MULTISCALE SIMULATION AND STATISTICAL ANALYSIS OF NANOPARTICLES SIZE EFFECT ON NANOFLUIDS EFFECTIVE THERMAL CONDUCTIVITY

by

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**Multiscale analysis of nanoparticles properties effect on nanofluids effective thermal conductivity**

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Abstract

Recent developments in nanofluids have led to a renewed interest in the nanoparticles effect on the effective thermal conductivity (ETC) of nanofluids. There are three parameters that define the nanoparticles properties: size, shape, and material. The effect of nanoparticle shape is simplified to the nanoparticle’s aspect ratio. Although the experimental data for the effect of nanoparticles aspect ratio and material on ETC are quite consistent, there are still controversial results regarding the effect of the nanoparticles size. Limitations in nano-scale experimental observations would make it even harder to approach into this topic. Thus, researchers have proposed many different macroscopic (continuum-based)/microscopic (molecular scale) numerical schemes as an alternative for experimental investigations. However, these studies are sporadic, meaning that there is not a consistent methodology to investigate the effect of the same type of a nanoparticle property in multiple scales. Here, a multiscale numerical analysis, is implemented to study the effect of nanoparticle properties on the nanofluids thermal conductivity. The multiscale analysis consists of macroscale (Navier-Stokes equation), mesoscale (Lattice Boltzmann method), and microscale (Molecular Dynamics). A Finite Element Method is implemented for the continuum-based method. At the mesoscale, results of a Lattice Boltzmann method (LBM) are taken into further statistical analysis. Using the statistical analysis on LBM results would further improve the acceptability of this method. At the microscale, a Molecular Dynamic simulation is used to investigate the effect of nanoparticles size, aspect ratio, and material on thermal energy conduction. The results demonstrate that the nanofluids thermal conductivity and the nanoparticles volume fraction can be linearly correlated. In addition, increasing the nanoparticles aspect ratio can improve ETC of nanofluids. However, the nanoparticle size is not statistically significant ($P$-Value > 0.050) to be considered as an influencing parameter when the interfacial phenomena (interfacial thermal resistance, nano-liquid layering, etc.) are not taken into account as they are largely affected by other parameters such as nanoparticles/base fluids material. The pure effect of nanoparticles size is
compensated by other parameters such as the distribution regime. This leads to the conclusion that nanoparticles size cannot play an important role in enhancing the thermal properties of nanofluids.
Lay summary

Solar energy systems required a circulating fluid that absorbs and transfers the thermal energy generated by Sun. The ability of this fluid to capture the generated heat defines the efficiency of the solar thermal system. As a novel solution, a new type of material (nanofluids) is used to be used as a heat transfer fluid in the solar thermal system. In this fluid, nano-sized solid particles in a very small amount (0.1% volume fraction) are added to conventional heat transfer fluid. The size of these nanoparticles is of great importance in terms of production costs and technical issues such as clogging in the piping, and pressure drop throughout the system. In this research, the effect of nanoparticles size is investigated using computer simulations. The results showed the size of the nanoparticles cannot have a direct effect on the thermal energy transfer efficiency of nanofluids.
Preface

The research presented in this thesis is the original work performed by the author. This thesis was supervised by Dr. Mina Hoorfar at the Advanced Thermo-Fluidic Laboratory (ATFL) in the School of Engineering, University of British Columbia. Parts of this thesis have been published in different journals. The details of the publications and the author’s contributions in them are explained below:

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<tr>
<td>A Cross section</td>
<td>a Interface of material a</td>
</tr>
<tr>
<td>$C_p$ Pressure constant specific heat</td>
<td>$b$ Interface of material b</td>
</tr>
<tr>
<td>c Lattice pseudo sound speed</td>
<td>$eff$ Effective</td>
</tr>
<tr>
<td>$D_B$ diffusivity of the nanoparticles</td>
<td>$f$ Fluid index</td>
</tr>
<tr>
<td>d Nanoparticles diameter</td>
<td>$s$ Solid index</td>
</tr>
<tr>
<td>e Lattice unit vector</td>
<td>$H$ Hot</td>
</tr>
<tr>
<td>f Distribution function</td>
<td>$C$ Cold</td>
</tr>
<tr>
<td>g Energy distribution function</td>
<td>Greek symbols</td>
</tr>
<tr>
<td>$h$ Enthalpy</td>
<td>$v$ Particles velocity</td>
</tr>
<tr>
<td>$k$ Thermal conductivity coefficient</td>
<td>$\rho$ Density</td>
</tr>
<tr>
<td>$l$ Nanoparticles aspect ratio</td>
<td>$\Gamma$ Diffusion coefficient</td>
</tr>
<tr>
<td>$m$ Mass</td>
<td>$\tau_s$ Relaxation factor</td>
</tr>
<tr>
<td>$n$ Unit normal vector</td>
<td>$\Phi_p$ Solid volume fraction</td>
</tr>
<tr>
<td>$q$ Heat flux</td>
<td>$\varphi_n$ Network ratio</td>
</tr>
<tr>
<td></td>
<td>$\varphi$ Advection-diffusion variable</td>
</tr>
<tr>
<td>$t$ Time</td>
<td>$\omega_i$ Weight coefficient</td>
</tr>
<tr>
<td>$u$ Velocity</td>
<td>$\alpha$ Significance level</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$ Potential well depth</td>
</tr>
<tr>
<td>$v$ Volume</td>
<td>$\sigma$ Distance at zero potential</td>
</tr>
<tr>
<td>$x$ Length variable</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>ETC</td>
<td>Effective Thermal Conductivity</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>FVM</td>
<td>Finite Volume Method</td>
</tr>
<tr>
<td>LBM</td>
<td>Lattice Boltzmann Method</td>
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<tr>
<td>MD</td>
<td>Molecular Dynamic</td>
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I would like to express my gratitude to my supervisor Dr. Mina Hoorfar, who offered me the opportunity for a Master’s in mechanical engineering here at UBC, Okanagan. It was a long journey that it could not be fulfilled without her kind support and supervision.

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Chapter 1: Background

1.1 Nanoparticles size and aspect ratio effect

The ever-increasing trend of energy demand has introduced major economic and political crisis in the last decades. Consequently, research regarding renewable sources of energy has attracted significant attention to provide solutions for the future of energy generation. Implementation of these research-based scenarios in real-world applications, however, demands for high capital costs and acceptable reliability and efficiency. In this situation, sustainable consumption of the current energy resources appears to be a more achievable midterm alternative. Optimization of thermal energy production, as the primary output of fossil fuels, is the first step toward sustainability and the critical step for the transition to renewable resources.

Nanofluids, dispersed thermally conductive nanoparticles in a heat transfer fluid (HTF), is one of the most creative innovation toward achieving these goals when it comes to thermal energy production and transfer. Considering the common applications of HTFs [1] thermal conductivity of HTF is the most important property that affects both thermal diffusivity and thermal convection efficacy. Therefore, the synthetization of nanofluids should be based on optimization of this property. Among all the design parameters, e.g. material, concentration, aggregation, the nanoparticles size is the most controversial factor, as there are many contradicting reports on its effect on nanofluids thermal conductivity. The importance of nanoparticles size is not limited to thermal conductivity enhancement. Challenges like pressure drop, pumping power required due to high viscosity, erosion of piping system, clogging in capillaries, are all practical obstacles that specifically initiate from the nanoparticles size effect [2].

\(^1\) Parts of this chapter have been published/submitted as a full paper in Int. Commun. Heat Mass Transf.
A prodigious number of researchers have reported the inverse relation between the size and the thermal conductivity of nanofluids [3,4]. What follows is a concise report of literature in the last 10 years that concluded the inverse relation between effective thermal conductivity (ETC) and the diameter of the nanoparticle. Teng et al. [5] examined 0.5% to 2.0% of nanoparticles weight fraction in water to determine the effect of different properties (e.g., temperature, particle size, etc.) on the thermal conductivity ratio. They concluded that smaller nanoparticles and higher base-fluid temperature can result in a higher ETC value. The probable reason was stated as the smaller the particles the larger the random movement velocity (Brownian motion) and the higher the surface area. Kazemi-Beydokhti et al. [6] discussed the same parameters affecting nanofluids heat conductivity, as well as ultrasonic mixing time, and elapsed time (the period of time that nanofluid is set to relax). Al, Al2O3, SiO2, SnO2, CuO, and TiO2, in ethylene glycol (EG) and water were used. Since decreasing the particle size results in an increase in the surface-to-volume ratio and a reduction in particle sedimentation, they reported that the size can adversely affect the nanofluids effective thermal conductivity. Cui et al. [7] conducted a simulation-based study using molecular dynamics method and found that ETC increases with an decrease in the nanoparticles diameter. In their research, water as the base fluid was mixed with Fe-based magnetic nanoparticles of three diameters (37 nm, 71 nm, and 98 nm). They suggested the inverse relation between the size of the nanoparticle and thermal conductivity is because of the nano-liquid layering (NLL) formation on the nanoparticles surface. Kalantari et al. [8] obtained the same results with silver nanoparticles in water and attributed this phenomenon to the high specific surface area and nanoparticles Brownian motion.

The controversy related to the effect of nanoparticles size on ETC is recently introduced by several studies indicating the positive effect of larger nanoparticles on nanofluids ETC [9–12]. Beck et al. [9] experimentally studied the alumina nanoparticles with different diameters dispersed in water and EG. Due to the phonon scattering at the solid/liquid interface, they showed that the largest particles have the
largest ETC. A similar experiment has been conducted by Timofeeva et al. [10] on water-based α-SiC nanofluids. The increase in ETC by increasing the nanoparticle size was observed and attributed to the increased effective volume of the solids. This conclusion was proven in another study by the same group, taking SiC in a 1:1 water-EG mixture [11]. Yu et al. [13] reviewed a few of the experimental reports on the effect of spherical particles size (Al₂O₃/EG and CuO/ water) and concluded that the larger the particle size, the larger the value of ETC. Warrier and Teja [14] conducted several experiments for different nanoparticle sizes and volume fractions and presented a one-parameter model for silver/EG nanofluids. They discussed that ETC increases by increasing the particles size which is attributed to the nanoparticle’s aggregation. They claimed that nanoparticles form conductive paths in an aggregated structure, and larger the particles, the higher the aggregations, enhancing ETC. Chauhan and Singhvi [15] applied an artificial neural network model to four combinations, namely water/CuO, EG/CuO, water/Al₂O₃, and EG/Al₂O₃. According to this study, the direct relation between the thermal conductivity and nanoparticle size attributed to greater stability of thermal conductive pathways (aggregation) for larger particles since the thinner conductive pathways are more likely to be disrupted. Pryazhnikov et al. [16] performed their experiments using CuO, Al₂O₃, SiO₂, ZrO₂, and TiO₂ and nanoparticles (10-150 nm) in water. They demonstrated the direct correlation of ETC on the nanoparticles size. Achhal et al. [17] used the equilibrium molecular dynamics method to investigate a Argon based nanofluid thermal conductivity with copper nanoparticles in solid volume fraction of 0.19% to 7.66%. The reason behind ETC enhancement and increase in nanoparticles size was assigned to the interfacial thermal resistance (ITR) at the solid/liquid interface and the decrease in the fluid condensation rate around the nanoparticle.

