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A new model for thermal conductivity in nanofluids

Pei Tillman
University of Wollongong, ptillman@uow.edu.au

James M. Hill
University of Wollongong, jhill@uow.edu.au

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Pei Tillman and James M. Hill
Nanomechanics Group
School of Applied Mathematics & Statistics
University of Wollongong, NSW 2522 Australia
Email: ptillman@uow.edu.au, jhill@uow.edu.au
Telephone: +61 2 42213845, Fax: +61 2 42214845

Abstract: **Nanofluids exhibit enhanced thermal conductivity superior to traditional heat transfer fluids. The conventional theoretical models cannot explain the large enhancement of the thermal conductivity of nanofluids. It has been proposed that an interfacial structure formed by liquid molecular layering might play an important role. To date there is no known procedure to properly calculate the nanolayer thickness, and all previous investigators arbitrarily adopt a layer thickness which is consistent with experimental results. Here we investigate the thermal conductivity structure of this interfacial layer and its impact on the effective thermal conductivity and an expression for the thermal conductivity profile in the nanolayer is investigated using matching boundary conditions for the general heat conduction equation. An expression for the thickness of the nanolayer is derived. The assumed profile for the thermal conductivity within the nanolayer, $k = k_o(1-\alpha r)^m$, is found to be appropriate when m > 15. It is found that the thickness of the nanolayer is approximately 19% and 22% of the radius of a nanoparticle, for Al_2O_3/Ethylene glycol and CuO/H_2O nanofluids, respectively. This evaluation of the nanolayer thickness is consistent with the range of values used by several authors in their theoretical models for the thermal conductivity of nanofluids which include a nanolayer.**

Keywords: nanofluids, nanoparticles, nanolayer, mathematical model, thermal conductivity, heat conduction, temperature field.

I. INTRODUCTION

Nanofluids are engineered as a suspension of solid nanoparticles or nanofibers into conventional heat transfer fluids. These new fluid composites have attracted considerable attention since anomalously large thermal conductivity enhancement of nanofluids has been reported over the past ten years.

Although some properties of multiphase mixtures may be obtained by simply averaging the properties of the pure phases, the relation of the thermal conductance of such mixtures to the conductance of the pure phases represents a complex problem. Large enhancement in the thermal conductivity of nanofluids cannot be explained by the traditional heat conduction model (Maxwell formula [1]). As a result, within the past ten years, several new theoretical models have been proposed [2]. Some of these models are based on the Brownian motion of nanoparticles to explain the anomalous thermal conductivities. Others have focused on including control factors which affect the thermal conductivity behavior of nanofluids. Experimental data shows that the thermal conductivity behavior of a composite fluid can be strongly dependent on the thermal conductivities of the solid and the liquid, particle volume concentrations, particle size, particle shape and temperature. It is well known that many physical properties of nanoparticles are changed in the micro scale regime. New theoretical descriptions may be needed to properly account for the unique features of nanofluids, in particlauler the small particle size which results in large surface-to-volume ratios.

A nanofluid is a multiphase system consisting of the host liquid and percolation patterned cluster inclusion. It has long been known that liquid molecules close to a solid surface form a layered solid-like structure, but little is known about the connection between this nanolayer and the thermal properties of the solid/liquid suspension. A few studies suggest that the solid-like nanolayer acts as a thermal bridge between a solid particle and a bulk liquid, and so is key to enhanced thermal conductivity [3-5]. However, the thermal conductivity profile of the nanolayer and the nanolayer thickness are unknown. In the most recently renovated models for the inclusion of a nanolayer, the constant thermal conductivity in the nanolayer and the value of the nanolayer thickness are chosen as input data to fit the experimental results. In Xie et al's model [6], a linear variation of the thermal conductivity of the nanolayer is assumed. Therefore, there is a need to develop an innovative concept or method to accurately evaluate the thermal conductivity of the nanolayer and the nanolayer thickness for improving current theoretical models. In this study, we propose a procedure which predicts the nanolayer thickness rather than just choosing it to fit the data.

