Chapter 3

Theoretical Models for Thermal Conduction in
Polymeric nanofluids
and nanosolids

3.1 Introduction

The theoretical models describing effective thermal conductivity of two component mixtures have been derived based on the assumption that all mixtures constitute a continuous base medium called the matrix with a discontinuous solid component called particles embedded in it. As mentioned in chapter 1, thermal properties of a two component mixture depend on the details of their microstructures, such as component properties, component volume concentrations, particle dimensions, particle geometry, particle distribution, particle motion and matrix-particle interfacial effects. The transport properties of heterogeneous mixtures have attracted the interest of researchers ever since the time of Maxwell in the nineteenth century. The reason for this interest is, of course, due to the enormous variety of physical systems in which inhomogeneities occur and their practical applications. Among various transport properties, the conductivity properties, comprising the dielectric constant, magnetic permeability, electrical conductivity and thermal conductivity, may be treated together in an analogous manner because of the comparable form of conduction laws. Maxwell was one of the first to investigate conduction properties analytically for a mixture consisting of particles embedded in a base medium following the effective medium theory.
Effective Medium Theory or Effective Medium Approximation denoted as EMT or EMA). The effective medium theory describes the macroscopic properties of a medium based on the properties of the components and their relative volume fractions. Later, using a mean field approach, Maxwell and Garnett modified the effective medium theory originally developed by Maxwell (Maxwell, 1873) to derive the expressions for effective dielectric properties of a two component mixture. Then, it has been extended to thermal conductivity so as to express the effective thermal conductivity or simply thermal conductivity of a binary mixture in terms of its corresponding component properties.

### 3.2 The Maxwell- Garnett model

The Maxwell - Garnett model or M-G model (Maxwell, 1873) is the first theoretical model used to describe the effective thermal conductivity of two component mixtures. Maxwell had followed an effective medium theory to express effective properties of a binary mixture. The properties considered have generally been the electrical conductivity $\sigma$ as well as the dielectric constant $\varepsilon$ of the medium. The conductivity $\sigma$ and dielectric constant $\varepsilon$ are interchangeable due to the wide applicability of the Laplace transforms. An analogous approach has been adopted to arrive at the effective thermal conductivity of a homogeneous mixture in terms of the thermal conductivity of its constituent phases.

#### 3.2.1 M-G model for effective dielectric constant of a binary mixture

Maxwell and Garnett followed a self consistent approximation or Mean Field Theory (MFT) to derive effective properties of homogeneous mixtures. The main idea of MFT has been to replace all multiple body interactions in a system to any single body one with an average or effective interaction between
them. This reduces any multi-body problem into an effective one-body problem. A many-body system with interactions is generally very difficult to solve exactly, except for extremely simple cases. In the effective medium approach, an n-body system is replaced by a one-body system with a chosen good external field. The external field replaces the interactions of all the other particles to an arbitrary single particle. The ease of solving problems following MFT provides some insight into the overall behavior of the system on an average, which suffices for most applications. In order to derive the effective dielectric properties of a medium, Maxwell- Garnett model considered systems under the following conditions.

(i) a mixture which is electro dynamically isotropic, non parametric and linear (none of its constitutive parameters depends on the intensity of electromagnetic field).

(ii) inclusions are separated by distances greater than their characteristic sizes.

(iii) the characteristic size of inclusions is small compared to the wavelength of the electromagnetic field in the effective medium.

(iv) inclusions are arbitrary randomly distributed.

Consider an effective medium consisting of a matrix medium with dielectric constant $\varepsilon_m$ and inclusions of dielectric constant $\varepsilon_p$ having volume fraction $\phi_v$. Suppose the effective medium is subjected to an electric field $\mathbf{E}$. In order to derive the Maxwell-Garnett equation, let us start with an array of polarizable particles. By using the Lorentz local field concept, it is rather straightforward to get the Clausius Mosotti Equation (Griffith, 1999) as
\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum_j N_j \alpha_j
\]

(3.1)

where \(\alpha_j\) is the polarizability of the \(j^{th}\) component and \(N_j\) is the number of components. By using elementary electrostatics, we get the following expression for the polarizability for a spherical inclusion with radius \(r\) as

\[
\alpha = \frac{(\varepsilon_i - 1)}{(\varepsilon_i + 2)} r^3
\]

(3.2)

If we combine this with the Clausius - Mosotti equation we get,

\[
\left(\frac{\varepsilon_{\text{eff}} - 1}{\varepsilon_{\text{eff}} + 2}\right) = \phi_v \left(\frac{\varepsilon_p - 1}{\varepsilon_p + 2}\right)
\]

(3.3)

where \(\varepsilon_{\text{eff}}\) is the effective dielectric constant of the mixture. As the model of Maxwell and Garnett is a composition of a matrix medium with inclusions we rewrite the above equation for such a system as

\[
\left(\frac{\varepsilon_{\text{eff}} - \varepsilon_m}{\varepsilon_{\text{eff}} + 2\varepsilon_m}\right) = \phi_v \left(\frac{\varepsilon_{\text{eff}} - \varepsilon_m}{\varepsilon_{\text{eff}} + 2\varepsilon_m}\right)
\]

(3.4)

This is the Maxwell-Garnett equation. When \(\varepsilon\) belongs to the real number set, we can simplify the Maxwell-Garnett equation to obtain the following expressions for \(\varepsilon_{\text{eff}}\)

\[
\varepsilon_{\text{eff}} = \varepsilon_m \frac{\varepsilon_p (1 + 2\phi_v) - \varepsilon_m (2\phi_v - 2)}{\varepsilon_m (2 + \phi_v) + \varepsilon_m (1 - \phi_v)}
\]

(3.5)

This is the Maxwell- Garnett equation which expresses the effective dielectric properties of a mixture in terms of its component values. Due to the interchangeability of conduction laws, it is possible to convert the above
expression into respective thermal conductivity terms by replacing the dielectric constant of the effective medium, matrix and inclusion by the corresponding thermal conductivities. Obviously, one has to rewrite the relevant steps of the derivation of Maxwell –Garnett formula (Maxwell, 1873) for effective thermal conductivity of mixtures following Laplace equation with the temperature \( T \) as the forcing field instead of the electric field \( E \).