To better investigate the effect of the nanoparticles size (d), one should also consider the particles shape (aspect ratio (l)) as these two together can represent the geometry of particles in a more inclusive way [2,18,19]. For example, one may make a comparison between a small cylindrical particle and a large spherical one in terms of their effect on nanofluids thermal conductivity. Clearly, this comparison cannot
be answered solely based on the effect of the particles size. That is the reason why the effect of the nanoparticles shape should also be investigated if a comprehensive study on the nanoparticles size is intended. To conduct a quantitative investigation on this parameter, the particle shape can be simplified as the aspect ratio of $l=\text{length/width}$ which can be used in comparing the vast results presented in the literature for different particle shapes. There are many parameters that define nanoparticles shape (sphericity, ovality, surface roughness, etc.). Depending on the topology of the surface, their properties can change dramatically. However, here only the effect of nanoparticles aspect ratio is used. The most important reason for this simplification is that the effect of other shape parameters (sphericity, surface roughness and specific surface area, etc.) is completely known and there is no controversy in the literature. Therefore, there is no need to investigate their effect. It has been explored in several studies that increasing the nanoparticles aspect ratios increases ETC of nanofluids. For instance, the model presented by Ooi and Popov [20] showed that the oblate spheroids (with the largest aspect ratio of $l=10$) causes the largest enhancement in ETC. Jeong et. al [21] experimentally investigated the ZnO nanofluids with spherical and rectangular nanoparticle, ranging from 0.05% to 5.0% of the solid volume content (vol.%). It was shown that ETC was almost 4% higher for the rectangular shape at the same volume concentration. Alawi et al. [22] utilized different shapes (spherical, bricks, blades, cylindrical, and platelets) and different metallic oxides (ZnO, SiO$_2$, Al$_2$O$_3$, and CuO) with concentrations of 1.0 to 5.0 vol.%. In general, the nanofluid with cylindrical nanoparticle ($l=8$) had the maximum ETC while platelets ($l=1/8$) had the least. Recently, Omrani et al. [23] studied the effect of the aspect ratio and the temperature on the dispersion energy, thermal conductivity and rheological behavior of the nanofluids. They dispersed multi-walled carbon nanotubes of different aspect ratios (between 10 to 3750) in water. The largest enhancement of thermal conductivity was 36% for the sample with the highest aspect ratio at 45 °C, and the least (almost 3%) was obtained for the smallest aspect ratio at 10 °C. As it was shown in all the available reports in literature, the nanoparticles aspect ratio always has a direct effect on ETC
of nanofluids. This fact is important as it can be implemented to validate numerical models and help us to explain the complex nanoscale thermal phenomena in a more intuitive way. It should be noted that the nanoparticles shape is simplified to the nanoparticle’s aspect ratio. There are many parameters that define nanoparticles shape (sphericity, surface area, and roughness, etc.), however, here only the effect of nanoparticles aspect ratio is investigated.

The contradictory reports on the effect of nanoparticles size on the nanofluids ETC needs to be wisely addressed. Considering the enormous expenses required for fabrication of very fine nanoparticles, acquiring a solid understanding of the size effect on nanofluids ETC will highly reduce the production costs and tackle the obstacles of the commercialization of nanofluids. Although there is a significant number of reports on nanoparticles size effect, none of them have drawn a generalized framework in which the effect of the size can be independently investigated due to the following deficiencies: first, experimental studies suffer from random errors and measurement errors. Also, there are many nanoscale thermal phenomena, such as nano-liquid layering [24], interfacial thermal resistance [25], etc., that each may happen for a specific combination of nanoparticles/base fluids material. Therefore, there are many contradicting reports on the effects of the size of the nanoparticles when it comes to different materials (e.g., different phonon scattering models at the interface [26]). Second, computer simulations lack either accuracy or extra magnification at the nanoscale. The molecular dynamic (MD) method, for instance, disregards the fact that nanofluids are colloidal material and their effective properties initiate from the collective behavior of nanoparticles. In fact, nanoparticles distribution regime and their orientation in regard to the thermal energy diffusion path cannot be modeled using the MD method due to the extremely high simulation cost. The effect of the nanoparticles size should be reflected in the changes of the distribution regime as small nanoparticles have more statistical states to occupy in contrast to larger nanoparticles. Therefore, investigating the effect of the particles size is the same as the study of probable enhancement due to different nanoparticles special distribution. To overcome the interfering parameters
observed in the experiments and deficiencies mentioned in both macroscopic and microscopic numerical models, and investigate the effect of particle distribution regime originated from the size, a suitable strategy is through a mesoscopic numerical simulation namely Lattice-Boltzmann (LBM).

1.2 Nanoparticles clustering effect

Nanofluid, as a modern engineering material, has shown to provide promising solutions in heat transfer applications due to its significant thermal properties. In comparison to other multi-component thermal materials (such as composites) nanofluids have shown a much higher thermal energy conduction characteristic [27], due to, undoubtedly, the fluidity of the base material (referred to as the matrix). However, the experimental limitations in the nano-scale investigations have hindered the understanding of the primary mechanism behind this characteristic. This shortcoming has led to the proposition of different microscopic theories such as Browning motion, liquid layering, nanoparticles clustering, and ballistic phonon transport [28–31]. In this situation, numerical simulation can be implemented as a powerful tool to observe the working function of these mechanisms explicitly. Among all these theories, nanoparticles aggregation appears to be more plausible in explaining the reason behind this phenomena base on the numerous studies conducted [28,32–39]. Therefore, conduction heat transfer in nanofluids must be simulated by employing a numerical method which considers not only the microscopic nature of heat conduction in nanofluids but also the complicated stochastic geometrical structures in the computational domain. For such a numerical approach two main steps must be taken into account [40]: generating the microstructure (modeling of the aggregation process), and choosing the proper numerical solver (simulating the aggregation effect on nanofluids thermal conductivity). Nanoparticles may go under different processes in an aquatic environment such as homo/hetero-aggregation, dissolution and chemical transformation [41]. In fact, aggregation is a process during which nanoparticles may stick
together and form random structures (called aggregate) as they migrate through the base fluid. This phenomenon happens due to the interparticle forces and their interactions [42] (a complete explanation on the interfacial phenomena is provided in section 2.3).

The first strategy to introduce the effect of aggregates in the thermal conductivity calculations is through a size parameter in theoretical models [43,44]. This size parameter (equivalent radii) can be both experimentally and theoretically extracted. For instance, researchers [45] have proposed a relationship between different parameters: gyration radius, hydrodynamic radius and smallest sphere enclosing radius of an aggregate. Knowing two of these parameters through experimental investigations, the other one can essentially be derived, leading to the equivalent radii. Then, this parameter can be implemented in a mean-field theory model to import the effect of aggregation phenomenon. In another example, Wei et al. [46] derived a theoretical Hamilton-Crosser based model to import the aggregation shape effect into the effective thermal conductivity (ETC) calculation. They used the shape factor in the Hamilton-Crosser model to represent the aggregates configurations. But, since these are theoretical models, aggregates shape cannot be fully investigated in the first strategy (the theoretical approach) as it is imported within a sole number or some representative parameters. Therefore, the second strategy, numerical microstructure generation (NMG), sounds to be more promising for studying the aggregations shape effect on nanofluids ETC. Comprehensive NMG methods include those that implement the fractal theory. In the Fractal-based NMG methods, the results are more consonant with the natural behavior of the suspended nanoparticles.

The Diffusion-Limited Cluster Aggregation (DLCA) and Reaction-Limited Cluster Aggregation (RLCA) are among the mostly used fractal-based algorithms to model aggregation process [47–50]. Aside from fractal representation of aggregates, researchers [51] have implemented Population Balance Equation (PBE) method to capture the dynamic behavior of nanoparticles in terms of their aggregation,
nucleation and breakage. However, a Maxwell-based model is implemented for the ETC calculation through the Monte Carlo method. It should be noted that there are also some NMG reports in which aggregates are not modeled based on their natural behavior [52,53]. Lotfizadeh et al. [52] investigated the effect of simple regular aggregates on nanofluids ETC using Monte Carlo simulations. The aggregation growth trend and its shape evolution (aggregation middle steps) are not consonant with the real behavior of nanoparticles in nanofluids. Therefore, the exact effect of aggregation processes on the nanofluids thermal conductivity cannot be observed. Since the sizes of the nanoparticles are in the Nano range, continuum assumption for the domain does not conform to the physics of the problem, and utilizing the numerical approaches is not feasible to predict the transport phenomena in the nanofluids. In this case, the Discrete Simulation of Fluid Dynamic (DSDF) approaches such as Monte Carlo, molecular dynamics (MD), and lattice Boltzmann schemes must be employed to simulate heat transfer in the nanofluids [49,54,55].

Molecular Dynamics (MD) simulation is one of the well-known numerical methods that has been implemented by many researchers to investigate the effective thermal conductivity of nanofluids. There is a wide variety of combined methods of MD simulations [56–58]. A combined method of EMD (equilibrium molecular dynamics) and NEMD (non-equilibrium molecular dynamics) have been used by Mohebbi et al. [59]. Their simulation results revealed that the thermal conductivity computed in two separated temperatures was increased as the result of nanoparticles aggregation. In MD simulations, selecting a proper inter-atomic potential function can affect the outcome results. This function defines the position of every single particle with respect to time by considering their interactions. Kang et al. [60] studied this issue and improved the accuracy of MD simulation by implementing two potentials, the Lennard-Jones (L-J) and the Embedded Atom Method (EAM). In another study, Wang et al. studied the aggregation morphology of nanoparticles using the EMD method for copper-argon nanofluids [61]. They modeled two types of nanoparticles aggregations (loose and compact) and showed that the effective
thermal conductivity increases with decrease in aggregates fractal dimension, a parameter that mathematically defines the complex geometry of aggregates. Although MD is one of the best candidates to simulate the transport phenomena in nano-scale, the collective behavior of large body of aggregates cannot be investigated due to the significant computational cost of the MD method for simulation of the behavior of several particles.