Exploring the nanolayer structure might be a new way to produce nanofluids that are highly thermally conductive. In this article, we focus on the study of the thermal conductivity profile of a nanolayer through mathematical manipulation of the basic heat conduction among the nanoparticles, the nanolayer and the bulk fluid. The adequate thermal conductivity variation in the nanolayer and the nanolayer thickness are derived.

II. NANOLAYER STRUCTURE

A. Profile of thermal conductivity within nanolayer

When the nanoaprticles are dispersed in the base fluid, the liquid molecules close to the solid surface generally form an ordered layer that behaves like a solid structure, which is called a nanolayer. The nanofluid is a composite. Fig. 1 illustrates the schematic structure of a nanoparticle with an interfacial nanolayer when the particle is dispersed in a fluid. Generally, the thermal conductivity of the particles k_p is much higher than that of the base fluid k_f. The solid layered molecules in the nanolayer is in an intermediate state between the base liquid and the solid. Hence, the nanolayer would be expected to have an intermediate thermal conductivity between k_p and k_f. There is no available expression for the thermal conductivity distribution inside a nanolayer k or the nanolayer thickness ($R-r_p$). The thermal conductivity of the nanolayer k is proposed as a variable k(r). k is equal to the thermal conductivity of the nanoparticle k_p at its inner surface and the thermal conductivity of base fluid k_f at its outer surface, that is

$$k(r_p) = k_p, \quad k(R) = k_f. \tag{1}$$

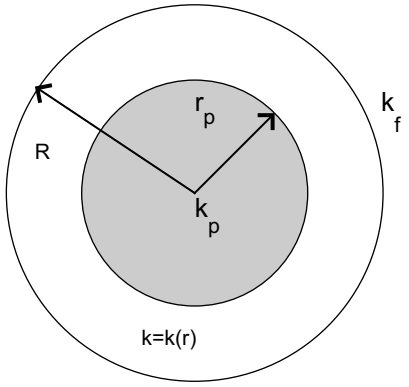

Figure 1. Schematic structure of a nanoparticle with interfacial nanolayer

To investigate the interfacial effect on the effective thermal conductivity of the nanofluid, we assume the nanolayer has continuous thermal conductivity and heat flux at its inner and outer surface. Assuming that the mixture system is subjected to steady state heat conduction, the temperature fields within a nanoparticle, nanolayer and fluid are governed by the steady heat conduction equation. The heat transfer rate in the material can be calculated by Fourier's law. We use $T_p(r,\theta)$, $T(r,\theta)$ and $T_f(r,\theta)$ to represent the temperature fields in a particle, nanolayer and fluid in spherical coordinates with axial symmetry. The steady-state heat conduction can be described by the following expression

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 k \frac{\partial T}{\partial r}\right] + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left[k \sin\theta \frac{\partial T}{\partial \theta}\right] = 0. \tag{2}$$

When the thermal conductivity k is a constant, the general solution of the above equation provides the temperature field in the homogeneous medium under equilibrium conditions. Hence, using the first order Legendre function, $T_p(r,\theta)$ and $T_f(r,\theta)$ can be given as follows:

Inside the nanoparticle ($r \le r_p$)

$$T_p(r,\theta) = Hr\cos\theta, \tag{3}$$

and in the base fluid ($r \ge R$)

$$T_f(r,\theta) = \left(D/r^2\right)\cos\theta. \tag{4}$$

$T(r,\theta)$ in the nanolayer ($r_p \le r \le R$) can be obtained by solving (2). Using separation of variables we let

$$T(r,\theta) = A(r)\cos\theta, \tag{5}$$

and substitute this into (2) to obtain

$$\frac{d^2A}{dr^2} + \left(\frac{2}{r} + \frac{1}{k}\frac{dk}{dr}\right)\frac{dA}{dr} - \frac{2}{r^2}A = 0. \tag{6}$$

