Effect of nanolayer on the thermal conductivity of nanofluids – A review of theoretical models

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Abstract

The thermophysical properties such as dynamic viscosity, thermal conductivity, specific heat, etc., of a nanofluids, having the uniform suspension of solid particles of nanosized and based fluid as a component, depends on the various parameters. Thermal conductivity is the primary reason to utilize the nanoparticles in the heat transfer processes. Different parameters affect the variation in thermal conductivity, such as Brownian motion, nanolayer, thermophoresis, size and concentration of nanoparticles. The present study provides a critical review on the theoretical models on the thermal conductivity of nanofluids based on the nanolayer (also known as electric double layer). It is found that the nanolayer affects the thermal conductivity of nanofluid only for the nanoparticles of small size and for the thickness of nanolayer almost equal to the radius of nanoparticle. For the same nanoparticle material, the thickness of nanolayer is a function of base fluid, water or ethylene glycol.

Keywords: *Nanofluid, thermal conductivity, concentration, particle size, nanolayer.*

INTRODUCTION

In 1995, SUS Choi used the advancement in the area of nanotechnology and used the nano-sized solid particles instead of micron sized particles in the base fluid and found the enhancement in the thermal conductivity without the sedimentation or clogging of application area. After his contribution, many researches organized to explore the importance of nanofluids in the heat transfer processes and observed the enhancement in the thermal conductivity of nanofluids. The measurement of thermal conductivity of nanofluids is further a challenging assignment as many variables affect the thermal properties. Puliti et al. (2011) reported that the thermal conductivity of nanofluids is affected by various variables such as nanoparticle material, size and shape of nanoparticle, particle concentration, temperature, dispersion of nanoparticles in base fluid, stability of suspension, nanoparticles clustering, pH variation, chemical additives and surfactant. To explore the effect of nanoparticles on the thermal conductivity of base fluids, a numerous theoretical and experimental investigations have been organized. These investigations were attentive to determine the dependency of thermal conductivity on the thermal and physical properties of nanoparticles.

Numerous models have been reported in the literature to estimate the thermal conductivity of suspension, but still some controversy is existed on some issues such as suitability or adequacy of classical models. The theoretical approaches considered only the thermal conductivity of nanoparticle, shape and concentration of nanoparticles with the temperature to estimate the thermal conductivity of nanofluids. Kumar et al. (2015) categorized the proposed models to estimate the thermal conductivity of suspension, such as classical models, modelling approaches, extension of conduction models, combination of conduction and convection, and development of new models using nano-convection due to Brownian motion. Further, the thermal conductivity of nanofluid is described as the combination of static thermal conductivity and dynamic thermal conductivity. In static thermal conductivity, the effect of nanoparticle and nanolayer, an ordered layer of liquid surrounded the nanoparticle, are investigated, whereas the effect of Brownian motion, due to the convection, on the thermal conductivity comes under the dynamic part of thermal conductivity. Puliti et al. (2011) conducted a review on the properties of nanofluids and found that four mechanisms: Brownian motion, nanolayer, aggregation and radiative heat transfer are responsible for the enhancement in the thermal conductivity of nanofluids.

CLASSICAL MODELS

The classical models by Maxwell model (1934), Hamilton-Crosser model (1962), Jeffery model (1973), etc. were investigated the thermal conductivity of solid suspension in liquid by considering only the particle concentration and thermal conductivity of base fluid and solid particles. The first reported investigation of thermal conductivity of solid suspension in a base fluid was conducted by the Maxwell (1934) by considering the thermal conductivity of suspended solid particles and base fluid, and particle concentration, as shown in equation 1.

$$\frac{k_{nf}}{k_{bf}} = \left[\frac{k_p+2k_{bf}+2(k_p-k_{bf})\phi}{k_p+2k_{bf}-(k_p-k_{bf})\phi}\right] \qquad (1)$$