### 3.2.2 M-G model for effective thermal conductivity of a binary mixture

In order to derive an expression for the effective thermal conductivity of a binary mixture following Maxwell’s idea, (Maxwell, 1873), M-G model considers a very dilute suspension of spherical particles by ignoring interactions between particles. For a mixture containing identical spherical particles of radius \( r_p \) in a field of temperature \( T \) and temperature gradient \( G \), the steady state-condition can be defined by the Laplace equation,

\[
\nabla^2 T(r) = 0 \tag{3.6}
\]

By introducing a large sphere of radius \( r_0 \) containing all the spherical particles dispersed in the matrix and being surrounded by the matrix, one can calculate the temperature \( T \) outside the sphere \( r_0 \) at a distance \( r > r_0 \) in the following two ways (Stratton, 1941; Van Beek, 1967).

First, the sphere \( r_0 \) is considered to consist of a heterogeneous system with an effective thermal conductivity \( k_{\text{eff}} \) embedded in a matrix with a thermal conductivity \( k_m \). The temperature \( T \) outside the sphere \( r_0 \) can therefore be expressed as,

\[
T(r) = \left( -1 + \frac{k_{\text{eff}} - k_m}{2k_m + k_{\text{eff}}} \frac{r_0^3}{r^3} \right) G \cdot r \tag{3.7}
\]
This is obtained by solving Laplace Equation together with the following boundary conditions:

\[
T(r) \bigg|_{r \to \infty} = -G \cdot r \\
T(r) \bigg|_{r \to r_0^-} = T(r) \bigg|_{r \to r_0^-} = 0
\] (3.8a)

\[
k_e \frac{\partial T(r)}{\partial r} \bigg|_{r \to r_0^-} = k_m \frac{\partial T(r)}{\partial r} \bigg|_{r \to r_0^-}
\] (3.8b)

Second, the temperature \( T \) is considered to be produced by all the spherical particles with thermal conductivity \( k_p \), embedded in a matrix with a thermal conductivity \( k_m \), and by following a similar procedure it can be calculated from the superposition principle as

\[
T(r) = \left( -1 + \frac{k_p - k_m}{2k_m + k_p} \phi_v \frac{r_0^3}{r^3} \right) G \cdot r
\] (3.9)

From the above equations, the effective thermal conductivity \( k_{eff} \) of a two component medium can be readily obtained after simple algebraic manipulations as

\[
k_{eff} = k_m + 3\phi_v \frac{k_p - k_m}{2k_m + k_p - \phi_v (k_p - k_m)}
\] (3.10)

Rearranging terms in the above equation, we can write

\[
\frac{k_{eff}}{k_m} = \frac{(1-\phi_v)(k_p + 2k_m) + 3\phi_vk_p}{(1-\phi_v)(k_p + 2k_m) + 3\phi_vk_m}
\] (3.11)

This is the conventional Maxwell –Garnett effective medium self consistent approximation that has been used to describe the effective thermal conductivity of two component mixtures. The Maxwell equation takes into account only the particle volume concentration and the thermal conductivities
of the particle and base medium. Later researchers introduced other classical models which include the effects of particle shape (Hamilton and Crosser, 1962), particle distribution (Cheng and Vachon, 1969), and particle-particle interactions (Jeffrey, 1973). However, all of these models predict more or less identical enhancements in thermal conductivity at low particle concentrations (<1 vol. %) for nanofluids under investigation. Therefore, the Maxwell model is used in this study as representative of all classical models. In this thesis we have used the Maxwell-Garnett model (Maxwell, 1873) and some of its extended forms (Yu and Choi, 2004; Liang and Tsai, 2011; Nan et al., 1997; Cheng and Vachon, 1969) to establish the mechanisms responsible for the observed enhancements in thermal conductivity and thermal diffusivity of Polymeric nanofluids and their solid counterparts, known as Polymeric nanosolids. In the following sections we discuss the details of the theoretical models that have been used for the theoretical calculations for comparison with experimental results.

3.3 Thermal Conduction in Polymeric nanofluids

3.3.1 Effect of adsorption layer on thermal conductivity

Adsorption is the adhesion of atoms or molecules of a fluid on to a rigid solid surface. This process creates a thin film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbant. In 1919, Langmuir introduced a model to quantify the amount of adsorbate adsorbed on an adsorbant as a function of the partial pressure or concentration of absorbate molecule at a given temperature. Langmuir’s model considers adsorption of fluid molecules onto an idealized surface.

The main physical process that determine adsorption as per this model are

i) the adsorbed fluid transforms into an immobile state or phase.
ii) all sites are equivalent.

iii) each site can hold at most one molecule (mono-layer coverage only).

iv) there are no interactions between adsorbate molecules on adjacent sites.

In a typical nanofluid system, it is assumed that the adsorption of liquid molecules on a nanoparticle surface is thought to be monolayer one. The way the molecules get organized on particle surface is generally considered to be hexagonal in nature. From the Langmuir formula of monolayer adsorption of molecules, the thickness of adsorption layer can be expressed as (Hua et al., 2008; Wang et al., 2009),

\[
t = \frac{1}{\sqrt{3}} \left( \frac{4M}{\rho_f N_A} \right)^{\frac{3}{4}}
\]

(3.12)

where \(M\) is molecular weight of the base fluid, \(\rho_f\) is the density of the liquid, and \(N_A\) is Avogadro’s constant (6.023×10^{23} \text{ / mol}).

