INVESTIGATING THE AGGREGATION EFFECT IN
NANOFLUIDS BY MOLECULAR DYNAMICS

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by
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Abstract

Nanofluids have been proposed to have superior heat transfer ability than typical coolant, but the mechanisms of thermal conductivity enhancement still remain obscure. This study, by using Molecular Dynamics simulation, specifically investigate the aggregation effect in nanofluids system. Non-Equilibrium Molecular Dynamics (NEMD) method is used to calculate the thermal conductivity of nanofluids system containing aggregated nanoparticles. The clustering phenomena is characterized and a simple model is proposed to explain the results qualitatively. Also the thermal properties of several nanofluids system consist of different shapes of aggregation are examined. A resistance-analogy model is found to explain the thermal transfer behavior between two limiting conditions.
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1.1 Overview

1.1.1 Why Nanofluids

Nanofluids is defined as a new class heat transfer fluids by suspending metallic or non-metallic nanoparticles in conventional heat transfer fluids [2]. Experiments have revealed that the addition of a very small volume fraction of nanoparticles into a liquid leads to a significant enhancement in thermal conductivity of the liquid [3, 4, 5]. Considering efficient dissipation of heat generated in compact electronics would increase their performance, the thermal management must be maintained for electronic systems. There is also a large number of engineering applications that can benefit the heat transfer enhancement of nanofluids such as coolant in machine [6], heat exchangers [7], fuel cells [2], home refrigerators [8, 9] and several medical applications [10]. Figure 1.1 shows the amount of papers published related to nanofluids up to May 2013. It is estimated that more than 300 companies and research groups are engaged in nanofluids field worldwide. The last two decades have seen growing importance placed on research in this topic.
1.1.2 Controversy over Nanofluids

In spite of the great potential of nanofluids system, the uncertainties over the fundamental effects of nanoparticles on thermal properties of solvent media still remain; the enhancement does not always follow the classical effective medium theory and the associated physical mechanisms are still a hotly debate topic. Maxwell was the first one proposed a theory to predict the thermal conductivity a composite system. The thermal conductivity of a perfectly dispersed spherical particles in a continuous liquid system could be precisely predicted with equation (1.1)[11].

\[
\frac{k}{k_f} = \frac{k_p + 2k_f + 2\phi(k_p - k_f)}{k_p + 2k_f - \phi(k_p - k_f)}
\]  (1.1)

This equation gives the ratio of the nanofluid thermal conductivity \(k\) to the thermal conductivity of the base fluids \(k_f\), \(k_p\) is the particle thermal conductivity and \(\phi\) is the particle volume fraction. It agrees well with experimental data when in the limit of \(\phi \ll 1\), in which particles could be considered as non-interacting [12]. Furthermore in the limit \(k_f \ll k_p\), equation (1.1) becomes \(k/k_f \simeq 1 + 3\phi\). In other words, when the thermal conductivity of solid is much higher than liquid,
the volume fraction of solid will be the only factor affects the thermal conductivity enhancement. Note this equation gives no dependence on the size of nanoparticles, pH value of solutions or temperatures. In other words, with the same volume fraction, \( k_f \) and \( k_p \), the heat transfer properties of two systems with different particle configuration are the same (see figure 1.2). Interestingly, experiments have shown disagreement with Maxwell model. The thermal conductivity is claimed to have a linearly increasing behavior with temperature [13, 14, 15] and an inverse dependence with nanoparticle size [16, 17, 18], also enhancements higher than the predictions from Maxwell’s model are reported [19, 20, 21]. Researchers believe there must be some hidden mechanisms behind these results.

\[
k_f = k_2
\]

**Figure 1.2.** Prediction from Maxwell’s theory.

### 1.2 Mechanisms of Nanofluids

To have a better, deeper understanding of nanofluids systems, some possible mechanisms have been proposed to explain the abnormal enhancement of thermal conductivity [22]. They are Brownian motion of nanoparticles, liquid layering of the base uid surrounding nanoparticles and nanoparticle aggregation respectively. Each mechanism is discussed in detail below.
1.2.1 Brownian motion

The term “Brownian motion” refers to the randomly moving behavior of particles suspended in a fluid resulted from their bombardment by the fast-moving atoms or molecules in the gas or liquid. Figure 1.3 shows the 2D Brownian motion process of a single particle by Mathematica®.

Brownian motion was first time discovered by the botanist Brown in 1827.

![Figure 1.3. Example of randomly 2D Brownian motion of a single particle.](image)

It has several properties: first the movement of particles never stop, secondly the temperature affects the movement significantly, thirdly there is no fixed trajectory of particles and finally, the movement has no dependence on the composition or density of particles. Brownian motion can be considered as a diffusive process with a diffusion coefficient $D$, which is characterized by Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi \eta a}$$

(1.2)

where $k_B$ is Boltzmann’s constant, $T$ is temperature, $\eta$ is the viscosity of fluids and $a$ is the radius of nanoparticles. By Brownian motion nanoparticles move through fluids and possibly will collide with each other, therefore enabling solid-solid heat
transport route directly, which is then expected to enhance the overall heat transfer properties.

Keblinski et al. discussed the effect of Brownian motion by estimating the time scale of the mass diffusion with that of heat diffusion [22]. The time scale for heat diffusion is

$$\tau_H = \frac{d^2}{6\chi} = \frac{d^2 c_p \rho}{6k_f}$$  \hspace{1cm} (1.3)

and to compare, the characteristic time scale of a nanoparticle to travel distance $d$ is given by

$$\tau_D = \frac{d^2}{D}$$  \hspace{1cm} (1.4)

where $D$ in equation (1.3) is the diffusion constant in equation(1.2) and $\chi$ is the thermal diffusivity, defined as thermal conductivity ($k$) divided by the heat capacity per unit volume of fluid ($\rho c_p$). For water at room temperature, the ratio of $\tau_D/\tau_H$ is $\approx 500$ which indicates the Brownian motion contribute very little to the heat due to the fact that time scale of heat transport is much smaller than diffusion phenomena. Wang et al. [23] claimed that the thermal conductivity of nanoparticle/fluid mixtures is dependent on the microscopic motion such as Brownian motion or inter-particle forces. Shukla et al. introduced a deep analysis to the Brownian motion effect in nanofluids system. By using a two-body interaction they showed for a typical nanofluid system which includes 1% volume fraction nanoparticles in water, the effect of kinetic contribution is negligible [24]. On the other hand, Prasher modeled the effect of Brownian motion for flow around spheres and they concluded that the convection due to Brownian movement of nanoparticles is the main reason of the enhancement of thermal conductivity. Jang in 2004 found that the Brownian motion to be the key mechanism governing the thermal conductivity of nanofluids. The model they proposed not only predicts the thermal behavior is size-dependent but also suggest the volume fraction and temperature dependence [25].
Based on Brownian dynamics, Bhattacharya et al. [26] proposed a method to calculate the thermal conductivity of nanofluid systems consisting of Cu/EG and alumina/EG and showed a nearly full agreement with the experiment data. Following this model, Sarkar et al. [27] established a model successfully predicting the thermal conductivity under various temperature and concentration situations. Evans also found that the hydrodynamic effects of Brownian motion have little correlation on the thermal properties in nanofluids [28]. In sum, the possible mechanism Brownian associated with Brownian motion is considered to be negligible with the enhancement of thermal conductivity while there is still some opacity to be clarified [29].

1.2.2 Liquid Layering Effect

From many experiments, researchers found the formation of an ordered liquid layering around the surface of nanoparticles solids [30] which is shown in figure 1.4. The strong interaction between solid-liquid atoms will force an oscillatory density profile in the direction perpendicular to the interface. The layering thickness is determined by the strength of atom bondings [31]. The thickness of this aligned layer of liquid molecules at the interface is at a magnitude of $10^{-9}$ meter, but due to the relatively high specific surface area of nanoparticles, this nanolayer may play an important role in heat transport from solid to adjacent liquid [32]. Given the fact that the thermal conductivities of perfect ordered crystalline materials are much larger than that of amorphous materials, the liquid layering phenomena is expected to have a positive effect on heat transfer behavior. In fact, this crystalline-like structure provides an exceptional ability for vibrational heat transfer (phonon mode) and has some effects on various dynamic properties such as viscosity and thermal conductivity [33, 34]. Zhou examined the effect of graded nanolayers and mutual interaction between nanoparticles on thermal conductivity of nanofluids. A conclusion was drawn that the nanolayer properties is an important mechanism
in conductivity enhancement, resulting in an effective thermal conductivity higher than Maxwell’s prediction [35]. He also commented that the mechanism of thermal transfer of nanofluids is complex, and it appears other factors such as Brownian motion, temperature should also be taken into account simultaneously. Results from molecular dynamics simulation indicated that the ordered liquid layering displays a higher thermal conductivity compared to that of bulk materials, which is in accordance with Zhou’s work [36].