Here k_{nf}, k_{bf}, k_p denotes the thermal conductivity of suspension, base fluid, suspended solid particles, respectively and ϕ is particle concentration of suspended solid particles. The Maxwell model is a representative of all classical models to estimate the thermal conductivity of suspension. The Maxwell model did not consider the shape of suspended solid particles, which later considered by the Hamilton and Crosser (1962) for estimating the thermal conductivity, theoretically, as shown in equation 2 and also conducted the experiments using the micron sized solid particles, Aluminium and Balsa wood, dispersed in the rubber.

$$k_{nf} = k_{bf}\left[\frac{k_p+(n-1)k_{bf}-(n-1)\phi(k_{bf}-k_p)}{k_p+(n-1)k_{bf}+\phi(k_{bf}-k_p)}\right] \qquad (2)$$

Here n is a function of sphericity (Ψ), which is a measure of shape with respect to the sphere. The sphericity is defined, by Hakon (1935), as the ratio of the surface area of a sphere, having the equal volume as the particle, to the surface area of the particle and given as:

$$\Psi = \frac{\pi^{1/3}(6V_p)^{2/3}}{A_s} \qquad (3)$$

Here the V_p and A_s are volume and surface area of the solid particle. The maximum value of sphericity is equal to 1, for the sphere. Hamilton and Crosser (1935) upgraded the Maxwell model (equation 2) by adopting the effect of particle shape on the thermal conductivity in the form of n, equal to $3/\Psi$. The effect of shape on solid suspended particle was not important in Hamilton and Crosser model (equation 3), when the ratio of the thermal conductivities of the particle and base fluid is below about 100, while the thermal conductivity of suspension increased with the particle concentration. Another model was proposed by the Jeffrey (1973), as given in equation 4;

$$\frac{k_{nf}}{k_{bf}} = 1 + 3\beta\phi + \phi^2 \left(3\beta^2 + \frac{3\beta^3}{4} + \frac{9\beta^3}{16} . \frac{\alpha+2}{2\alpha+3} + \frac{3\beta^4}{2^6}\right) \quad (4)$$

Where α and β are constants and defined as:

$$\alpha = \frac{k_p}{k_{bf}};\ \beta = \left(\frac{k_p}{k_{bf}} - 1\right) \Big/ \left(\frac{k_p}{k_{bf}} + 2\right) \quad (5)$$

Jeffrey (1973) extended the Maxwell model to estimate the thermal conductivity of suspension, with the consideration of interaction between the pairs of suspended spheres.

EFFECT OF NANOLAYER

In the suspension of solid particles in the base fluid, an ordered layer of base fluid molecule covers the particle, as depicted in figure 1. The ordered layer is a solid-like structure and has different thermal properties than the particle and base fluid. This ordered layer is known as nanolayer, in case of nanofluids, or interface layer. When heat from the suspended solid particle is conducted to the base fluid, a discontinuous temperature distribution is occurred at the nanolayer and causes a temperature gradient. The generated temperature gradient is proportional to the heat flow, and the ratio of temperature gradient to the heat flow is known as thermal resistance at the nanolayer and inversely proportional to the nanolayer area. The thermal resistance at nanolayer, which is occurred when the heat flow from particle to base fluid, is known a Kapitza resistance.

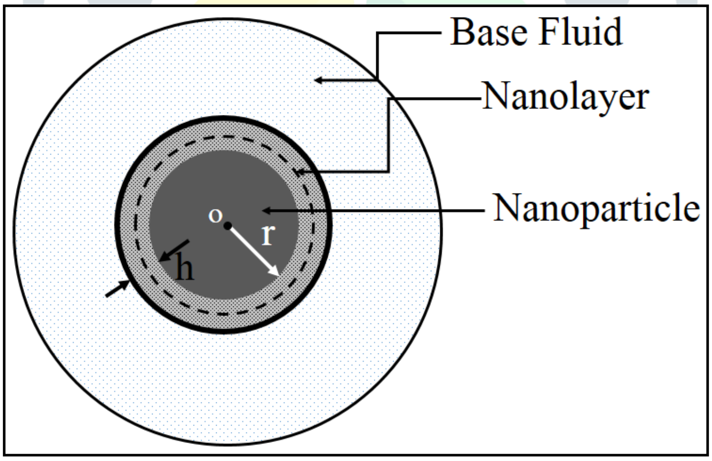

Figure 1: Schematic of nanolayer around the nanoparticle in base fluid.

