On the Effective Thermal Conductivity of metallic and oxide Nanofluids

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Abstract

Intriguing heat transfer characteristics of nanofluids have drawn widespread attention of researchers in the last decade. These highly stable colloids have a large potential to be future industrial coolants and finds application in various biomedical applications including cancer therapy. In this paper, we present an analytical derivation of effective thermal conductivity of nanofluids which incorporates the contribution of interfacial layer as well as the Brownian motion. A new form of thermal conductivity profile for interfacial layer around the nanoparticles has been proposed. All the material parameters that contribute to the variation of thermal conductivity with volume concentration have been taken into account. A comparison with the other models and experimental results for various nanofluids brings out the merit of the present effort. This model is also found to work even for large nanoparticles.

Keywords: Nanofluid, Nanoparticle, Interfacial Nanolayer, Heat Transfer, Thermal conductivity.

List of Symbols

\begin{itemize}
\item $k_f$: Thermal conductivity of the fluid
\item $k_p$: Thermal conductivity of the nanoparticle
\item $k_e$: Effective thermal conductivity of the nanofluid
\item $k_i$: Average thermal conductance coefficient of the nanolayer
\item $r_r$: Outer radius of the nanoparticle
\item $d$: Ratio of the outer and inner radius of the interfacial layer
\item $\phi$: Volume fraction of the nanoparticle
\item $k_b$: Boltzmann Constant
\item $Pr$: Prandtl Number
\end{itemize}
**1. Introduction**

Thermal conductivity of various heat transfer fluids has become a subject of immense research interest as it plays an important role in the development of heat transfer equipments with increased energy efficiency. Considerable energy and cost savings can be expected in heat exchangers by employing nanofluids. It finds enormous significance in this age of accelerating miniaturization which leads to fast increasing heat fluxes. Numerous studies have been carried out to understand the effective thermal conductivities of nanofluids which are liquids containing suspended nanoparticles. Nanofluids, a term coined by Choi (1995) [1], are engineered stable colloidal suspensions of nanoparticles in the thermal base fluids such as water, ethylene glycol, etc. These have been found to show conspicuous enhancement in their thermal conductivity at a very low volume fraction of suspended nanoparticles as compared to that of the base fluids.

For about past-one decade, many theoretical and experimental efforts have been put into this area to study such an anomalous behavior at the nanoscale. A number of physical and chemical factors are responsible for the heat transfer characteristics of nanofluids such as volume fraction, size, shape and species of nanoparticles, pH value and temperature of fluid, aggregation of nanoparticles and Brownian motion, etc. The typical behavior is evident from the fact that by loading less than 6% of volume fraction of aluminium oxide or copper oxide nanoparticles with an average size of 30 nm in water, the thermal conductivity of nanofluids increases up to three times the value of the base fluid [2-4]. Since Masuda et.al [5] reported the prominent increase in thermal conductivity with ultrafine particles for the first time in 1993, one has not been able to construct an efficient model to explain the effective thermal conductivity behavior of the nanofluids. The study becomes all the more important because nanofluids find vast applications in many industrial processes, chemical processes, heat exchangers, biomedical engineering, medicine, microelectronics, etc. This has generated interest both among academia and industries [6].
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In spite of numerous models for thermal conductivity of fluids starting from the traditional macroscopic theory put forward by Maxwell [7], Hamilton and Crosser [8], Maxwell-Garnet [9], etc. to the Brownian motion model by Prasher et al [10], Interfacial layer model and so on, this unusual behavior still lacks a proper explanation. A number of models have assumed nanoparticle to be a composite formed by a nanoparticle as a core, surrounded by a liquid layering at the liquid particle interface [11,12] known as nanolayer which, in turn, is immersed in the base fluid. The dependence of thermal conductivity on other variables like particle size, shape and temperature has also been investigated [12,13]. Experiments show that the enhanced thermal conductivity depends on many physical properties of nanoparticles due to their large specific area to volume ratio. Recently, a model was proposed by Murshed and Castro [14] wherein they incorporated the renovated dynamic part by using the effective diffusion coefficient concept in Brownian motion. Xie et al [15] have also shown experimentally that the thermal conductivity of nanofluids could be manipulated by controlling the morphology of the inclusions in the base fluid.