For a typical water based nanofluid system, the thickness of adsorption layer calculated using Langmuir formula, is 1.8–2.3 nm. The involved for the derivation of Equation (3.12) is well documented in literature and available elsewhere (Yan, 1986). Researchers have tried to establish the anomalous enhancement observed in effective thermal conductivity of low molecular weight based nanofluids (Yu and Choi, 2003; Yu and Choi, 2004; Xie et al., 2005; Wang et al., 2003) in terms of the phenomenon of adsorption of base fluid molecules around nanoparticle surfaces. But experimental studies (Buongiorno et al., 2009) have shown that this adsorption layers have no significant influence on the effective thermal conductivity of nanofluids made from low molecular weight base nanofluids like water, Ethylene Glycol etc.
However, for a polymer based nanofluid consisting of solid particle suspensions embedded in a polymer fluid, the adsorption of liquid molecules on the surface of solid material is a well defined phenomenon (Becker et al., 1989; Klein and Luckham, 1986). There are a number of studies reported in literature (Klein and Luckham, 1986; Glass, 1968; Witt and Ven, 1992; Nash et al., 1996) on the adsorption characteristics of a polymer liquid like PVA. Schematic illustration of the formation of a polymer layer around solid nanoparticle is shown in Figure 3.1.

![Figure 3.1 Schematic illustration of the formation Polymeric nanolayer around a spherical nanoparticle.](image)

For a polymeric fluid, the apparent thickness ($t_{ad}$) of the adsorption layer formed around the nanoparticle is obtained by subtracting the radius of the bare nanoparticle ($r$) from the hydrodynamic radius ($R_h$) of the layered nanoparticle. The hydrodynamic radius of the layered nanoparticle can be estimated from the Stokes- Einstein equation as,

$$R_h = \frac{kT}{6\pi\mu D} \quad (3.13)$$
where \( \mu \) the viscosity of the base fluid and \( D \) is the diffusion coefficient of the layered nanoparticle. Studies on the adsorption of PVA like liquid polymers around solid particles (Becker et al., 1989) have shown that the effective adsorption layer thickness \( t \), varies with nanoparticle radius \( r \) as

\[
t = \left[ \frac{(r + t_{ad})^3 - r^3}{3r^2} \right]
\]

(3.14)

Upon performing this calculation we obtain an apparent adsorption layer thickness in the range 1-5 nm for a typical polymeric nanofluid.

We try to explain the observed effective thermal conduction in a polymeric nanofluid in terms of the formation of adsorption layer and the associated nanoparticle clustering. Though different authors have modified the effective medium theory including the formation of liquid adsorption layer around particles, most of these modifications have been done for nanofluids made of low molecular weight base fluids. We adopt similar formalism to the two systems studied in this work. For polymeric nanofluids, we have tried to establish the thermal conduction properties analytically following the theoretical models given by Yu and Choi (2003), and Liang and Tsai (2011) which consider the particle clustering in the nanofluid. Detailed descriptions of the theoretical models that we have adopted in our theoretical analysis and their comparison are given in the following sections.

### 3.3.2 Renovated Maxwell–Garnett model including adsorption layers

Yu and Choi (2003) modified the Maxwell–Garnett model to derive the effective thermal conductivity of nanofluids composing of nanoparticles with adsorption layer as follows.
In order to include the effect of the liquid adsorption layer, Yu and Choi (2003) considered that nanoparticles of radius $r$ and volume fraction $\phi_v$ are suspended in a base fluid. Assume that the solid-like adsorption layer of thickness $t$ around the particles is more ordered than the bulk liquid and that the thermal conductivity $k_{layer}$ of the ordered liquid layer is higher than the base liquid. In high molecular weight based fluid, $t$ is estimated as a difference between the hydrodynamic radius and the radius of the suspended nanoparticles in the medium (Becker et al., 1989). One can find theoretical as well as experimental findings on this subject in literature (Becker et al., 1989, Schwartz et al., 1995).

In order to simplify the analysis, assume that the nanolayer around each particle could be combined with the particle to form an equivalent particle and that the particle volume fraction is so low that there is no overlap of these equivalent particles. The above assumptions result in an equivalent particle radius $r+t$ and an increased volume fraction $\phi_v'$, which can be expressed as

$$\phi_v' = \frac{4}{3} \pi (r+t)^3 n = \frac{4}{3} \pi r^3 n (1 + \frac{t}{r})^3 = \phi_v (1 + \beta)^3$$  \hspace{1cm} (3.15)

where $n$ is the particle number per unit volume and $\beta = t/r$ is the ratio of the nanolayer thickness to the original particle radius.

Based on the effective medium theory, Schwartz et al. (1995) investigated the electrical conductivity of mortars including the enhanced electrical conduction in the matrix-sand grain inter-facial region. They evaluated the electrical conductivity by a combination of finite element, finite difference, and random walk methods for periodic and disordered models for the mortar. Since the effective conductivity within the inter-facial zone is often much higher than the bulk matrix conductivity, the qualitative features of
transport in these systems is often controlled by the connectivity of the interfacial zone. A family of effective medium approximations has given a good qualitative description of the effective electrical properties of this physical system in terms of the properties of its components, interfacial layer and that of the base matrix. The detailed mathematical steps followed by Schwartz et al. are available in literature (Schwartz et al., 1995). Adapting an analogous mathematical formalism to the case of nanofluids having layered nanoparticles, Yu and Choi (2003) have expressed the effective thermal conductivity of layered nanoparticle in terms of the nanoparticle thermal conductivity \( k_p \), thickness of the adsorption layer and thermal conductivity of the base medium \( k_m \).

Following the above approach, equivalent thermal conductivity \( k_{pe} \) of the equivalent particles can be obtained as (Schwartz et al., 1995)

\[
k_{pe} = \frac{\left[2(1 - \gamma) + (1 + \beta)^3(1 + 2\gamma)\right] \gamma}{-(1 - \gamma) + (1 + \beta)^3(1 + 2\gamma)} k_p
\]  

(3. 16)

where \( \gamma = k_{layer}/k_p \) is the ratio of nanolayer thermal conductivity to particle thermal conductivity. For the extreme case of \( k_{layer} = k_p \) (i.e. \( \gamma = 1 \)), Equation (3. 16) reduces to \( k_{pe} = k_p \). This model assumes that the value of \( k_{layer} \) lies in between \( k_m \) and \( k_p \).

