

## **The role of interfacial layers in the enhanced thermal conductivity of nanofluids: A renovated Maxwell model**

W. Yu and S.U.S. Choi\*

*Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA;*

*\*Author for correspondence (Tel.: +1 630-252-6439; Fax: +1 630-252-5568; E-mail: choi@anl.gov)*

Received 27 November 2002; accepted in revised form 10 February 2003

*Key words:* nanofluids, nanoparticles, solid/liquid suspensions, thermal conductivity, nanolayers, heat exchanger

### **Abstract**

Nanofluids, a new class of solid/liquid suspensions, offer scientific challenges because their measured thermal conductivity is one order of magnitude greater than predictions. It has long been known that liquid molecules close to a solid surface form layered solid-like structures, but little is known about the connection between this nanolayer and the thermal properties of the suspensions. Here, we have modified the Maxwell equation for the effective thermal conductivity of solid/liquid suspensions to include the effect of this ordered nanolayer. Because this ordered nanolayer has a major impact on nanofluid thermal conductivity when the particle diameter is less than 10 nm, a new direction is indicated for development of next-generation coolants.

### **Introduction**

With an ever-increasing thermal load due to trends toward smaller microelectronic devices, greater power output for engines, and brighter beams for optical devices, cooling of such devices and related systems is a crucial issue in high-tech industries such as microelectronics and transportation. The conventional approach for increasing cooling rates is the use of extended surfaces such as fins and microchannels. However, current designs have already stretched this approach to its limits. Therefore, there is an urgent need for new and innovative concepts to achieve ultra-high-performance cooling. Taking a different tack, Argonne National Laboratory has pioneered ultra-high-thermal-conductivity fluids, called nanofluids, by suspending nanoparticles in conventional coolants (Choi, 1995).

Dispersing solid particles into liquids to improve the physical properties of liquids is hardly new, since the idea can be traced back to James Clerk Maxwell's theoretical work (Maxwell, 1873). Despite numerous

studies for more than a century on the thermal conductivity of traditional solid/liquid suspensions containing millimeter- or micrometer-sized particles, the rapid settling of these meso- or microparticles in fluids has been a major hurdle to developing suspensions for practical applications. In contrast, two salient features – well-suspended particles and high-thermal conductivities far above those of traditional solid/liquid suspensions – make nanofluids strong candidates for the next generation of coolants for thermal management systems.

Above all, nanofluids offer theoretical challenges because the measured thermal conductivity of a nanofluid containing a low concentration (<1 vol.%) of copper nanoparticles or carbon nanotubes is one order of magnitude greater than that predicted by existing theories (Eastman et al., 2001; Choi et al., 2001). This discovery clearly suggests that conventional heat conduction models for solid-in-liquid suspensions are inadequate. An understanding of this anomalous enhancement is critical to the design of nanofluids for cooling applications.

## Nanostructure

Although liquid molecules close to a solid surface are known to form layered structures (Henderson & Swol, 1984; Yu et al., 2000), little is known about the connection between this nanolayer and the thermal properties of solid/liquid suspensions. We propose that the solid-like nanolayer acts as a thermal bridge between a solid nanoparticle and a bulk liquid and so is key to enhancing thermal conductivity. From this thermally bridging nanolayer idea, we suggest a structural model of nanofluids that consists of solid nanoparticles, a bulk liquid, and solid-like nanolayers. Figure 1 shows a schematic cross section of the proposed nanofluid structure. Conventional pictures of solid/liquid suspensions do not have this nanolayer.

The thermal conductivity of the nanolayer on the surface of the nanoparticle is not known. However, because the layered molecules are in an intermediate physical state between a bulk liquid and a solid (Yu et al., 2000), the solid-like nanolayer of liquid molecules would be expected to lead to a higher thermal conductivity than that of the bulk liquid. Based on this assumption, we have modified the Maxwell equation for the effective thermal conductivity of solid/liquid suspensions to include the effect of this ordered nanolayer.

