The Interfacial Layer Effect on Thermal Conductivity of Nano-Colloidal Dispersions

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Abstract—A mathematical model has been proposed for calculating the effective Thermal Conductivity of nano colloidal dispersions by incorporating a thermal conductivity profile for the interfacial layer. The present model has been successfully applied to the colloidal dispersions containing rod shaped nanoparticles as well as those containing spherical nanoparticles. The results have also been compared with other existing models.

Index Terms—Thermal conductivity, nanofluids, colloidal dispersion and interfacial layer.

I. INTRODUCTION

About a decade ago Choi at Argonne National Laboratory coined a word ‘nanofluid’ for fluid containing dispersed nanoparticles. Since then nanofluids have attracted a worldwide attention from researchers across the world due to their wide range of potential applications. They are a two phase system with a solid phase and a liquid phase. These find applications in the field of electronics, transportation, space and defense, drug delivery and the areas where energy saving and cooling is the key issue [1]. The major reasons attributed are to their showing intensified heat transfer properties than the conventional solid liquid suspensions are the higher specific surface area, higher stability of dispersion, reduced pumping power and lesser particle clogging. Due to the above stated reasons, some of the thermophysical properties of nanofluids have been found to be enhanced in comparison to the conventionally used base fluids like water, ethylene glycol etc. These include thermal conductivity, thermal diffusivity, viscosity and the heat transfer coefficients. These enhanced properties have been the main driving force for instigating interest amongst the research community towards these nano colloidal dispersions.

There has been a large scale research to study the anomalous enhancement in effective thermal conductivity of nanofluids both theoretically as well as experimentally [2]-[8]. The most commonly employed experimental methods have been Temperature oscillation technique [4], [5] and a Transient hot-wire method [6]-[9] to determine thermal conductivity of the nanofluids. All the experiments have reported unusually higher increase in the effective thermal conductivity values of the nanofluids. About 4% volume fraction of Al$_2$O$_3$ nanoparticles when dispersed in water shows an increase of 30% in thermal conductivity as reported by Masuda et al. [10]. Similarly a 4 volume percent of CuO nanoparticles with average diameter of 35nm in ethylene glycol dispersion show a 20% increase in thermal conductivity of the dispersion obtained as shown by Eastman et al. [11]. More interestingly, above 100% enhancement in thermal conductivity in case of CNT based nanofluids. There has been a wide variety of experimental works with a dispersed range of values for different nanoparticle volume fraction which has tempted the research community to look for theoretical physical mechanisms or models that can explain such an anomalous enhancement in effective thermal conductivity of dispersions with nano-sized particles.

A number of theoretical mechanisms proposed so far [12], [13] have been unable to account for one or the other important factors affecting the effective thermal conductivity of a nanofluid. These include thermal conductivity of the fluid medium, thermal conductivity of the nanoparticle dispersed, nanoparticle size and its volume fraction, formation of layer around the nanoparticle etc. Yu and Choi [14] have improved the Maxwell model to incorporate the concept of interfacial layer as a more ordered layer is found to have major impact on the nanofluids thermal conductivity. But this model remained silent about the interaction between nanoparticles and the fluid medium. Many interfacial layer models have come up so far which presented empirical formulae for describing the profile of thermal conductivity of the Interfacial nanolayer. Some of these include Tillman et al. [15], Nsofor et al. [16] and Xie et al. [17] among others.

In the present theoretical formulation, a general empirical form of thermal conductivity profile inside the interfacial layer has been proposed. This is then used to develop a model for calculating the effective thermal conductivity of the colloidal dispersion containing nanoparticles. The parameters involved in the present study are the effect of Nanoparticle size, the volume fraction of the nanoparticles, thermal conductivity of the base fluid and the thermal conductivity of the nanoparticle itself.

