Chapter 3

Role of particle shape and interfacial layer in thermal conductivity of nanofluids

In the present chapter, a theoretical model based on the effective medium approximation has been discussed to find the effective thermal conductivity of nanofluids by considering the interfacial layer around the particle with ellipsoidal shape. Nanoparticles, soon after dispersion, develop an interfacial layer around them. The density of this interfacial layer is intermediate between the liquid and the solid. The packing of the fluid atoms around the nanoparticle is quite dense. Also, it is found experimentally that in the dispersed state, the active particle and its distribution could be quite different from that of particle before dispersion. Processes such as agglomeration, coagulation and particle cohesion and adhesion to the walls of the vessel may cause the shape of the particle to deviate from perfect sphericity. In the formulation of the proposed model, it is presumed that some nanoparticles in nanofluids may group together to form clusters. The nanoparticle with interfacial layer is considered to be equivalent nanoparticle. It is also postulated that nanofluids may consist of two portions: non-aggregating particles and aggregating particles. Few of these nanoparticles may just touch each other whereas others remain well dispersed. The variation in thermal conductivity has been studied with particle concentration, particle size, eccentricity and thickness of interfacial layer.

3.1 Transfer of Heat

Properties of a material characterize its ability to conduct heat which varies dramatically both with magnitude and temperature; for example metals conduct heat
rapidly whereas others such as wood act as thermal insulators. Heat energy can be transmitted through solids by means of electrons or holes, lattice waves (phonons) or other excitations. The physical property that describes the rate at which heat is conducted is the thermal conductivity \( k \). Heat conduction in fluids can be thought of as molecular energy transport which is a basic mechanism as much as the motion of constituent molecules. Transport of heat which depends on the density of fluid \( \rho_f \) is termed as convective energy transport. Another mechanism is that of diffusive energy transport, which occurs in mixtures that are inter diffusing. In addition, energy can be transmitted without any mediating material termed as radiative energy transport as in conduction and convection. Thermal conductivity is defined by Fourier Law [1, 2], according to which thermal conductivity \( k \) is defined as the coefficient of proportionality between the heat flux vector \( q \) and temperature gradient \( \nabla T \), i.e.

\[
q = -k \nabla T, \tag{3.1}
\]

Here, \( q \) is the rate of heat flow through a unit cross-section perpendicular to it. This equation describes the molecular transport of heat in isotropic media. In case of anisotropic materials such as noncubic crystals, fibrous materials, laminates, heat is given as

\[
q = -k_{ij} \nabla T, \tag{3.2}
\]

where the coefficient \( k_{ij} \) is a symmetric second rank tensor called as thermal conductivity tensor.

### 3.2 Effective Medium Theory

The thermal conductivity of nanofluids could be analyzed on the basis of Effective medium approximations (EMA) derived from continuum formulations and the concept of nanoparticle clusters. EMA is used to calculate the thermal conductivity of the nanofluids without taking in to consideration the size, geometry, distribution or the motion of dispersed particles, while only thermal conductivities of base fluids and particles and the particle volume fraction are considered. EMA are physical models that describe the macroscopic properties of a medium based on the properties and the relative fractions of its components. There are two methods commonly used in effective medium theory to treat the effective transport coefficient of mixture and composites: the
Maxwell–Garnett (MG) self consistent approximation [3] and the Bruggeman approach [4]. For particle-fluid mixtures, numerous theoretical studies have been conducted dating back to the classical work of Maxwell [3]. Maxwell considered a heterogeneous mixture of suspension of spherical particles in which the interaction between the particles was ignored in the dilute limit. Effective medium theory is discussed in Appendix-A at the end of thesis.