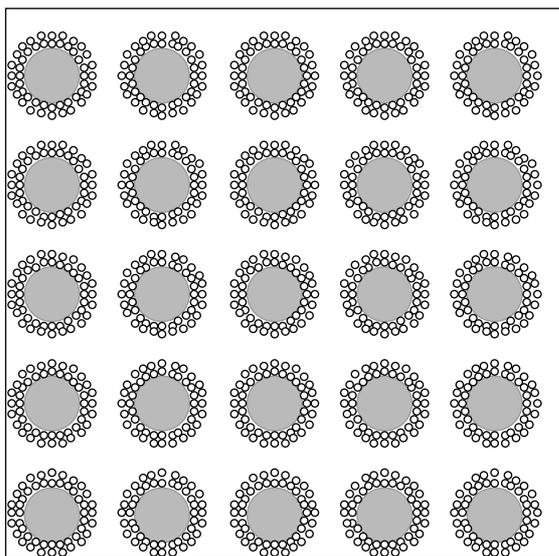


Figure 1. Schematic cross section of nanofluid structure consisting of nanoparticles, bulk liquid, and nanolayers at solid/liquid interface.

## Maxwell equation

To show a new connection between the nanolayers and thermal conductivity increase in nanofluids, we assume that the thermal energy transport in nanofluids is diffusive. This is feasible because the average interparticle distance in nanofluids is much greater than the mean free path of the liquid molecules. This allows us to use classical models to show the effect of the nanolayer. The Maxwell equation takes into account only the particle volume concentration and the thermal conductivities of particle and liquid. Other classical models include the effects of particle shape (Hamilton & Crosser, 1962), particle distribution (Cheng & Vachon, 1969), and particle/particle interaction (Jeffrey, 1973). However, all of these models predict almost identical enhancements at the low concentrations (<1 vol.%) of interest in our nanofluid study. Therefore, the Maxwell model is used in this study as representative of all classical models. Particle size and the nanolayer have not been accounted for in any classical models.

Based on Maxwell's work, the effective thermal conductivity of a homogeneous suspension can be predicted as (Maxwell, 1873)

$$k_{\text{Maxwell}} = \frac{k_p + 2k_l + 2(k_p - k_l)\phi}{k_p + 2k_l - (k_p - k_l)\phi} k_l \quad (1)$$

where  $k_p$  is the thermal conductivity of the dispersed particles,  $k_l$  is the thermal conductivity of the dispersion liquid, and  $\phi$  is the particle volume concentration of the suspension.

## Nanolayer impact

Many studies have focused on the effect of a solid/solid interface on effective thermal conductivity (Every et al., 1992; Davis & Artz, 1995; Torquato & Rintoul, 1995; Chen, 1997; Devpura et al., 2001). Because of the imperfect contact of the solid/solid interface, the interface resistance (also called Kapitza resistance) is a barrier to heat transfer and lowers the overall effective thermal conductivity. In contrast, this solid/solid contact resistance phenomenon is not dominant at the solid/liquid interface of particle-in-liquid suspensions. Moreover, we expect the nanolayer to enhance thermal conductivity of particle-in-liquid suspensions.

In order to include the effect of the liquid layer, we consider a nanoparticle-in-liquid suspension with

monosized spherical particles of radius  $r$  and particle volume concentration  $\phi$ . We assume that the solid-like layer of thickness  $h$  around the particles is more ordered than that of the bulk liquid and that the thermal conductivity  $k_{\text{layer}}$  of this ordered layer is higher than that of the bulk liquid. To further simplify our analysis, we assume that the nanolayer around each particle could be combined with the particle to form an equivalent particle and that the particle volume concentration is so low that there is no overlap of those equivalent particles. The above assumptions result in an equivalent particle radius  $r + h$  and an increased volume concentration  $\phi_e$ , which can be calculated as