II. THEORETICAL FORMULATION

A. The Nanoparticle Structure and the Thermal Conductivity Profile

The equivalent nanoparticle consists of nanoparticle and interfacial nanolayer consisting of the orderly arrangement of base fluid molecules around the nanoparticles. This nanoparticle is dispersed in the base fluid forming a colloidal suspension called ‘nanofluid’ or nano colloidal dispersion. This orderly arrangement is expected to have intermediate thermal conductivity profile between the base fluid and the dispersant nanoparticle. The nanoparticle structure is

Manuscript received September 30, 2013; revised January 13, 2014.

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DOI: 10.7763/IJAPM.2014.V4.244
depicted in the Fig. 1.

![Fig. 1. The nanoparticle structure.](image)

The thermal conductivity of the nanolayer is supposed to vary with distance $r$ from inner radius $r_p$ of the nanoparticle to the entire thickness of the interfacial layer around the nanoparticle before it becomes equal to the $k_f$ at the interface. Here, the empirical formulation is introduced based on the assumptions that thermal conductivity equals the thermal conductivity of the nanoparticle $k_p$ at the inner interface and that at the outer interface it is equal to base fluid’s thermal conductivity i.e $k_f$ so that

$$
\begin{aligned}
  k(r) = \\
  \begin{cases}
    k_p & \text{size} \leq r_p \\
    f(r) & r_p \leq r \leq r_p + d \\
    k_f & r_p + d \leq \text{size}
  \end{cases}
\end{aligned}
$$

(1)

Size in the equation (1) refers to radius of the nanoparticle. Here, the following tangential variation of $f(r)$ is proposed

$$
  f(r) = k_p + \frac{(k_f - k_p)}{\tanh m} \tanh \left( m \frac{r - r_p}{d} \right)
$$

(2)

where, $m$ is a real positive integer. The corresponding thermal conductivity profile within the interfacial layer is displayed in Fig. 2.

![Fig. 2. The thermal conductivity profile versus radius of the nanoparticle.](image)

The above graph shows the thermal conductivity profile of the Interfacial nanolayer for Al$_2$O$_3$ nanoparticles in Ethylene Glycol with size of 35nm. The graph is plotted for different values of $m$ ($m=1, 2, 0.5$). The value of $m$ as decreased from 1.0 shift towards a linear profile while $m$ if increased from 1.0 show a fast decrease moving towards being a step function profile. In the present model the value of $m$ is taken as 1 in each type of nanofluid system.

**B. Dispersions with Spherical Nanoparticles**

It is assumed that the Al$_2$O$_3$ and CuO nanoparticles are spherical when dispersed in base fluids, ethylene Glycol and water respectively. The thermal conductivity of the interfacial layer is a continuous function of $r$ within the nanolayer. The thermal resistance offered by the nanolayer is given by

$$
  R_L = \frac{1}{4\pi k_f} \left( \frac{1}{r_p} - \frac{1}{r_p + d} \right)
$$

(3)

Also the resistance is related to the thermal conductivity distribution between $r_p$ and $r_p+d$ as

$$
  R_L = \int_{r_p}^{r_p+d} \frac{dr}{4\pi r^2 f(r)}
$$

(4)

Combining the preceding two equations, we get

$$
  k_i = \frac{d}{r_p (r_p + d) \int_{r_p}^{r_p+d} \frac{dr}{r^2 f(r)}}
$$

(5)

**C. Dispersions with Rod Shaped Nanoparticle**

In case the nanoparticles are assumed to be cylindrical like rod shaped nanoparticles then the thermal resistance offered by the nanolayer will be given by

$$
  R_L = \frac{1}{\pi K_i} \left[ \frac{l}{r_p^2} - \frac{(l + 2d)}{(r_p + d)^2} \right]
$$

(6)

where $l X r_p$ are the dimensions of the nanoparticle.