Yu and Choi, in other way, modified Maxwell’s model, take the liquid layering structure as solid atoms, then replace the $k_p$ with new thermal conductivity of particles $k_{pe}$. $k_{pe}$ is calculated based on effective medium theory

$$k_{pe} = k_p \frac{2(1 - \gamma) + (1 + \beta)^3(1 + 2\gamma)\gamma}{-(1 - \gamma) + (1 + \beta)^3(1 + 2\gamma)}$$

(1.5)

where $\gamma$ is the ratio of the thermal conductivity of liquid layering to nanoparticles, $\gamma = k_{layering}/k_p$. And $\beta$ is the ratio of layer thickness to the radius of nanoparticle, $\beta = h/\gamma$. Then the effective thermal conductivity would be

$$k_{eff} = k_f \frac{k_{pe} + 2k_f + 2(k_{pe} - k_b)(1 - \beta)^3\phi}{k_{pe} + 2k_f - (k_{pe} - k_b)(1 - \beta)^3\phi}$$

(1.6)

This equation gives good result when the liquid layering thickness is below 10 nm.
Despite the possible positive enhancement due to the special structure, it is proposed this layering phenomena may also decrease the heat transfer because of the interfacial resistance between solid and liquids. This interfacial thermal resistance is known as Kapitza resistance ($R_k$) since the pioneering work on the metal-liquid helium interface by Kapitza [38]. Acoustic mismatch model (AMM) considers the transmission and reflection of classical heat waves around the interface [39]. It says the heat flux over these phases can be related to the temperature gradient

$$J = G \Delta T$$  \hspace{1cm} (1.7)

where $G$ is the reciprocal of Kapitza resistance and the thermal conductivity then can be expressed as

$$h = \frac{k}{G}$$  \hspace{1cm} (1.8)

where $h$ is called Kapitza radius, defined as the the distance over which the temperature drop is the same as at the interface. From literature, the scale of Kapitza resistance is usually too small to be considered as a hinder to heat transfer; in other words, the liquid layering effect cannot act as a barrier to heat transfer [40] and the thermal interfacial resistance of most solid-liquid interfaces could be neglected in large grainsized materials [39]. However the AMM is derived only with the bulk properties of two materials and failed to consider the natural bonding between liquid and solid at the interface.

It is the first time through molecular dynamics, the thermal resistance is analysed [41]. The study exhibited that a thermal resistance cannot be neglected over a liquid-solid interface when the system size is very small, i.e. the importance of thermal resistance to heat conduction is relatively small. Xue et al. [34], with Molecular Dynamics simulations, discovered that when computing the thermal resistance over the solid-liquid interface, the inter-forces between solid atoms and
liquid atoms play a very important role. There were apparent liquid layering phenomena observed but no significant temperature change over those regimes. In 2004, Xue analyzed the thermal transfer properties in the direction perpendicular to the solid-liquid layering structure with Molecular Dynamics. They found out the thickness of liquid layering was no more than one atom and there was no apparent temperature drop. This indicates the layering has very little effect on the thermal transport in nanofluids system [33].

Also there is a large body of experimental data suggesting that the interfacial resistance is not significant in nanofluids even when the particle sizes are nanometer orders [14, 42, 43, 44]. So far there is still controversy over the effect of liquid layering [45, 46], and whether the thermal resistance around this layer is negligible. The reason makes this problem difficult to solve is that, to investigate a liquid layer width within $\approx 10 \text{ nm}$ scale is experimentally not viable. Most computational works suggested the existence of liquid layering and no obvious thermal property change over it.

1.2.3 Aggregation Effect

1.2.3.1 Aggregation of nanoparticles

For Maxwell’s theory, the thermal conductivity can only be predicted under the condition that all particles are spherical and perfectly dispersed (no interaction with each other), but this will never be the true case in reality. Nanoparticles have been experimentally observed to aggregate into clusters when dispersed in the liquid [17]. It can be experimentally characterized by optical absorption spectroscopy [47], small-angle X-ray scattering [48], and transmission electron microscopy (TEM) [49]. Figure 1.5 reveals the images of aggregated silica nanoparticles under TEM [50]. Aggregation is a common yet complicated phenomenon for nanoparticles. It could be resulted from several factors, $pH$ value of solution, surfactant of nanoparticles, temperature, van der Waals forces or chemical bonding between atoms. Some
techniques, such as surface treatment of nanoparticles[17], ultrasonic agitation[51] or mixing of dispersants[52] are often used to improve the dispersion behavior.

In former literature, it is suggested that the aggregation would not only cause the clogging but also affect the thermal properties. In a nanofluids containing metal oxide particles and carbon nanotubes, great thermal conductivity enhancement was observed by Wensel. The possible mechanism is the aggregation of metal oxide particles on the surface of nanotube by electrostatic attraction [53]. Hong found described the influence of the nanoparticle dispersion on thermal conductivity, proposing the thermal property is closely related to the clustering of nanoparticles [17]. As a result, many model were proposed to explain the aggregation effect on nanofluids system.

![TEM images of synthesized silica nanoparticles dispersed in water.](image)

**Figure 1.5.** TEM images of synthesized silica nanoparticles dispersed in water.

### 1.2.3.2 Parallel and series Model

Most intuitively, there is two simplest configuration could be drawn is arranging particles in series and parallel (See figure 1.6). The effective thermal conductivity under these two conditions are then given by [54]

\[
\frac{1}{k_e} = \frac{1 - \phi}{k_f} + \frac{\phi}{k_p}
\]  

(1.9)
where \( k_s \) and \( k_p \) are the series and parallel mode thermal conductivities, \( k_f \) and \( k_p \) are the bulk thermal conductivity of base fluids and nanoparticles. Although it is nearly impossible that in nanofluids system we have such ideal configuration of nanoparticles, it still establish two bounds which the thermal conductivity should be lying between.

### 1.2.3.3 Extension from Maxwell’s Model

Considering different shapes of aggregation, Hamilton and Crosser extended Maxwell’s equation with a shape factor \( n \), which is an empirical shape factor \( n = 3/\psi \). \( \psi \) is defined as the ratio of the surface area of a sphere which has the same volume fraction as the particle equal to the surface area of the particle [55]. Thus equation (1.1) becomes

\[
\frac{k}{k_f} = \frac{k_p + (n - 1)k_f + (n - 1)(k_p - k_f)\phi}{k_p + (n - 1)k_f - (k_p - k_f)\phi}
\]

Maxwell model can be considered as a special case of Hamilton’s model with \( n = 3 \).

In 1962, Hashin and Shtrikman developed a set of bounds which is more strict.
than the series-parallel model [56]. This theory assumes, in one limiting cases, all the particles are perfectly dispersed in the liquid thus liquid is considered as continuous phase (see figure 1.7(a)); while in another one case, the particles are linked together to “trap” liquid inside, making solids being the continuous phase (figure 1.7(b)).

Figure 1.7. 2D illustration of H-S bounds. (a)Upper bound (b)lower bound

The equation associated with this theory is

\[ k_f \left[ 1 + \frac{3\phi (k_p - k_f)}{3k_f + (1 - \phi)(k_p - k_f)} \right] \leq k \leq k_p \left[ 1 - \frac{3(1 - \phi)(k_p - k_f)}{3k_p - \phi(k_p - k_f)} \right] \tag{1.12} \]

The lower bound of this equation gives the situation that heat conduction is along the path in which liquid forms the “surrounding” (i.e. liquid is the continuous phase), while the upper bound provides the heat conduction path in which particles is the continuous phase. Naturally neither lower bound nor upper bound will not be achieved, then the effective thermal conductivity lie in between these two limiting bounds. Please note \( k_p \) is assumed to be larger than \( k_f \) or the lower bound and upper bound would reverse; the lower bound actually matches Maxwell’s theory [57, 56, 54] or it is also true for the upper bound, if \( k_p \) and \( k_f \) are reversed with \( \phi \) being replaced by \( 1 - \phi \). Classical models above were proposed under assumptions that the system is continuous and the heat is transferred by thermal diffusion. However the thermal conductivity measured during experiment were much larger
than the prediction from those models. Therefore Keblinski claimed there must be something need to be considered such as the size of nanoparticles, liquid layering and clustering effect [22]. Figure 1.8 graphically summarizes these models, please note the Maxwell’s prediction actually overlaps with HS lower bound and the parallel-series model gives the widest range of thermal conductivity.

