canonical ensemble (NVT) and micro canonical ensemble (NVE) while the equilibration steps were ignored for the data production.

**Table 3.2 Various ensembles used in MD (Lee, 2017)**

| Ensembles | Fixed variables | Remarks |
|---|---|---|
| Microcanonical | N, V, E | Isolated system<br>Very common in MD<br>$S = k \ln \Omega_{NVE}$ |
| Canonical | N, V, T | Very common in MC<br>Common in MD<br>$F = -kT \ln \Omega_{NVT}$ |
| Isobaric-isothermal | N, P, T | $G = -kT \ln \Omega_{NPT}$ |
| Grand canonical | μ, V, T | Rarely in MD, more in MC<br>$\mu = -kT \ln \Omega_{NPT}/N$ |

Table 3.3 shows various ensembles used in MD with different fixed variables. This simulate same as actual experiment in a lab, where we impose the external constraints on ensembles to have properties out after a run.

### 3.2.6 Data Production

Data production can be begun to computer the transport and structural properties once the system has attained equilibrium state. A 500,000 time steps was used for data production under canonical ensemble (NVT) and microcanonical ensemble (NVE). The transport properties data such as thermal conductivity and shear viscosity were collected. Each transport properties were averaged over five different initial velocities in order to improve the statistics.

#### 3.2.6.1 Transport Properties

**a) <u>Thermal Conductivity</u>**

In this project thermal conductivity, $k$ was calculated by using the Green-Kubo formula:

$$k = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \mathbf{j}(0)\mathbf{j}(t)\rangle dt \qquad (3.11)$$

Where $V$ is the volume of simulation box, $T$ is the system temperature, $k_B$ is the Boltzmann constant and $\langle \mathbf{j}(0)\mathbf{j}(t)\rangle$ is the heat current autocorrelation function (HCACF). The microscopic heat current is given by:

$$\mathbf{j}(t) = \sum_i \mathbf{v}_i e_i + 0.5 \sum_{i<j} \mathbf{r}_{ij}\left[\mathbf{F}_{ij} \cdot \left(\mathbf{v}_i + \mathbf{v}_j\right)\right] \quad (3.12)$$

Where $\mathbf{v}_i$ is the velocity of particle i and $\mathbf{F}_{ij}$ is the force on atom i due to its neighbour j from the L-J potential. The site energy $e_i$ is given by:

$$e_i = 0.5\left[m_i|\mathbf{v}_i|^2 + \sum_j \emptyset\mathbf{r}_{ij}\right] \quad (3.13)$$

The Green-Kubo formalism allows us to calculate many dynamical properties such as viscosity, thermal conductivity and electrical conductivity from equilibrium simulations of atomic systems.

**b) <u>Shear Viscosity</u>**

The Green-Kubo relation for shear viscosity, $\mu$ is given:

$$\mu = \frac{V}{k_B T}\int_0^\infty dt\langle P_{xy}(0)P_{xy}(t)\rangle \quad (3.14)$$

Where $\langle P_{xy}(0)P_{xy}(t)\rangle$ is autocorrelation function (SACF). The stress tensor $P_{xy}$ is given by:

$$P_{xy} = \sum_{i=1}^{N} \frac{P_i^x P_i^y}{m_i} - \sum_{i>j}^{N}\left(x_i - x_j\right)\frac{\partial u_{ij}}{\partial y_j} \quad (3.15)$$

Where $P_{xy}$ is momentum component, $u_{ij}$ is an interaction potential, $m_i$ is a mass, $x_i$ is a component of radius vector $i$ and $j$ are number of particles. The SACF is derived from the scalar of off-diagonal components of the stress tensor while HCACF is calculated from the vector of heat flow in the system.

### 3.2.6.2 Structural Property

**a) <u>Bulk modulus</u>**

Bulk modulus is defined as how much volume is changed with apply pressure,

$$B_v = -V\left(\frac{\partial P}{\partial V}\right)_{NVT} \quad (3.16)$$

For example, in FCC structures, it can be obtained by taking the second derivative (curvature) of a potential curve at the equilibrium lattice constant, $r_0$:

$$B_v = \frac{r_0^2}{9\,\Omega}\left(\frac{d^2U}{dr^2}\right)_{NVT} \quad (3.17)$$

Where Ω is atomic volume.