The experimental methods commonly used to determine thermal conductivity of the nanofluids include the steady state parallel plate technique [3], the transient hot wire method [16,17] and the temperature oscillation method [18,19]. Amongst these, the transient hot wire technique has been widely used. In steady state method, a heat flux is applied to develop a steady state temperature difference across a layer of the liquid. In transient hot wire method, temperature difference in created by immersing metallic rod which acts as one arm of the Wheatstone bridge in the sample nanofluid. The transient hot wire method is a low cost method and allows us to minimize the natural convection effects over extended measurement time thereby reducing experimental uncertainties. Accordingly, if \( q \) is the heat flux and if the temperature of the hot-wire at two different times \( t_1 \) and \( t_2 \) are \( T_1 \) and \( T_2 \) respectively, then thermal conductivity of the nanofluid will be given by

\[
k_{\text{eff}} = \frac{q}{4\pi} \frac{\ln(t_1 / t_2)}{T_1 - T_2}
\]

Some workers have also considered the contribution of liquid molecular layering between the solid particle and the base fluid in terms of thermal bridge acting between the two phases [13,20,21]. Computer simulations have also demonstrated [22] that molecular - level layering of the liquid at the solid–liquid interface could play a significant role in the interaction of dynamic nanoparticles with the base fluid molecules. Because of interfacial layer, a larger effective volume fraction of the particle – layered-liquid structure also plays significant role in enhancing the thermal conductivity of nanofluids. While investigating the thermal conductivity profile as a function of nanolayer thickness, Xie et.al [20] assumed a linear variation of thermal conductivity of nanolayer. Tillmann and Hill [23] used another function

\[
k = k_0 (1 - \alpha r)^n
\]

and predicted nanolayer thickness of various nanofluid systems. Nsofor and Gadge [24] assumed alternative variation of \( k \) as
\[
k(\mathbf{r}) = k_f + \frac{k_p - k_f}{\delta} \sqrt{\delta^2 - (\mathbf{r} - \mathbf{r}_p)^2}
\]

(where \( \delta \) is the interfacial layer thickness) and following the approach used by Xie et al. [20] elaborated the enhancement in thermal conductivity of some of the nanofluids. Although the already existing models, as listed above, show agreement with the experimental results, a widely accepted model is still not available. So there is need to develop a concept that could accurately explain the role of nanolayer in the thermal conductivity property of the nanofluids and improve upon the empirical relations used for this purpose, keeping this in mind we propose the present model for heat conduction wherein the concepts of nanolayer as well as the Brownian motion have been used.

In the present work, we have assumed an exponential variation in the thermal conductivity contribution of interfacial layer and thermal resistance of the fluid in order to include the Brownian motion contribution and developed an analytical model for the effective thermal conductivity of the nanofluid. The study also incorporates the effect of volume concentration and nanoparticle size on the ratio of effective thermal conductivity of nanofluid and the base fluid.

2. Modeling of Effective Thermal Conductivity of Nanofluids

In order to develop a model for effective thermal conductivity of nanofluids, the involved heat transfer mechanisms have been presumed to be collective contributions of mainly two types: one is considered to be a result of conduction heat transfer mechanism through the interfacial layer developed around the nanoparticles of intermediate density and second is a result of Brownian motion which involves convective heat transfer mechanism caused by the relative random motion between the nanoparticles and the surrounding base fluid.

2.1 Contribution of Interfacial Nanolayer.

When nanoparticles are dispersed in the base fluid, the latter is assumed to form a layer around nanoparticles which certainly has different thermal conductivity profile as compared to the nanoparticles and the base fluid. The nanolayer has an ordered structure and an intermediate density between the nanoparticle and the base fluid. In addition, the layer thickness is an important parameter as it would influence the overall thermal conductivity of the nanofluid. The thermal conductivity profile of the nanolayer is chosen to be a continuous function \( f(\mathbf{r}) \) of position \( \mathbf{r} \) within the layer such that it varies from thermal conductivity of the nanoparticle material \( (k_p) \) to that of the base fluid \( (k_f) \). Hence, if we consider the spherical nanoparticles with ratio of outer radius \( r_T \) to the inner radius \( r_p \) as \( d \), then thermal conductivity of the single particle system is expected to satisfy the following conditions:
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\[ k(r) = \begin{cases} 
  k_p & r \leq r_p \\
  f(r) & r_p \leq r \leq r_T \\
  k_f & r_T \leq r 
\end{cases} \]  