The Lattice Boltzmann method (LBM) is another microscopic method that can handle complex geometries and requires a reasonable computational time (compared to MD) for simulation of transport phenomena in a medium. Considering the advantages of LBM for micro-scale simulations, there is a great opportunity to utilize this method to investigate nanofluids thermal conductivity which is a complex function of the nanoparticles size, aspect ratio, distribution regime, and material. LBM is capable of importing the effect of all these parameters into simulations while keeping the simulation cost comparable to conventional CFD methods (this can be observed in a few simulations conducted for other two-component systems, such as porous media, cement paste or aerogels [62–64]). For instance, Fang et al. [65] have generated microstructures for cement pastes using the open-cell and diffusion-limited cluster-cluster aggregation (DLCA) methods. Then, the LBM is implemented to solve the conduction-radiation equation to acquire the effective thermal conductivity (ETC) coefficient. The main difference between these materials and the nanofluids is the ability of nanoparticles to migrate in the base fluid which may lead to a higher heat transfer rate. Therefore, the application of LBM in nanofluids thermal energy conduction simulations would not be different from that of other materials if the migration of nanoparticles is carefully considered.
1.3 Objectives

In this project, the effects of the size and aspect ratio of nanoparticles on ETC of nanofluids is investigated using MD and FEM method and compared with statistical analysis results from LBM. This provides a robust mathematical set of tools that overcomes the deficiencies of the other numerical methods and the experimental studies suffering from variability and conflicting results. LBM analyzes the effect of nanoparticles size/aspect ratio in the presence of collective characteristics of nanofluids (i.e., nanoparticles distribution regimes). MD, investigate the atomic scale integrations for nanoparticles and the base fluid. Then, a comprehensive statistical analysis, analysis of variances (ANOVA), is performed on the numerical results to test whether the calculated discrepancies in the value of ETC can be assumed significant enough to draw a meaningful conclusion.

1.4 Organization of thesis

In this thesis, the second chapter entails the theoretical background and the governing equations of FEM and LBM. These methods include macroscale method (continuum mechanics, Navier-Stocks equation), mesoscale (Lattice Boltzmann method), and microscale (Molecular Dynamics). Chapter 3, explains the macroscale and mesoscopic methods. FEM method is used to investigate the effect of nanoparticles sizes. Then, a statistical analysis (ANOVA Test) is conducted on the FEM and available LBM results, and conclusions are made based on the statistical analysis outcomes. After that, chapter 4 talks about the microscale simulations (Molecular dynamics). The effect of nanoparticles aspect ratio (shape) is also investigated using MD. The combination of these methods together would provide a comprehensive investigation on the controversies about the nanoparticle’s properties on nanofluids thermal conductivity. The conclusion and overall findings of this thesis is summarized in chapter 5.
Chapter 2: Theory and governing equations

2.1 Macroscale governing equations

The Bhatnagar–Gross–Krook (BGK) lattice Boltzmann method fundamentally attempts to retrieve conservation equations of mass, momentum and energy [66]. Therefore, this method cannot violate the basic principles of heat transfer physics achieved by the macroscopic conservation equations. As an open topic, many researchers are presenting innovative methods to capture deficiencies of LBM when it comes about unsteady conjugate heat transfer[67–73]. In this paper, however, the interest is around effective properties (thermal conductivity coefficient) rather than time-dependent properties (in case of reacting fluids or combustion). Thus, there is no need to investigate unsteady conditions. The advection-diffusion equation with the dependent variable \( \varphi \) in the general form without the source term is [69,74,75]

\[
\frac{\partial}{\partial t}(\rho \varphi) + \frac{\partial}{\partial x_i}(\rho \varphi u_i) = \frac{\partial}{\partial x_i}\left(\Gamma \frac{\partial}{\partial x_i} \varphi\right) \tag{1}
\]

where, \( \Gamma \) is the diffusion coefficient, \( t \) is time, and \( u \) is velocity. Considering \( \varphi = h \) (\( h \) represents enthalpy) and \( \Gamma \nabla \varphi = k \nabla T \), (where \( k \) and \( T \) are thermal conductivity coefficient and temperature, respectively), Eq. (1) can be written in the following form:

\[
\frac{\partial}{\partial t}(\rho h) + \frac{\partial}{\partial x_i}(\rho hu_i) = \frac{\partial}{\partial x_i}(k \frac{\partial T}{\partial x_i}) \tag{2}
\]

Then, substituting \( h = C_p T \) (\( C_p \) is the specific heat capacity) in Eq. (2) yields:

---

2 Parts of this chapter have been published/submitted as a full paper in Int. Commun. Heat Mass Transf.
\[
\frac{\partial}{\partial t} (\rho C_p T) + \frac{\partial}{\partial x_i} (\rho C_p T u_i) = \frac{\partial}{\partial x_i} (k \frac{\partial T}{\partial x_i}) \tag{3}
\]

Effective properties of two-component systems (e.g. thermal conductivity of nanofluids) should be modeled through a steady-state solid-fluid conjugate heat transfer problem. For steady-state heat conduction in solid, Eq. (3) can be simplified as:

\[
\frac{\partial}{\partial x_i} (k \frac{\partial T}{\partial x_i}) = 0 \tag{4}
\]

Eq. 4 shows that steady-state heat conduction in solids is a function of thermal conductivity \((k)\), rather than the specific heat \((C_p)\). This rule should remain unchanged in conjugate heat transfer for any combination of materials (solid-solid, solid-fluid). In solid-solid conjugate heat transfer, temperature and heat flux continuities must be satisfied when there is no thermal resistance at the interfaces:

\[
T_{int.a} = T_{int.b} \tag{5}
\]

\[
K_a \frac{\partial T}{\partial n}_{int.a} = K_b \frac{\partial T}{\partial n}_{int.b} \tag{6}
\]

where the subscript “\(int\)” corresponds to the interfaces, \(n\) represents the unit normal vector, and \(a\) and \(b\) represent each phase. The thermal conductivity variation can be due to non-homogeneity of the material, as in a composite material. To satisfy heat flux continuity, our main objective is to obtain a valid representation for the heat flux \(q_{int}\) at the interface:

\[
q_{int} = -\frac{2k_a k_b}{k_a + k_b} \frac{T_b - T_a}{x_b - x_a} \tag{7}
\]

Here the harmonic mean of the thermal conductivities \((k_b,k_a)\) and the piecewise linear temperature profile have been employed to evaluate the heat flux at the interface to ensure the overall energy balance of the computed results. Since this is a steady-state conduction heat transfer in solid, the heat flux at the interface is dependent only on thermal conductivity of each phase, as it was declared by Eq. (4).
As mentioned earlier, effective thermal conductivity of nanofluids can be modeled through a steady-state solid-fluid conjugate heat transfer problem. Therefore, Eq. (3) is implemented in the following form (Eq. 8):

$$\frac{\partial}{\partial x_i} \left( \rho T u_i \right) = \frac{\partial}{\partial x_i} \left( \frac{k}{C_p} \frac{\partial T}{\partial x_i} \right)$$  \hspace{1cm} (8)

In contrast to Eq. (4), it can be seen that $C_p$ remains in the equation (Eq. 8). Following the same procedure, Eq. (9) can be derived for solid-liquid conjugate heat transfer [69]:

$$q_{int} = \frac{-2k_s k_f}{(k_s C_{ps} + k_f C_{pf})} \frac{T_s - T_f}{x_s - x_f}$$  \hspace{1cm} (9)

In the above equation $C_{ps}$ and $C_{pf}$ are the specific heat capacity for solid and fluid, respectively. Since steady-state heat conduction is sought, Eq. (9) cannot be accepted due to that fact that it wrongly shows the dependence of the heat flux to $C_p$ in the solid phase (in contradiction to Eq. (4)). This error can be avoided by replacing these two specific heat capacity terms with that of the fluid. As a result, the actual solid specific heat capacity does not affect the computed temperature field. However, as it is shown by Eq. (4), the heat flux at the steady-state condition is only a function of thermal conductivity, rather than heat capacity ($C_p$). This is physically accepted by the macroscopic conservation equation of energy. Since LBM tries to resemble this equation, it is expected that implementing $C_p$ in LBM mathematical machinery would not affect calculated temperature field, if the system has been allowed to reach the steady condition.
2.2 Mesoscale theoretical background

LBM can be used to simulate heat transfer phenomenon by proposing a different approach: as it is a bottom-to-top approach, one can relate the molecules’ velocity to their thermal energy content. In fact, temperature can be retrieved through definitions found in the kinetic theory [74,76].

LBM is founded on a parameter called distribution function \(f\). There are different explanations for this term, however a simple approach to define this parameter in an intuitive way is through dimensional analysis \([f] = kg \times \frac{1}{m^3} \times \frac{1}{(m/s)^3}\) [74]. In fact, it shows density of a medium \(\rho(x,t)\) consisting of particles traveling with the three-dimensional velocity \(v\) (molecules velocity) at time \(t\). Thus, this function can be defined as:

\[
\rho(x,t) = \int f(x,v,t) \, d^3v
\]  

(10)

By knowing the distribution function \(f\), other macroscopic parameters such as the momentum density, total energy density and internal energy can be defined. At the thermodynamic equilibrium state, the distribution function is denoted by \(f^{eq}\) and calculated by the Maxwell-Boltzmann distribution function, as shown below:

\[
f^{eq}(x,v,t) = \left(\frac{\rho}{2\pi RT}\right)^{3/2} \exp \left[ -\frac{(v-u)^2}{2RT} \right]
\]  

(11)

where \(R\) is gas constant, \(T\) is temperature, \(u\) is macroscopic velocity, and \(\rho\) is macroscopic density. The LBM algorithm calculates the evolution of the distribution function \(f\) at every node and defines its deviation from the equilibrium distribution function \(f^{eq}\). This can happen through the Boltzmann equation that tracks the distribution functions in a phase space consisting of time, location and velocity.

\[
\frac{\partial f}{\partial t} + v \nabla f + F_v f = -\frac{1}{\tau} (f - f^{eq})
\]  

(12)
In the above equation, the time that it takes for the distribution function \( f \) to have the equilibrium state is relaxation factor \( \tau \) that links material thermal properties to LBM. In this paper, a D2Q9 standard single relaxation-time lattice Boltzmann method is used [76]. In fluid flow application of LBM, the distribution function \( f \) stands for mass ensembles, while in Thermal LBM (TLBM) ‘\( g \)’ shows the energy distribution function. In pure thermal conduction problems, fluid macroscopic velocity is zero \( (u = 0) \) that leads to a simplified form of Eq. (13) and (14), the diffusion equation with the temperature \( (T) \) as the diffusion variable:

\[
T_{eq}^i = \omega_i T
\]  

(13)

\[
T = \sum T_{eq}^i = \sum g_i
\]  

(14)

where, \( \omega_i \) is a weighting factor. The above equation is obtained from the Chapman–Enskog Expansion [76]. Thus, the local temperature can be calculated using the discretized Boltzmann equation below:

\[
g_i(x + e_i \delta t \cdot t + \delta t) - g_i(x, t) = -\frac{1}{\tau} (g_i - g_i^{eq})
\]  

(15)

where, \( e_i \) is the lattice velocity vector for \( i = [2, 8] \) in a D2Q9 LBM model. The relaxation factor \( (\tau_g) \) can be introduced using either physical parameters or lattice parameters (lattice units). However, in both \( \tau_g \) is dimensionless. The relaxation factor defines material thermal properties. Having said that, each node in the computation domain should be assigned to a specific relaxation factor regarding its property constants. The solver distinguishes each node property, then decides which of the following relations should be used:

\[
\tau_f = \frac{3}{2} \frac{k_f}{(\rho C_p)_f c^2 \delta t} + 0.5
\]

(16)

and

\[
\tau_s = \frac{3}{2} \frac{k_s}{(\rho C_p)_s c^2 \delta t} + 0.5
\]

(17)
where $c$ is the pseudo sound speed ($c = \frac{\delta x}{\delta t}$). As it was declared before, pure conduction in the solid phase should be independent of $(\rho Cp)_s$ in steady-state condition which is violated in Eq. (16) and (17). Therefore, the term $\rho Cp$ in the solid phase is assumed to be identical to that of the fluid phase[69].

