Thermal Conductivity Modeling of Nanofluids

Kazem FARHADI [1,*], Nick T. CROFT [2]

* Corresponding author: Tel.: ++44 (0)1792 295197; Fax: ++44 (0)1792 295197; Email: 497120@swansea.ac.uk
1: School of Engineering, Swansea University, UK
2: School of Engineering, Swansea University, UK

Abstract In the present work, a mathematical model for predicting effective thermal conductivity of nanofluids containing spherical nanoparticles is developed. This model takes into account the effects of an interfacial nanolayer formed by liquid molecule layering on the particle liquid interface as well as micro-convection caused by thermal motion of nanoparticles. The present model has been proposed in order to calculate the effective thermal conductivity of nanofluids. The model accounts for the enhancement in effective thermal conductivity of a nanofluid with respect to the suspended nanoparticles size, volume fraction, temperature and thermal conductivities of the nanoparticle and base fluid. The results show that the prediction capability of the developed model is good by the way of comparison with the existing recent experimental data.

Keywords: Nanofluids, Thermal Conductivity, Heat Flux, Nanolayer, Micro-Convection

1. Introduction

Nanotechnology is foreseen by scientists to be one of the remarkable forces that drive the next major industrial revolution of this century. It represents the most relevant technological cutting edge currently being explored. The goal is to manipulating the structure of the matter at the molecular level with the goal for innovation in virtually every industry and public endeavor including biological sciences, physical sciences, electronics cooling, transportation, the environment and national security. Low thermal conductivity of conventional heat transfer fluids such as water, oil, and ethylene glycol mixture is a primary limitation in enhancing the performance and the compactness of many engineering electronics devices. To overcome this drawback, there is a strong motivation to develop advanced heat transfer fluids with substantially higher conductivities to enhance thermal characteristics. Nanoparticles (small particles) stay suspended much longer than larger particles. Should particles settle rapidly (microparticles), more particles need to be added to replace the settled particles, resulting in extra cost and degradation in the heat transfer enhancement. As such an innovative way in improving thermal conductivities of a fluid is to suspend metallic nanoparticles within it. The resulting mixture referred to as a nanofluid possesses a substantially larger thermal conductivity compared to that of traditional fluids (Choi, 1995). The presence of the nanoparticles in the fluids increases significantly the effective thermal conductivity of the fluid and therefore enhances the heat transfer characteristics. Nanofluids have distinctive characteristics, which is quite different from those of traditional solid-liquid mixtures in which millimeter and/or micro-meter-sized particles are involved. Such particles can clot equipment and can increase pressure drop due to settling effects. Moreover, they settle rapidly, creating substantial additional pressure drop. However, nanofluids exhibit little or no penalty in pressure drop when flowing through the passages. Moreover, they flow smoothly through microchannels without clogging them. Thus, nanofluids are best for applications in which fluid flows through small passages

because nanoparticles are small enough to behave similar to liquid molecules. Nanofluids increases heat transfer rates and this associated with minimum pressure drop. Enhancements were recently reported for copper nanofluids, where just a 0.3% volume fraction of 10 nm diameter copper nanoparticles led to an increase of up to 40% in the thermal conductivity of ethylene glycol (Choi, 1995). Researchers have demonstrated that nanofluids, containing a small amount of metal (for example Cu) or nonmetal (for example SiC, Al2O3 and CuO) nanoparticles, exhibits substantially enhanced thermal conductivities compared with those of the base fluids Eastman et al. (2001), Xie et al. (2002), Xie et al. (2002) and Lee et al. (1999). The enhanced thermal conductivities have been found to be much higher even up to an order of magnitude greater than those values predicted by the traditional models. Namely Maxwell model (Maxwell, 1881), Hamilton and Crosser model (Hamilton and Crosser, 1962) and Davis model (Davis, 1986) which are satisfactory for computing the effective thermal conductivity for mixture consisting of fluid and micro-or larger-sized solid particles. In particle-fluid mixtures, the liquid molecules close to a particle surface are known to form layered structures and behave much like a solid, Yu et al. (2000). The thickness of this aligned solid-like layer of liquid molecules at the interface is at a magnitude of nanometer. This nanolayer has a significant impact in heat transport form solid to adjacent liquids Lee et al. (1999), Keblinski et al. (2002) and Yu and Choi (2003). The weakness of traditional models in predicting the thermal conductivities of nanofluids indicates that some mechanisms are not considered. Therefore, nanofluids not only offer an opportunity for upgrading traditional thermal engineering but also present a theoretical challenge to explain their heat transport mechanisms. In this work, an attempt made to investigate theoretically the mechanism of the effective thermal conductivity of nanofluids. In building up the present model, it is assumed that the nanoparticle and the attached nanolayer as a complex nanoparticle.