![Figure 1.8. Significant temperature drop around the “necking” of a silicon doublet under vacuum.](image)

### 1.2.3.4 Other Models

Bruggeman developed a model for a binary mixture if homogeneous spherical inclusions [58]. The implicit equation reads

\[
\phi \left( \frac{k_p - k}{k_p + 2k} \right) + (1 - \phi) \left( \frac{k_f - k}{k_f + 2k} \right) = 0
\]

For low particle concentrations Bruggeman’s model agrees with Maxwell’s theory, however the discrepancy increase as the concentration increases.
Xuan et al., by introducing a factor $r_c$, the effective radius of aggregation, into Maxwell’s model, proposed an equation [59]

$$k = k_b \frac{k_p + 2k_f - 2(k_f - k_p)\phi}{k_p + 2k_f + (k_f - k_p)\phi} + \frac{\rho_p c_p}{2} \sqrt{\frac{k_B T}{3\pi r_c \mu}}$$

(1.14)

where $\rho$ is the density of nanoparticles and $c_p$ is the specific heat of solids. This model, which is proportional to the square root of temperature ($\propto T^{1/2}$), however, can not agree with experimental data from Das [14].

1.2.3.5 Current research

From literature survey, many computational studies suggested that clustering has a positive effect on thermal conductivity of nanofluids system [60, 45, 61], while there is still a comparable number of researchers claiming aggregation of nanoparticles would decrease the enhancement of thermal conductivity [62, 63, 17]. No general consensus has been made on what essential knowledge base of the aggregation effect.

1.2.4 Motivations

Because of the contradiction of the conclusions from past studies, we are motivated to investigate what exactly is the clustering effect over nanofluids system. With proper boundary conditions and ample particles numbers, MD could be used to obtain macroscopic dynamic properties of fluids. It is common that MD is applied on complicated fluids system such as microscopic heat transfer [64], analysis of carbon nanotubes [65]. Lee et al. applied MD to compute dynamic properties of liquid argon, including diffusion coefficient, thermal conductivity and viscosity in his study [66]. Due to the former success, MD is chosen to be the tool to compute thermal conductivity of nanofluids in this project. The questions we are trying to answer with this study is
1. What is the influence of aggregation effect in nanofluids? With molecular dynamics we try to focus on this possible mechanism. More specifically, what is the difference if the nanoparticles of nanofluids system have the shape of figure 1.9 (a) and (b)?

![Figure 1.9.](image)

Figure 1.9. Different configuration of aggregations. (a) Perfectly-dispersed (b) A doublet

2. From former study in our co-op, the thermal conductivity has a dramatically drop around the “necking” in a silicon doublet. In other words, under vacuum condition, the thermal conductivity is expected to drop when nanoparticles aggregate [67]. The significant temperature drop $\Delta T$, in figure 1.10 indicates a relatively low thermal conductivity according to Fourier’s Law. However, what will be the case if this solid doublet is put into a fluids system instead of vacuum? Will there be any difference and if so, why?

$$q = -k \nabla T$$ (1.15)

Interestingly, will it be the same case in nanofluids system which consists of both liquid and solid atoms instead of solid only?

3. If the aggregation effect is confirmed to play an important role in nanofluids system by using molecular dynamics, is it possible to propose a model explaining it?
Figure 1.10. Significant temperature drop around the “necking” of a silicon doublet under vacuum.
Chapter 2

Methodology

2.1 Molecular Dynamics

2.1.1 History

Molecular Dynamics simulation (MD) is a technique for computing the equilibrium and transport properties of a classical many-body system[68]. It was first used in the late 1950s by Alder and Wainwright for a system of hard spheres[69], where particles move at constant velocity between perfectly elastic collisions. It was not until the mid-1960s that MD was first used to solve the equations of motion for a set of LJ particles[70]. Nowadays there are commercial, open-source software available which provide sufficient features, easy-manipulated graphic interface. The Package used in this study is LAMMPS, abbreviated from Large-scale Atomic/Molecular Massively Parallel Simulator (http://lammps.sandia.gov/).

2.1.2 Fundamentals of Molecular Dynamics

Ergodic hypothesis states

\[
\overline{M} = \lim_{t \to \infty} \frac{1}{t} \int_{0}^{t} dt' M(t) = \langle M \rangle = \frac{1}{N} \sum_{i=1}^{N} M_i
\] (2.1)
where left hand side is clearly a time average and the angular brackets in the right hand side denote an ensemble average. Under this postulate, given a mechanical variable $M$ and an equilibrium thermodynamic system of interest, the long time average (i.e. in the limit that $t \to \infty$) of $M$ is equal to the ensemble average of $M$ (in the limit $N \to \infty$).

The process of Molecular Dynamics in many aspects is very similar to the real experiments. In experimental studies, we proceed as follows. First we prepare a sample of materials that we are interested in, then connect it to the instruments which we used to measure a specific property (temperature, thermal conductivity, viscosity, etc.) during a time interval. We could have reduce the statistical noise by extend the time we take measurement. In MD simulation we follow the same approach. We set a system consisting of $N$ atoms we are studying up, and by solving Newton’s equation of motion till the dynamic properties do not change with time (e.g. equilibrated system). Then we perform measurement of quantity. This can be done by expressing these observables as a function of the momenta and position of the particles.

Considering a system with $N$ atoms, the total energy of the system equals to the kinetic energy of atoms plus the potential energy of the system.

$$E_{total} = E_{kinetic} + U_{total} \quad (2.2)$$

Potential energy is a function of atom positions, $U(r_1, r_2, \ldots, r_N)$, and generally it can be divided into two parts which are interatomic van der Waals force and internal potential energy.

$$U_{total} = U_{VDW} + U_{int} \quad (2.3)$$
van der Waals force can be approximated to the summation of every atom pair

\[ U_{VDW} = u_{12} + u_{13} + ... + u_{1n} + u_{23} + u_{24} + ... \]

\[ = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} u_{ij}(r_{ij}) \] (2.4)

And total potential energy is the summation of potential energy in different coordinate system. According to classical mechanics, the force exerted on any atom \( i \) in the system is the gradient of potential energy,

\[ \vec{F}_i = -\nabla_i U \]

\[ = -\left( \frac{\partial}{\partial x_i} + \frac{\partial}{\partial y_i} + \frac{\partial}{\partial z_i} \right) U \] (2.5)

Combined with Newton’s Law, the acceleration of atom \( i \) is

\[ \ddot{a}_i = \frac{\vec{F}_i}{m_i} \] (2.6)

Integrate this equation with time, we can predict

\[ \vec{v}_i = \vec{v}_i^0 + \ddot{a}_i t \] (2.7)

\[ \vec{r}_i = \vec{r}_i^0 + \vec{v}_i^0 t + \frac{1}{2} \ddot{a}_i t^2 \] (2.8)

where \( \vec{v} \) indicates the velocity and the subscript 0 is for the initial value of any physical properties. By solving Newton’s Law numerically, calculating the force and acceleration exerted on every single atom in the system, predicting the position after a short time period \( \delta t \), then repeat everything, again computing the new force, acceleration and then new positions. The trajectory, velocity and force of every atom will be recorded.

To solve Newton’s equation numerically, the most common way to do it is Verlet algorithms. Expanding the position equation with Tyler’s series:
\[ r(t + \delta t) = r(t) + \frac{dr(t)\delta t}{dt} + \frac{1}{2!} \frac{d^2r(t)(\delta t)^2}{dt^2} + ... \]  \hspace{1cm} (2.9)

Substitute \( \delta t \) with \(-\delta t\)

\[ r(t - \delta t) = r(t) - \frac{dr(t)\delta t}{dt} + \frac{1}{2!} \frac{d^2r(t)(\delta t)^2}{dt^2} + ... \]  \hspace{1cm} (2.10)

Add (2.9) to (2.10)

\[ r(t + \delta t) = -r(t - \delta t) + 2r(t) + \frac{d^2r(t)(\delta t)^2}{dt^2} \]
\[ = -r(t - \delta t) + 2r(t) + a(t)(\delta t)^2 \]  \hspace{1cm} (2.11)

Thus the position at \( t+\delta t \) can be predicted by poistion at \( t \) and \( t-\delta t \).