After enough time steps, the solution reaches steady state, and the effective thermal conductivity ($k_{eff}$) can be estimated using the following equation[77,78]:

$$k_{eff} = \frac{L \int q \, dA}{\Delta T \int dA}$$  \hspace{1cm} (18)

where, $q$ is the heat flux, $dA$ is the area, $L$ is the distance, and $\Delta T$ is the temperature differences.

2.3 Solid-liquid interfacial interactions in mesoscopic method

There are two main interfacial phenomenon that may enhance or hinder thermal energy conduction in nanofluids; interfacial thermal resistance (ITR) [79,80] and Nano liquid layering (NLL)[81,82]. NLL is expected to enhance the effective thermal conductivity of nanofluids as it forms a crystal-like layer of base fluid molecules around nanoparticles. On the other hand, ITR works as an obstacle for thermal waves (phonons) at the solid-fluid interface that reduces the nanofluids effective thermal conductivity. To explain the complexity of this issue, a review on literature is provided here.

There are diverse theoretical and experimental contradictory reports on the existence of each of these mechanisms. In a recent study, Guo and Zhao investigated the probability of formation of the interfacial layer around 2, 4 and 6 nm nanoparticles in a Cu-Ar nanofluid using the large-scale atomic/molecular massively parallel simulator molecular dynamics package [83]. They concluded that the interfacial nanolayer (NLL) can be formed and it is thicker for larger nanoparticles. However, the effective thermal conductivity is said to be increased when nanoparticles diameter decreases due to larger solid surface
area. On the contrary, in [28] authors showed that long sonication time can break nanoaggregates into small pieces and reduce the thermal conductivity of nanofluid. They inferred that generation of more solid surface area, and consequently, higher interfacial thermal resistance (ITR) oversees this occurrence. Alawi et. al. measured the thermal conductivity of four types of distilled water based nanofluids (Al$_2$O$_3$, CuO, SiO$_2$ and ZnO) with nanoparticles diameter of 20–100 nm [84]. In all cases, the effective thermal conductivity decreased with increase in particles size. They claimed that this enhancement is because of larger specific surface area of small size nanoparticles which can lead to the augmentation of NLL effect. This conclusion however, is in contrast to the previous findings that state NLL accrues when nanoparticles diameter is below 10 nm [79,85]. Liu et al. developed an analytical model to investigate the effect of aggregation and interfacial thermal resistance on nanofluid thermal conductivity for different nanoparticles including Alumina[79]. They showed that larger nanoparticles work better for enhancing the effective thermal conductivity. The reason was stated that the larger nanoparticles decrease the total interfacial surface geometrically. In another study, a molecular dynamics simulation by Xue et. al. indicated that NLL cannot happen at solid-liquid interfaces [86], while many other studies indicated that Nano liquid layering exists[83,87,88].

Several MD simulations showed that surface wettability (the level of contact between the base fluid and the nanoparticles surface) is the main parameter to distinguished whether interfacial thermal resistance is decreasing the thermal transport efficacy or formation of a nanometer liquid layer around particles enhances thermal transport property of nanofluids[89–92]. Hydrophobic interfaces can have 2-3 times greater ITR in comparison to hydrophilic ones [93]. Surface geometry is another interfering parameter. In an investigation, Gao et. al. measured the thermal conductivity of graphene nanoplatelet (GNP) ethylene glycol (EG) base nanofluids [94]. They proposed that the lower thermal conductivity enhancement at subzero temperatures may be due to the larger interfacial thermal resistance between GNP and EG caused by high viscosity of EG. In a recent study, Milanese et al. investigated metal and
metal oxide nanoparticles/water for the effect of nanolayer both experimentally and using MD simulations[95]. In contrast to others, their results showed that formation of nanolayer is not a function of nanoparticles diameter. Also, they showed that a nanolayer forms around Cu nanoparticles while no specific layering happens for CuO nanoparticles. This indicate the fact that Nano liquid layering can have a crucial role in some nanofluids but no effect in some other types. Atomic structure of nanoparticles/base fluid is another influencing parameter that defines the dominant phenomenon at the solid-liquid interface. For instance, monoatomic molecules are not much affected by the interfacial phenomena while the thermal transport efficacy in complex liquids such as polymers are shown to be more sensitive to the thickness of interfacial layer around nanoparticles[96,97]. The debate on the liquid nanolayer does not limit to its existence. There are conflicting hypothesizes about the thickness of this layer (0.5 to 2nm) [98,99] as well as its thermal conductivity value (1.6-3 times of base fluid’s) [100,101].

It can be inferred from these inconsistent reports that not all nanofluid systems can benefit from Nano liquid layering or suffer from interfacial thermal resistance. In LBM, Importing the effect of NLL and ITR is through adding a source term to Boltzmann equation. However, the exact value of thermal conductivity for the Nano liquid layer and interfacial thermal resistance as well as the thickness of NLL are yet to be defined by researchers. Therefore, it would lead to more uncertainty about the results. In this case, one should consider the overall effect of these mechanisms on aggregation and see how they interact if they are supposed to be considered simultaneously. If ITR exits, aggregation (solid-solid contact) would diminish ITR resulting in TC enhancement and, if NLL exists, aggregation would enhance TC more than the amount that NLL can do. Considering the mentioned overall uncertainties in literature about these two mechanisms and the ultimate target of this paper which is investigating the pure effect of aggregation through a mesoscopic approach, these nanoscale solid-liquid interactions are not considered.
2.4 Boundary conditions for mesoscopic/macroscopic method

Fig. 2.1 shows the computational domain and its boundary conditions (BCs). To investigate the effective thermal conductivity, the temperature-constant boundary conditions (Dirichlet BCs) are assigned to the right and left walls, and the zero-flux boundary conditions (Neumann BCs) are assigned to the top and bottom walls. In this figure, \( g_3, g_6, g_7 \) are known and \( g_1, g_5, g_8 \) are unknown distribution functions on the left isothermal wall (higher temperature wall with \( T_H = 350^\circ \text{C} \)). For the right isothermal wall (lower temperature wall with \( T_C = 300^\circ \text{C} \)), known and unknown distribution functions are reversed. These unknown distribution functions in TLBM are defined using the flux conservation principle (see the following equation) for a bounce-back boundary condition scheme [76,102].

\[
g_i^{neq} = g_i - g_i^{eq}
\]  \hspace{1cm} (19)

For the insulated walls, the Neumann boundary condition is used:

\[
\frac{\partial T}{\partial x} = 0
\]  \hspace{1cm} (20)

Also, the initial condition of the whole domain is set to be at \( T_C \). All the simulations in this paper are conducted in 2D. To evaluate the effect of the third dimension, we should study the geometry and the boundary conditions to see if there are any parameters that may affect. The first parameter to evaluate the probable effect is the nanoparticles aggregates. Nanoparticles aggregates are fully defined through their fractal dimensions, chemical dimension, etc. It is believed that as far as the fractal theory-based parameters of aggregates stay the same, disregarding the third dimension would not miss any extra information in explaining the geometry of aggregates. Therefore, their effect on thermal energy conduction would be the same. Horizontal walls of the domain are adiabatic (zero heat flux) and the other two walls are at constant temperature. Therefore, they can be simplified to 2D[78]. Second, the accuracy of TLBM should be checked to see if it can add any unexpected error into the results. Another
parameter is the complex geometry of interfaces (curved boundaries). In an extensive study conducted by Demuth et al., it was demonstrated that this parameter does not affect the accuracy of results[78]. More important than that, they showed that D2Q9 (as implemented here) can produce the most accurate results as well as D3Q15 in two-component thermal energy conduction (D2Q9: 2D LBM, D3Q15: 3D LBM). Therefore, two-dimensional LBM can be used interchangeably by three-dimensional LBM if the characteristics of geometry of the problem can be defined in two dimensions (which is the case for fractal objects).

![Diag](image)

Fig. 2.1. Computational domain and boundary conditions. Two walls are adiabatic, and the other opposite walls are at fix-temperature $T_C$ (300 °C) and $T_H$ (350° C).

### 2.5 Microscale theoretical background

The classic molecular dynamic governing equations are based on the Newton second law, Eq. (21). In fact, the strategy in classical molecular dynamic simulation is to calculate the interatomic forces for each particle within a limited spatial interval (neighbor particles).

$$F = ma \quad (21)$$
The governing equation for classic molecular dynamics is not provided here. In the following, the strategy for calculation of the nanofluid effective thermal conductivity is explained.

There two main categories for molecular dynamic simulations: Non-equilibrium molecular dynamics (NEMD), and Equilibrium molecular dynamics (EMD). Regarding the thermal energy conduction, NEMD calculated the effective thermal conductivity by creating a temperature gradient within the simulation box. Therefore, there will be a heat flux in the computational domain. In contrast, EMD solved the ETC without using a temperature gradient. In fact, EMD uses the strategy known as Green-Kubo formulations [103]. In Green-Kubo formulation (Eq(22)), the heat flux is calculated using the kinetic energy and potential, and stress per atom when the system is at the equilibrium state [104]

\[
J = \frac{1}{V} \left[ \sum_i e_i v_i - \sum_i S_i v_i \right] = \frac{1}{V} \left[ \sum_i e_i v_i - \sum_{i<j} (F_{ij} \cdot v_i) r_{ij} \right] \tag{22}
\]

where, \(J\) is the heat flux, \(e_i\) is the total (potential and kinetic) energy of the system (per atom), \(S_i\) is the per atom stress tensor, and \(V\) is the system volume.