$$\phi_e = \frac{4}{3}\pi(r+h)^3 n = \frac{4}{3}\pi r^3 n(1+h/r)^3 = \phi(1+\beta)^3 \quad (2)$$

where  $n$  is the particle number per volume and  $\beta = h/r$  is the ratio of the nanolayer thickness to the original particle radius. Based on effective medium theory, the equivalent thermal conductivity  $k_{\text{pe}}$  of the equivalent particles can be calculated as (Schwartz et al., 1995)

$$k_{\text{pe}} = \frac{[2(1-\gamma) + (1+\beta)^3(1+2\gamma)]\gamma}{-(1-\gamma) + (1+\beta)^3(1+2\gamma)} k_p \quad (3)$$

where  $\gamma = k_{\text{layer}}/k_p$  is the ratio of nanolayer thermal conductivity to particle thermal conductivity. For the extreme case of  $k_{\text{layer}} = k_p$  (i.e.  $\gamma = 1$ ), Eq. (3) reduces to  $k_{\text{pe}} = k_p$ .

Based on the above discussion, the Maxwell equation (1) can be modified into

$$k_e = \frac{k_{\text{pe}} + 2k_1 + 2(k_{\text{pe}} - k_1)(1+\beta)^3\phi}{k_{\text{pe}} + 2k_1 - (k_{\text{pe}} - k_1)(1+\beta)^3\phi} k_1 \quad (4)$$

Figure 2 shows the thermal conductivity enhancement predicted by the modified Maxwell equation (4) normalized to the increase predicted by the Maxwell equation as a function of particle radius for a copper-particle-in-ethylene-glycol suspension. It can be seen in Figure 2 that the nanolayer impact is significant for small particles (for  $r \sim h$ ). A three- to eight-fold increase in the thermal conductivity of nanofluids compared to the enhancement without considering the nanolayer occurs when nanoparticles are smaller than the critical radius of 5 nm and where there is a clear change in the slope. However, for large particles ( $r \gg h$ ,  $\beta \rightarrow 0$ ), the nanolayer impact is small and the modified Maxwell equation reduces to the original Maxwell equation.

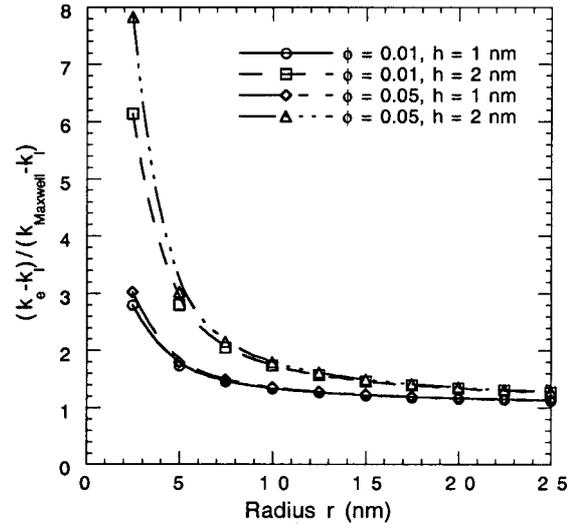


Figure 2. Thermal conductivity enhancement ratio as a function of particle radius for copper-in-ethylene-glycol suspensions ( $k_{\text{layer}} = k_p$ ).

Figure 3A shows the effects of the thickness and thermal conductivity of the nanolayer on thermal conductivity enhancement for a 1.0 vol.% copper-particle-in-ethylene-glycol nanofluid. Thermal conductivity enhancement is strongly dependent on the thickness of the nanolayer, but is almost invariant to the thermal conductivity of the nanolayer when  $k_{\text{layer}} > 10k_1$ . Therefore, we conclude that nanolayer thickness is crucial to thermal conductivity enhancement. As shown in Figure 3B, the dramatic thermal conductivity enhancement with smaller nanoparticles ( $< 5$  nm) is attributed primarily to increased volume fraction by nanolayer per Eq. (2). This suggests that the increased effective volume fraction due to the existence of a thermally bridging nanolayer is a new mechanism of enhanced thermal conductivity in nanofluids. Because this mechanism is most effective when the nanoparticles are  $< 10$  nm in diameter, it can be concluded that the smaller the particle, the higher the thermal conductivity increase. In addition, the very small size of the nanoparticles should markedly improve the stability of the suspension.