The presence of nanolayer around the solid particle was experimentally confirmed by Yu et al. (2000) using the X-ray reflectivity study. The density oscillation near the solid-liquid interface was observed in three layers with the spacing of molecular size. As mentioned, the thermal properties of nanolayer are different from the particle and base fluid and can lead to the enhancement in thermal conductivity of nanofluid. Yu and Choi (2003) involved the effect of nanolayer, the solid-like layer of base fluid molecules around the suspended solid particle, in to Maxwell's model to estimate the thermal conductivity of suspension. It was assumed that the base fluid molecules in this nanolayer had the intermediate physical properties than the solid particle and base fluid and expected to contribute in to increased thermal conductivity of suspension.

Yu and Choi (2003) assumed an equivalent particle, which was formed by combining the effect of nanolayer with the suspended particle, and used very low particle concentration to prevent the overlapping of the equivalent particles. The assumption was resulting in an increased particle concentration (ϕ_e), as:

$$\phi_e = \phi \left(1 + \frac{h}{r}\right)^3 \tag{6}$$

where, h is nanolayer thickness and r is radius of suspended particle. The model was proposed to estimate the thermal conductivity of suspension as:

$$k_{nf} = \left[\frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\left(1+\frac{h}{r}\right)^3 \phi}{k_p + 2k_{bf} - (k_p - k_{bf})\left(1+\frac{h}{r}\right)^3 \phi} k_{bf}\right] \tag{7}$$

The effect of nanolayer on the thermal conductivity of suspension was found significant only for the particle of small size ($r \sim h$) and observed a three to eight-fold enhancement in thermal conductivity of suspension for the suspended solid particles of radius smaller than 5 nm. But equation 7 reduced to the Maxwell's model for larger solid particles ($r >> h$).

Leong et al. (2006) proposed a model to predict the thermal conductivity of nanofluid by taking the thermal conductivity and thickness of the nanolayer at nanoparticles. In the proposed model, nanolayer was taken as a separate component along with the nanoparticle and base fluid and model was formulated in two steps; (1) modelling of temperature field and gradient, and (2) formulation of the effective thermal conductivity model, as given in equation 8.

$$k_{nf} = \frac{(k_p - k_{nl})\phi\left(\left(1+\frac{h}{r}\right)^3 - 1\right)k_{nl}\left[2\left(1+\frac{h}{2r}\right)^3 - \left(1+\frac{h}{r}\right)^3 + 1\right]}{\left(1+\frac{h}{2r}\right)^3 (k_p + 2k_{nl}) - (k_p - k_{nl})\phi\left(\left(1+\frac{h}{r}\right)^3 - 1\right)\left[\left(1+\frac{h}{2r}\right)^3 + \left(1+\frac{h}{r}\right)^3 - 1\right]} + \frac{(k_p + 2k_{nl})\left(1+\frac{h}{2r}\right)^3\left[\phi\left(\left(1+\frac{h}{r}\right)^3 - 1\right)\left(1+\frac{h}{r}\right)^3 (k_{nl} - k_f) + k_f\right]}{\left(1+\frac{h}{2r}\right)^3 (k_p + 2k_{nl}) - (k_p - k_{nl})\phi\left(\left(1+\frac{h}{r}\right)^3 - 1\right)\left[\left(1+\frac{h}{2r}\right)^3 + \left(1+\frac{h}{r}\right)^3 - 1\right]} \tag{8}$$

Where, k_p, k_{nl}, k_f are thermal conductivity of solid particle, nanolayer and base fluid; ϕ is particle concentration. In the absence of nanolayer, the equation 6 reduced to the Maxwell's model. The presented model was found in agreement with the thermal conductivity of water based Al_2O_3 nanofluid measured by the transient hot wire method.