2.6 Microscale Job algorithm

Large-scale Atomic/Molecular Massively Parallel Simulator known as LAMMPS is used for the MD simulations in this chapter [104]. LAMMPS, a molecular dynamic simulator developed by Sandia National Laboratories, is one of the most open source codes used for molecular dynamics simulations. Before using LAMMPS as the solver for thermal energy conduction, there are many steps need to be taken. These steps can be categorized into two groups: 1) atoms coordinates 2) interatomic forces. In MD simulations, the position of every single atom (x, y, and z coordinates) needs to be known. PDB (Program database) files contains the exact location of every atom. For simple structure, the PDB files
ca be generated using a simple script (e.g., water molecules). For the complicated structures, the PDB files are generated by experts and are available online³.

After the coordinates of the atoms are defined, the interatomic forces need to be declared. This is done using the forcefields. The interatomic forces can be defined using a function that calculates the amount of repulsion or attraction force. There are different types of force field, each of which can be used for a specific type of material. Here, one of the most practical forces fields is implemented, the Lennard-Jones force field⁴. The formulation for Lennard-Jones potential is represented as (Eq (23)):

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

(23)

where, \(\sigma\) us the cut off distance by which the interatomic potential tends to zero (neighbor definition), \(r\) is the interatomic distance, and \(\epsilon\) is the depth of the potential well. The Lennard-Jones potential can be used for two-body systems and is mostly defined as the potential between two similar atoms (e.g., H-H bonds). Here, to define the interatomic potential between other types of atoms (e.g., H-O bonds), the mix arithmetic method is used. In this strategy, LAMMPS implements an algorithm to average and calculate the potential. After defining the interatomic forces, the solver is able to run the simulation and calculate the effective thermal conductivity of the system.

³http: wiki.crystallography.net/cod/citing/webpaegs
Chapter 3: Macroscopic and mesoscopic numerical analysis of nanoparticles size effect on nanofluids effective thermal conductivity

3.1 Benchmark problems

The mesoscopic and the macroscopic methods are intrinsically bonded to each other. Although the mesoscopic method (LBM) has kinetic theory-based roots, it retrieves the continuum mechanics equations of heat transfer. Therefore, these two methods are explained together in this chapter.

LBM and FEM (Finite Element Method) results are compared with those obtained using theoretical solution for a standard test problem, i.e., a two-component heat conduction in parallel and series modes. Fig. 3.1 (a) and (b) show the parallel and series modes, respectively, and their theoretical solution used for calculation of the effective thermal conductivity ($k_{eff}$).

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5 Parts of this chapter have been published as a full paper in Analytica Chimica Acta,
The two-component system resembles a nanofluid system with solid and fluid components. Thermal conductivity of the fluid phase is selected as of water, \( k_f = 0.613 \text{ (W/mk)} \), i.e., the most common base fluid in nanofluids [105–113]. The thermal conductivity coefficients of the solid phase are assumed as \( k_{s1} = 40 \text{ [W/mk]} \) and \( k_{s2} = 11.7 \text{ [W/mk]} \) for \( \text{Al}_2\text{O}_3 \) [53,114–119] and \( \text{TiO}_2 \) [81,107,111,120–123], respectively (used as nanoparticles).

Tables 3-1 and 3-2 list the effective thermal conductivity values calculated using LBM, FEM and theoretical solution for the parallel and series modes for \( \text{Al}_2\text{O}_3/\text{water} \) and \( \text{TiO}_2/\text{water} \) combinations, respectively. Two numerical methods (FEM and LBM) are in great agreement with the theoretical results. The largest deviation of the LBM results from the theoretical solution (\( \frac{\text{LBM Value} - \text{Theoretical Value}}{\text{Theoretical Value}} \)) is less than 0.03.

The solid volume fraction \( (\phi_p) \) is chosen to be 0.15 for the test problems through this thesis. The reason is that in \( \phi_p = 0.15 \), solid volume fraction is large enough to observe the effect of nanoparticles size and aspect ratio.

Table 3-1. The ETC values for LBM, FEM, and the theoretical solution in \( \text{Al}_2\text{O}_3/\text{water} \) system at the solid volume fraction of \( \phi_p = 0.15 \).

<table>
<thead>
<tr>
<th>( k_{\text{eff}} \text{ [W/mK]} )</th>
<th>Al(_2)O(_3/\text{water} )</th>
<th>Parallel</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical Solution</td>
<td>6.916</td>
<td>0.728</td>
<td></td>
</tr>
<tr>
<td>FEM</td>
<td>6.915</td>
<td>0.727</td>
<td></td>
</tr>
<tr>
<td>LBM</td>
<td>6.917</td>
<td>0.738</td>
<td></td>
</tr>
<tr>
<td>Deviations from Theoretical Solution</td>
<td>FEM</td>
<td>( 1 \times 10^{-4} )</td>
<td>0.001</td>
</tr>
<tr>
<td>LBM</td>
<td>( 1 \times 10^{-4} )</td>
<td>0.013</td>
<td></td>
</tr>
</tbody>
</table>
Table 3-2. The ETC values for LBM, FEM, and the theoretical solution in TiO_2/water system at the solid volume fraction of $\phi_P = 0.15$.

<table>
<thead>
<tr>
<th>$k_{\text{eff}}$ [W/mK]</th>
<th>Parallel</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Solution</td>
<td>2.387</td>
<td>0.722</td>
</tr>
<tr>
<td>FEM</td>
<td>2.387</td>
<td>0.722</td>
</tr>
<tr>
<td>LBM</td>
<td>2.409</td>
<td>0.742</td>
</tr>
<tr>
<td>Deviations from Theoretical Solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FEM</td>
<td>0</td>
<td>0.009</td>
</tr>
<tr>
<td>LBM</td>
<td>0.009</td>
<td>0.028</td>
</tr>
</tbody>
</table>

3.2 Numerical microstructure generation

The numerical microstructure generation (NMG) algorithm is implemented to generate the nanoparticles distribution in the computational domain. The nanoparticles are distributed randomly in terms of their spatial location and orientation (for nanorod particles). The solid volume fraction ($\phi_P$) as well as the particles size and aspect ratio can be controlled using the parameters defined in microstructure generator algorithm. Also, the NMG algorithm is prohibited from generating a repetitive configuration so that increasing the number of trials leads to error reduction and covering all the possible states that nanoparticles can occupy in real distribution. It should be noted that the algorithm avoids nanoparticles to form aggregations through defining a minimum proximity distance.
3.3 Results and discussions

This section is divided into two categories. First the effect of nanoparticles size is explained. Next, the effect of nanoparticles aspect ratio is discussed.

3.3.1 Effect of nanoparticles size

There are two steps prior to utilization of LBM for studying the nanoparticles size effect. In the first step, the square particles are uniformly distributed (homogenous regime). Then, the particles are allowed to randomly distribute in the entire computational domain (heterogenous regime) and the ETC value is calculated. The use of the square particles simplifies the problem by eliminating any nuance effects of curved boundaries for the conjugate heat transfer. The reason behind having two distribution regimes is to precisely evaluate the effect of geometry on the results. In both regimes, the computational domain is dimensionless. For the homogenous regime, results of FEM, LBM and the analytical solution are provided. Based on the results of these methods, LBM and FEM are selected to calculate the ETC for the heterogenous regime. When particles randomly distribute (heterogenous regime), there is an interval of answer as the simulations are replicated to cover more possible states that nanoparticles can distribute. Therefore, a statistical analysis is conducted to evaluate the answer intervals. Having different calculation methods for different distribution regimes provides a preliminary analysis through which LBM is validated to be used for the real nanofluid system, i.e., the second step.

3.3.2 Benchmark for nanoparticles size effect

The square particles distributed in a homogenous regime (chequered pattern) are shown in 3.2 (a-d). These conditions simplify the problem so other numerical methods and the analytical solution can be implemented. The particles size in regard to the computational domain is normalized in this way: the
network ratio \((\varphi_n)\) which is the ratio of the number of the nodes used to define a particle \((n)\) to the total number of nodes in the computational domain \((N)\).

\[
\varphi_n = \frac{n}{N}
\]  

(1)

This parameter indicates how many particles are considered to form the solid phase in different volume fractions. Smaller value of this parameter means more particles in the network. This would lead to more permutations that the particles can put together, while large values show a smaller statistical sample size. In this way, we have implicitly generated microstructures capable of resembling nanoparticles in different sizes in a dimensionless computational domain.
Fig. 3.2. Temperature distribution for homogenous and random (heterogenous) distribution of nanoparticles for a) $\phi_n=0.15$ b) $\phi_n=0.03$ c) $\phi_n=0.005$ d) $\phi_n=0.001$.

The simulation is conducted for water as the base fluid, and Al$_2$O$_3$ as the solid phase ($K_{Solid}=40$ [W/mK], and $K_{Fluid}=0.613$ [W/mK]). First, the homogenous systems are discussed (Fig. 3.2 (a, b, c, d)). The 1D and 2D resistor network are implemented here as well.

The homogenous pattern results for different methods are presented in Table 3. The 1D resistor circuit method predicts smaller values for the effective thermal conductivity of Al$_2$O$_3$/water at solid volume fraction of $\phi_P=0.15$, while the largest difference between FEM and LBM is around 8%. The difference between the values of the network ratio for each of the numerical methods is lower than 1%, and the
difference between the ETC mean values of FEM and LBM is not more than 2%. The 1D resistor network calculates identical results for all values of $\varphi_n$ ($k_{eff}=0.7721$). This happens due to over simplifying the problem by considering one dimensional heat conduction.

Next, a random distribution (heterogenous distribution) of particles is generated and ETC is calculated. Fig. 3.2 \((a, b, c, d)_i\) to \((a, b, c, d)_{ii}\) show examples of the random distribution of the nanoparticles as well as the temperature field for different values of $\varphi_n$. The random distribution of particles in the computational domain leads to variations of the results. Therefore, in contrast to the previous homogenous distribution, the calculated ETC differs in every simulation resulting in a set of values (answer interval) for the value of ETC. In the other word, the calculated ETC is a random variable in this study. Next, a random distribution (heterogenous distribution) of particles is generated and ETC is calculated. Fig. 3.2 \((a, b, c, d)_i\) to \((a, b, c, d)_{ii}\) show examples of the random distribution of the nanoparticles as well as the temperature field for different values of $\varphi_n$. The random distribution of particles in the computational domain leads to variations of the results. Therefore, in contrast to the previous homogenous distribution, the calculated ETC differs in every simulation resulting in a set of values (answer interval) for the value of ETC. In the other word, the calculated ETC is a random variable in this study. Here, random variable refers to a variable that changes when the simulation geometry (computational domain) changes. In other word, every distribution of particles has a different ETC value as particles are in a configuration different from the previous one. ETC is a random variable because its value is affected by another random phenomena (random spatial distribution of particles).
Table 3-3. Comparison of the methods for ETC with the volume fraction of 0.15 with homogenous distribution of square particles (Fig. 3.2. (a), (b), (c), (d)).