2. Mathematical Modeling

For constructing the present model, it is assumed that the nanoparticle and the attached nanolayer as a complex nanoparticle. The aforementioned complex nanoparticles undergo restless motion which arises from the random thermal agitation of the molecules in the surrounding liquid. These smaller entities act both as the driving force for the nanoparticle fluctuations (due to the impact of the liquid molecules on the nanoparticles) and as a means of damping these motions (due to the viscosity experienced by the nanoparticles), Parisi (2005). The nanoparticle motions produce micro-convection of the suspending fluid. Consequently enhance the overall heat transfer in nanofluids.

There exist four heat transport modes in a nanofluid. These are by the base fluid, by the nanoparticle, by the nanolayer and by the micro-convection, respectively. Figure 1 schematically shows the four different heat transport modes involved in the present modeling. The overall heat flux can be stated as

$$\langle \vec{q}_t \rangle = \langle \vec{q}_f \rangle + \langle \vec{q}_{e,p} \rangle + \langle \vec{q}_{e,l} \rangle + \langle \vec{q}_{e,c} \rangle \quad (1)$$

Where $\langle\rangle$ denotes the volume-averaged value, $\vec{q}$ is the heat flux and the subscript {t, f}, {e, p}, {e, l} and {e, c} represent the total value, base fluid, extra value of nanoparticle, extra value of nanolayer and extra value of micro-convection, respectively. The three parameters, $\langle \vec{q}_f \rangle$, $\langle \vec{q}_{e,p} \rangle$ and $\langle \vec{q}_{e,l} \rangle$ can be written as (Lu and Song, 1996)

$$\langle \vec{q}_f \rangle = -k_f \langle \nabla T \rangle \quad (2a)$$

$$\langle \vec{q}_{e,p} \rangle = \frac{1}{V}\frac{k_p - k_f}{k_p}\int_{V_p} \vec{q} dV = \frac{1}{V}\frac{k_p - k_f}{k_p}\int_{S_p} \vec{r}\vec{q}.\vec{n} dS \quad (2b)$$

$$\langle \vec{q}_{e,l} \rangle = \frac{1}{V}\frac{k_l - k_f}{k_l}\int_{V_l} \vec{q} dV = \frac{1}{V}\frac{k_l - k_f}{k_l}\int_{S_p+S_l} \vec{r}\vec{q}.\vec{n} dS. \quad (2c)$$

Here ∇T represents temperature gradient vector, V the total volume of the observed composite system, $\vec{r}$ the position vector and $\vec{n}$ the unit outward normal vector of the bounding surface. Where S_p and S_l denote the inner and outer bounding surface of the

nanolayer. In addition, k_p and k_f represent the thermal conductivity of the nanoparticle and the base fluid.

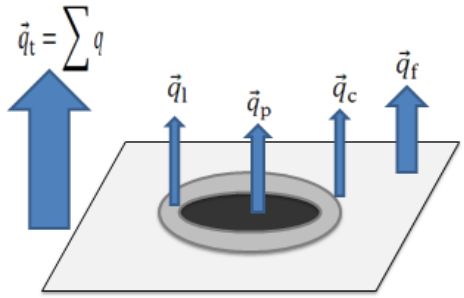

Fig. 1. *Four heat flux modes in a nanofluid where $\vec{q}_t$, $\vec{q}_p$, $\vec{q}_l$, $\vec{q}_c$ and $\vec{q}_f$ represent the total heat flux, heat flux through the nanoparticle, heat flux through the nanolayer, heat flux caused by micro-convection and heat flux through the base fluid, respectively.*

The present effective thermal conductivity model is based on a nanoparticle-liquid mixture with monosized spherical inclusions of radius r_p and particle volume concentration ϕ. The alignment of the liquid molecules inside the solid-like interfacial nanolayer of thickness d is more ordered than that of the bulk liquid. The thickness, the microstructures and the physicochemical properties of this nanolayer are highly dependent on the suspended nanoparticles, the base fluid, and the interaction between them. The accurate thermophysical behaviour of the aforesaid interfacial nanolayer may be studied by analyzing the effect of these factors. A literature survey suggests that there is not an expression for calculating the thermal conductivity of the nanolayer on the surface of the nanoparticle. The solid-like nanolayer would be expected to have an intermediate thermal conductivity between that of the bulk liquid and that of the solid. This is logic since the layered molecules are in an intermediate physical state between the bulk liquid and the solid, Yu (2003). Assuming the distribution of the thermal conductivity inside the nanolayer to be given by

$k(r)\left(r_p \le r \le r_p + d\right)$.