### Comparison with experimental results

Figure 4 compares the predictions of the Maxwell equation (1) and modified Maxwell equation (4) with the limited experimental data currently available for

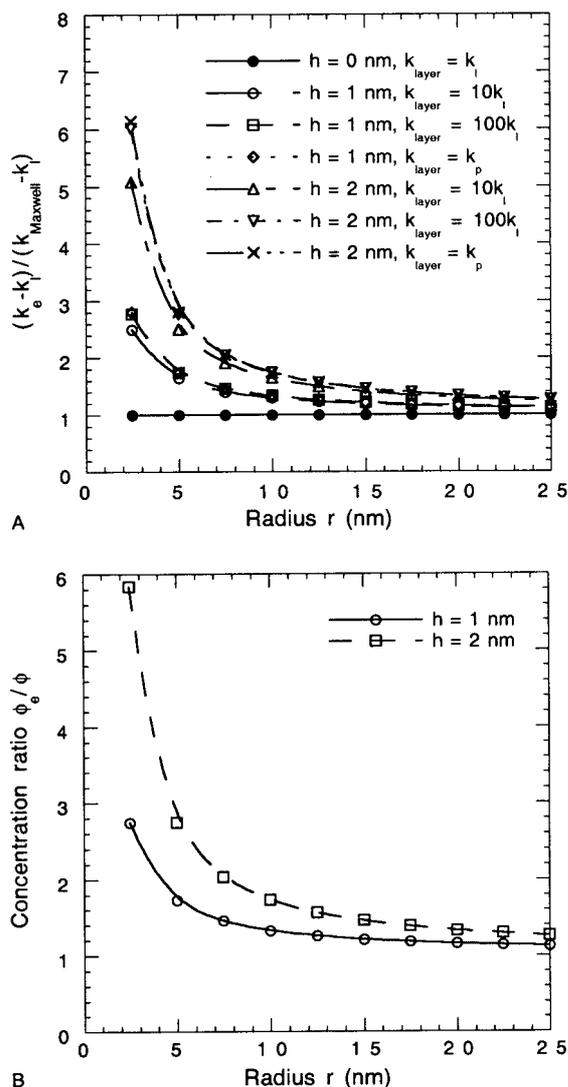


Figure 3. (A) Thermal conductivity enhancement ratio as a function of particle radius for copper-in-ethylene-glycol suspensions ( $\phi = 0.01$ ); (B) nanoparticle volume concentration ratio as a function of particle radius.

two nanofluids: copper oxide nanoparticles in ethylene glycol, and copper nanoparticles in ethylene glycol (Lee et al., 1999; Eastman et al., 2001). The calculation radii for the particles were chosen as 15 nm (copper oxide particles) and 3 nm (copper particles), based on their average radii and agglomerates from transmission electron micrographs (Lee et al., 1999; Eastman et al., 2001). Nanolayer thickness was chosen as 2 nm. It can be seen in Figure 4A and B that the modified Maxwell equation with nanolayer