<table>
<thead>
<tr>
<th>Method</th>
<th>Network ratio ($\varphi_n$)</th>
<th>ETC [W/mk]</th>
<th>ETC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1D resistor circuit</strong></td>
<td>0.15</td>
<td>0.7721</td>
<td>1.2596</td>
</tr>
<tr>
<td></td>
<td>0.036</td>
<td>0.7721</td>
<td>1.2596</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>0.7721</td>
<td>1.2596</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>0.7721</td>
<td>1.2596</td>
</tr>
<tr>
<td><strong>2D resistor circuit</strong></td>
<td>0.15</td>
<td>0.92869</td>
<td>1.51499</td>
</tr>
<tr>
<td></td>
<td>0.036</td>
<td>0.91825</td>
<td>1.4979</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>0.96957</td>
<td>1.5816</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>1.03797</td>
<td>1.69327</td>
</tr>
<tr>
<td><strong>FEM</strong></td>
<td>0.15</td>
<td>0.841424</td>
<td>1.372</td>
</tr>
<tr>
<td></td>
<td>0.036</td>
<td>0.83868</td>
<td>1.368</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>0.8406</td>
<td>1.371</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>0.84088</td>
<td>1.371</td>
</tr>
<tr>
<td><strong>LBM</strong></td>
<td>0.15</td>
<td>0.852</td>
<td>1.3906</td>
</tr>
<tr>
<td></td>
<td>0.036</td>
<td>0.8527</td>
<td>1.3911</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>0.858</td>
<td>1.4004</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>0.8694</td>
<td>1.4182</td>
</tr>
<tr>
<td><strong>Maxwell Model</strong></td>
<td>-</td>
<td>0.894</td>
<td>1.46</td>
</tr>
</tbody>
</table>

In order to compare the values of ETC in each sample, the analysis of variance (ANOVA) test is conducted [124]. This statistical technique is able to detect any significant difference between the means of any samples. One of the most recent investigations was conducted by Joseph et al. on SiO$_2$/Ag-CuO
water-based nanofluid showing the impact of the particle and surfactant concentrations [125]. ANOVA was used to evaluate the significance of the interfering parameters. Iranmanesh et al. [126] developed a mathematical model for the viscosity and ETC of aqueous graphene nanosheets nanofluids by taking into account the concentration, temperature and specific surface area of the nanosheets. The significance of the model was tested using ANOVA. Most relevant to this study, Esfe et al. [127] used ANOVA to study the effect of temperature, size and volume fractions of nanofluid on ETC of MgO/water nanofluid. The outcome of their study showed the negligible effects of the particle sizes on ETC.

The interval plot of LBM and FEM results are shown in Fig. 3.3. As mentioned above, an ANOVA test is conducted for these responses. The $P$-value for the effect of particles size (comparison of the ETC values for different particle sizes) is more than the assumed significance level ($\alpha=0.05$), meaning that the effect of the particles size is not statistically significant. Therefore, the effect of the particles size on ETC is negligible.

Fig. 3.3. ETC [W/mK] as a function of the network ratio change at $\phi_P=0.15$ using LBM and FEM.
Fig. 3.3 shows an important phenomenon happening in the simulated system. When there is only one particle, the answer span (changes of ETC value due to the variations of the distribution regime) is smaller than the other two configurations (4 and 25 particles). The reason can be justified by the number of states that particles can occupy within the base fluid. In another word, the number of spatial configurations that 4/25 particles can occupy relative to each other is higher than that of a single particle. This leads to more variations in the ETC value indicating the effect of distribution regime on the ETC. However, when the number of particles increases from 25 to 64, the response variations decrease again. Although the number of spatial configurations for 64 particles is larger than the other systems, their effect is not significant that can fluctuate the ETC value the way 4/25 particles do. On the other hand, this system has a large number of small particles where particle-free zones (acting as a thermal resistant) are minimized. In systems with 4/25 particles, depending on the spatial distribution of particles, particle-rich zones can occur and affect the ETC value significantly. In a 64-particle system, particles are almost occupying everywhere so that there cannot be a relatively large particle-free zones/particle-free zones. That leads to a smaller range of responses (fewer variations of the ETC value).

3.3.3 Nanofluid system

Regarding the ANOVA results for the benchmark problem, the effect of the particles size was found to be insignificant on ETC. At the next step, the geometry and the scale of the computational domain is changed to that of the nanofluids. The microstructure generated for real nanofluids is demonstrated in Fig. 3.4 the random distribution of nanoparticles agrees with the normal behaviour of nanoparticles in a base fluid. Fig. 3.4 (a) shows the smallest diameters; while Fig. 3.4 (c) presents the largest size considered for the particles. The simulation has been performed for the diameters of 10, 20, and 40 nm.

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6 The LBM results are previously published somewhere else. They are provided here for the statistical analysis and comparisons made with FEM results and MD simulations: H. Tahmoressi, MSC. Thesis, energy systems (technology of energy), Faculty of New sciences and Technologies, University of Tehran, Iran, 2017.
for the solid volume fraction of 2, 4, 6, 8, and 10. Also, each particle is considered to be circular so that a fixed diameter can be considered.

![Image of nanoparticle sizes](image)

**Fig. 3.4.** Different size of the nanoparticle for spherical nanoparticles for (a) d=10nm, (b) d=20nm and (c) d=40nm.

The calculated thermal conductivity enhancement for Al₂O₃/water and TiO₂/water for d=10, 20, and 40 nm are shown in and Fig. 3.5, respectively. The results are also compared with the Maxwell model.

![Graph of thermal conductivity enhancement](image)

**Fig. 3.5.** ETC (%) for Al₂O₃/water nanofluid (LBM simulation) at different volume fractions for d=10nm, d=20nm, and d=40nm.
Before making any conclusion, a comprehensive statistical analysis is needed for the results presented in Fig. 3.5 and Fig. 3.6. The first observation from these figures implies that the smaller nanoparticles enhance ETC more than the larger nanoparticles. However, the degree of this enhancement should be statistically tested to see if it can be defined as a meaningful signal rather than noise in the responses. Fig. 3.7 shows the interval plot for the mean of nanoparticles sizes at each volume fraction for both Al₂O₃ and TiO₂. In all cases (Fig. 3.7), the P-Value is more than the assumed significance level (α=0.05) indicating that there is not enough evidence to reject the hypothesis stating that the samples’ means are different. Therefore, it cannot be statistically concluded that nanoparticle size affects the nanofluids thermal conductivity coefficient. In some cases, e.g., TiO₂, Φp =0.08, P-Value is very close to the assumed significance level. This means that there are errors, such as limited randomness due to the developed numerical microstructure generator, affecting the results. Also, understanding the physics behind parameters affecting nanofluids thermal conductivity value is crucial in drawing a conclusion on the effect of the nanoparticle size. When the nanoparticle size decreases, the surface to volume ratio
increases. Hence, depending on the solid/fluid combination, the size is not the only parameter affecting ETC; other mechanisms (e.g., surface chemistry that may lead to interfacial thermal resistance or nano-liquid layering) can also play a role.

In addition to the Maxwell Model, the LBM simulation results are compared with a few experimental results available for TiO$_2$/water (Fig. 3.8). Although the nanoparticles size in all the experimental results for similar nanofluids are approximately 10nm, the ETC values differ significantly. This supports the fact that in the experiments, there are many other variables that are not reported or cannot be controlled.

Additionally, the ETC is mostly reported as a single value rather than a set of values for a number of experimental replications. In fact, if a thorough design of experiment (DOE) and a subsequent statistical analysis has been done for each of these experiments, the conclusion on nanoparticles size effect could

![Fig. 3.7. ETC [W/mK] interval plot for different nanoparticles sizes and volume fractions. Several simulations are conducted for each nanoparticles size. Figures above show the changes of ETC at each nanoparticle sizes. The P-Values are calculated from the ANOVA test. Al$_2$O$_3$: (a) $\Phi_p=0.2$, P-Value=0.23 (b) $\Phi_p=0.04$, P-Value=0.56 (c) $\Phi_p=0.06$, P-Value=0.13 (d) $\Phi_p=0.08$, P-Value=0.22 (e) $\Phi_p=0.1$, P-Value=0.22. TiO$_2$: (f) $\Phi_p=0.2$, P-Value=0.1 (g) $\Phi_p=0.04$, P-Value=0.29 (h) $\Phi_p=0.06$, P-Value=0.16 (i) $\Phi_p=0.08$, P-Value=0.056 (j) $\Phi_p=0.1$, P-Value=0.059]
be potentially different. These are the reasons why numerical simulations are of great importance when it comes to nanoparticles size effect on the ETC.

![Graph showing ETC (%) for TiO$_2$/water (LBM simulation) at different volume fractions for nanoparticles with approximate size of d=10nm; Angayarkanni and Philip [126], Timofeeva et al. [52], Patel et al. [127], Pak and Cho [128], and Zhao et al. [129].]

3.3.4 Effect of nanoparticle aspect ratio (shape)$^7$

To investigate the effect of the nanoparticle shape on the ETC of nanofluids, microstructures for rod-like nanoparticles in different aspect ratios ($l$) have been developed. Nanorods are the nanostructures with higher aspect ratios than sphere shaped particles. The effects of the particle’s aspect ratio are studied using three different configurations shown in Fig. 3.9. For TiO$_2$/water, the values of $l = 7, 9, \text{ and } 29$, and for $\text{Al}_2\text{O}_3$/water, $l = 2, 3, 4, 7, \text{ and } 8$ have been generated.

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$^7$ These results are previously published somewhere else. They are provided here for the statistical analysis and comparisons made with FEM results and MD simulations: H. Tahmoressi, MSC. Thesis, energy systems (technology of energy), Faculty of New sciences and Technologies, University of Tehran, Iran, 2017.
Fig. 3.9. Different aspect ratios for rod-like nanoparticles generated for the LBM simulation. Aspect ratios of TiO2/water, $l = 7$, 9, and 29, and for Al2O3/water, $l = 2$, 3, 4, 7, and 8.

As it was mentioned in Section (2.2), the value of effective properties, e.g. thermal conductivity coefficient ($k_{eff}$), stabilizes at the steady-state condition. The temperature field evolution in the LBM simulation is shown in Fig. 3.10. The temperature of the left and right side of the domain is 350K and 300K, respectively. The effect of temperature is not investigated in this project. Therefore, this temperature is selected as the common working temperature of nanofluids. For instance, the working temperature of small-scale solar thermal collectors is under 100° C. The temperature distribution has a nonlinear behaviour at the beginning (Fig. 3.10 (a)). By approaching to the steady state condition, the temperature field stabilizes to a linear distribution (Fig. 3.10 (d)). It should be noted that the temperature gradient slope of the particle is distinguishable from the base fluid due to the different values of thermal conductivity coefficients.
The LBM simulation results for Al₂O₃/water nanofluid in 5 different aspect ratios are shown in Fig. 3.11. As it can be seen, increasing the nanoparticles aspect ratio results in the ETC enhancement. To further validate the LBM results, Hamilton–Crosser (HC) model [128] and Timofeeva’s experimental results [129] for the aspect ratio of 8 are also provided. LBM, HC and Timofeeva’s result are in great agreement. The deviation between the LBM and the HC is about 2%.