**b) <u>Radial Distribution Function</u>**

The radial distribution function (RDF), g(r), is used to study the structure of crystalline solid, liquid and gas as it can show how atoms are distributed around a reference atom. This can be obtained by summing the number of atoms found at given distance in all directions from a particular atom (Lee, 2017):

$$g(r) = \frac{dN/N}{dV/V} = \frac{V}{N}\frac{\langle N(r,\Delta r\rangle}{4\pi^2\Delta r} \quad (3.18)$$

Where $r$ is the radial distance, $N(r,\Delta r$ is the number of atoms in shell volume of $4\pi^2\Delta r$ between $r$ and $\Delta r$, and the brackets denote the time average.

## 3.3 Validation

In this project the validation is not done by conducting the experiment. The validation of the simulation is done by comparing the real properties of pure water with the result that got from the MD simulation of pure water (system #1). The data collection of viscosity and thermal conductivity are compared to the reference water properties at atmospheric pressure.

# CHAPTER 4: RESULTS AND DISCUSSION

This chapter aims to present results and discussions on the objectives of this thesis.

## 4.1 Effect of number of nanoparticles in a system

### 4.1.2 Density

Density is a characteristic property of a substance. It is the relationship between the mass of the substance and how much space it takes up (volume). The density also depending on the mass, size and the arrangement of the atoms in the substances. Table 4.1 is the data obtained from the simulation. From the data collected, the density value of each system is calculated.

**Table 4.1 Number of nanoparticles and number of water molecules in the particular volume.**

| System | No. of nanoparticle | No. of water molecules | Volume of the system (Å$^3$) |
|---|---|---|---|
| #1 | 0 | 1000 | 29,970.65 |
| #2 | 8 | 1000 | 30,065.57 |
| #3 | 16 | 1000 | 30,159.46 |
| #4 | 24 | 1000 | 30,254.52 |

Before determining the density of the substances in the system, we need to find the mol first. The mol is calculated by using Avogadro constant, $A = 6.022 \times 10^{23}$. Mol is calculated by:

$$n = \frac{N}{A} \tag{4.1}$$

Where *N* is number of molecules or atoms.

Mol of water,

$$n = \frac{1000}{6.022 \times 10^{23}}$$

$n = 1.66 \times 10^{-21}$mol

Then mass of water is calculated by equation,

$$m = M \times n \tag{4.2}$$

Where *M* is molecular/atomic weight.

Mass of water,

$$m = (18) \times (1.66 \times 10^{-21})$$

$$m = 2.988 \times 10^{-20} g / 2.988 \times 10^{-23} kg$$

The density, $\rho$ is calculated by,

$$\rho = \frac{m}{V} \tag{4.3}$$

Where *V* is volume in $m^3$.

$$\rho = \frac{2.998 \times 10^{-23}}{29970 \times 10^{-30}}$$

$$\boldsymbol{\rho = 1000.334\ kg/m^3}$$

**Table 4.2 Comparison of water density from simulation and theoretical at temperature 300K.**

| Density of water from simulation, $(kg/m^3)$ | Theoretical density of water, $(kg/m^3)$ | Difference (%) |
|---|---|---|
| 1000.334 | 996.53 | 0.382 |

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**Table 4.3 Comparison of copper density from simulation and theoretical**

| Density of copper from simulation, $(kg/m^3)$ | Theoretical density of copper, $(kg/m^3)$ | Difference (%) |
|---|---|---|
| 8894.203 | 8941 | 0.523 |

The percentage difference of water density between MD simulation and theoretical value is 0.382%. while for copper is 0.523%. This difference is quite low and can be accepted. Then, density of each system is calculated to show how number of nanoparticles effect the density value of the system. The density of the nanofluids are calculated by this equation (Pak BC, Cho Y., 1998),

$$\rho_{nf} = (1 - \emptyset)\rho_{bf} + \emptyset\rho_s \quad (4.4)$$

Where, $\rho_{nf}$ is the density of nanofluid, $\rho_{bf}$ is the density of base fluid, $\rho_s$ is the density of solid particles and $\emptyset$ is the volume concentration.

For example, for density of system #2,

$$\rho_{nf} = (1 - 3.16 \times 10^{-3})1000.334 + [(3.16 \times 10^{-3})(8894.203)]$$

$$\boldsymbol{\rho_{nf} = 10025.279\ kg/m^3}$$

**Table 4.4 Density of the systems calculated from MD simulation data**

| System | No. of nanoparticles | Volume Concentration, % | Density, ($kg/m^3$) |
|---|---|---|---|
| #1 | 0 | 0.0 | 1000.334 |
| #2 | 8 | 0.32 | 1025.279 |
| #3 | 16 | 0.63 | 1049.750 |
| #4 | 24 | 0.94 | 1074.378 |