Replacing \( k_p \) by \( k_{pe} \) and \( \phi_v \) by \( \phi_v' \), the Equation (3. 11) can be modified into

\[
k_{eff} = \frac{k_{pe} + 2k_m + 2(k_{pe} - k_m)(1 + \beta)\phi_v'}{k_{pe} + 2k_m - (k_{pe} - k_m)(1 + \beta)^3 \phi_v'} k_m
\]  

(3. 17)

This Equation (3. 17) represents the effective thermal conductivity of a nanofluid having nanoparticles with adsorption layers around them.
In addition to the formation of adsorption layer around the nanoparticle, another mechanism simultaneously at work in a nanofluid system is the formation of nanoparticle clusters in the liquid medium at comparatively high particle concentrations (Liang and Tsai, 2011). In order to include the effect of clustering along with interfacial layering we have followed the modified form of effective medium theory introduced by Liang and Tsai (2011).

### 3.3.3 Effective medium theory including clustering of nanoparticles with interfacial adsorption layers

Liang and Tsai (2011) developed a modified form of a three-level particle clustering model originally developed by Prasher (Prasher et al., 2006) assuming the formation of nanoparticle clusters along with formation of interfacial layers. They have used the nonequilibrium Molecular Dynamics (MD) simulation for a nanofluid assuming it as an inhomogeneous system in which the solid-liquid interactions are assumed to be much stronger than liquid-liquid interactions. They have incorporated the simulation results into a three-level clustering model to evaluate the effective thermal conductivity of nanofluids. They have assumed that the nanoparticle clusters are embedded in a sphere of radius $R_a$ and the cluster spheres are uniformly distributed in the liquid medium. Each cluster consists of linear chains of nanoparticles, termed back-bone of the cluster, and side chains called dead-end particles. These clustered nanoparticles are assumed to have a significant influence on the thermal conductivity of the interfacial layers. By combining the idea of nanoparticle clustering with liquid layering, Liang and Tsai have introduced a new model to evaluate the thermal conductivity of nanofluids. As mentioned above, Liang and Tsai (2011) assumed that particle clusters are embedded within a sphere of radius $R_a$ and these cluster spheres are uniformly distributed.
in the liquid. Clustering of nanoparticles including the back-bone of the cluster and dead-end particles are pictorially demonstrated in Figure 3.2.

![Figure 3.2 Schematic of a single nanoparticle cluster consisting of the backbone (black circles) and dead ends (gray circles). The nanoparticle cluster is decomposed into dead ends with the fluid and the backbone. Thermal conductivity of the aggregate only with particles belonging to the dead ends $k_{nc}$. Linear chains are embedded inside a medium with effective conductivity of $k_{nc}$. Here $k_a$ is the overall thermal conductivity of a single cluster consisting of back-bone particles and dead end particles.](image)

The volume fractions of the nanoparticles ($\phi_{int}$), the backbone particles ($\phi_c$), and the dead-end particles ($\phi_{nc}$) in the cluster spheres are, obtained from fractal theory (Hui and Stroud, 1990; Hui and Stroud, 1994) as

\[
\begin{align*}
\phi_{int} &= \left( \frac{R_a}{a} \right)^{d_j - 3} \\
\phi_c &= \left( \frac{R_a}{a} \right)^{d_1 - 3} \\
\phi_{nc} &= \phi_{int} - \phi_c
\end{align*}
\]  (3.18)
where $d_f$ and $d_l$ are, respectively, the fractal dimensions and chemical dimensions of clustered spheres. In this calculation, we assume $R_o = 5a$ and set $d_f = 1.8$ and $d_l = 1.4$, following Prasher et al. (2006). Due to number conservation of the particles, we can write

$$\phi_v = \phi_{int} \phi_a$$

(3.19)

where $\phi_v$ and $\phi_a$ are the volume fractions of nanoparticles and cluster spheres in the liquid respectively. After defining the above parameters, Prasher’s model (Prasher et al., 2006) starts with the first level of homogenization, which is performed with only particles belonging to the dead ends. The effective thermal conductivity of the cluster sphere in the presence of the dead-end particles only, $k_{nc}$, can be determined based on the Bruggeman model, which has adopted a mean field approach (Bruggeman, 1935). The Bruggeman equation to determine $k_{nc}$ can be easily derived from the Maxwell-Garnett equation, given by Equation (3.11), by applying an integration scheme to take into account of the concentration of dispersed particles in the immediate neighborhood of a certain particle. For this, assume that the large sphere of radius $R_0$ is embedded in the matrix of thermal conductivity $k_{eff}$ rather than $k_m$; then rearrange and differentiate equation (3.11) to obtain

$$\frac{dk_{eff}}{d\phi_v} = \frac{1}{1-\phi_v} \frac{3k_{eff}(k_p-k_{eff})}{2k_{eff}+k_p}$$

(3.20)

which upon integration from $\phi_v = 0$ ($k_{eff}=k_m$) to $\phi_v = \phi_{nc}$ ($k_{eff}=k_{nc}$) leads to

$$1 - \phi_v = \frac{k_p-k_{nc}}{k_p-k_m} \left( \frac{k_m}{k_{nc}} \right)^{1/3}$$

(3.21)
Rearrangement of terms in equation (3.21) leads to a model which is particularly suitable for composites with high-concentration of additives and is given by,

\[
\phi_{nc} \left( \frac{k_p - k_{nc}}{k_p + 2k_{nc}} \right) + (1 - \phi_{nc}) \left( \frac{k_f - k_{nc}}{k_f + 2k_{nc}} \right) = 0
\]  
(3.22)