Fig. 3.11. ETC (%) for Al₂O₃/water nanofluid (LBM simulation) compared with the theoretical model and with the experiment conducted by Timofeeva et al. [52] for l=2, 3, 4, 7, and 8.
Next, LBM is used for TiO$_2$/water nanofluid (Fig. 3.12) for the aspect ratios similar to the Murshed’s analysis [130]. Increasing the aspect ratio enhances the heat conduction rate. For example, at the fixed solid volume fraction of 0.060, the ETC of $l = 29$ is 1.32, that is 13% higher compared to that obtained for $l = 7$ (ETC = 1.17%). The effect of the aspect ratio is negligible for the aspect ratios close to each other (such as $l = 7$ and $l = 9$) at low solid volume fractions; for instance, for solid volume fraction of $\phi_P = 0.02$, the thermal conductivity enhancement value for all aspect ratios are equal, but as the volume fraction increases, the values of ETC grows in different rate resulting in a higher enhancement of ETC for higher aspect ratios (at volume fraction of $\phi_P = 0.08$, ETC = 1.27 for $l = 9$, and ETC = 1.22 when $l = 7$). When the particles have larger aspect ratio, the particles aligned with the heat flux direction are longer and as a result, it provides a longer pathway for thermal energy conduction within a solid phase. This thermal energy pathway leads to a higher thermal conductivity coefficient in nanofluids.

![Fig. 3.12. ETC (%) for TiO$_2$/water nanofluid (LBM simulation) for $l = 7, 9,$ and 29.](image-url)
Chapter 4: Microscopic numerical analysis of nanoparticles size effect on nanofluids effective thermal conductivity

4.1 Crystal structure of nanoparticles

Microscale simulation consists of modeling the atomic structure of the material in a nanofluid system. This means that the atomic structure of the material should be exactly defined within the simulation. Here, there are two types of material: water; nanoparticles. The molecular structure of water (base fluid) does not need extra explanations as it is very common. However, metal oxide nanoparticles crystal structure is of a great importance. In fact, in classic molecular dynamic simulations, the lattice properties define the way energy dissipate within the structure. The lattice structure and the vibrational modes are the key parameters for thermal energy conduction throughout the material. In the following, the crystal structure of the nanoparticles used in this research are explained[131]. The following illustrations for the nanoparticles atomic structures are generated using VMD[132].

4.1.1 Alpha-alumina nanoparticle

For alumina nanoparticles, the alpha type (corundum) is the most common used nanoparticle in the literature. There are other types of alumina nanoparticles (e.g., Gamma), they are not explained here. The lattice constant in direct a and b are equal to \( a = b = 4.759 \), and \( c = 12.991 \) in the third direction. Fig 4.1 shows the unit cell for the alpha-alumina structure in which \( a, b, \) and \( c \) are unit cell physical dimensions (lattice constants) in \( x, y, \) and \( z \) directions.

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\(^8\) Parts of this chapter have been published/submitted as a full paper in Int. Commun. Heat Mass Transf.
Fig. 4.1. Alpha-alumina crystal unit cell with unit cell physical dimensions of $a=b=4.759$, and $c=12.991$. The unit cell is shown in top view (left), and isometric view (right) [131,132]

4.1.2 Titanium dioxide nanoparticle

Titanium dioxide nanoparticles, similar to alumina nanoparticles have different crystal structures. Here, the Anatase structure is used as it is the most common type of Titanium dioxide nanoparticles used in nanofluids [133]. This crystal structure with the lattice constants of $a = b = 3.776\,\text{Å}, c = 9.486\,\text{Å}$ has a tetragonal structure (Fig. 4.2). The other crystal structure for Titanium dioxide is the Rutile with lattice constants of $a = b = 4.594\,\text{Å}, c = 2.959\,\text{Å}$. Fig. 4.3 shows the unit cell for this crystalline structure. Finally, the third crystalline structure for this material is the one known as Brookite. Fig. 4.4 shows the unit cell and the lattice constants ($a = 9.166\,\text{Å}, b = 5.436\,\text{Å}, c = 5.135\,\text{Å}$).
Fig. 4.2. Anatase crystalline structure for titanium dioxide. The unit cell physical dimensions are:
\[ a=b=3.776\text{Å}, c=9.486\text{Å} \] [131,132]

Fig. 4.3. Rutile crystalline structure for titanium dioxide. The unit cell physical dimensions are:
\[ a=b=4.594\text{Å}, c=2.959\text{Å} \] [131,132]
Fig. 4.4. Brookite crystalline structure for titanium dioxide. The unit cell lattice constants are: 
\[a=9.166\text{Å}, b=5.436\text{Å}, c=5.135\text{Å}\] [131,132]

4.2 Effect of nanoparticle size in Al₂O₃/water nanofluid

The effect of nanoparticles sizes has been investigated by other researchers using MD simulation[55]. However, the main advantage of the strategy implemented here is the consistency of the comparison. The material used for all the simulations in different scales are the same. Therefore, a more safe and comprehensive comparison can be made.

The solid volume fraction for all of the simulations in this chapter is chosen to be \(\Phi_p = 0.1\) as in the previous section. In contrast to the previous chapter where meso/macroscale simulations were conducted at different volume fractions, here only one volume fraction is selected. The reason is that: it was shown that the effect of nanoparticle size and volume fraction do not have interactions. This fact is also pointed out by other authors as discussed in chapter 1.

Fig. 4.5 indicates three different sizes of nanoparticles selected in this chapter. These sizes are a) \(d_p = 18.14\text{Å}\), b) \(d_p = 22.86\text{Å}\), c) \(d_p = 28.8\text{Å}\). It should be noted that the dimensions cannot be the same
as those in the previous chapter. The reason is the intrinsic feature of MD simulations which is in micro scale. In mesoscale simulations, the window can be larger as the interatomic interactions are simplified by considering an ensemble of molecules, kinetic theory. Here, the window through which we look at the thermal energy conduction is at the molecular level; therefore, the collective behaviour of nanoparticles cannot be seen.

![Fig. 4.5. Alpha-alumina spherical nanoparticles in different sizes. a) d\_p=18.14 Å, b) d\_p=22.86 Å, c) d\_p=28.8 Å [132].](image)

The next step is to disperse the nanoparticles in the base fluid. This step is done using the open source code develop by [134]. Figs. 4.6 to 4.8 shows the dispersed nanoparticle sin the base fluid, water. As it can be seen, for nanoparticle with $d_p = 18.14$ Å, 4 particles are needed to achieve the solid volume fraction of $\Phi_p = 0.1$. Hence, for nanoparticle with the $d_p = 28.8$ Å, only one particle will produce the desired solid volume fraction. In fact, these sizes are selected in a way that the solid volume fraction is kept constant.
Fig. 4.6. Alpha-alumina nanoparticles with $d_p=18.14 \, \text{Å}$ dispersed in the base fluid (water) with the simulation box of $a=b=c=50\text{Å}$ [132].

Fig. 4.7. 2 Alpha-alumina nanoparticles with $d_p=22.86 \, \text{Å}$ dispersed in the base fluid (water) with the simulation box of $a=b=c=50\text{Å}$ [132].
As we are working at the molecular level, the solid volume fraction definition needs to be defined based on the non-continuous definitions, i.e. the number of molecules. Here, the simulation box dimension is chosen to be 50 Å. For this simulation box, the total number of 3762 water molecules are selected. Considering the density of water as 1 [g/mL] and the molar mass of 18 [g/mol], the solid volume fraction of $\Phi_p = 0.1$ can be achieved.

4.3 Effect of nanoparticle size in TiO$_2$/water nanofluid

The solid volume fraction for the titanium dioxide nanoparticles are chosen to be $\Phi_p = 0.1$. Fig. 4.9 indicates three different sizes of nanoparticles, selected similar to the alumina nanoparticles. These sizes are a) $d_p = 18.14$ Å, b) $d_p = 22.86$ Å, c) $d_p = 28.8$ Å.
Fig. 4.9. Anatase titanium dioxide spherical nanoparticles in different sizes. a) $d_p=18.14$ Å, b) $d_p=22.86$ Å, c) $d_p=28.8$ Å[132].

Similar to the alumina nanoparticles, the titanium nanoparticles are dispersed in the base fluid using Packmol code. Figs. 4.9 to 4.12 shows the dispersed nanoparticle sin the base fluid, water. As it can be seen, for nanoparticle with $d_p = 18.14$ Å, 4 particles are needed to achieve the solid volume fraction of $\Phi_p = 0.1$. Hence, for nanoparticle with the $d_p = 28.8$ Å, only a single particle is enough.
Fig. 4.10. 4 titanium dioxide nanoparticles with d_p=18.14 Å, dispersed in the base fluid (water) with the simulation box of a=b=c=50Å [132].