In another study, Xue and Xu (2005) investigated the effect of complex nanoparticle, composed of interfacial shell and nanoparticle, on the thermal conductivity of nanofluid along with the particle size and proposed a model based on the Fourier's law of heat conduction, as given in equation 9.

$$\left(1 - \frac{\phi}{k_p/k_{bf}}\right)\frac{k_{nf} - k_{bf}}{2k_{nf} + k_{bf}} + \frac{\phi}{k_p/k_{bf}} \frac{(k_{nf} - k_p)(2k_p + k_{nl}) - \frac{k_p}{k_{bf}}(k_{nl} - k_p)(2k_p + k_{nf})}{(k_p + 2k_{nf})(2k_p + k_{nl}) + 2\frac{k_p}{k_{bf}}(k_{nl} - k_p)(k_p - k_{nf})} = 0 \tag{9}$$

The results of theoretical model, equation 9 were in agreement for the experimental results of thermal conductivity of CuO/water and CuO/EG nanofluids.

The former studies involved the effect of nanolayer in determining the thermal conductivity, but were incapable to provide the method or procedure to measure the thickness of nanolayer. Tso et al. (2014) predicated thermal conductivity of nanofluid after accounting the nanolayer effect by formulating a semi-analytical model, an improved model presented by Leong et al. (2006), and also determine the thickness of nanolayer. A linear variation in thermal conductivity in the nanolayer, decreasing from nanoparticle to the base fluid, was assumed.

$$\frac{k_{nf}}{k_{bf}} = \frac{3\phi v_2^3 k_{nl}[3r^3 k_p + v_1(k_p+2k_{nl})] + r^3(1-v_2^3\phi)[v_2^3(2k_{bf}+k_{nl})(k_p+2k_{nl})+2(k_{bf}-k_{nl})(k_{nl}-k_p)]}{3\phi v_2^3 k_{nl}[3r^3 k_f + v_1(k_p+2k_{nl})] + r^3(1-v_2^3\phi)[v_2^3(2k_{bf}+k_{nl})(k_p+2k_{nl})+2(k_{bf}-k_{nl})(k_{nl}-k_p)]} \quad (10)$$

Where $v_1 = 3r^2h+3rh^2+h^3$ and $v_2 = 1+h/r$.

The nanolayer thickness (*h/r*) was also determined based on the semi-analytical value based on proposed model, equation 11 with the linear variation in thermal conductivity of nanolayer and given as;

$$\frac{h}{r} = D_1 a^{-D_2} \quad (11)$$

Where the values of D_1 and D_2 for the water based Al_2O_3 nanofluid are 3.042 and 1.059, and for EG based Al_2O_3 nanofluid are 1.8082 and 0.912, respectively. It was also observed from equation 11 that the thickness of nanolayer depends on the base fluid. For the same nanoparticle material, the increased nanoparticle size caused to decrease in the nanolayer thickness for the water based nanofluid, while opposite was found for the ethylene glycol based nanofluid, the larger nanoparticle radius resulted in the thicker nanolayer.