(1)

The schematic diagram of the nanoparticle (assumed to be spherical) is projected in Fig 1.

\[ R_L = \frac{1}{4\pi k_p r_p}(1 - \frac{1}{d}) \]  

(2)

The average thermal conduction coefficient of the nanolayer is given as

\[ k_l = \frac{r_T - r_p}{r_p \# r_T} \int_{r_p}^{r_T} \frac{dr}{r^2 f(r)} \]  

(3)

Little is known about the functional form of thermal conductivity of the nanolayer except the criteria that at \( r=r_p \), it should yield \( k_p \) and at \( r=r_T \), it should reduce to \( k_f \). As such, the exact form is still not established and its prior assumption is necessary. Therefore, we propose the following empirical form of exponential variation of the thermal conductivity within the interfacial layer and as such take

\[ f(r) = k_f + \frac{(k_p - k_f)}{(1 - e^m)} \left[ 1 - e^{\frac{m(r_T - r)}{r_T - r_p}} \right] \]  

(4)

where \( m \) is a real number. Another possible form of \( f(r) \) is given below which also has exponential form.

\[ f(r) = k_f + \frac{(k_p - k_f)}{(1 - e^{m(d-1)})} \left[ 1 - e^{\frac{m(d-r)}{r_p}} \right] \]  

(5)

However, we expect to observe similar variations with this form as that given by eqn.(4) and therefore the analysis in this paper has been carried out by only using
eqn.(4). The variation of $f(r)$ with $r$ within the interfacial layer (i.e. $r_p < r < r_T$) for different $m$ values is shown in Fig.2. From the plot, it is evident that the variation in $f(r)$ is in conformation with the boundary conditions that for $r = r_T = r^*_p d$, $f(r)$ must reduce to the thermal conductivity of nanofluid, $k_f$, whereas for $r = r_p$, the thermal conductivity should be the same as that of the particle i.e. $k_p$. We also note that as $m$ increases to a large value, say 10, $f(r)$ takes the form of a step function which points to the situation that there is no formation of interfacial layer around the dispersed nanoparticles in base fluid. Thus, the role of interfacial layer is relevant only for lower values of $m$.

![Fig 2 Thermal conductivity profile of the nanolayer as function of r for different values of m for the system Al$_2$O$_3$-water $r_p=33$nm.](image)

### 2.2 Convective Heat Transfer Mechanism

The heat transfer mechanism proposed here involves the Brownian motion wherein the convective heat transfer mechanism is caused by the relative motion between the nanoparticles and the surrounding base fluid. The Brownian motion in the system causes a correlation mechanism for the convective heat transfer. Thus, the resistance offered by the thermal base fluid is given by

$$ R_f = \frac{1}{4\pi h r_p^2 d^2} $$

(6)

where

$$ h = \frac{k_f}{d_p} (1 + A \text{Re}^\alpha \text{Pr}^{1/3} \phi_r) $$

(7)

Here, $h$ is the heat transfer coefficient developed by Prasher et al [10]. In the above expression, $A=4 \times 10^4$ is a constant [25] and $n$ is a positive number that measures the Reynold number’s, Re, contribution of the specific base fluid and is found to be different for different nanofluids i.e. it depends on the type and size of the
nanoparticle and the choice of the base fluid. Here, \( \phi_T \) is the total volume fraction of the nanoparticle along with the nanolayer and is given by

\[
\phi_T = \frac{4}{3} \pi r_T^3 \rho_n = \frac{4}{3} \pi r^3 d^3 \rho_n = \phi(d)^3
\]  

(8)

where \( \rho_n \) is the number density [20]. Prandtl number of liquid (Pr) gives a measure of the ratio of kinematic viscosity to thermal diffusivity. Reynolds number is defined as

\[
Re = \frac{1}{v_{bf}} \sqrt{\frac{9k_p T}{\pi \rho_p r_p}}
\]  

(9)