Since (6) is a second-order differential equation, there are two non-linear independent solutions, $y_1(r)$ and $y_2(r)$ so that $A(r)=Ey_1(r)+Fy_2(r)$. The temperature field $T(r,\theta)$ in the nanolayer ($r_p \le r \le R$) can be given as follows

$$T(r,\theta) = \left[Ey_1(r) + Fy_2(r)\right]\cos\theta, \tag{7}$$

where H, E, F and D are parameters to be determined through imposition of the relevant boundary conditions on $T_p(r,\theta)$, $T(r,\theta)$ and $T_f(r,\theta)$. The temperature and heat flux continuity boundary conditions at the two interfaces are:

$$T_p\big|_{r=r_p} = T\big|_{r=r_p}, \frac{\partial T}{\partial r}\bigg|_{r=r_p} = \frac{\partial T_p}{\partial r}\bigg|_{r=r_p}, \tag{8}$$

$$T_p\big|_{r=R} = T\big|_{r=R}, \frac{\partial T}{\partial r}\bigg|_{r=R} = \frac{\partial T_p}{\partial r}\bigg|_{r=R}. \tag{9}$$

B. Determination of nanolayer thickness

The critical nanolayer thickness may exist where the thermal conductivity, temperature and heat fluxes maintain continuity. In the renovated Maxwell and Hamilton-Crosser models by Yu and Choi [3, 4], the thickness of the nanolayer is required as input data, while in the fractal model by Wang et al [5] the thickness of the nanolayer is evaluated from the adsorption layer thickness by liquid molecular theory. In this paper, the expression of the critical nanolayer thickness is derived from the system of equations for the unknown coefficients D, H, E and F. From the boundary conditions at the inner and outer interfaces of the nanolayer, (8) and (9), we obtain a linear system of four equations for D, H, E and F. Through elimination of E and F and simplifying the system of equations, the resulting two equations for H and D are

$$\begin{bmatrix} \dfrac{r_p \dfrac{dy_2(r_p)}{dr} - y_2(r_p)}{\omega(r_p)} & \dfrac{R^2 \dfrac{dy_2(R)}{dr} + 2Ry_2(R)}{\omega(R)} \\ \dfrac{r_p \dfrac{dy_1(r_p)}{dr} - y_1(r_p)}{\omega(r_p)} & \dfrac{R^2 \dfrac{dy_1(R)}{dr} + 2Ry_1(R)}{\omega(R)} \end{bmatrix} \begin{bmatrix} H \\ \dfrac{D}{R^4} \end{bmatrix} = 0, \quad (10)$$

where the function ω(x) is the Wronskian of the two independent solutions of the ordinary differential equation defined by

$$\omega(x) = y_1(x)\frac{dy_2(x)}{dx} - y_2(x)\frac{dy_1}{dx}. \quad (11)$$

Equation (10) has a non-trivial solution if and only if the determinant is zero, that is

$$\frac{\dfrac{d}{dr}\left[\dfrac{y_1(r_p)}{r_p}\right]}{\dfrac{d}{dr}\left[\dfrac{y_2(r_p)}{r_p}\right]} = \frac{\dfrac{d}{dr}\left[R^2 y_1(R)\right]}{\dfrac{d}{dr}\left[R^2 y_2(R)\right]}. \quad (12)$$

If we use δ to denote the ratio between the radius of the outer and inner interface of the nanolayer, that is $\delta = R/r_p$, substituting $R = \delta r_p$ into (12) gives

$$\frac{\dfrac{d}{dr}\left[\dfrac{y_1(r_p)}{r_p}\right]}{\dfrac{d}{dr}\left[\dfrac{y_2(r_p)}{r_p}\right]} = \frac{\dfrac{d}{dr}\left[\delta^2 r_p^2 y_1(\delta r_p)\right]}{\dfrac{d}{dr}\left[\delta^2 r_p^2 y_2(\delta r_p)\right]}. \quad (13)$$

It is clear that the critical nanolayer thickness can be determined by solving (13) for δ and then evaluating the nanolayer thickness by $(\delta-1)r_p$. For any given k(r) and k_p, k_f and r_p, the first step is to find the temperature profile $T(r,\theta)$ by solving (6).