The direct effect of nanolayer on the thermal conductivity of nanofluid was investigated by Alipour et al. (2014) and proposed a model to estimate the thermal conductivity of nanofluid, as given in equation 12.

$$k_{nf} = \left[\frac{(k_p+2k_{nl})\beta_1^3[\phi\beta^3(k_{nl}-k_f)+k_{bf}]+k_{nl}\phi(k_p-k_{nl})[2\beta_1^3-\beta^3+1]}{\beta_1^3(k_p+2k_{nl})-(k_p-k_{nl})[\beta_1^3+\beta^3-1]}\right] + \left[\frac{\left(\frac{6\phi}{\pi}\right)^{\frac{1}{3}}}{d_p\left(\frac{\alpha_{nf}\mu_{nf}}{k_b k_p T}+\frac{h}{4\pi r(r+h)k_{nl}}\right)}\right] \quad (12)$$

Where $\beta = 1 + h/r$; $\beta_1 = 1 + h/2r$; α_{nf} and μ_{nf} are thermal diffusivity and dynamic viscosity of nanofluid, k_b is Boltzmann's constant, d_p is diameter of nanoparticle. The first term in right side of equation 12 denotes the static thermal conductivity, while second term represents the dynamic thermal conductivity due to Brownian motion. The effect of nanolayer on the thermal conductivity of nanofluid was significant only when the ratio of particle radius to the nanolayer thickness (*r/h*) was almost small. In the opposite case, the nanolayer did not affect the heat conduction in the nanofluid, as a part of dynamic thermal conductivity. The proposed model was found in agreement with the experimental values of thermal conductivity of water based Al_2O_3 and CuO nanofluids.

Another important model to estimate the thermal conductivity of nanofluid, as a function of size and concentration of nanoparticles, thermal conductivity of nanoparticles and base fluid and thickness of nanolayer, was proposed by the Feng et al. (2007) based on the 2D lattice model which was used due to the random distribution of nanoparticles in nanofluid. The term 'equivalent nanoparticle' was used for the combination of nanoparticle and nanolayer. The presented model was formulated in two distinct portions: for non-aggregated nanoparticles, and for clusters (aggregated nanoparticles), the first and second terms in right side of equation 13, respectively.

$$k_{nf} = (1-\alpha)\left[\frac{k_p+2k_{bf}+2(k_p-k_{bf})\left(1+\frac{h}{r}\right)^3\phi}{k_p+2k_{bf}-(k_p-k_{bf})\left(1+\frac{h}{r}\right)^3\phi}k_{bf}\right] + \alpha\left[\left(1-\frac{3}{2}\left(1+\frac{h}{r}\right)^3\phi\right)k_{bf}\frac{3\left(1+\frac{h}{r}\right)^3\phi\, k_{bf}}{\beta}\left[\frac{1}{\beta}ln\frac{r+h}{(r+h)(1-\beta)} - 1\right]\right] \quad (13)$$

Where $\beta = 1 - (k_{bf} / k_{pe})$ and k_{pe} is thermal conductivity of equivalent nanoparticle and given as:

$$k_{pe} = \frac{\left[2\left(1-\frac{k_{nl}}{k_p}\right)+\left(1+\frac{h}{r}\right)^3\left(1+\frac{2k_{nl}}{k_p}\right)\right]\frac{k_{nl}}{k_p}}{\left(\frac{k_{nl}}{k_p}-1\right)+\left(1+\frac{h}{r}\right)^3\left(1+\frac{2k_{nl}}{k_p}\right)}k_p \quad (14)$$

When the thermal conductivity of nanolayer is twice the thermal conductivity of base fluid, the thermal conductivity of nanofluid is decreased with the increased particle size and when the thermal conductivity of both nanolayer and base fluid is equal, no effect of nanolayer was observed on the thermal conductivity of nanofluid. Feng et al. (2007) also concluded for the constant particle concentration that the probability of aggregation of nanoparticles is increased when the size of nanoparticle is decreased. It is caused due strong van der Waals forces for small interparticle distance. By using the molecular dynamics modelling of inter and intra-molecular interactions of the components including the nanoparticle, base fluid and nanolayer, Puliti et al. (2011) reported a highly ordered layer of base fluid molecules around the nanoparticles and higher heat flux at the nanolayer, which resulted in the increased thermal conductivity of nanofluids.