Therefore, the thermal resistance resulted from this layer (R_l) can be written as

$$R_l = \int_{r_p}^{r_p+d} \frac{dr}{4\pi r^2 k(r)} \tag{3}$$

The layer thermal resistance (R_l) can also be stated by the average thermal conductivity of the nanolayer (k_l) as

$$R_l = \frac{1}{4\pi k_l}\left(\frac{1}{r_p} - \frac{1}{r_p + d}\right) \tag{4}$$

On substituting Equation (3) into Equation (4), one obtains

$$k_l = \frac{d\left(r_p + d\right)^{-1}}{\int_{r_p}^{r_p+d} \frac{dr}{r^2 k(r)}} \tag{5}$$

Due to the complexity of physicochemical interactions betweens nanoparticle and the base fluid, it is assumed that the variation of the thermal conductivity inside the nanolayer is linear. In other words

$$k(r) = r\left(\frac{k_f - k_p}{d}\right) + \frac{k_p\left(r_p + d\right) - k_f r_p}{d} \tag{6}$$

Substituting Equation (6) into Equation (5), there results in

$$k_l = \frac{k_f A^2}{(A-\eta)\ln(1+A) + \eta A} \tag{7}$$

Where $A = \varepsilon_p(1+\eta) - 1$ with ε_p which is the ratio of the thermal conductivity of the solid to that of the base liquid and η is the ratio of the nanolayer thickness to the original particle radius. The total volume fraction (ϕ_T) is defined as

$$\phi_T = \frac{4}{3} n\pi\left(r_p + d\right)^3 = \phi(1+\eta)^3 \tag{8}$$

where $\phi = \left(4n\pi r_p^3\right)/3$ is the original volume fraction of nanoparticle and n is the particle number per volume. It is known that a nanofluid comprising a base fluid and complex nanoparticles is statistically homogenous and isotropic. Following Fourier's law of heat conduction, the effective thermal conductivity

of the complex nanoparticles $\left(k_{eff}\right)$ is defined as

$$\langle \vec{q}_t \rangle = -k_{eff} \langle \nabla T \rangle \quad (9)$$

Combining Equations (1) and (9) one arrives at the effective thermal conductivity $\left(k_{eff}\right)$. The temperature distributions inside nanoparticle-fluid mixture should be evaluated in order to determine $\langle \vec{q}_{e,p} \rangle$ and $\langle \vec{q}_{e,l} \rangle$, respectively. An investigation was carried out by Lu and Song (1996) in connection with the heat conduction in a suspension with random arrays of coated or debonded spherical inclusions by adopting equivalent hard sphere fluid model to represent the microstructure of mixtures and considering two interacting particles. Based on the same methods of Lu and Song, the total volume-averaged heat fluxes through the base fluid, the nanoparticles and the nanolayers can be rewritten as

$$\langle \vec{q}_f \rangle + \langle \vec{q}_{e,p} \rangle + \langle \vec{q}_{e,l} \rangle = -k_f (\nabla T) \times \left[1 + 3\theta\phi_T + \frac{3\theta^2\phi_T^2}{1-\theta\phi_T} + H\left(r_p, d, \phi, k_f, k_p, k_l\right) \right] \quad (10)$$

$$\text{with } \theta = \frac{\psi_{lf}\left[\left(1+\eta\right)^3 - \left(\psi_{pl}/\psi_{fl}\right)\right]}{\left(1+\eta\right)^3 + 2\psi_{lf}\psi_{pl}} \quad (11)$$

where $\psi_{lf} = \dfrac{\left(k_l - k_f\right)}{\left(k_l + 2k_f\right)}$, $\psi_{pl} = \dfrac{\left(k_p - k_l\right)}{\left(k_p + 2k_l\right)}$, $\psi_{fl} = \dfrac{\left(k_f - k_l\right)}{\left(k_f + 2k_l\right)}$ and $H\left(r_p, d, \phi, k_f, k_p, k_l\right)$ is the higher order pair interactions related to the detailed microstructure of a specified nanofluid. It is obvious that the sum of the first three terms of the right side in Equation (10) is with a truncation error of $O\left(\phi^2\right)$. In order to simplify Equation (10), it is assumed that $H\left(r_p, d, \phi, k_f, k_p, k_l\right)$ is negligible for low particle loading. In other words

$$\langle \vec{q}_f \rangle + \langle \vec{q}_{e,p} \rangle + \langle \vec{q}_{e,l} \rangle = -k_f \langle \nabla T \rangle \left[1 + 3\theta\phi_T + \frac{3\theta^2\phi_T^2}{1-\theta\phi_T} \right] \quad (12)$$