Solution of this equation yields the value of \(k_{nc}\) as,

\[
k_{nc} = (3\phi_v - 1)k_p + [3(1 - \phi_v) - 1]k_f + \sqrt{\Delta}
\]  
(3.23)

where

\[
\Delta = (3\phi_v - 1)^2 k_p^2 + [3(1 - \phi_v) - 1]^2 k_m^2 + 2[2 + 9\phi_v(1 - \phi_v)]k_pk_m
\]  
(3.24)

where \(k_p\) is the thermal conductivity of the nanoparticle. Equation (3.22) does not consider the effect of interfacial layers. In order to include the influence of the interfacial layers, consider each nanoparticle with radius of \(r\) to be covered with an interfacial layer of thickness \(t\). The volume fraction of a nanoparticle in this structure, therefore, is

\[
\phi_e = r^3 / (r + t)^3
\]  
(3.25)

The effective thermal conductivity of the particle-interfacial layer structure for dead-end particles, \(k_{ed}\), can be obtained by solving Equation. (3.22) after necessary substitutions.

Then we get

\[
\frac{k_{ed}}{k_{layer}} = \frac{k_p + 2k_{layer} + 2\phi_e(k_p - k_{layer})}{k_p + 2k_{layer} - \phi_e(k_p - k_{layer})}
\]  
(3.26)
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The numerical steps for solving this equation are available in literature (Xue and Xu 2005). The results of the MD simulation performed by Liang and Tsai (2011) have shown that \( k_{\text{layer}} = 2k_m \) and \( k_p = 200k_m \). While incorporating the effect of interfacial layers we have to replace \( k_p \) and \( \phi_{nc} \) in equation (3. 22) by \( k_{ed} \) and \( \phi_{nc} / \phi_e \), respectively.

In the second level of homogenization in Prasher’s model \( k_a \), the effective thermal conductivity of the cluster sphere, including the particles belonging to the back-bone, is calculated assuming that the backbone is embedded in a medium with an effective thermal conductivity \( k_{nc} \) obtained from Equation (3. 21). A methodology to predict the effective thermal conductivity of particulate composites with interfacial thermal resistance following the effective medium approach, combined with interfacial thermal resistance, or Kapitza resistance, was developed by Nan et al. (1997). The details of Nan et al. ’s model for effective thermal conductivity of nanosolids will be discussed in the next section. This approach has been able to predict the thermal conductivity of a composite medium with particle inclusions. When this model is adapted to a nanofluid system, the value of \( k_a \), the effective thermal conductivity of the cluster sphere, can be obtained as

\[
\frac{k_a}{k_{nc}} = \frac{3 + \phi_e [2\beta_{11}(1-L_{11}) + \beta_{33}(1-L_{33})]}{3 - \phi_e (2\beta_{11}L_{11} + \beta_{33}L_{33})}
\]  

(3. 27)

where, \( L_{11} = 0.5 p^2 / (p^2 - 1) - 0.5 p / (p^2 - 1)^{1.5}. \cosh^{-1} p \)

\[
p = R_a / r ; L_{33} = 1 - 2L_{11}
\]

\[
\beta_{11} = \frac{(k_e - k_{dc})}{(k_{dc} + L_{11}(k_e - k_{dc}))}
\]

\[
\beta_{33} = \frac{(k_e - k_{dc})}{(k_{dc} + L_{33}(k_e - k_{dc}))}
\]
However in back-bone structure of clustered sphere, the nanoparticles belonging to the backbone are so close to each other that the interfacial layers are connected to one another and they form a percolating network. Thus by assuming the nanoparticles in the backbone are embedded in the interfacial layer medium, we can also calculate the effective thermal conductivity of the backbone-interfacial layer structure \( k_e \) using the Bruggeman model (1935) as has been performed above. So we have

\[
\phi_e \left( \frac{k_p - k_e}{k_p + 2k_e} \right) + (1 - \phi_e) \left( \frac{k_{layer} - k_e}{k_{layer} + 2k_e} \right) = 0
\]  

(3.28)

While incorporating the effect of interfacial layers, the \( k_p \) and \( \phi_e \) in Equation (3.27) have to be replaced by \( k_e \) and \( \phi_e / \phi_e \). By including the effects of particle clustering and interfacial adsorption layering, the expression for effective thermal conductivity based on EMT can be obtained as

\[
\frac{k_{eff}}{k_m} = \frac{k_a + 2k_m + 2\phi_a (k_a - k_m)}{k_a + 2k_m - \phi_a (k_a - k_m)}
\]  

(3.29)

This expression gives the effective thermal conductivity of nanofluids consisting of clustered nanoparticles with interfacial layers. Equations (3.11), (3.17) and (3.29) have been used to evaluate the effective thermal conductivity of polymeric nanofluids in this work.

In this work we have presented the thermal conduction mechanisms in nanofluids by measuring the variations of effective thermal diffusivity with particle volume fraction using a thermal wave interference technique. Since the parameter measured is thermal diffusivity \( (\alpha_{eff}) \), it is required to express thermal conductivity in terms of thermal diffusivity. These two are related through the following expression (Zhang et al., 2006b),
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\[ \alpha_{\text{eff}} = \frac{k_{\text{eff}}}{\rho_{\text{eff}} c_{\text{eff}}} \]  \hspace{1cm} (3. 30)

where \( \rho_{\text{eff}} \) and \( c_{\text{eff}} \) defines the effective mass density and effective specific heat capacity of nanofluids. In an effective medium approach, these are given by

where \( \rho_{\text{eff}} = \phi_w \rho_p + (1-\phi_w) \rho_m \) \hspace{1cm} (3. 31)

\[ c_{\text{eff}} = \phi_w c_p + (1-\phi_w) c_m \]  \hspace{1cm} (3. 32)

Here \( \rho_p, \rho_m \) are the densities of the nanoparticle and base fluid respectively, and \( c_p \) and \( c_f \) are the specific heat capacities of the nanoparticle and the base fluid respectively. These expressions also follow from the respective effective medium approximations.