3.3 Theoretical Modelling for Thermal Conductivity

Here, we make use of the involved static or structural mechanisms such as liquid layering at the particle-liquid interface as heat transfer bridge, which was first proposed by Choi et. al. [5] and the concept of nanoparticle aggregation which is termed as clusters, formation of these have been confirmed experimentally [6-10] for explaining the substantially high thermal conductivity in carbon nanotube suspensions. Particle in nanofluids may aggregate with each other to form chain structures which are termed as fractal aggregates and may resemble solid like structure. The heat conduction could be enhanced due to particle aggregations because these clusters allow more heat to transfer along the direction of heat flux [11]. It is assumed that there are two paths of heat flow through the nanoparticle –liquid suspension: one through the medium and the other by aggregating particles. It is proposed that some nanoparticles form clusters when they just touch each other with an interfacial layer around them. Also, the nanoparticles inside the fluid no longer retain their original shape but deviate slightly form sphericity which, in turn, enhances their surface properties. This is supported by TEM images provided by Premkumar and Geckeler [12] and Lee et al. [13] for CuO and Al2O3 nanoparticles. These particles may take some irregular shape due to coagulation, particle adhesion to wall of the vessel and agglomeration. It may also be due to induced charges, if the charged nanoparticles are considered. However, for the present case, the deviated shape of nanoparticles has been taken to be a simple prolate spheroid in order to reduce the mathematical complexity. The overall heat transfer of the system for one dimensional heat flow may be expressed as

\[ q = q_m + q_{ir} \]  

Where the subscripts \( m \) and \( il \) denote quantities of medium, and of clusters of
particles with interfacial layer respectively. After dispersion of nanoparticles in the base fluid, there is formation of interfacial layer around the nanoparticles, which is expected to be consisting of atoms more ordered than that of bulk liquid as shown in Fig. 3.1. Hence thermal conductivity of this ordered layer should be higher than that of bulk liquid with different thermo physical properties [14-19]. Nanoparticles with nanolayer developed around them are termed as equivalent nanoparticles suspended in the base fluid [17]. The thermal conductivity of the equivalent particles can be analyzed using the concept of effective medium theory [17, 19] as:

\[
k = \frac{2(1 - \sigma) + \left[1 + \delta_{\text{med}} \right] \left[1 + \delta_{\text{min}} \right]}{\left[1 + \delta_{\text{med}} \right] \left[1 + \delta_{\text{min}} \right]},
\]

where \( \sigma = k_{\text{med}} / k_n \) is the ratio of thermal conductivities of interfacial layer to that of the nanoparticle, respectively. Due to these equivalent nanoparticles, volume fraction \( \phi \) of nanoparticles also gets modified and results in an equivalent volume fraction given by

\[\phi_{\text{med}} = \phi \left[1 + \delta_{\text{med}} \right] \left[1 + \delta_{\text{min}} \right].\]

Here,

\[
\delta_{\text{med}} = \frac{h}{a}, \quad \delta_{\text{min}} = \frac{h}{b},
\]

where \( h \) is the nanolayer thickness, \( a \) and \( b \) are the semi major and minor axes of prolate spheroid nanoparticle. The effective thermal conductivity for the medium due to these equivalent nanoparticles for low volume concentration [17] is obtained to be

\[
K = \frac{k_n + 2k_f + 2(k_n - k_f)\phi_{\text{med}}}{k_n + 2k_f - (k_n - k_f)\phi_{\text{med}}}.\]

Following Feng et al. [20], theoretical formalism has been developed for aggregation structure formed by the prolate shaped nanoparticles based on the fact that thermal conductivity increases because of aggregating nanoparticles [21-23]. The particles are generally taken to be in small volume fraction so that the chance of agglomeration is very low Fig. 3.1 (a). However, with lapse of time they start forming aggregate structures as shown in Fig. 3.1(b).
Aggregations formed by nanoparticles occupy more space than the individual nanoparticles that make up the aggregation as these are porous in nature. The effective volume concentration of aggregates is larger than that of nanoparticles making up the cluster because there is interspace between the aggregated nanoparticles [21].

Aggregating model has contribution due to two parts [22, 23]: one due to coherent base fluid and the other due to the contribution from one fourth of column of length \(2(h + \delta)\) as shown in Fig. (3.2).

**Figure 3.1:** Schematic cross section of nanofluid after dispersion of nano-sized particle in base fluid (a) Well dispersed prolate shaped nanoparticle with nanolayer around them which deviates from the spherical shape with no overlapping. (b) Morphological structure aggregate of few nanoparticles inside the fluid.