Minus (2.9) from (2.10), the velocity is then expressed as

\[ v(t) = \frac{dr}{dt} = \frac{1}{2\delta t}(r(t + \delta t) - r(t - \delta t)) \]  \hspace{1cm} (2.12)

This equation tells that the velocity at \( t \) could be computed from velocity at \( t-\delta t \) and \( t+\delta t \). However a problem with Verlet algorithm is that it includes \( 1/\delta t \) term (2.12) which leads to significant error if \( \delta t \) is too small. To solve this issue, Verlet developed another algorithm called "leap-frog method" [71]. It uses different equation to compute velocities and positions of atoms,

\[ \vec{v}_i(t + \frac{1}{2}\delta t) = \vec{v}_i(t - \frac{1}{2}\delta t) + \vec{a}_i(t)\delta t \]  \hspace{1cm} (2.13)

\[ \vec{r}_i(t + \delta t) = \vec{r}_i(t) + \vec{v}_i(t + \frac{1}{2}\delta t)\delta t \]  \hspace{1cm} (2.14)

\[ \vec{v}_i = \frac{1}{2}(\vec{v}_i(t + \frac{1}{2}\delta t) + \vec{v}_i(t - \frac{1}{2}\delta t)) \]  \hspace{1cm} (2.15)

Leap-frog method not only saves the memories needed to store velocity data, it is
also simple and has high accuracy.

2.1.2.1 Force Fields

The potential used in this project is a typical 12-6 Lennard-Jones potential. It is a mathematically simple model that approximates the interaction between a pair of neutral atoms or molecules. A form of the potential was first proposed in 1924 by John Lennard-Jones[72]. The most common form of L-J potential is

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

(2.16)

where \(\varepsilon\) is the depth of the potential well, \(r\) is the distance between the particles, and \(\sigma\) is the distance at which the potential reaches its minimum. These parameters can be fitted to reproduce experimental data or accurate quantum chemistry calculations. Due to its computational simplicity, the Lennard-Jones potential is used extensively in computer simulations even though more accurate potentials exist. Figure 2.1 shows typical Lennard-Jones curves of common molecules. The minimum of potential is at \(r = 2^{1/6}\sigma\).

![Lennard-Jones potential graph of common molecules.](image)

**Figure 2.1.** Lennard-Jones potential graph of common molecules.
2.1.2.2 Boundary Condition

Computational simulation are normally performed on a small number of atoms, $10 \leq N \leq 10000$. The size of simulation domain is crucially limited to the speed of CPUs as the time taken to execute a double loop of force calculation is proportional to $N^2$. The problem of surface effect could be overcome by conducting periodic boundary conditions. Periodic boundary conditions (PBC) are a set of boundary conditions that are usually used to simulate a large system by modeling a small part that is far from its edge. The simulation box is replicated throughout space to form an infinite lattice (see figure 2.2). The duplicated boxes are labelled A, B, C, etc. As the atom 1 moves cross a boundary between two boxes, its images, $1_A, 1_B$, etc. also move through their corresponding boundaries. Thus the density in every box is then conserved, however we only have to store the information in the central box to save the limited memory. In some special simulation cases, non-periodic boundary conditions such as “fixed” or “shrink-wrapped” may be used as well.

2.1.2.3 Minimum Image Criterion

When calculating the interacting forces between atoms, we generally apply nearest mirror image method. As figure 2.3 shows, the force between $1$ and $5$ is computed by taking $E1$ and $B5$ for consideration instead of $E1$ and $E5$. Thus a "cut-off" radius idea is introduced to prevent from incorrect results. In Molecular Dynamics, the cut-off distance can not exceed half of the box length, i.e. $r_c \leq L/2$. Normally the cut-off distance is around $10 \text{ Å}$. In non-cubic simulation boxes, $r_c$ may be larger value than in the cubic boxes for a given density and number of particles.
2.1.3 Equilibrium Molecular Dynamics (EMD)

The Green-Kubo relations can give the exact mathematical expression for transport coefficients in terms of integrals of time correlation functions under a equili-
brated system [73, 74]. It is shown as:

\[ k = \frac{V}{3k_BT^2} \int \langle \vec{J}(0) \cdot \vec{J}(t) \rangle \, dt \]  
(2.17)

where \( V \) is the volume of system, \( T \) is the system temperature and \( J \) is the heat flux which can be expanded to:

\[ \vec{J}(t) = \frac{1}{V} \sum_i \left( (E_{k;i} + E_{p;i} - \langle h_i \rangle) \vec{v}_i + \sum_{j \neq i} (\vec{f}_{ij} \cdot \vec{r}_{ij}) \vec{v}_j \right) \]  
(2.18)

In (2.18), \( E_{k;i} \) and \( E_{p;i} \) stand for the kinetic energy and potential energy of \( i^{th} \) atom; \( \vec{f}_{ij} \) is the force exerted on \( i^{th} \) atom from \( j^{th} \) atom; \( \vec{r}_{ij} \) is the distance between \( i^{th} \) and \( j^{th} \) atoms; \( \vec{v}_i \) is the velocity of \( i^{th} \) atom and \( \langle h_i \rangle \) is the average enthalpy of \( i^{th} \) atom which can be computed with

\[ \langle h_i \rangle = \langle E_{k;i} \rangle + \langle E_{p;i} \rangle \]  
(2.19)

To further understand the physical mechanism, the heat flux is divided into several terms to recognize the contribution of each part. First, the heat flux in equation (2.18) can be expressed as

\[ \vec{J}_c(t) = \frac{1}{V} \sum_i \left( (E_{k;i} + E_{p;i} - \langle h_i \rangle) \vec{v}_i \right) \]  
(2.20)

\[ \vec{J}_i(t) = \frac{1}{V} \sum_i \sum_{j \neq i} \left( \vec{f}_{ij} \cdot \vec{r}_{ij} \right) \vec{v}_j \]  
(2.21)

In (2.17), the bracket denotes for the autocorrelation of heat flux. It can also be expressed in discrete form which is applicable in Molecular Dynamics simulation.

\[ k = \frac{\Delta T}{3Vk_BT^2} \sum_{m=1}^{M} \frac{1}{N-m} \sum_{n=1}^{N-m} J(m+n)J(n) \]  
(2.22)
2.1.4 Non-equilibrium Molecular Dynamics (NEMD)

Non-equilibrium Molecular Dynamics has seen a huge growth in the past years due to its ability to study transport coefficients and rheological properties of fluids mimicking real experiments[75]. What makes it different from Equilibrium Molecular Dynamics (EMD) is the presence of an external force field that drives the system arbitrarily away from equilibrium. The basic principles are common to these algorithms, namely to solve numerically Newton’s equations of motion (which determines the systems of interest) and computing the physical properties of the system as a function of its phase-space variables. However, while the theoretical framework for equilibrium systems is well established by equilibrium Statistical Mechanics, for non-equilibrium systems it is still developing [76]. It nowadays becomes a very useful tool to recreate and test real experiments or otherwise situations impossible or very difficult to obtain in a laboratory. Other approaches exist in the field of numerical simulation, such as Monte Carlo methods, first introduced by Metropolis et al. [77]. However they rely mainly on the calculation of equilibrium ensemble probabilities and are therefore not well suited for non-equilibrium processes. Since then the field has evolved significantly and now complex molecular systems, polymers, DNA filaments polymers, etc. can be simulated with the usage of appropriate theoretical models and rapidly-developed computer hardware.

A classical non-equilibrium Molecular Dynamics method for computing the thermal conductivity is developed by Muller[78]. According to Fourier’s law,

\[ q = -k \nabla T \]  

(2.23)

where \( q \) is heat flux, \( k \) is the thermal conductivity and \( \nabla T \) is the temperature gradient. A known heat flux is imposed on the system and thus the temperature gradient is obtained from the simulation record. Besides being very simple to implement, the scheme also offers several advantages such as compatibility with
often used periodic boundary conditions, conservation of total energy and total linear momentum, and the sampling of a rapidly converging quantity (temperature gradient) rather than a slowly converging one (EMD).

Figure 2.4. Illustrative figure of M-P method.