Equation (12) illustrates the heat fluxes through the base fluid and the complex nanoparticles in a nanofluid. To include the effect of micro-convection caused by the thermal motion of complex nanoparticles more physics of the process must be explored. Based on the molecular theory of heat, the mean value of the instantaneous velocity which a particle may possess at the absolute temperature $\left(T\right)$ can be calculated. Therefore, the kinetic energy of the motion of the centre of gravity of a particle is independent of the nature of its environment. For example the liquid in which the particle is suspended. This kinetic energy corresponds to that of a monoatomic gas molecule. Consequently, the mean velocity $\left(u_{mean}\right)$ of the complex nanoparticle is determined by Equation (13), Einstein (1959)

$$u_{mean} = \sqrt{\frac{3kT}{m_c}} \quad (13)$$

where m_c is the mass of the complex nanoparticle, and $k = 1.38 \times 10^{-23}\, JK^{-1}$ is Boltzman constant. However, the mass of the complex nanoparticle can be calculated by

$$m_c = \frac{4}{3}\rho_p \pi r_p^3 \left\{ \frac{\rho_l}{\rho_p} \left[\left(1 + \frac{d}{r_p} \right)^3 - 1 \right] + 1 \right\} \quad (14)$$

The overall heat transport augmented through micro-convection. The relative motion between the suspended complex nanoparticle and the suspended base fluid creates micro-convection. An investigation was carried out by Gupte et al. (1995) who investigated the effect of this micro-convection in the enhancement of the heat transfer at a macroscopic scale and established an expression to describe the extra heat flux. This extra heat flux is given by

$$\langle \vec{q}_{e,c} \rangle = -k_f \langle \nabla T \rangle F\left(Pe\right) \quad (15)$$

$$F\left(Pe\right) = 0.055Pe + 0.1649Pe^2 - 0.0391Pe^3 + 0.0034Pe^4 \quad (16)$$

In the present work $\left(Pe\right)$, Gupte et al. (1995) is defined as

$$Pe = \frac{u_{mean} L}{\alpha_f}\left(\phi_T^{0.75}\right) \quad (17)$$

The specific length can be calculated from Equation (18)

$$L = \left(r_p + d\right)^3 \sqrt{\frac{4\pi}{3\phi_T}} \qquad (18)$$

On substituting Equations (12) and (15) into Equation (1) results in

$$\langle \vec{q}_t \rangle = -k_f \langle \nabla T \rangle \left[1 + F\left(Pe\right) + 3\theta\phi_T + \frac{3\theta^2\phi_T^2}{1-\theta\phi_T} \right] \qquad (19)$$

The expression for effective thermal conductivity $\left(k_{eff}\right)$ can be calculated as

$$k_{eff} = k_f \left[1 + F\left(Pe\right) + 3\theta\phi_T + \frac{3\theta^2\phi_T^2}{1-\theta\phi_T} \right] \qquad (20)$$

It is clear that Equation (20) relates the thermal conductivity enhancement of a nanofluid to the system parameters such as the thermal conductivities of the base fluid, nanoparticle and nanolayer, the volume fraction, the particle size of nanoparticle, the thickness of nanolayer and the temperature.

3. Results and discussion

The effective thermal conductivity of a nanofluid is related to the system parameters such as the thermal conductivities of the base fluid, nanoparticle and nanolayer, the volume fraction, the particle size of nanoparticle, the thickness of nanolayer and the temperature. This is shown in Equation (20). Equation (20) is the result of the present model deduced for evaluating the effect of the nanoparticle presence as well as the particle motion on the effective thermal conductivity of a nanofluid. It is expected that the thermal conductivity of a nanofluid will vary significantly with the temperature. This is because the thermal motion of the suspended nanoparticles shows a strong dependence on temperature. This is indeed the case and Das et al. (2001) reported similar temperature dependent thermal conductivity enhancement tendency for water-based nanofluids containing 38.4 nm Al_2O_3 nanoparticles.