By analyzing the experimental results obtained with polymeric nanofluids, we have tried to describe the effective thermal conductivity of a polymeric nanofluid by comparing the experimental results with the corresponding ones calculated using the above mentioned theoretical models (Equations (3. 11), (3. 17) (3. 29) and (3. 30)). Our experimental results agree best with the conventional mean field theory with an essential concept of interfacial layering. The detailed descriptions of the experimental results on thermal conduction properties of polymeric nanofluids obtained as a function of nanoparticle volume fraction and nanoparticle sizes are presented in the following chapters.

3.4 Thermal conduction in polymeric nanosolids

While comparing thermal conduction properties of polymeric nanofluids with values derived from the above described theoretical models, it can be
clearly seen that the mechanisms which mainly control the effective thermal properties of liquid composites is the diffusion of thermal waves through the solid inclusions. But in the case of a solid composite mixture the situation is rather different especially in the case of a polymeric nanosolid material obtained by condensing the respective polymeric nanofluid. In a nanosolid material another mechanism which works dominantly in transporting thermal energy is the scattering of thermal waves at matrix-particle interfaces. This is due to the smaller dimensions of the solid particle inclusions compared to the mean free path of phonons in the solid matrix. The interfacial thermal wave scattering, demonstrated pictorially in Figure 3.3, causes an interfacial thermal resistance, known as Kapitza resistance $R_k$, which constitutes a barrier to heat flow at the nanoparticle-matrix boundaries. The magnitude of the Kapitza resistance at an interface can be estimated following an acoustic mismatch model (AMM) or a diffusion mismatch model (DMM). Even while phonons are backscattered from the interfaces, normal thermal diffusions through the nanoparticles do occur as demonstrated in Figure 3.3. This can be accounted for in terms of the transmission probability of the propagating thermal waves through the dispersed nanoparticles in the host matrix. The strength of diffusion would be greater at an interface of a nanoparticle with higher mass density and thermal conductivity (higher transmission probability), compared to the host matrix, while back scattering would be predominant when the nanoparticles have a lower mass density and thermal conductivity (lower transmission probability). While dealing with a nanosolid consisting of nanoparticles embedded in a base material like a polymer, a combination of above two mechanisms (diffusion and scattering) will control the overall thermal conduction in the material.
In the present work on thermal conductivity of nanosolid materials obtained by condensing nanofluids we have tried to establish the validity of our experimental results by combining relevant theoretical models which include the modified form of the Maxwell-Garnett effective medium model for this special material. We have employed a modified EMT which takes into account

(i) Thermal diffusion through the constituent phases of the composite medium, and

(ii) Interfacial scattering of thermal waves at matrix-particle interfaces.

Figure 3.3: Demonstration of heat flow in a nanosolid, controlled by interfacial scattering at matrix-particle interfaces and diffusion through particles

We have followed the modified model based on EMT, including the above two mechanisms. These mechanisms have been considered earlier for other systems by previous workers; interfacial scattering by Nan et al. (1997) for composites in which the phonon mean free path are greater than the size of constituent phases and diffusion by Cheng and Vachon (Cheng and Vachon, 1969) for general solid composite mixtures. We have employed Nan’s model (Nan et al., 1997) for describing the scattering part of thermal conduction mechanisms through polymeric nanosolids. The role of thermal diffusion mechanisms has been included in the Cheng-Vachon model (Cheng and Vachon, 1969; Shabde et al., 2006). An expression for the overall thermal
conductivity of polymeric nanosolids has been derived combining these two mechanisms and adopting these to polymeric nanosolids.

3. 4. 1 EMT in the limit of diffusion

As mentioned earlier, thermal diffusion through the particles play a significant role in determining the thermal conduction in a nanosolid sample. Conventionally, for a two component mixture, earlier researchers have generally tried models such as the series and parallel resistance models to describe effective thermal conductivity of composites. Cheng and Vachon (1969) proposed a modified form of effective medium theory following an analogy between heat flow and electric current flow to express the effective thermal conductivity of a composite as determined by thermal diffusion. Cheng and Vachon started their theoretical formalism by modifying Tsao’s model (Tsao, 1961) for predicting the thermal conductivity of a two phase material. This model assumes a discontinuous material phase (one component) dispersed in a continuous material phase. They have assumed a parabolic distribution of the discontinuous phase in the background matrix. The constants of the parabolic distribution are determined by a numerical analysis and are presented as a function of the volume fraction of the discontinuous phase. The equivalent thermal conductivity of a unit cube of the mixture is derived in terms of a distribution function, and the thermal conductivity of the constituents. In order to derive the expression for effective thermal conductivity of a two component heterogeneous mixture, Cheng and Vachon model makes the following assumptions.

For a unit cube of the mixture in an x-y-z co-ordinate system

(i) the heat flux is unidirectional in the x-direction,

(ii) thermal convection and radiation are negligible,
(iii) contact resistance between the continuous and discontinuous phases is negligible,

(iv) no porosity exists in the mixture,

(v) the discontinuous phase is uniformly dispersed in the continuous phase,

(vi) thermally, the mixture is isotropic,

(vii) in a mechanical mixing process, no chemical reaction occurs.

Assume that the unit cube cell of the nanosolid is sliced into differential elements of width $dx$ which are perpendicular to the direction of the heat flow. Here it is assumed that $dx$ is parallel to the $y$-$z$ plane. A two dimensional picture of this assumption is shown in Figure 3.4.