**Figure 3.2:** One dimensional heat flow through network consisting of infinitesimal layers of thickness \(dx\).
Thus, the total volume fraction $\phi$ corresponds to one fourth of column in the aggregation model as shown in Fig. 3.2 with the dotted line. The volume of nanoparticles in a quarter of column is

$$V_{\nu} = \frac{\pi AB^2}{3} \quad (3.8)$$

Here, $A=a+h$ and $B=b+h$ denotes the effective semi major and semi minor axis of prolate shape particle with interfacial layer, respectively and the total volume of the aggregation model is given by

$$V_{\nu} = \frac{V_{\nu}}{\phi_{\text{mod}}} = \frac{\pi AB^2}{3\phi_{\text{mod}}} \quad (3.9)$$

The total volume of the quarter of column is given by

$$V_c = \frac{\pi AB^2}{2} \quad (3.10)$$

Therefore, the volume fraction of the base fluid inside the quarter of the column is

$$\phi = \frac{V_c - V_{\nu}}{V_c} = \frac{\pi AB^2}{2\phi_{\text{mod}}} - \frac{\pi AB^2}{3\phi_{\text{mod}}} = \frac{\phi_{\text{mod}}}{2} \quad (3.11)$$

Thus, the total volume of the quarter of column is

$$\phi = \phi_{\text{mod}} + \phi_{\text{p}} = 1.5\phi_{\text{mod}} \quad (3.12)$$

Here, $\phi_{\text{p}}$ is the volume fraction of base fluid inside the column. Thus, the upper limit of porosity is $\phi_{\text{mod}}=2/3$. As $\phi_{\text{mod}} \to 2/3$, the aggregation model contains only a one-fourth column of length $2(b+h)$ and all the particles are in touching state. In this way the aggregation model can be approximately used to describe a cluster. The effective thermal conductivity, $\kappa$, of the aggregation model is

$$K_c = (1-1.5\phi_{\text{mod}})k_f + 1.5\phi_{\text{mod}}k_c \quad (3.13)$$

Here, $k_c$ is the effective thermal conductivity of a quarter of a column. For the one dimensional heat flow model, application of thermal electrical analogue for the thermal conductivity for touching model has been evaluated as shown in Fig. 3.2. $T_f$ and $T_c$ are
the temperatures of the top and bottom surfaces of aggregation column, respectively. The thermal resistance of the layer is in series with infinitesimal thickness $dx$ for each layer. Let $\delta_{p}, \delta_{p'}$, $\delta_{f}$ and $\delta_{r}$ be the thermal resistances of the upper and bottom parts of equivalent particle, of the base fluid and of the total resistance, respectively. Equation for an ellipsoid with symmetry along $y$ and $z$ axis and elongated along $x$ axis reads

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1,$$

where $a$ and $b$ are the semi-major and semi-minor axes, respectively. Interfacial layer of thickness $h$ enlarges the ellipsoid to make the semi-major and semi-minor axes as $A=a+h$ and $B=b+h$ respectively. Accordingly, the equation describing this becomes

$$\frac{x^2}{A^2} + \frac{y^2}{B^2} + \frac{z^2}{C^2} = 1.$$

Now consider hollow cylindrical part of the two particles in contact with each other with axis along $z$ axis as shown in Fig. 3.2. It has height $z_p$ in the upper equivalent particle $dr_{p1}$ as well as the lower equivalent particle $dr_{p2}$. The base of this cylinder will be elliptical and let the semi-major axis of this ellipse be $x$ and thickness along this axis be $dx$. A part of this cylindrical body will lie in the particle and a part in the fluid.

Nanoparticle part corresponding to the upper equivalent particle $dr_{p1}$ will be

$$PQ = z_p = \begin{cases} 
B & \text{when } x = 0 \\
0 & \text{when } x = A 
\end{cases}$$

This implies that $z_p = B \sqrt{1 - \frac{x^2}{A^2}}$. The area of the elliptical base ring will be circumference of ellipse of semi-major axis times thickness $dx$.