Figure 2.4 illustrate the system we apply M-P method. By changing the velocity of the hottest atom in the "cold region" with the coldest atom in the "hot region", an known heat flux will be generated thus a temperature gradient will occur as a response to the imposed heat flux. It can be expressed as

\[
J_{z,\text{heat}} = -\sum_{\text{transfer}} \frac{m(v_h^2 - v_c^2)}{2tA} \tag{2.24}
\]

where \( m \) is the mass of atom, \( v_h \) is the hot atom velocity \( v_c \) is the cold atom velocity, \( t \) is time and \( A \) is the cross-sectional area. After heat flux is manually generated, the temperature of each defined region could be valued by

\[
E = \frac{3}{2}k_BT \tag{2.25}
\]

where \( E \) is the kinetic energy of atoms. Then by equation(2.23), thermal conductivity of this system is then obtained.
2.1.5 EMD or NEMD?

These two methods are most common way to compute the thermal properties in MD simulation. Schelling et. al have discussed the difference of EMD and NEMD[79]. The results were very close under a system associated with silicon particles. Each method exhibits its own pros and cons. The direct method, compared to Green-Kubo method, shows a faster convergence. Although some non-linearity is observed in, it is suggested the nonlinear effect could be small in this temperature regime. Both methods have been used to study the thermal properties of nanofluids in literature. In fact, for an inhomogeneous system the direct method is preferred due to the capability to compute the Kapitza resistance [80]. Because of the simplicity and fastness of NEMD, it is applied in this study.

2.1.6 Simulation Details

2.1.6.1 Initial Configuration

The simplest way of constructing a liquid structure is placing the atoms randomly in the simulation box. However the difficulty is there may be many atoms overlapping which will result in unreasonable potential calculations. It is more usual to start from a lattice and allow the system to equilibrate. The proper lattice configuration is chosen depends on which material we are dealing with. Typically the face-centred cubic structure (fcc) with its $4M^3(M = 2, 3, 4, 5...)$ lattice points has been the starting configuration for many simulations. Figure 2.5 shows the fcc lattice configuration. During the process of simulation the lattice structure will disappear and replaced by a typical liquid structure (which could be confirmed by radial distribution function).
2.1.6.2 Initial Velocity Distribution

It is a must that the velocities of atoms should be specified before the MD simulation starts. The velocities is generally assigned to each atoms according to Gaussian distribution.

\[ p(v_{ix}) = \left( \frac{m_i}{2\pi k_B T} \right)^{\frac{1}{2}} e^{-\frac{m_i v_{ix}^2}{2k_BT}} \]  

(2.26)

where \( p(v_{ix}) \) is the probability density for velocity component \( v_{ix} \). Note the overall momentum is set to be zero.

\[ P = \sum_{i=1}^{N} m_i v_i = 0 \]  

(2.27)

2.1.6.3 Force Field Description

Lennard-Jones potential is chosen to apply on this study. Although most accurate potential for simulating copper atoms is embedded atom method (EAM) potential as it considers of metallic bonding [81], the LJ potential also can predict the qualitative trend of thermal conductivity enhancement pretty well [26, 27]. Also the goal of this study is to understand the aggregation effect, the simplicity of two-pair potential would make it convenient to adjust the interacting force between
solid-liquid atoms. According to literature, the typical Lennard-Jones potential of these two material are: $\epsilon_{\text{argon}} = 0.0104 \text{eV}$, $\epsilon_{\text{copper}} = 0.4096 \text{eV}$, $\sigma_{\text{argon}} = 3.405 \text{Å}$, $\sigma_{\text{copper}} = 2.338 \text{Å}$ [82, 26]. From our preliminary simulation, the thermal conductivity of this copper material is about 400 W/m-K, which is 3300 times larger than argon (0.121 W/m-K). To decrease the difference to a reasonable ratio, $\epsilon_{\text{copper}}$ is halved to 1.669 Å, making the thermal conductivity of this “modified copper” particles to be reduced 20 W/m-K. This can diminish the discrepancy of thermal conductivity between two materials in the nanofluids system.

Lorentz-Berthelot mixing rule is used for argon to copper Lennard Jones parameters[83].

\begin{equation}
\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{2.28}
\end{equation}

\begin{equation}
\epsilon_{ij} = \sqrt{\epsilon_{ii} \epsilon_{jj}} \tag{2.29}
\end{equation}
Thermal Conductivity of nanofluid Systems

3.1 Properties of base argon fluids

Before constructing the nanofluid system, the dynamic properties of base fluid, argon, will be examined as a way of validating the computational model. Argon is chosen to be the base fluid since its simplicity in modelling; it is monatomic element with full outer shell of electrons thus it generally does not form chemical bonds and is easy to simulate in molecular dynamic simulation. The usual Lennard-Jones (LJ) 12-6 potential for the interaction between atoms is used with LJ parameters, $\sigma = 0.34 \text{ nm}$ and $\epsilon/k = 120 \text{ K}$, where $k$ is the Boltzmann constant. The interatomic potential is truncated at 0.85 nm, which is the cut-off distance used in many other simulations [84]. A $8 \times 8 \times 8$ face-centred cubic system with lattice constant 5.376 Å is defined as simulation box and argon atoms with mass weight 39.948 (g/mole) are placed into this box according to the fcc lattice rules. There are totally 2048 argon atoms, making the system density being 1.374 g/cm$^2$. The periodic boundary conditions are applied in all three dimensions to keep the density constant. During the simulation, the velocities and configurations of argon atoms in each time steps are stored in memories for further analysis.
To analyze the liquid system, radial distribution function is chosen to be the first thing to look at. RDF method is widely used to characterize material state [85]. If the material we are interested is at solid state, then it should be ordered and dense, showing very slight compressibility and has definite shape and volume. Thus neighbouring atoms are found at characteristic distances. For liquid material, it is more disordered and usually slightly less dense. The spacing is irregular compared to solids, which indicates a smooth variation in atoms distance. RDF is a particularly effective way of describing the structures of disordered molecular systems (liquids). Based on this idea, the distance of particles to their neighbours are measured during simulation, then averaged over number of atoms and time. The radial distribution function $g(r)$ is defined by

$$g(r) = \frac{1}{V\rho^2} \left( \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right) = \frac{V}{N^2} \left( \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right)$$

(3.1)

where $\rho = N/V$ is the number density and $\langle \rangle$ denotes the above average over configurations with Boltzmann weighting dependent on the potential energy $U(r_N)$ that depends on the collection of coordinates for the N particles: $r_1, r_2, ..., r_N$.

Figure 3.1 is the radial distribution function of argon at its initial configuration. As stated earlier, the initial configuration is face-centred cubic lattice and it is reflected in the four peaks in figure 3.1.

However, this made-to-be-ordered system needs to be relaxed to achieve the real properties of argon fluids. After equilibrating under isothermal-isobaric ensemble ($NPT$) and canonical ensemble ($NVT$), the RDF of this system becomes figure 3.2. For this liquid argon system, $g(r)$ exhibits several peaks, revealing that at certain radius, it is more likely to find particles than at others. This is a result of the attractive nature of the interaction at such characteristic distances. The $g(r)$ plot shows that there is literally zero probability of finding particles at distances less than about 3.1 Å from each other. This is because of the presence of very strong repulsive interatomic forces at short distances of argon.
After the liquid structure of argon is confirmed by radial distribution function, thermal conductivity of bulk argon at 90 K is then calculated by two methods men-
tioned before. First, thermal conductivity is obtained with equation (2.22) under micro-canonical ensemble ($NVE$). This is a very common way to evaluate the theoretical thermal conductivity of liquid argon at low temperature that is difficult to conduct experiment[86, 87]. The heat flux over the system in $x, y, z$ directions is recorded and the autocorrelation function in Green-Kubo equation is also computed as simulation time goes by. Please note the thermal conductivity shown in figure 3.4 is averaged over three dimensions. The equilibrium result 0.121 (W/m-K) is achieved at about 6,000,000 steps and very close to literature value 0.125 (W/m-k)[88].