Fig. 4.11. 2 titanium dioxide nanoparticles with d_p=22.86 Å, dispersed in the base fluid (water) with the simulation box of a=b=c=50Å [132].
4.4 Effect of nanoparticles aspect ratio in Al$_2$O$_3$/water nanofluid

In this section, the effect of nanoparticles shape is investigated using the molecular dynamic simulations. The effect of nanoparticles shape is studied using the definition of shape factor or aspect ratio ($l$). This is simply defined as the ratio of length to the width of nanoparticles. In the previous section, 2d simulations were conducted for macro/mesoscopic scales. Therefore, rectangular nanoparticles were used for the shape effect study. Here, as the simulations are conducted in 3D, cylindrical nanoparticles are used. Therefore, the aspect ratio is defined as the ratio of the height to the diameter of cylindrical nanoparticles ($l = h/d$). Three cylindrical nanoparticles with aspect ratio of $l = 1$, $l = 2$, and $l=3$ is designed. Fig 4.13 shows different aspect ratios for alumina nanoparticles. Next, these nanoparticles are dispersed into the base fluid in a way that the solid volume fraction is $\Phi_p = 0.1$ (figure not provided).
4.5 Effect of nanoparticle aspect ratio in TiO$_2$/water nanofluid

For the titanium dioxide nanoparticles, the same strategy is considered. Three cylindrical nanoparticles with the aspect ratios of $l = 1$, b) $l = 1.62 = 5$, c) $l = 2$ are designed (Fig. 4.14). Later, using Packmol code, these nanoparticles are immersed into the base fluid.
4.6 Results and discussion

4.6.1 Effect of nanoparticle size in Al₂O₃/water nanofluid

The effective thermal conductivity of Al₂O₃/water nanofluid is calculated using the MD simulations. The solid volume fraction is set to $\Phi_p = 0.1$ for different nanoparticle sizes with a) $d_p = 18.14 \, \text{Å}$, b) $d_p = 22.86 \, \text{Å}$, c) $d_p = 28.8 \, \text{Å}$. The simulation box dimensions are $a = b = c = 50 \, \text{Å}$. The ensemble considered for this simulation is NVT, where the number of particles, volume and temperature (300K) are constant during the simulation. Fig. 4.15 indicates the ETC for the alumina/water nanofluid. As it can be seen, the effective thermal conductivity of the nanofluid does not change for different nanoparticles sizes. In contrast to the meso/macro-scale methods, multiple simulations are not considered for the MD simulations. The reason is that in micro-scale, atoms and molecules are allowed to have the chaotic motion and change their location. Also, the ETC is calculated over a time average. Therefore, the calculated value is intrinsically averaged.
4.6.2 Effect of nanoparticle size in TiO$_2$/water nanofluid

For the TiO$_2$/water nanofluid, similar to the previous section, the ETC is calculated using the MD simulations. The solid volume fraction is set to $\Phi_p = 0.1$ for different nanoparticle sizes with a) $d_p = 18.14$ Å, b) $d_p = 22.86$ Å, c) $d_p = 28.8$ Å. The simulation box dimensions,ensample, and the temperature is the same as before. Fig. 4.16 indicates the ETC for the TiO$_2$/water nanofluid. Interestingly, the ETC calculated for this system does not show a noticeable change in regard to the nanoparticles diameters. There are some fluctuations, however, the reported values here are averaged and the overall trend is depicted.
Fig. 4.16. The effective thermal conductivity of TiO$_2$/water nanofluid for different particles sizes of $d_p=18.14$ Å, b) $d_p=22.86$ Å, c) $d_p=28.8$ Å.

4.6.3 Effect of nanoparticle aspect ratio in Al$_2$O$_3$/water and TiO$_2$/water nanofluid

In contrast to the nanoparticles size, the effect of aspect ratio is not debated in literature. In most of the cases, the aspect ratio is shown to have a positive effect on nanofluids thermal conductivity. However, it should be noted that the aspect ratio can have a significant effect, when nanoparticles are aligned with the heat conduction direction. Then, the ETC in that direction can show a huge enhancement. Here the calculated ETC is the average over three directions.

Fig. 4.17 reports the ETC values calculated for two nanofluid systems. The ETC shows an enhancement when the aspect ratio changes from 1 to 2. Also, the results are compared with the mesoscale simulations. It can be seen that the effect of aspect ratio is less significant in MD simulations. There can be several reasons for these results. The most important working mechanism is believed to be the effect of system scale. In mesoscale, there are more nanoparticles engaged in the simulation. Therefore, more nanoparticles are prone to be aligned with the heat conduction direction. This will increase the ETC
significantly. However, here there is only one nanoparticle. Also, the reported value here is the averaged ETC, while the calculated value for the mesoscale is the ETC in heat conduction direction.

![Graph showing the effective thermal conductivity of Al₂O₃ and TiO₂/water nanofluid for different aspect ratios of a) l=1 , b) l=1.62, c) l=2.](image)

Fig. 4.17. The effective thermal conductivity of Al₂O₃ and TiO₂/water nanofluid for different aspect ratios of a) l=1 , b) l=1.62, c) l=2.
Chapter 5: Conclusions and future work

5.1 Summary

Multiscale numerical simulations using the Lattice Boltzmann (LBM) method, finite Element Method (FEM), and Molecular Dynamic (MD) were first conducted to investigate the effect of the nanoparticles size and aspect ratio on the TiO$_2$/water and Al$_2$O$_3$/water nanofluids effective thermal conductivity. The results were partially validated with other conventional numerical methods and the experimental data. In addition, a comprehensive statistical analysis (ANOVA) was performed to evaluate the confidence level of the simulation results. Based on the ANOVA test and the LBM simulations, these conclusions can be drawn:

There is a linear correlation between ETC of nanofluids and the nanoparticles volume fraction. Increasing the nanoparticles aspect ratio can enhance the effective thermal conductivity of nanofluids.

Statistical analysis regarding the nanoparticles size effect on ETC indicated that there is not enough evidence to reject the hypothesis that smaller nanoparticles increases ETC more than larger nanoparticles ($P$-Value > 0.05). Therefore, the pure effect of nanoparticle size in the absence of other interfering parameters (e.g., nanoparticles aggregation, Brownian motion, solid/liquid interfacial thermal resistance, nano-liquid layering, etc.) was declared to be not statistically significant enough to be considered as an affecting parameter on the nanofluids effective thermal conductivity. In another word, the changes of ETC value due to the variations of distribution regime was larger than the changes in ETC value due to the nanoparticles size variations. Depending on the material of the base fluid/nanoparticles, when nanoparticles size increases, the interfacial phenomena can enhance (nano-liquid layering, nanoparticles aggregation), or decrease (solid/liquid interfacial thermal resistance) the ETC value. Disregarding these
interfacial interactions helps us to make a conclusion on the pure effect of nanoparticles size on nanofluids effective thermal conductivity coefficient.

5.2 Comparing FEM/LBM and MD results

Three different method are used in this thesis to investigate the effect of nanoparticles size and aspect ratio on nanofluids thermal conductivity. In this comparison, same material (Al$_2$O$_3$ and TiO$_2$/water nanofluid) are used. However, due to the limitations of microscale simulation, it is not possible to have the same nanoparticles size and aspect ratio. The reason is that in MD simulation, calculation of the interatomic interactions, which is a many-body problem, will significantly increase the computation cost. That is the reason why in most of the published papers, nanoparticles are modeled with diameter lower than 10 nm. [55]. Although this is a limitation, it cannot be considered as an obstacle to make rational conclusions. The more we go small into interatomic details, the more we lose the large-scale phenomena and collective behaviours. In fact, this is the reason why only a multiscale analysis can help us find the answer as it investigates all the possible interfering phenomena happening at different scales.

Another important point that needs to be mentioned is that in MD simulation, the solid-liquid interface is affecting the results as interatomic potentials are specifically defined for each atom type (O, H, Ti, and Al). Therefore, the results cannot be generalized as for any given nanofluid system. As it was said, this was not an issue in FE/LB methods as the interfacial phenomena could be disregarded due to the intrinsic properties of the methods.

The results of FEM/LBM were incomplete before the statistical analysis. Therefore, an ANOVA test were conducted to understand if the calculated fluctuations are acceptable signals or the system noise. In contrast, MD simulations do not need any further analysis. The reason is that in MD simulations,
nanoparticles are allowed to have the Brownian motion and freely move around. In this way, the system would experience all the possible configurations that a nanoparticle can float in a base fluid.

5.3 Contribution to the field

Nanofluids, as a new generation of heat transfer fluids, are on their way toward commercialization and real-world industrial applications. However, reaching the mass production level needs a systematic research on the parameters affecting the production expenses. Undoubtedly, the nanoparticles size is the most crucial aspect of nanofluids production cost as the utmost effort and high-level technologies are exerted for fabrication of finer nanoparticles. Hence, it is necessary to understand whether there is a real need to fabricate finer nanoparticles (10 nm). Otherwise, larger nanoparticles (40 nm) with lower production cost can accelerate the commercialization of nanofluids. Here, the lattice Boltzmann method (LBM) and FEM results are statistically investigated (ANOVA test). Then, a MD simulation is used to consider the probable microscale phenomena. The MD simulations were conducted for two different materials, three different sizes and three different aspect ratios. The important contribution of the MD simulations was that fact that the shared the same materials, aspect ratios used in the macro/mesoscale simulations. Compared to other methods, LBM is superior due to its mesoscopic approach that can consider the collective behavior of nanoparticles. Collective behaviour is a critical aspect of nanofluids thermal conductivity as the value is a random variable that depends on the nanoparticle’s distribution regime in the base fluid. Considering the numerous conflicting experimental studies on the literature that suffer from inconsistency and extra variability, these findings are of a great importance as they answer a controversial question.
5.4 Future work

It was shown that LBM can be a better numerical simulation method in terms of accuracy, cost of simulation and the scale. In the future, LBM can be extended the atomic scale by developing a new collision operator based on nanoscale phenomena. Currently, the collision operator of LBM is based on the kinetic theory principles. This means that LBM considers an ensemble of particles (atoms/molecules), rather than single particles. Developing such a collision operator, LBM will be able to capture more interatomic phenomena, enhancing its capability and accuracy. This can be done by the help of molecular dynamic simulations and density functional theory (DFT) as they calculate the atomic level assurances. This research provided a path for future researchers to have a better understanding of how they can combine different scale simulations and probably, combine them into a novel method that enjoys from each method’s advantage.
References


Appendix

Assumptions for ANOVA test

Analysis of Variances (ANOVA) has three main assumptions that need to be met before the analysis [124]. These include 1) randomness in experiments 2) equal variances 3) normally distributed residuals. Before conducting the ANOVA test, one should conduct a preliminary test to see if these assumptions are met. As mentioned before, the computational domain geometry is randomly generated using the developed code. Therefore, the first assumption is considered. The other two assumptions, however, need to be checked. In the following, normality in residual distribution and the equality of variances is checked.

The figure below shows the distribution of variances for the data indicated in Fig. 3.3. Here, the LBM and FEM responses are combined and shown for each $\varphi_n$. As it can be seen visually, variances are not equal.

![Image](image.png)

**Fig. A.1.** Multiple comparison intervals for the standard deviation, $\alpha = 0.05$. 
When the variances are not equal, ANOVA test results are not accepted. To solve this problem, the data should be transferred so that the variances can be equal. Therefore, a Johnson transformation is conducted and the results are shown in the fig. A.2.

![Fig. A.2. Multiple comparison intervals for the standard deviation for transformed data, $\alpha = 0.05$.](image)

After transforming the data, the variances are equal and ready to conduct the ANOVA test. The next step is to test the normality of the distribution. The distribution of the data needs to be a normal distribution. The figure below shows the raw data (simulation results).

![Fig. A.3. Normality test for the data shown in fig. 3.3. the data is not normally distributed as the P-Value is lower than 0.05.](image)
As can be seen, the data is not normally distributed. The P-Value for the normality test is P-Value < 0.005. Similar to the previous step, a Johnson transformation is conducted and the data is transferred into a normal distribution. Now, the data can be used for further analysis. It should be noted that using the transformation technic does not change the overall results as the same remedy is implemented on the whole data set.

Fig. A.3. Normality test for the data shown in fig. 3.3. the transferred data is normally distributed.