Accordingly, one quarter of this area $= \frac{1}{4}$ Circumference of ellipse of semimajor axis $x$ $dx$

$$= \frac{1}{4} 4\pi e(x) dx$$

(3.16)
Using the fact that circumference of ellipse with eccentricity \( e \) and semi-major axis \( a \) is
\[
4aE(e)
\]
where
\[
E(e) = \int_0^{\pi/2} \sqrt{1 - e^2 \sin^2 \theta} d\theta.
\]
is the complete elliptic integral of 2\(^{nd}\) kind. Here
\[
E(e) = \frac{\pi}{2} \left[ 1 - \frac{1}{2} \sum_{n=1}^{\infty} \frac{\epsilon^{2n+1}}{2n-1} \left( \frac{2n-1}{2n} \right)^2 \frac{e^{2n}}{2n-1} \right]
\]
Obviously, for a circle eccentricity \( e = \sqrt{1 - \frac{B^2}{A^2}} \) is zero as \( A=B \) and \( E(e) = \frac{\pi}{2} \). In our problem, thermal resistance of the part of the upper equivalent particle \( dr_{p1} \) in the cylinder is
\[
dr_{p1} = \frac{B}{k_p E(e)} \sqrt{1 - \frac{x^2}{A^2}} dx.
\]
Here, \( k_p \) is the thermal conductivity of the equivalent particle including the contribution of the interfacial layer. Similarly, thermal resistance for lower equivalent particle,
\[
dr_{p2} = \frac{B}{k_p E(e)} \sqrt{1 - \frac{x^2}{A^2}} dx.
\]
Fluid between the two equivalent particles in the cylindrical strip \( z_f = \begin{cases} 0 & \text{for } x = 0 \\ 2B & \text{for } x = A \end{cases} \).
Therefore,
\[
z_f = 2B \left[ 1 - \sqrt{1 - \frac{x^2}{A^2}} \right].
\]
Thermal resistance of the part of the fluid in the cylinder is given by
Total thermal resistance of the infinitesimally thick cylindrical strip would then be

\[
\frac{dR}{k_e(x)dx} = \frac{2B \left(1 - \frac{x^2}{A^2}\right)}{k_e(x)}
\]

(3.22)

Here, \(\gamma = 1 - k_f/k_p\) and it is a positive fraction. Thus, the total resistance of a quarter of the column is

\[
\frac{1}{R} = \frac{k_e(x)}{2B} \gamma \left[\frac{1}{\gamma} \ln \frac{1}{1 - \gamma} - 1\right].
\]

(3.24)

Using the Fourier law of heat conduction, the effective thermal conductivity of quarter of column \(k_{eff}\) is obtained to be

\[
k_{eff} = \frac{4k_e(x(a + h))}{\gamma^{1/2} - \gamma} \left[\frac{1}{\gamma} \ln \frac{1}{1 - \gamma} - 1\right].
\]

(3.25)

The effective thermal conductivity of equivalent nanoparticles defined by the formation of clusters is given by

\[
K_e = \frac{6\phi_{eq} E(x(a + h))}{\pi \gamma^{1/2} - \gamma} \left[\frac{1}{\gamma} \ln \frac{1}{1 - \gamma} - 1\right].
\]

(3.26)

Some nanoparticles may aggregate to form clusters, while others remain well dispersed. Therefore the effective thermal conductivity of medium and aggregating particles is given by

\[
K_{eff} = (1 - \alpha)K_m + \alpha K_{eff}
\]

(3.27)

Dimensionless thermal conductivity is given by

\[
K_{eff}^* = K_m^* + K_e^*
\]

(3.28)

where

\[
K_e^* = \frac{6\phi_{eq} E(x(a + h))}{\pi \gamma^{1/2} - \gamma} \left[\frac{1}{\gamma} \ln \frac{1}{1 - \gamma} - 1\right].
\]

(3.39)
Expressions (3.29) and (3.30) show that the thermal conductivity is dependent upon the thermal conductivity of nanoparticles and base fluid, nanoparticle size, thickness of the nanolayer and effective particle volume fraction. For calculations, $\alpha = \phi \text{vol}$ is taken.