![Thermal conductivity computed from EMD method.](image)

**Figure 3.3.** Thermal conductivity computed from EMD method.

From the non-equilibrium molecular dynamic simulation, thermal conductivity could be obtained from heat flux and temperature gradient. The imposed, known heat flux will naturally result in a temperature gradient over the liquid system, thus gives us thermal conductivity by Fourier’s Law [78]. The heat flux resulted from exchanging hot and cold atoms over this system is calculated by equation (2.24) and recorded during each simulation time step. Figure 3.5 shows heat flux versus time. Note the heat flux reaches a steady value 1.1 MW/m$^2$ after 1 million
steps. At this moment the system already reaches its transient equilibrium state. The heat flux imposed could be controlled manually by changing the number of atoms we exchange each time step. Higher exchange frequency gives higher heat flux but also makes the system more difficult to be equilibrated. The temperature profile of this simulation box is also computed by equation (2.25) and averaged over a finite area. Figure 3.5 is the temperature profile of the system. By fitting the temperature with linear regression method, the slope \((dT/dX)\) term in Fourier’s Law) is 0.895, with coefficient of determination being 1.00. Note the temperature profile here only stands for half of the argon fluid system, but the other half has a symmetric temperature distribution as well.

Combining the slope fitted from the temperature distribution and the heat flux, using equation (2.23), the thermal conductivity of base argon fluids is then calculated. The result 0.123 (W/m-K) is also close to the literature value 0.125 (W/m-k) and is in good agreement with result from EMD. This could be viewed as a indication of thermal dynamically equilibrated system.

![Heat flux of base argon fluid](image)

**Figure 3.4.** Heat flux of base argon fluid.
3.2 Thermal conductivity of nanofluid systems

After the base argon fluid system is well constructed, nanofluid systems are then built to study the mechanisms that we are interested in. The first task is to validate if Maxwell’s prediction could be applied in this MD system. As introduced in former chapter, Maxwell presented method to predict system thermal conductivity by considering the nanoparticles are spherical, isolated in the base medium and there is no thermal interaction between the nanoparticles [11]. In other words, if these restriction are achieved, the overall thermal conductivity will only be a function of the volume fraction of nanoparticles, instead of the configuration, size, species or temperature of nanoparticles. This theory was developed based on the effective medium theory.

To test Maxwell’s theory, a nanofluid system with 4% particle volume fraction is established. Nanoparticles are created by defining a 3-D area with lattice constant 3.61 Å, replacing argon atoms within this area according the the fcc lattice rules with solid atoms, of which molar weight is 63.5 (g/mole). Different shapes
of nanoparticles such as cube, cylinder or cone could be created by carving different shapes area. The velocity distribution is initially assigned with Maxwell distribution. Relaxation of this newly created nanofluid system is needed, thus isothermal-isobaric ensemble and canonical ensemble are again used to equilibrate this system. Followed by running micro-canonical ensemble, thermal conductivity is then calculated by NEMD method.

The system size is $20 \times 10 \times 10$ with lattice constant 5.376 (7655 liquid atoms in total), and the nanoparticle size is 2.50 nm in diameter (1276 solid atoms in total), making the volume fraction equal to four percent. Figure 3.6 shows the images of the nanofluid system created by VMD [89]. White atoms stand for fluids and yellow ones are for solid. According to the NEMD method, the thermal conductivity calculated is 0.137 (W/m-K). Compared to Maxwell’s prediction from equation (eqn:1.1), which is 0.138(W/m-K), it matches the theoretic number well. Moreover, a nanofluid system with 8% volume fraction is tested as well. The nanoparticle size remain 2.50 nm in diameter while the system size is shrink to $15.5 \times 8 \times 8$ with same lattice constant to make the volume fraction 8% (3684 liquid atoms in total).

![Figure 3.6](image)

**Figure 3.6.** Atom configurations of 4% nanofluid with single spherical solid particle created by VMD.

The results show, for 8% volume fraction nanofluid, the thermal conductivity is 0.148 (W/m-K), which is lower than the theoretical value 0.153 (W/m-K). Consid-
When constructing the simulation system, the solid particle that we created is not a perfect sphere, which means some atoms may be cut by the program to match a closed shape, resulting in a volume fraction that is lower than the desired value, 8%. The actual volume fraction calculated is 7.9%.

To further validate the Maxwell’s theory, another nanofluid system is considered. The sphere in former case is split into two separated smaller spheres with diameter 1.98 nm (see figure 3.7). Since the spherical particles are separated too far to have atomic interaction with each other, the Maxwell’s prediction could still be applied. During the simulation the two particles are always separated. Thus the volume fractions are kept at 4% and 8%; only the configuration of solid particle is changed. Results from NEMD method reveals that the thermal conductivities of this system including smaller solid particles are 0.134 and 0.146 (W/m-K) for 4% and 8% respectively. This indicates the even the particles configuration changes, as long as the volume fraction and materials remain the same, thermal conductivity from simulation results would still be close to Maxwell’s prediction. In sum, according our MD simulation, Maxwell’s prediction works well on low volume fraction nanofluid with dispersed sphere particles.

Table 3.1 and figure 3.8 describe the results of 4% and 8% nanofluid, as we can see, thermal conductivities of 4% nanofluid from molecular dynamics simulation are close to Maxwell lower bound while the conductivities of 8% are below the bound. But it appears there is no difference between different nanoparticles configurations. This graph tells that the Maxwell’s prediction is applicable in our molecular dynamics simulation system; the heat transfer behaviour is the same even the larger sphere is split into smaller, spherical and well-dispersed particles.

So far, the Maxwell’s theory is validated by molecular dynamics simulation.
Figure 3.7. Atom configurations of 4% nanofluid with two separated solid particles created by VMD.

Figure 3.8. Thermal conductivity of 4% & 8% nanofluid in two different configurations.

The Kapitza resistance (thermal boundary resistance), caused by the mismatch in thermal properties between two connected material is also a possible dominant factor that may affect the heat transfer behaviour of nanofluid [39]. Originally this
Table 3.1. Thermal conductivity of 4% and 8% nanofluid containing single and two separated nanoparticles.

<table>
<thead>
<tr>
<th>Case</th>
<th>$k$ (W/m·K)</th>
<th>4%</th>
<th>8%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>●</td>
<td>0.137</td>
<td>0.148</td>
</tr>
<tr>
<td>2</td>
<td>◆</td>
<td>0.134</td>
<td>0.146</td>
</tr>
</tbody>
</table>

The thermal conductivity refers to the resistance at the interface between two solids or between a liquid and a dielectric at low temperatures. Even when materials are in perfect contact with each other, reflections happen when phonons travel toward the boundary, due to the difference in acoustic properties of adjacent materials. It has been shown that the heat flux across the boundary of a perfectly joined interface between two phases is proportional to the difference in the fourth power of temperature on each side of the interface [90]. Also, since Kapitza resistance could be a considerable mechanism around the solid-liquid contact phase, for higher contact area the resistance would be higher.

By solving the equation of phonon radiative transfer (EPRT), the thermal boundary resistance can be analytically solved, given [91]

$$R_b'' = \frac{30h^3T^{-3}}{\pi^2k_BT^2\sum_j v_{j1}^{-2}}$$  \hspace{1cm} (3.2)

where $\Gamma_{12}$ is the heat flux from medium 1 to medium 2 and the summation term is the propagation speed of longitudinal phonons to medium 1.

To investigate the role that Kapitza resistance plays in nanofluid system, a single cubic shape nanoparticle with length 2.3 nm (1183 atoms in total) is put into the argon base fluid and its thermal conductivity is calculated (see figure 3.9). Since the surface-area-to-volume ratio of sphere to cube under same volume is about 0.806, which means if the resistance over solid-liquid interface is important, an apparent difference in thermal conductivity should be observed since the thermal
boundary resistance is a geometry-independent property [39]. However, our results reveal that the thermal conductivity of 4% nanofluid system containing cubes is 0.136 (W/m-K), which could be simply justified as the same heat transfer efficiency as the former cases (0.137 and 0.134 W/m-K). Same thing is also observed when the volume fraction is increased to 8%, the thermal conductivity of cubic system, 0.147 (W/m-K), is close to the result 0.148 and 0.146. Figure 3.10 and Table 3.2 organize the results.

**Figure 3.9.** Atom configurations of 4% nanofluid with a cube solid particles created by VMD.

In sum, according to our simulations, no significant difference can be seen between the thermal conductivities of nanofluid systems with same volume fraction but different nanoparticles shapes, indicating that the interfacial resistance between solid-liquid is negligible. The possible reason is according to equation (3.2) the resistance is proportional to the reciprocal of third power of temperature. The Kapitza resistance is first time proposed in the studies of liquid helium, but in this molecular dynamics system the temperature is 90 Kelvin, which is relatively high, thus the boundary resistance effect could not be observed.