Clearly, it includes the effect of kinematic viscosity of the base fluid (\( \nu_{bf} \)), particle size, \( (r_p) \), temperature (T) and density (\( \rho_p \)) of the nanoparticle. Thus, the coefficient \( h \) includes all the necessary parameters that can influence the thermal conductivity of the nanofluid including volume concentration and the conductivity of the base fluid itself. Now, the effective thermal resistance of the nanoparticle-fluid mixture is sum of the two thermal resistances and is obtained to be [25]

\[
R_{\text{eff}} = R_L + R_f.
\]  

(10)

Where expressions for \( R_L \) and \( R_f \) are given by eqns.(2) and (6) respectively. The effective thermal resistance that controls the rate of heat transfer between the nanoparticles and the base fluid is given as

\[
R_{\text{eff}} = \frac{1}{4\pi k_e r_p} (1 - \frac{1}{R_0})
\]  

(11)

where \( R_0 = R_0/r_p \) is the dimensionless radius of a sphere formed around each nanoparticle in the base fluid. Substituting equation (10) and using above relations, one obtains the expression for effective thermal conductivity as

\[
\frac{k_e}{k_f} = \left(1 - 3\sqrt{\phi_T} \left[ \frac{k_f}{K_L} \left(1 - \frac{1}{d} \right)^{\frac{1}{2}} + \frac{k_f}{hr_p d^2} \right] \right)^{-1}
\]  

(12)

3. Graphs and discussions

When nanoparticles are dispersed in the fluid, adsorption of liquid molecules takes place on the surface of the nanoparticles resulting in the formation of a thin nanolayer around the nanoparticles. The liquid molecules get closely arranged on the surface resulting in a layer with density slightly more than that of the fluid medium. To study the overall enhancement of thermal conductivity, we use eqn.(12) to draw a plot of effective thermal conductivity as a function of size of the nanoparticles. Fig.3 displays this variation for Al\(_2\)O\(_3\)/water system for volume fraction 0.01, 0.04 and 0.05. Based on heat conduction mechanism, Tillman and Hill [23] found the ratio of \( r_f/r_p \) to be \( d=1.2 \text{ nm} \). In this investigation, we have incorporated the Brownian motion involving convective heat transfer mechanism in addition to heat conduction phenomena in the particle-layered-liquid structure. We have chosen \( d \) to be 1.6 nm [25] since equation (12) yields compatible results with this value for three different kinds of nanofluid
systems. Here, values of $m$ and $n$ are found using least square fitting by using the experimental data as taken from the papers given in the table below. From the curve, we observe that the effective thermal conductivity of nanofluid decreases with increase in the size of the nanoparticle. As we increase the size of the particle from 20 nm to 50 nm the effective conductivity decreases from 1.67 to 0.98 for volume fraction of 0.04. This behavior of the curves can be easily understood when one realizes that as the particle size increases for one particular system and keeping all other conditions constant, there starts an onset of the process of sedimentation of these particles. As the size of nanoparticles increases, they start sinking down to the bottom of the container owing to their heavy mass and eventually their participation in the thermal conductivity process decreases and thus reducing the overall effective thermal conductivity of nanofluids. This aspect has also been kept in mind while formulating the form of the function for thermal conductivity of the nanolayer as given by eqn.(4)

Alternatively, this can also be understood in terms of the very definition of nanofluids which demands them to be a ‘stable’ colloidal dispersion. This is possible only if the dispersed nanoparticles are so small in size that their mass has negligible role in the whole process. Hence, with increase in the size of the nanoparticles, their colloidal dispersion remains no longer a stable one. Also, for one value of size of the nanoparticle, the ratio of effective thermal conductivity to that of the base fluid increases with the increase of volume fraction.