CONCLUSIONS

Based on the above presented models, the effect of nanolayer on the thermal conductivity of nanofluid can be summarized as:

- The nanolayer affects the thermal conductivity of nanofluid only for the nanoparticles of small size and for the thickness of nanolayer almost equal to the radius of nanoparticle, ($r \sim h$).
- An enhancement in thermal conductivity of nanofluid having the nanoparticle of radius smaller than 5 nm was occurred.
- For the same nanoparticle material, the thickness of nanolayer is a function of base fluid, water or ethylene glycol.
- With increasing the nanoparticle size, thickness of nanolayer is decreased for the water based nanofluid, while it is increased for the ethylene glycol based nanofluid.
- When the thermal conductivity of nanolayer is twice the thermal conductivity of base fluid, the thermal conductivity of nanofluid is decreased with the increased particle size.

REFERENCES

1. Alipour, R., Ghoranneviss, M., Mirzaee, M.¸ Jafari, A. (2014) The direct effect of interfacial nanolayers on thermal conductivity of nanofluids, Heat Mass Transfer, vol. 50, pp. 1727–1735.

2. Choi, S.U.S.¸ Eastman, J.A. (1995) Enhancing thermal conductivity of fluids with nanoparticles, ASME International Mechanical Engineering Congress & Exposition, San Francisco, pp. 12-17.
3. Feng, Y.¸ Yu, B.¸ Xu, P.¸ Zou, M. (2007) The effective thermal conductivity of nanofluids based on the nanolayer and the aggregation of nanoparticles, J. Phys. D: Appl. Phys., vol. 40, pp. 3164–3171.
4. Hakon, W. (1935) Volume, shape, and roundness of quartz particles, The Journal of Geology, vol. 43, pp. 250-280.
5. Hamilton, R.L.¸ Crosser, O.K. (1962) Thermal conductivity of heterogeneous two-component systems, Ind. Eng. Chem. Fundamen., vol. 1, pp. 187–191.
6. Jeffrey, D.J. (1973) Conduction through a random suspension of spheres, *Proceedings of the Royal Society of London, Series A: Mathematical and Physical Sciences*, vol. 335, pp. 355-367.
7. Kumar, P.M., Kumar, J.¸ Tamilarasan, R.¸ Sendhilnathan, S., Suresh, S. (2015) Review on nanofluids theoretical thermal conductivity models, *Engineering Journal*, vol. 19, pp. 67 – 83.
8. Leong, K.C.¸ Yang, C., Murshed, S.M.S. (2006) A model for the thermal conductivity of nanofluids–the effect of interfacial layer, *Journal of Nanoparticle Research*, vol. 8, pp. 245–254.
9. Maxwell, J.C. (1934) A Treatise on Electricity and Magnetism, vol. 1, 3rd Ed., Dover, New York.
10. Puliti, G., Samuel, P., Sen, M. (2011) Nanofluids and their properties, *Applied Mechanics Reviews*, vol. 64, pp. 030803:1 – 23.
11. Tso, C.Y., Fu, S.C., Chao, C.Y.H. (2014) A semi-analytical model for the thermal conductivity of nanofluids and determination of the nanolayer thickness, *International Journal of Heat and Mass Transfer*, vol. 70, pp. 202–214.
12. Xue, Q.¸ Xu, W.M. (2005) A model of thermal conductivity of nanofluids with interfacial shells, *Materials Chemistry and Physics*, vol. 90, pp. 298–301.
13. Yu, C.J., Richter, A.G., Datta, A.¸ Durbin, M.K., Dutta, P. (2000) Molecular layering in a liquid on a solid substrate: a X-ray reflectivity study, *Physica B*, vol. 283, pp. 27-31.
14. Yu, W., Choi, S.U.S. (2003) The role of interfacial layers in the enhanced thermal conductivity of nanofluids: A renovated Maxwell model, *Journal of Nanoparticle Research*, vol. 5, pp. 167–171.