We now switch our interest to the aggregation effect in nanofluid system. In literature, people have discussed a lot about the clustering. Particularly in simulation studies, aggregations are created by Monte Carlo algorithm [59, 45], mathematical algorithms [92, 93, 62, 61], kinetic model [60] and molecular dynamic algorithms
Figure 3.10. Thermal conductivity of 4% & 8% nanofluid containing sphere and cube nanoparticles.

Table 3.2. Thermal conductivity of 4% and 8% nanofluid containing sphere and cube nanoparticles.

<table>
<thead>
<tr>
<th>Case</th>
<th>$k$ (W/m-K)</th>
<th>4%</th>
<th>8%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>●</td>
<td>0.137</td>
<td>0.148</td>
</tr>
<tr>
<td>3</td>
<td>■</td>
<td>0.136</td>
<td>0.147</td>
</tr>
</tbody>
</table>

[67]. Molecular dynamics is specifically used to investigate any possible microscopic phenomena because the atomic interaction force is considered.

To study the aggregation effect in nanofluid system, the simplest clustering case, doublet aggregated particles are put into the argon fluid system. In former cases, nanoparticles are dispersed around the fluids, but by defining two adjacent spherical regions (diameter 2.50 nm) with their distance between their centres equal to their diameters, a doublet could be created (solid atoms 831 in total, see
Comparing to figure 3.7, the solid particles in figure 3.11 are created to be touched, and due to the stronger interaction force between solid atoms, this aggregate will remain its shape during the simulation.

**Figure 3.11.** Atom configurations of 4% nanofluid with a doublet particles created by VMD.

In former Molecular Dynamics simulations, the thermal conductivity of aggregated particles in vacuum was shown to decrease dramatically due to the nanosized constrictions around the necking area between two nanoparticles [67]. However in nanofluid system, fluid atoms should be taken into account, so the heat flux will have an alternative route to go through the system instead of being forced to pass by the necking. This may be a possible reason makes the aggregation effect an enhancement over heat transfer behaviour in nanofluid system.

The simulation appears with this doublet aggregation, the thermal conductivity of 4% nanofluid system is 0.147 compared to the separated particle case, of which is 0.134 (W/m-K). The results have significant enhancement (9.7%). This apparent increase can also clearly justified by comparing to the Maxwell lower bound in figure 3.13. The ★ symbol standing for the thermal conductivity in this case, is above the lower bound. Same behaviour could also be seen in 8% nanofluid; in the nanofluid with doublet, the thermal conductivity increase to 0.168 from 0.146 (W/m-K), showing 15% enhancement. Thus we propose that aggregation has a positive effect on the heat transfer in nanofluid system.
The aggregation effect is so far confirmed to be positive when the aggregation in nanofluid is doublet, to extend our conclusion, triplet cases are also studied. A triplet aggregation is created by the similar algorithm as doublet with same volume fraction. (0.86 nm in diameter of each particle, see figure 3.12). Compared to the doublet case, the triplet case has smaller volume of each particles but two “neckings” area. Not too surprising, the simulation results indicate it has even higher thermal conductivities than the doublet cases, which are 0.165 and 0.196 (W/m-K) for 4% and 8% nanofluid, respectively. These simulations confirm that the clustering phenomena in nanofluid systems increases the effective thermal conductivity; more the aggregation, higher the thermal conductivity.

Figure 3.12. Atom configurations of 4% nanofluid with a triplet particles created by VMD.

The conclusion we made from this simulation has several intriguing point: fist, this is contradictory to the literature conclusions. In those papers, people proposed the aggregation effect is negative because of that the larger cluters (which means larger gyration radius) move slower in per unit time and invoke a weaker energy transport inside the nanofluid [59]. But what we saw here is under the same volume fraction, aggregation would result in an enhancement of heat transfer ability. Second, this conclusion explain something Maxwell did not consider in his theory; aggregation effect is excluded in the the theory by assuming all nanoparticles are “well-dispersed”, however this will never be the reality since all
realistic particles are inevitably aggregated, partially or completely as stated in section 1.2.3.1. Third, in a former aggregation study [67], the “necking” is said to be a obstruction of heat transfer under vacuum environment, however in our simulation by introducing fluid atoms into the system, the “necking” leads to an enhancement.

![Figure 3.13. Thermal conductivity of 4% & 8% nanofluid containing aggregated solid nanoparticles.](#)

### 3.3 Resistance analogy model explaining the aggregation effect

All the results are integrated in figure 3.14 and Table 3.4.

A resistance-analogy model is used to explain the increased thermal conductivities of doublets in nanofluid system. Figure 3.15 shows the simplified resistance
Table 3.3. Thermal conductivity of 4% and 8% containing aggregated solid nanoparticles.

<table>
<thead>
<tr>
<th>Case</th>
<th>k (W/m-K)</th>
<th>4%</th>
<th>8%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>◆</td>
<td>0.134</td>
<td>0.146</td>
</tr>
<tr>
<td>4</td>
<td>★</td>
<td>0.147</td>
<td>0.168</td>
</tr>
<tr>
<td>5</td>
<td>▼</td>
<td>0.165</td>
<td>0.196</td>
</tr>
</tbody>
</table>

Figure 3.14. Thermal conductivity in 4% and 8% nanofluid system with different nanoparticle configurations.

model of heat transfer behavior; in (a) when the heat flux is flowing from left to right, it passes through the resistance of bulk material ($R_m$), resistance of fluids ($R_f$) and then the resistance of bulk material again, showing a series heat circuit. Same structure could be considered for (b), while the resistance of fluids is replaced by the resistance from the “necking” area ($R_n$), which is two orders larger than $R_m$. However, it is noticed that in (c), the fluids around the aggregated particles
Table 3.4. Thermal conductivity of 4% and 8% nanofluid in different aggregation configurations.

<table>
<thead>
<tr>
<th>Case</th>
<th>$k$ (W/ m-k)</th>
<th>4%</th>
<th>8%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>●</td>
<td>0.137</td>
<td>0.148</td>
</tr>
<tr>
<td>2</td>
<td>◆</td>
<td>0.134</td>
<td>0.146</td>
</tr>
<tr>
<td>3</td>
<td>■</td>
<td>0.136</td>
<td>0.147</td>
</tr>
<tr>
<td>4</td>
<td>★</td>
<td>0.147</td>
<td>0.168</td>
</tr>
<tr>
<td>5</td>
<td>▼</td>
<td>0.165</td>
<td>0.196</td>
</tr>
</tbody>
</table>

Actually create another route for heat flux, making the circuit parallel.

Assuming $R_m = 1$, $R_f = 50$, $R_n = 100$, the effective thermal resistance of these three heat circuit will be 52, 102 and 35.3 respectively. This is quite interesting since the thermal conductivity was confirmed to be lower for a cluster under vacuum condition [67], but when the cluster is taken into fluids system, the thermal conductivity would increase on the contrary. Actually the effective resistance of (a), (b) and (c) can be mathematically expressed as

\[
R_a = R_m + R_f + R_m 
\]

(3.3)

\[
R_b = R_m + R_n + R_m 
\]

(3.4)

\[
R_c = R_m + \frac{1}{\frac{1}{R_f} + \frac{1}{R_n} + \frac{1}{R_f}} + R_m 
\]

(3.5)

where $R_c$ is always smaller than $R_a$ as long as $R_f$ and $R_n$ are larger than zero, which is always true. This simple model qualitatively reveals the aggregation would actually provide a parallel route for heat transfer, enhancing the effective thermal conductivity in nanofluid system.
Figure 3.15. Resistance-analogy model of (a) Dispersed particles in fluids (b) Aggregated particles in vacuum (c) Aggregated particles in fluids.

3.4 Further study of aggregation effect

From the above-mentioned results, nanofluid with aggregation has a significant enhancement on thermal conductivities. Motivated by this result, additional simulations are conducted to investigate the aggregation effect. The question we would like to answer is “How will the thermal conductivity change while the degree of aggregation change?”. From the simulation case 1 and 2, we know that the thermal conductivity meets the Maxwell’s lower bound in both cases, and from case 4 and 5, aggregation is confirmed to have a positive effect. If we image it is a continuous
process from case 2 to case 1, i.e., two separated particles are approaching to each other little by little, finally merging into a single one. Interesting we know the thermal conductivity at the beginning and the end are the same, but conditions in between remain unanswered (see figure 3.16).