III. ANALYSIS AND DISCUSSION

The nanolayer is a transition zone for the thermal conductivity. Whichever function k(r) is proposed for the nanolayer, it must produce a solution for $\delta > 1$ to be physically acceptable. With this criterion, we analyze the applicability of any proposed function of k(r). For $k(r) = k_o(1-\alpha r)^m$, when $m > 10$ δ is greater than 1 and gradually approaches 1.19 with increasing m (see Fig. 2). This indicates the thickness of the nanolayer for a Al_2O_3/Ethylene glycol (EG) nanofluid is about 19% of the radius of a Al_2O_3 nanoparticle, which is approximately the same order of other references. For a CuO/H_2O nanofluid, calculations indicate δ = 1.22, which means the nanolayer thickness is about 22% of radius of CuO nanoparticle.

The average thermal conductivity of the nanolayer k_a can be evaluated by

$$k_a = \frac{\int_{r_p}^{R} r^2 k(r) dr}{\int_{r_p}^{R} r^2 dr}. \quad (14)$$

When the particles of the dispersed phase consist of an inner sphere of radius r_p and conductivity k_p, covered by an outer spherical shell of radius R and conductivity k_l, Maxwell's treatment results in the following expression for the effective thermal conductivity of a nanofluid k_{eff} [7]:

$$\frac{k_{eff} - k_f}{k_{eff} + 2k_f} = \frac{(k_a - k_f)(2k_a + k_p)\delta + (2k_a + k_f)(k_p - k_a)}{(k_a + 2k_f)(2k_a + k_p)\delta + 2(k_a - k_f)(k_p - k_a)}\varphi. \quad (15)$$

where φ is the volume fraction of the loaded nanoparticles. For given k_p, k_f, r_p and $k(r) = k_o(1-\alpha r)^m$, we solve (13) for the ratio of the outer surface radius of the nanolayer to the inner surface radius δ and then calculate the effective thermal conductivity of the nanofluid k_{eff} from (14) and (15). The comparison between predicted and measured thermal conductivity k_{eff} [6, 8-11] is displayed in Fig.3 and Fig.4. The result shows general agreement between the present prediction and measured data.

TABLE I. MATHEMATICAL ANALYSIS OF DIFFERENT VARIATIONS OF THERMAL CONDUCTIVITY OF THE NANOLAYER IN A AL_2O_3/EG NANOFLUID (K_P=46 W/M.K AND K_F=0.253 W/M.K).

k(r) and the relevant ordinary differential equation	**m**	**δ=R/r_p**
$k(r) = k_o(1-\alpha r)^m$ $\frac{d^2A}{dr^2} + \left[\frac{2}{r} - \frac{m\alpha}{1-\alpha r}\right]\frac{dA}{dr} - \frac{2}{r^2}A = 0$ $k_o = \frac{(\delta k_p^{1/m} - k_f^{1/m})^m}{(\delta-1)^m}$ $\alpha = \frac{k_p^{1/m} - k_f^{1/m}}{r_p(\delta k_p^{1/m} - k_f^{1/m})}$	1	0.0204
	2	0.1180
	10	0.5946
	11	0.6233
	12	1.3978
	15	1.3035
	20	1.2572
	30	1.2255
	40	1.2128
	50	1.2059
	60	1.2016
	100	1.1934