![Figure 3.4](image)

**Figure 3.4** Model used for the study of the thermal conductivity of a two-phase mixture.

Here the thermal conductivity of the composite medium is evaluated in terms of $y(x)$ in the configuration given in Figure 3.4. It can be shown the equivalent resistance of the solid composite as per the configuration given in Figure 3.4 is;
\[ R_e = \int_{0}^{x} \frac{dx}{k_m + (k_p - k_m)y} + \frac{1-2x}{k_m} \]  

and thermal conductivity \( k_{\text{eff}1} \) is given by,

\[ k_{\text{eff}1} = \frac{1}{R_e} \]  

Here \( y(x) \) represents the volume fraction of dispersed discontinuous phase. It is a normal distribution curve due to the assumed randomness of the discontinuous phase embedded in the continuous phase. Thus,

\[ y = C \exp(-C_2 x^2) \]  

\[ y = C_1 \left(1-C_2 x^2 + \frac{C_3 x^4}{2!} - \ldots \right) \text{ for } -1/2 \leq x \leq +1/2 \]  

or \( y = B + C x^2 \)  

Thus the normal distribution can be reduced into a parabolic distribution. So it is possible to express the constants \( B \) and \( C \) as a function of the given volume fraction of \( \phi_v \) of the discontinuous phase. Since the discontinuous volume fraction would be a known volume for a given two phase mixture, we can write

\[ \phi_v = 2 \int_{0}^{1/2} y \, dx \]  

In order to evaluate \( B \) and \( C \) one can apply the following boundary conditions,

\[ y = 1 \quad \text{at} \quad x = 0 \]

and

\[ y = 0 \quad \text{at} \quad x = 1/2 \]
This represents the maximum volume fraction for the discontinuous phase.

Equation (3.37) is an even function of $x$, hence only the positive value of $x$ need to be considered. i.e. $0 \leq x \leq \frac{1}{2}$. Applying this boundary conditions, one obtain $B = 1$ and $C = -4$.

Now, the maximum volume fraction $\phi_v$ of the discontinuous phase is calculated to be 0.669 which is the maximum volume fraction for discontinuous phase which equation (3.37) can accommodate. The boundary conditions will change as $\phi_v$ deviates from the maximum value.

When $\phi_v < 0.669$, the general conditions are,

$$y = B + Cx^2 \quad \text{at} \quad |x| \leq \frac{1}{2},$$

$$y = 0 \quad \text{at} \quad |x| \leq \frac{1}{2}, \quad \text{and}$$

$$y < 1 \quad \text{at} \quad x = 0$$

It is easy to show that, $B = \frac{-4}{C}$.

Thus it is possible to calculate $B$ and $C$ in terms of $\phi_v$ as follows;

$$\phi_v = 2 \int_0^{B/2} y \, dx$$

$$= 2 \int_0^{B/2} (B + Cx^2) \, dx$$

$$= \frac{2B^2}{3} + C'$$
Or $B = \sqrt{\left(\frac{3\phi_v}{2}\right)}$ and $C = -4\sqrt{\frac{2}{3}\phi_v}$

This is the situation when a two-phase mixture is reduced to the limiting case of single phase when $y = 0$ at $x = 0$ and $\phi_v = 0$. Substituting Equation (3.37) in (3.33) and letting $C=C'$ since $C<0$ yield

$$R_e = 2 \int_0^{B/2} \frac{dx}{\left[ k_m + B(k_p - k_m) \right] - C(k_p - k_m) - C(k_p - k_m)x^2 + \frac{1-B}{k_m}}$$  \hspace{1cm} (3.39)

Rearranging the first term in the denominator of Equation (3.39), one gets

$$k_m + B(k_p - k_m) = Bk_p + k_m(1-B),$$

which is always greater than zero since $B$ varies from 0 to 1. Integration of Equation (3.39) resulting in the effective thermal conductivity ($k_{eff1}$) due to diffusion of thermal waves through nanoparticles having volume fraction $\phi_v$.

Consider the following two cases.

(i) $k_m > k_p$

In this case Equation (3.39) reduces to

$$k_{eff1} = R_e^{-1} = \frac{2}{\sqrt{C(k_m - k_p)}} \times \arctan\left( B \frac{C(k_m - k_p)}{2 \sqrt{k_p + B(k_m - k_p) + \frac{1-B}{k_m}}} \right)$$ \hspace{1cm} (3.40)

(ii) $k_m < k_p$

In this case Equation (3.39) reduces to
Theoretical Models for Thermal Conduction in Polymeric nanofluids and nanosolids

\[
\frac{1}{k_{\text{eff}}} = \frac{1}{\sqrt{C(k_m-k_f)(k_m+B(k_f-k_m))}} \ln \left( \frac{k_m + B(k_f - k_m) + 0.5B\sqrt{C(k_m-k_f)}}{k_m + B(k_f - k_m) - 0.5B\sqrt{C(k_m-k_f)}} \right) + 1 - \frac{B}{k_m} \tag{3.41}
\]

Equations (3.40) and (3.41) express the effective thermal conductivities of medium embedded with particles. This model describes the effective thermal conductivity of composites as an overall effect of thermal diffusion among spherical nanoparticles distributed parabolically in a continuous base matrix.

3.4.2 EMT in the limit of interfacial scattering

As has been outlined earlier, while dealing with nanoparticle inclusions in a continuous base matrix, thermal wave scattering plays a significant role in determining the effective thermal conductivity of nanosolids. So we have employed a modified effective medium theory (EMT) including the contributions from interfacial thermal wave scattering, proposed earlier by Nan et al. (1997), to describe the role of thermal wave scattering at matrix-particle interfaces on the effective thermal conductivity of these nanosolids. Nan et al. modified Maxwell’s model including the concept of interfacial thermal resistance to describe the thermal conductivity of a two-component composite (Nan et al., 1997), under the following basic assumptions.

(i) A composite material consists of different constituent phases; the different mechanical or chemical adherences at the interfaces, as well as thermal expansion mismatch result in the scattering of thermal waves at the interfaces.

(ii) Scattering rates at the interfaces vary with the aspect ratio (ratio of the longitudinal to transverse dimensions) of the dispersed particles.