It is shown that nanofluids utilize completely the size effect of nanoparticles. The effective thermal conductivity of Cu-EG nanofluids with copper nanoparticle concentration of 5.0% is calculated in order to evaluate the nanoparticle size effect. In the evaluation, the thermal conductivities were taken as 398 $Wm^{-1}K^{-1}$ for Cu and 0.258 $Wm^{-1}K^{-1}$ for EG. Figure 2 show the results which reveal the fact that the enhancement in the effective thermal conductivity increases with the reciprocal of the nanoparticle radius. The figure show that the effective thermal conductivity augments with very large slope at small particle sizes. This is due to the contributions of the nanolayer and the particle motion.

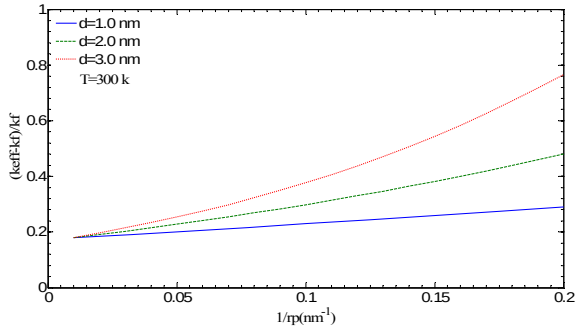

Fig. 2. *Variations of the thermal conductivity enhancement versus the reciprocal of nanoparticle radius* $\left(\phi = 0.05\right)$.

Figure 2 also show that an increase in nanolayer thickness leads to a larger enhancement in the effective thermal conductivity. This has a remarkable implication that exploiting the nanolayer structure might be an innovative approach to produce nanofluids that are highly thermally conductive. It is possible to manipulate the thermal conductivity of nanoparticle and base fluid mixture through nanoparticle surface process.

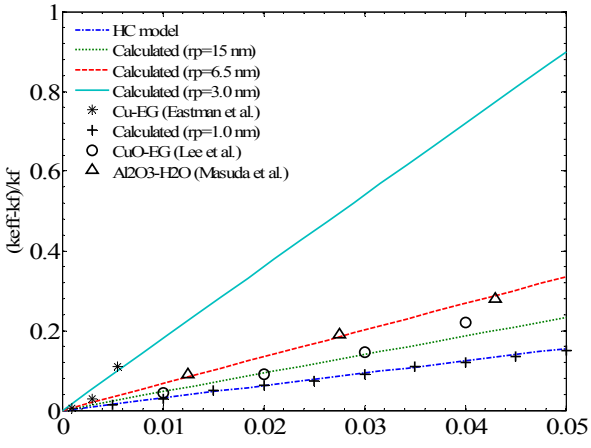

Fig. 3. *Comparison between the results obtained from the present model and the*

existing experimental data.

Figure 3 shows the comparisons of the computed values by the present model to some available experimental data. Copper nanoparticles in EG (Eastman et al., 2001), copper oxide nanoparticles in EG (Lee et al., 1999) and alumina nanoparticles in water (Masuda et al., 1993) are the observed nanofluids. For the calculation, the particle sizes were taken as 3 nm for copper nanoparticle, 15 nm for copper oxide particle and 6.5 nm for alumina nanoparticle from the measured data Eastman et al. (2001), Lee et al. (1999) and Masuda et al. (1993). A 2 nm thick nanolayer was considered. This is because the thickness of the nanolayer is at a magnitude of nanometer. The thermal conductivities were taken as 32.9 $Wm^{-1}K^{-1}$ for CuO,36.0 $Wm^{-1}K^{-1}$ for Al_2O_3 and 0.610 $Wm^{-1}K^{-1}$ for water. Figure 3 describes the present model including the effects of nanolayer and nanoparticles motion and show good agreement with experimental data. Also shown in the figure are the values calculated by the Hamilton and Crosser (HC) model (1962). The Hamilton and Crosser model has the following expression for a suspension containing spherical particles

$$\frac{k_{eff}}{k_f} = \frac{\varepsilon_p + 2 - 2\left(1-\varepsilon_p\right)\phi}{\varepsilon_p + 2 + \left(1-\varepsilon_p\right)\phi} \qquad (21)$$

Equation (21) results in an effective thermal conductivity which is independent of the particle size. It is shown that the experimental data and the predicted values of the present model are much larger than those values calculated by the HC model. This indicates that the traditional model which gives reasonable predictions for the effective thermal conductivity of mixtures comprising fluids and micro-or larger-sized particles can not be used to predict the effective thermal conductivity of a nanofluid containing nanoscale particles. The larger the size of the suspended particles, the weaker appears the effects of the nanolayer and the thermal motion. Figure 3 shows when the average particle size reaches 1000 nm, the prediction of the current model is the same as that of a traditional model, HC model, without considering the interfacial layer and the particle motion.