IV. CONCLUSION

In this paper, we propose a procedure to properly determine the nanolayer thickness to improve the prediction of the thermal conductivity of nanofluids in the most recent theoretical models. It is the first attempt to determine the nanolayer thermal conductivity structure and nanolayer thickness from mathematical manipulation. A model including the consideration of the role of a nanolayer and variable profile

of thermal conductivity of the nanolayer has been proposed. We have used the basic principle of heat conduction in the composite medium to study the thermal conductivity in the nanolayer and then determine the nanolayer thickness. From a mathematical point of view, the temperature profiles in the nanoparticle, the nanolayer and the base fluid have to be determined individually from the steady-state solution of heat conduction with individual thermal conductivities which satisfy continuous interface boundary conductions. An expression for the nanolayer thickness is derived from the condition for the existence of a non-trivial solution. We have explored the variation of the thermal conductivity nanolayer assuming that $k(r) = k_o (1 - \alpha r)^m$. The ratio between the radius of outer and inner interface of the nanolayer δ approaches its limit when m increases. The calculation indicates that the nanolayer thickness for Al_2O_3/EG and CuO/H_2O nanofluids are approximately 19% and 22% of the corresponding nanoparticle radius respectively, which is consistent with some data used in other studies. Using the proposed thermal conductivity function of the nanolayer and its derived thickness, the Maxwell model for inclusion of the nanolayer shell in the nanoparticle has been applied to evaluate the effective thermal conductivity of the nanofluid. The calculated values agree well with experimental data. As a nanoparticle is so small, the effects of particle size and nanolayer thickness become much more significant, which implies that exploring the nanolayer structure is an effective method to understand the high thermal conductivity of nanofluids.

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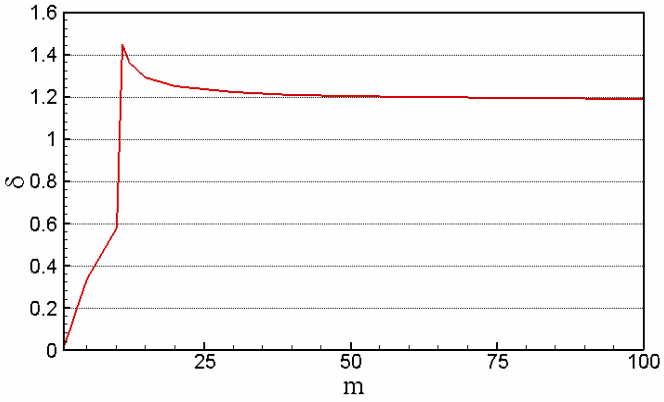

Figure 2. The critical nanolayer thickness δ for the Al_2O_3/EG nanofluid (k_p=46 W/m.K and k_f=0.253 W/m.K) when the thermal conductivity of nanolayer is of the form $k(r) = k_o (1 - \alpha r)^m$

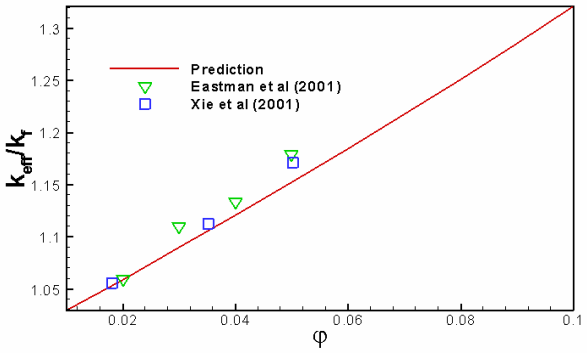

Figure 3. Comparison between the present prediction and some experimental data for the Al_2O_3/EG nanofluid

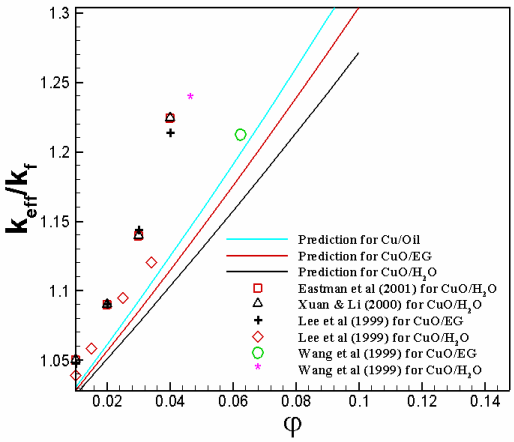

Figure 4. Comparison between the present prediction and some experimental data for the CuO/EG, Cu/Oil, CuO/Water nanofluids