(iii) The interfacial thermal resistance influences the total thermal conductivity of the composite significantly.
In order to obtain an expression for thermal conductivity, this model considers a composite medium with multiple scatterers in the medium. In such a situation the thermal conductivity inside the composite varies from point to point. The variations in thermal conductivity can be written as,

\[ k(r) = k^0 + k'(r) \]  

(3. 42)

where \( k^0 \) is the constant part of the thermal conductivity for the homogeneous medium and \( k'(r) \) is the arbitrary fluctuating part. Using Green’s function \( G \) for a homogeneous medium defined by \( k^0 \) and the transition matrix \( T \) for the entire composite medium, a rigorous solution for the distribution of the temperature gradient can be obtained. The resulting effective thermal conductivity \( k^* \) is given by

\[ k^* = k^0 + \langle T \rangle (I + \langle GT \rangle)^{-1} \]  

(3. 43)

where \( I \) is the unit tensor and, symbol \( \langle \ \rangle \) denotes spatial averaging. The matrix \( T \) is

\[ T = \sum_n T_n + \sum_{n,m=n} T_n GT_m + \ldots, \]  

(3. 44)

Here the first term is the sum of the \( T \) matrices of \( n \) particles and the succeeding term represents the interaction between particles. An accurate calculation of \( T \) is a formidable problem. For simplicity of calculation we approximate \( T \) as,

\[ T \approx \sum_n T_n = \sum_n K'_n (I - GK'_n)^{-1} \]  

(3. 45)

there by neglecting inter-particle multiple scattering. Obviously, this approximation is valid only when the inclusion particles are dispersed uniformly in the base matrix.
Now, let us consider an ellipsoidal particle in the matrix, which is surrounded by a semisolid interface layer of thickness $\delta$ and thermal conductivity $k_s$, as a composite unit cell. Substituting $k_0 = k_s$ we directly obtain the equivalent thermal conductivities $k_{ii}^{C}$ ($i=1, 2, 3$) along the $X_i$ symmetric axis of this ellipsoidal composite unit cell as

$$k_{ii}^{C} = k_s \frac{k_s + L_{ii}(k_p - k_s)(1-u) + u(k_p - k_s)}{k_s + L_{ii}(k_p - k_s)(1-u)}$$

(3.46),

with

$$u = a_1^2 a_3^2 / (a_1 + \delta)^2 (a_3 + \delta)$$

Here $k_p$ is the thermal conductivity of the ellipsoidal particle; $a_1$ and $a_3$ are respectively, the radii of the ellipsoid along the $X_1$ and $X_3$ axes; and $L_{ii}$ are the well known geometrical factors dependent on the particle shape, and are given by (Nan et al. 1997)

$$L_{11} = L_{22} = \frac{p^2}{2(p^2 - 1)} - \frac{p^2}{2(p^2 - 1)^{3/2}} \cosh^{-1} p \text{ for } p > 1,$$

(3.47)

and

$$L_{33} = 1 - 2L_{11}$$

(3.48)

Also, $L_{33} = 1 - 2L_{11}$.

In the above expressions, $p = a_3/a_1$ is the aspect ratio of the ellipsoid, and $p > 1$ and $p < 1$ are for a prolate $(a_1=a_2<a_3)$ and an oblate $(a_1=a_2>a_3)$ ellipsoidal inclusion, respectively.
By ultimately passing to the limit that $$\delta \to 0$$ at $$k_x \to 0$$, the interfacial thermal resistance is thought of as the limiting case of heat transport across bulk phase by a thin, poorly conducting interface region, we rewrite Equation (3.46) as

$$k_{ii}^C = k_p/(1 + \gamma L_{ii} k_p/k_m)$$ \hspace{1cm} (3.49)

with

$$\gamma = (2+1/p)\alpha \quad \text{for} \quad p \geq 1$$ \hspace{1cm} (3.50)

and, $$\gamma = (1+2p)\alpha \quad \text{for} \quad p \leq 1$$

Here a dimensionless parameter, $$\alpha$$, is introduced, which is defined by

$$\alpha = a_k/a_i \quad \text{for} \quad p \geq 1$$ \hspace{1cm} (3.51)

$$\alpha = a_k/a_s \quad \text{for} \quad p \leq 1$$

where $$a_k$$ is the Kapitza radius defined by $$a_k = R_{bd}k_m$$, where $$R_{bd}$$ is the interfacial Kapitza resistance, and $$k_m$$ is the thermal conductivity of the host matrix phase.

When the inclusions become spheres, $$p=1$$, so that

$$L_{11} = L_{33} = 1/3, \text{ and } \langle \cos^2 \theta \rangle = 1/3$$

then Equation (3.49) reduces to

$$K_{11}^C = K_{22}^C = K_{33}^C = k_p/(1 + \alpha k_p/k_m)$$

and thermal conductivity limited by interfacial scattering is then given by,

$$k_{eff}^2 = k_m \frac{k_p(1+2\alpha) + 2k_m + 2\phi_v[k_p(1-\alpha) - k_m]}{k_p(1+2\alpha) + 2k_m - \phi_v[k_p(1-\alpha) - k_m]}$$ \hspace{1cm} (3.52)
This expression represents the thermal conductivity under the effective medium approximation including interfacial thermal resistance. It is evident that a large enough value for $\alpha$ can give rise to a de-enhancement in the effective thermal conductivity for a nanosolid of this type. Here also assuming an analogy between thermal conductivity and electrical conductivity we can also express $k_{eff2}$ in terms of corresponding resistance value as expressed in the diffusion limited case.

3. 4. 3 Overall effective thermal conductivity of a nanosolid

From the foregoing discussions we can see that it is possible to combine the resistance due to diffusion and scattering of thermal waves at the interfaces. We define the overall conductivity of a polymeric nanosolid as a combined effect of the mechanisms described by Equations (3.41) and (3.52). Assuming that the two mechanisms work in parallel we can write the effective thermal conductivity of a nanosolid as

$$k_{ns} = \frac{k_{eff1} * k_{eff2}}{k_{eff1} + k_{eff2}}$$

(3.53)

In this work we have employed Equation (3.53) to compute and discuss the variations in effective thermal properties of polymeric nanosolids. Experimental and theoretical variations of the thermal conduction properties of polymeric nanosolids are presented and discussed in chapter 6.