![Fig 3 Effective thermal conductivity versus diameter of the nanoparticle](image)

Next, we study the variation of effective thermal conductivity as a function of volume fraction for various systems such as CuO / Water, Al$_2$O$_3$ / Water, Al$_2$O$_3$ / EG, and CuO / EG for given particle sizes as depicted in Fig.4. Again, the choice of the particle size is guided by the availability of experimental results in the literature. For CuO / water system, the particle size is chosen to be 23.6 nm. The results have been compared with the available results [10,25,26]. Our results are found to agree well with those of Wang and Mujumdar [26] for $m=0.1$ and $n = 2.202$. We note that as the volume fraction of nanoparticles increases, the effective thermal conductivity of nanofluid also increases. This is so because with increase in volume fraction, more nanoparticles become available for participation in the thermal conductivity process.
and this, in turn, enhances the effective thermal conductivity of the nanofluids. For Al₂O₃ / water system the size of the particle has been chosen to be 33 nm for which we find that n = 2.236 and m=0.4 gives us the best fitting with the experimental values [26]. For CuO/water, size of nanoparticles is 23.6nm and for Fe/Water system particle size has been chosen to be 26nm and the values for m and n are found to be 1.7 and 2.083 respectively. Comparison has also been carried out with other works [10,25,26] as shown in Fig.4. Similarly, Al₂O₃ / EG, and CuO / EG systems have also been investigated and compared with the other available results [4,10,25] and [10,25,26] respectively. The values of n for different systems of nanofluids used here are listed in Table 1.

Table 1. The values of n for graphs of thermal conductivity ratio of nanofluid versus volume fraction at 300K

<table>
<thead>
<tr>
<th>S.No.</th>
<th>System</th>
<th>Dp</th>
<th>Value of m</th>
<th>Value of n</th>
<th>Ref for Expt. values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al₂O₃ / Water</td>
<td>80nm</td>
<td>0.1</td>
<td>2.013</td>
<td>Murshed et.al 2008</td>
</tr>
<tr>
<td>2</td>
<td>Al₂O₃ / Water</td>
<td>33nm</td>
<td>0.4</td>
<td>2.236</td>
<td>Wang et.al 2007</td>
</tr>
<tr>
<td>3</td>
<td>Al / EG</td>
<td>80nm</td>
<td>1.6</td>
<td>1.407</td>
<td>Murshed et.al 2008</td>
</tr>
<tr>
<td>4</td>
<td>Fe / Water</td>
<td>26nm</td>
<td>1.7</td>
<td>2.083</td>
<td>Li et.al 2005</td>
</tr>
<tr>
<td>5</td>
<td>Al₂O₃ / EG</td>
<td>35nm</td>
<td>1.3</td>
<td>1.492</td>
<td>Eastman et.al 2001</td>
</tr>
<tr>
<td>6</td>
<td>CuO / water</td>
<td>23.6nm</td>
<td>0.1</td>
<td>2.202</td>
<td>Wang et.al 2007</td>
</tr>
<tr>
<td>7</td>
<td>CuO / EG</td>
<td>35nm</td>
<td>0.5</td>
<td>1.423</td>
<td>Eastman et.al 2001</td>
</tr>
</tbody>
</table>

![Image of graphs](4(a)) ![Image of graphs](4(b))
Lastly, we have also tested the present model for particles as large as 80 nm in diameter. The corresponding graphs for Al / EG and Al₂O₃ / Water systems are depicted in fig.5 for the values of n and m calculated to be 1.407 and m=1.6, n=2.013 and m=0.1, respectively. These findings also match well with the experimental data [11,28]. We also note that the present model certainly has an edge over the results reported by Sohrabi et al [10] and Prasher et al (2005) for Al / EG system and those reported by Leong et al [28] and Sohrabi [10] for Al₂O₃ / Water system. Thus, this model is found to work not only for small sized nanoparticles as is true with various models proposed earlier by other workers but it also yields very good results for large sized nanoparticles.
4. Conclusions
A new expression for the thermal conductivity profile of the nanolayer has been put forth and has been used to find the effective thermal conductivity of the nanoparticle-fluid mixture. The results predicted by the proposed ansatz are found to be generally better than those reported in other works. This model shows a significant improvement over other models as it incorporates the formation of nanolayer around the dispersed nanoparticles which is found to play a significant role in accounting for the anomalous enhancement in thermal conductivity shown by nanofluids. Here, care has been taken to judiciously combine both the effects namely, the conduction mechanism in the particle-layered-liquid structure as well as the Brownian motion of the nanoparticles in the fluid. Also, this model gives significant improvement over the existing models even for larger nanoparticle diameters.

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References
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