4. Conclusion

This investigation presents a new thermal conductivity theoretical model for nanofluids. The developed theoretical model in the present work includes the effects of the interfacial nanolayer and the particle motion for explaining the enhancement in the effective thermal conductivity of nanofluids. The parameters of a nanofluid system, such as the temperature, nanoparticle size, volume fraction, nanolayer thickness and thermal conductivities of the nanoparticles and the base fluid, have been shown to affect the enhanced thermal conductivity ratio. The present model is validated with the experimental results of Al_2O_3 /water and CuO/water nanofluids and found that it fits well with the currently available experimental data.

Nomenclature

F	A function of Peclet number defined in Equation (15)
L	Specific length, m
T	Temperature, K
k	Thermal conductivity, $Wm^{-1}K^{-1}$

Greek letters

ϕ	Volume fraction (%)
α	Thermal diffusivity, m^2/s

Subscripts

nf	Nanofluids
f	Base fluid
p	Nanoparticle
eff	Effective

References

Choi, S. U. S. 1995, Enhancing thermal conductivity of fluids with nanoparticles, Development and Applications of Non-Newtonian Flows, FED-vol.231/MD-vol. **66**, pp. 99-105.

Davis, R. H., 1986. Int. J. Thermophys. 7, pp. 609.

Das, S. K, Putra, N., Thiesen, P., and Roetzel, W, 2003, Temperature dependence of thermal conductivity enhancement for nanofluids, ASME, Trans. J. Heat Transfer, **125**, pp. 567-574.

Eastman, J. A., Choi, S. U. S., Li, S., Yu, W. and Thompson, L. J. 2001, Anomalously increased effective thermal conductivities of ethylene glycol-based nanofluids containing copper nanoparticles, Applied Physics Letters **78** (6), pp. 718-720.

Einstien, A. 1959, Investigation on the Theory of the Brownian Movement (New York: Dover), pp. 64.

Gupte, S. K. Advani, S. G. and Huq, P., 1995, Role of micro-convection due to non-affine motion of particles in a mono-disperse suspension, Int. J. Heat Mass Transfer, Vol. **38**, No. 16, pp. 2945-2958.

Hamilton, R. L., and Crosser, O. K., 1962, Thermal conductivity of heterogeneous two-component systems, I&E. Ind. Eng. Chem. Fundamentals **1**, pp. 182-191.

Keblinski, P., Phillpots, S. R., Choi, S. U. S. and Eastman, J. A., 2002, Mechanisms of heat flow in suspensions of nano-sized particles (nanofluids), Int. J. Heat and Mass Transfer **45**, pp. 855-863.

Lee, S., Choi, S. U. S., Li, S. and Eastman, J. A., 1999, Measuring thermal conductivity of fluids containing oxide nanoparticles, J. Heat Transfer, **121**, pp. 280-289.

Masuda, H., Ebata, A., Teramae, K., and Hishimura, N., 1993, Alteration of thermal conductivity and viscosity of liquid by dispersing ultra-fine particles (dispersion of 7-AI_2O_3, SiO_2, and TiO_2 ultra-fine particles), Netsu Bus-sei (Japan), **7** (**4**), pp. 227-233.

Maxwell. J. C., 1881, A Treatise on Electricity and Magnetism, 2nd ed., Vol. 1 (Oxford: Clarendon), pp. 435.

Parisi, G. 2005, Nature, **433**, PP. 221.

Lu, S. Y. and Song, J. L. 1996. J. App. Phy. 79, pp. 609.

Xie, H., Wang, J, Xi, T., and Liu, Y. 2002, Thermal conductivity of suspensions containing nanosized SiC particles, Int. J. of Thermophysics. **23** (**2**), pp. 571-580.

Xie, H., Wang, J, Xi, T., and Liu, Y. and Wu. Q. 2002, Thermal conductivity enhancement of suspensions containing nanosized alumina particles, J. of Applied Phys. **91** (**7**)4568-4572.

Yu, C. J., Richter, A. G., Datta, A., Durbin, M. K. and Dutta, P. 2000, Physica B **283**, pp. 27.

Yu, W. and Choi, S. U. S. 2003, The role of interfacial layers in the enhanced thermal conductivity: A renovated Maxwell model, J. Nanopart, Res. **5** pp. 167-171.