3.4 Results

Results based on the model developed here have been compared with the experimental data on oxide nanofluids available in the literature. This clearly brings out the fact that the thermal conductivity enhancement of nanofluids is influenced by the volume fraction of nanoparticles, interfacial layer, eccentricity, thermal conductivity of nanoparticle and base fluid, aggregation and size of the dispersed nanoparticles.

3.4.1 Particle Volume Fraction

The thermal conductivity of a solid is much higher than that of a liquid. For example, the thermal conductivity of the most commonly used conventional heat transfer fluid, water is about 0.6 W/m-K at room temperature, while that of copper is higher than 400 Wm$^{-1}$K$^{-1}$, CuO is 69.0 Wm$^{-1}$K$^{-1}$ and multi walled carbon nanotube (MWCNT) 2000 Wm$^{-1}$K$^{-1}$. Therefore, particle loading proves as a chief factor that significantly influences the thermal transport in the nanofluids. Some researchers have observed anomalous thermal conductivity enhancement for dilute suspensions i.e. $\phi < 1$% by volume of nanoparticles [24-27]. In literature there are a number of reports on oxide based nanofluids, Masuda et al. [25] reported an enhancement of 32.4% for the effective thermal conductivity of 4.3% of Al$_2$O$_3$-H$_2$O nanofluid at 304.85K. Similarly study was performed by Wang et al. who examined the thermal performance of Al$_2$O$_3$-H$_2$O nanofluid, in the case of 8% volume fraction 40% enhancement was achieved [26]. Generally there is linear enhancement in thermal conductivity with particle volume fraction whereas there are other studies showing nonlinear relation between thermal conductivity ratio and particle volume fraction [5, 28, 30]. This non linear behaviour in the curve may correspond to interactions among particles [28].
Calculations have been carried out to study the effect of particle shape on thermal conductivity of nanofluids. For this analysis was performed by varying values of eccentricity. However, only those values of eccentricity have been reported for which the thermal conductivity values match well with the experimental values. For example in Fig 3.3 (a) the choice of eccentricity $e=0.1$ is found to give results for Al$_2$O$_3$-EG system whereas $e=0.9$ appears to be better choice for Al$_2$O$_3$-H$_2$O system as shown in Fig 3.3 (c). It is observed that $e=0.9$ lies closer to the experimental values as compared to other values of eccentricity. Our model has been built by modifying the model given by Feng et al. [20] and hence comparison has been carried out only with the values reported in [20]. Other works follow different approach and gives result which deviate from experiment data. There exist other experimental measurements also but for particle size different from the present case for a given system with different size for given system and thereafter results have not compared.

The calculations for Al$_2$O$_3$, CuO nanoparticles in C$_2$H$_5$OH and H$_2$O base fluids have been carried out using the values $k_p$(Al$_2$O$_3$)=46.0 W/m-K, $k_p$(CuO) =69.0 W/m-K, $k_f$(C$_2$H$_5$OH) =0.258 W/m-K and $k_f$(H$_2$O) =0.604 W/m-K [29], for different values of eccentricity and interlayer thickness and the results are plotted in Figs. 3.3 and 3.4. We have taken the thermal conductivity of interfacial layer to be 2 times that of base fluid. Obviously, thermal conductivity increases monotonically with the volume fraction. A perusal of Figs. 3.3 (a) to 3.3 (e) for Al$_2$O$_3$ in Ethylene glycol (EG) and water as a base fluid reveals that effective thermal conductivity increases nonlinearly with volume fraction which may correspond to the fact that suspensions are more prone to aggregation and deviation from sphericity with an increase in particle concentration. Formed clusters are of porous natures which actively participate in the heat transfer across the temperature gradient, by increasing the surface area.