To look at what happens between these two extreme situations, we define a variable \( d \) representing the distance between the centres of two particles and \( r \) is the radius of particles. Nanofluid systems with different aggregation configurations, said \( d = 2.0r, 1.8r, 1.5r, 1.0r, 0.8r, 0.5r, 0.0r, 0.8r, 0.5r \), are simulated. Figures 3.17 to 3.22 show the images of different degree of merging created by VMD. The “necking” area changes as \( d \) changes. Although these aggregate configurations may not be the real case that we could control in experiment, but by considering it as a continuous process, we could possibly have a deeper understanding of the effect of aggregation.

3.5 Results from different degree of merging

Those aggregates are then put into argon fluids to simulate nanofluid system with different degree of aggregations. Due to the strong interaction between solid
atoms, the configuration remain the same as the simulation goes by. Figure 3.23 reveals the thermal conductivity of different conditions. The value is also listed in Table 3.5. As the distance \( d \) increases from 0.0\( r \) to 0.5\( r \), thermal conductivity also increases to 0.178 (W/m-K) and it reaches its maximum when \( d = 0.8 \). Afterwards,
it keeps decreasing as the distance becomes farer from $1.0r$ to $2.0r$. These results match our former simulation: aggregation enhance the heat transfer, moreover, it says there is a maximum in the two extreme conditions which are single particle case and two separated particles case. This is interesting because by creating different degree of merging “aggregations”, the thermal conductivity will change as well, which is beyond Maxwell’s theory explanation.

Figure 3.22. Aggregated nanoparticle with $d = 0.5r$.

Figure 3.23. Thermal conductivity calculated from nanofluids containing different degree of aggregations.

So we know, between the two situations that nanoparticles are considered as “fully-dispersed”, there is a maximum of thermal conductivity lying in. To our
knowledge, no previous study has found this specifically using molecular dynamics. The finding provides us information that aggregation do have a positive effect when it comes to heat transfer; and the enhancement depends on how aggregated these particles are. This could be helpful in realistic nanofluid applications. Specific aggregation could be created to achieve the best condition that gives highest thermal conductivity.

3.6 Resistance-analogy-model

To explain this result, a two dimension resistance-analogy-model is proposed. In figure 3.24, a 2-D fluid system with width $2W$, length $L$ and thermal conductivity $k_f$ (blue area) is filled with two slabs with width $X$ and thermal conductivity $k_p$. Inset figure (a) shows the slabs are in touched while in (b) they are completely separated with a distance $2d$. The heat flux is assumed to flow from left to right over this 2-D system.

![Figure 3.24. Thermal resistance as a function of b from the simple model.](image)

The thermal resistance of (a) is then given by
\[ R_{\text{total},a} = \frac{W - X}{Lk_f} + \frac{X}{Lk_p} + \frac{W - X}{Lk_f} + \frac{X}{Lk_p} \quad (3.6) \]

and for (b), the overall thermal resistance is

\[ R_{\text{total},b} = \frac{W - X - d}{Lk_f} + \frac{X}{Lk_p} + \frac{d}{Lk_f} + \frac{W - X - d}{Lk_f} + \frac{X}{Lk_p} + \frac{d}{Lk_f} \quad (3.7) \]

Note equation (3.6) and (3.7) actually have the same thermal resistance. This implies that the heat transfer behaviour is not affected as long as it is under well-dispersed condition; in other words, figure 3.24 (a) is considered as a single particle and 3.24 (b) is two separated particles dispersed in fluid, giving the same system thermal resistance. However, if part of the slabs is (say C, see figure 3.25) cut to make a “bridge” between two slabs with the distance 2d fixed, then the thermal resistance is a function of C, given as

\[ f(C) = \frac{2(W - d - X + C)}{Lk_f} + \frac{2(X - C)}{Lk_p} + \frac{2d}{k_f(L - \frac{CL}{d}) + \frac{k_pCL}{d}} \quad (3.8) \]

Figure 3.25. Cut part of the slabs to create a “bridge”.

If we set \( W = 10, L = 10, k_f = 0.12, k_p = 20, d = 2, X = 3 \), then the thermal resistance can be calculated as it is the reciprocal of resistance. Results are shown in figure 3.26.

This model qualitatively explains figure 3.23. As we can see there is a maximum for thermal conductivity. Figure 3.27 (a) is when small amount of slabs are cut,
which makes a narrow “bridge”. As more amount is transferred into “bridge”, it becomes wider; since thermal resistance is proportional to heat flux flow cross-sectional area, this effect will increase the overall thermal conductivity; however, as part of the slabs is taken (Figure 3.27 (b) ), it becomes shorter, which increase the thermal resistance due to the replacement by liquid, which has lower thermal conductivity. The positive and negative effect both change the overall heat transfer behaviour, causing the extreme value between fully-aggregated and fully-dispersed conditions.
Figure 3.27. Configurations of the process of aggregation.
Conclusion and Future Work

4.1 Conclusion

We used Molecular Dynamics as a tool to investigate the possible mechanism of the abnormal thermal conductivity enhancement. This study specifically focus on the aggregation effect in nanofluids systems. First a valid atomic liquid argon system is established, and the dynamic properties of base fluids are examined with radial distribution function (RDF) and both Equilibrium Molecular Dynamics and Non-Equilibrium Molecular Dynamics. The RDF reveals that the created fluids system agrees with the characteristic of argon at 90 K; thermal conductivity from simulations also agrees with literature values.

Then different configuration of solid particles are added into the fluids to simulate the nanofluids. The results shows following points:

1. For nanofluids systems with well-dispersed nanoparticles, the thermal conductivities matches Maxwell’s theory, i.e. lying within the lower bound of H-S theory. This indicates that for nanofluids systems satisfying the Maxwell’s assumption, equation (1.1) gives a reliable prediction of this composite, heterogeneous system.
2. The role of Kapitza resistance, or so-called the Thermal Boundary Resistance (TBR) is examined. Due to the difference of surface-area-to-volume ratio, the system containing cube particles is expected to have higher TBR, i.e. lower effective thermal conductivity, if the resistance plays an important role in heat transferring; however, no significant difference is observed between these two systems, indicating the Kapitza resistance, which arises from the discontinuity between the contact surface of solid and liquid, is negligible.

3. To understand the aggregation effect in nanofluids, two different kinds of aggregated particles are created in argon fluids system. Results from our simulation show the clustering phenomena has a positive impact on thermal conductivity, in other words, aggregation is considered as a dominating factor to the significant enhancement beyond Maxwell’s prediction. This conclusion agrees with former study from other group[94]. Although clustering is claimed to have negative effect on heat transfer in the vacuum environment from former studies, on the contrary, it is proposed to enhance the thermal transfer behavior in nanofluids system. A simple resistance-analogy model is used to illustrate the aggregation effect. The liquid around the nanoparticles created other paths for heat transferring, making the a parallel system, which reduces the overall resistance.

4. Further simulations under different nanoparticle configuration are conducted. Nanoparticles with varying distances between their centers are put into the fluids system to investigate the effect of different aggregation. Our results reveal there is a maximum between two limiting conditions, which are considered as perfectly-dispersed situations. Another 2-D resistance-analogy model is proposed to qualitatively model the continuous aggregating process and it is shown that there are two factors simultaneously affecting the thermal properties; of which one is positive and another one is negative, causing the
5. The reason we used Molecular Dynamics as a research tool is that we want to see if there is any microscopic phenomena could be caught. However, the results from our simulation tells no significant behavior can only be seen within atomic scope. In other words, the mechanism of aggregation effect in nanofluids system could be explained well with a microscopic model.

4.2 Future work

From works so far, a few future works are suggested:

1. Predict the thermal conductivity of different aggregations from known configurations. It would greatly increase the potential of nanofluids system if we can predict the thermal properties precisely before we make the nanofluids.

2. Simulate realistic nanofluids that are currently applied in industry. For example water/ethylene glycol or oil/alumina nanofluids. See if the aggregation still has positive effect on heat transfer. However the potential of materials would be an issue, especially for complicated molecules.

3. Because none of any microscopic effect is observed by using Molecular Dynamics, different methodology such Monte Carlo simulation or Numerical Method, will be suggested to investigate aggregation effect. By comparing the results from simulation with different resolution, the mechanism would be further understood.
Bibliography