And the resistance is related to the thermal conductivity distribution between $r_p$ and $r_p+d$ as

$$
  R_L = \int_{r_p}^{r_p+d} \frac{dr}{2\pi r_p (r_p + l) f(r)}
$$

(7)

Using the two preceding equations we get

$$
  k_i = \frac{\int_{r_p}^{r_p+d} \frac{dr}{r_p^2 (r_p + l)^2 f(r)}}{\int_{r_p}^{r_p+d} \frac{dr}{2r_p (r_p + l) f(r)}}
$$

(8)

**D. The Expression for the Effective Thermal Conductivity**

The effective thermal conductivity is defined using Fourier’s law of heat conduction as

$$
  \langle \dot{q} \rangle = -k_{eff} \langle \nabla T \rangle
$$

(9)
\[ q = \langle q \rangle - k_f \nabla T > + \langle q_p \rangle + \langle q_i \rangle \]  \hspace{1cm} (10)

Lu and Song [18] used equilibrium hard sphere fluid model and determined the effective thermal conductivity by considering the inclusion which is the dispersed nanoparticle to be coated and debonded for two interacting particles. They considered temperature field to be linear and applied the ambient temperature gradient as unity along a specified direction to the system. The effective thermal conductivity is computed to be given by

\[ k_{eff} = k_f \left( 1 + 3F \phi_f + \frac{3F^2 \phi_f^2}{1 - F \phi_f} \right) \hspace{1cm} (11) \]

with

\[ F = \frac{\alpha_1[(1 + \beta)^3 - \alpha_2]}{(1 + \beta)^3 + 2(\alpha_1)(\alpha_2)} \hspace{1cm} (12) \]

and

\[ \alpha_1 = \frac{k_p - k_f}{k_p + 2k_f}, \hspace{1cm} \alpha_2 = \frac{k_f - k_f}{k_i + 2k_f} \hspace{1cm} \alpha_3 = \frac{k_f - k_f}{k_f + 2k_f} \hspace{1cm} (13) \]

The total volume fraction of the equivalent nanoparticle which is formed from the original nanoparticle of radius \( r_p \) and the nanolayer of thickness \( d \) is given by

\[ \phi_f = \frac{4}{3} \pi (r_p + d)^3 n = \phi (1 + \beta)^3 \hspace{1cm} (14) \]

where

\[ \phi = \frac{4}{3} \pi r_p^3 n \hspace{1cm} (15) \]

is the original volume fraction of the nanoparticle without including the nanolayer and \( n \) defines the number density of particles and \( \beta = d/r_p \).

The above graphs show that the effective thermal conductivity ratio increases with an increase in the volume fraction of the nano-dispersants in the base fluid. The results from this model have been compared with other theoretical models like Yu and Choi [14], Maxwell model [12] and Prasher model [19], [20].

The maximum deviation in case of Al₂O₃/EG nanodispersion is 0.75% in the present model whereas it is 1.3% in case of Xie model [17] and it is 1.07% in case of Nsofor model [16]. The maximum deviation in case of
CuO/Water nanodispersion is 0.7% in the present model and the maximum deviation in case of Xie model is 1.6% and in case of Nsofor model is 0.6%. In case of TiO2/EG our maximum deviation from experimental data is 0.5%. Also in case of CuO/water system, the present model overlaps the model by Yu and Choi when the thermal conductivity of the equivalent particle is taken to be equal to the thermal conductivity of the nanoparticle with an interfacial layer thickness of 1nm. The value for the interfacial layer thickness in each type of nanofluid system has been calculated using least square fitting method.

The system studied for rod shaped nanoparticle dispersion is TiO2/EG and the available experimental data by Murshed et al. [9] is used for comparison.

![Tangent hyperbolic profile with present model](image)

**Fig. 6.** The variation of effective thermal conductivity ratio with volume fraction for TiO2/EG system.

It is evident from the Fig. 6 that the proposed thermal conductivity profile (tangent hyperbolic) fits well with the available experimental values by Murshed [9]. It shows the comparison with the thermal conductivity profiles given by Xie et al. (linear Profile) and Nsofor et al. (Quadratic Profile).

### IV. CONCLUSION

The present model successfully explains the anomalous behavior of effective thermal conductivity of nanofluids containing spherical as well as cylindrical nanoparticles. The maximum deviation from the experimental result is 0.75% in case of present proposed semi empirical model.

### ACKNOWLEDGMENT

The authors are highly obliged to Dr. Vishwamittar for his useful comments and suggestions.

### REFERENCES