It is interesting to note that the nanofluids of both the oxide particles of the same size in EG have somewhat higher thermal conductivity than in water although the latter has larger thermal conductivity value. A possible explanation for this seems to be that the interfacial layer formed with EG is more densely packed than that in the case of water.
Figure 3.3: Plots of effective thermal conductivity as a function of particle volume fraction for Al₂O₃ in ethylene glycol (EG) and water as base fluid for different sizes and eccentricity. (a) Al₂O₃-EG \( r_p=7.5 \text{nm} \) (b) Al₂O₃-EG \( r_p=13 \text{nm} \) system (c) Al₂O₃-EG \( r_p=19.2 \text{nm} \) system (d) Al₂O₃-H₂O \( r_p=19.2 \text{ nm} \) system and (e) Al₂O₃-H₂O \( r_p=30.2 \text{ nm} \) system. Dash line/Solid Line (— or —), Dash dot dot (—...), and (△) are calculated results, Feng et al. and Expt. data respectively.
Figure 3.4: Effective thermal conductivity for CuO nanoparticle in ethylene glycol (EG) and water as base fluid for different size of nanoparticles. (a) CUO-EG ($r_p=11.9$ nm) (b) CuO-H$_2$O ($r_p=11.8$nm) system (c) CuO- H$_2$O ($r_p=14.3$ nm) system. Dash line/Solid line (--- or —), Dash dot dot (….) and (▲) are calculated results, Feng et al. and Expt. data respectively.
3.4.2 Particle size

Xie et al. [30] reported thermal conductivity of nanofluids containing different sizes of alumina nanoparticles and concluded that there is an optimal size of the particle which yields the greatest thermal conductivity enhancement. However, Kim et al. [33] measured thermal conductivity of nanofluids containing different sizes of Al₂O₃, TiO₂, and ZnO in water and in ethylene glycol and reported enhanced thermal conductivity for fluid containing smaller nanoparticles. For nanofluids containing 3 % TiO₂ in ethylene glycol, the thermal conductivity enhancement for the 10 nm sample (16 %) was approximately double the enhancement for the 70 nm sample. Li and Peterson [34] also observed up to 8 % enhancement in thermal conductivity for aqueous nanofluids containing 36 nm Al₂O₃ particles compared to nanofluids containing 47 nm Al₂O₃ particles. Fig. 3.5 presents the thermal conductivity enhancement as a function of particle size for Al₂O₃-EG. It also depicts that thermal conductivity values decrease with particle size, pointing to the fact that the contributions from clusters due to nanoparticle aggregation increase for small particle size as Al₂O₃-EG system for 7.5 nm. Also a dramatic enhancement in thermal conductivity is expected because a reduction in particle size can result in large interfacial area. For particle size <5 nm one can observe a sharp increase in thermal conductivity of nanofluids. However with increase in size beyond 5 nm, the thermal conductivity of nanofluid decreases and reaches an almost constant value which may corresponds to the thermal conductivity of colloidal mixture. Also, as concentration is increased the thermal conductivity curve approaches a higher constant value and hence one can conclude that the thermal conductivity of the nanofluids becomes independent of the size of nanoparticles. Figs. 3.3 (e) and 3.4 (a), (b) & (c) also showed that a smaller size particle contributes better to heat conduction.
3.4.3 Interfacial layer Thickness

The nanolayer thickness is considered as a critical parameter for thermal conductivity enhancement [35, 36]. Figs. 3.3 and 3.4 show plots of effective thermal conductivity for different interfacial layer thickness as function of particle loading for different nanofluid systems. From the calculations, it is reported that as thickness of interfacial layer around nanoparticle is increased, the thermal conductivity increases manifold. Fig. 3.3 (e) matches quite well for Al₂O₃-water at h=0.5nm, ε=0.9, showed particle of larger size deviates more from sphericity while Fig. 3.4 (c) for CuO-H₂O depicts that as thickness increases calculated results more close to expt. although the experimental behaviour is not clearly described using the present model.
3.5 Conclusions

Based on aggregation of nanoparticles and heat conduction through dispersed nanoparticles in base fluid, a model for effective thermal conductivity of nanofluids has been proposed. It is found that the thermal conductivity increases with decrease in particle size. This is attributed to the contribution from clusters due to nanoparticle aggregation with decrease in nanoparticle size at constant volume fraction. Also, we find that as thickness of interfacial layer is increased, the effective thermal conductivity also increases. This implies that the conductivity and thickness of interfacial layer play a major role. The model predictions are compared with the available experimental data, and a good agreement between them is obtained.
Bibliography