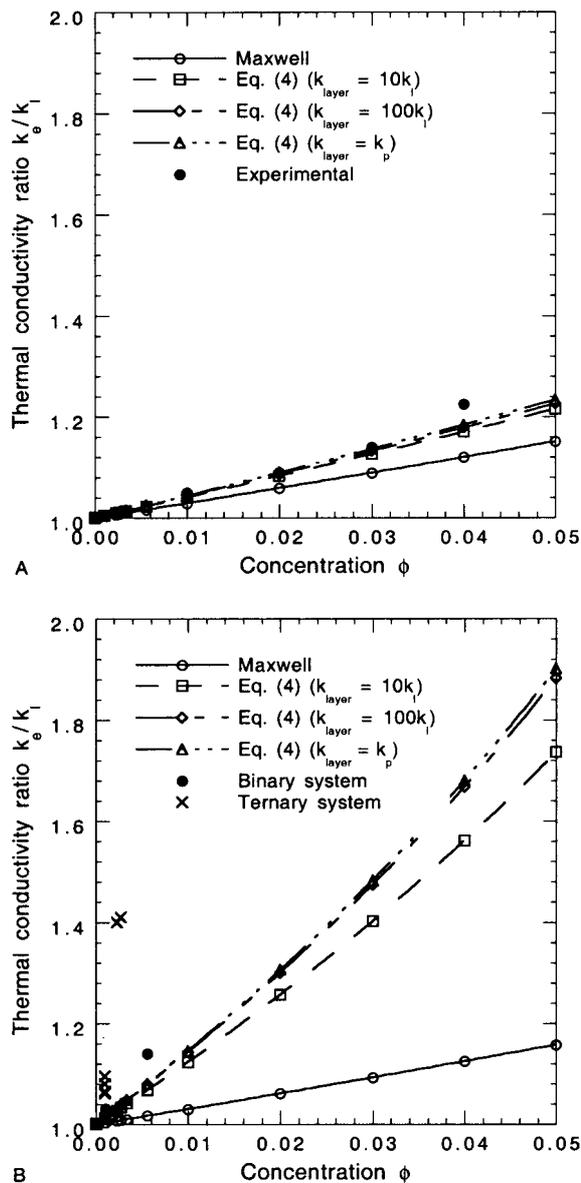


Figure 4. Experimental data compared with predictions. (A) Copper oxide-in-ethylene-glycol suspensions ( $h = 2$  nm,  $r = 15$  nm); (B) copper-in-ethylene-glycol suspensions with (ternary system) and without surfactants (binary system) ( $h = 2$  nm,  $r = 3$  nm).

predicts the experimental data quite well. In Figure 4B, nanofluid conductivity is clearly not sensitive to the conductivity of the nanolayer and the predictions agree with experimental data when  $k_{\text{layer}} > 10k_i$ . However, for ternary systems such as copper nanofluids with surfactants (Eastman et al., 2001), our model

predictions are still much lower than experimental data. Although our results show that the nanolayer is a key parameter, it appears that other parameters such as surface chemistry of nanoparticles should be considered.

### Conclusions

A modified Maxwell model, which includes a nanolayer, can predict that the presence of very thin nanolayers, even though only a few nanometers thick, can measurably increase effective volume fraction and subsequently the thermal conductivity of nanofluids, particularly when particle diameter is  $<10$  nm. The new model predictions show that when nanolayers are accounted for, there is potential for up to an eight-fold increase in the thermal conductivity of nanofluids over the enhancement predicted by the Maxwell model without the nanolayer. This has the significant implication that exploiting the nanolayer structure might be a new way to produce nanofluids that are highly thermally conductive.

Considering that one of the greatest drawbacks to traditional solid/liquid suspensions containing micro- and mesoparticles is that significant conductivity enhancement is achieved at high-particle concentration ( $>20$  vol.%), this study suggests the new approach that adding smaller ( $<10$ -nm diameter) particles could be potentially better than adding more particles to concoct next-generation coolants for faster cooling of high-heat-load devices and systems. The next-generation coolants produced by this new approach will be instrumental in advancing many miniaturization technologies.

### Acknowledgements

This work was supported by the US Department of Energy, Office of Basic Energy Sciences and Office of Heavy Vehicle Technologies, under Contract W-31-109-Eng-38.

### References

- Chen, G., 1997. Size and interface effects on thermal conductivity of superlattices and periodic thin-film structures. *J. Heat Transfer* 119, 220–229.
- Cheng, S.C. & R.I. Vachon, 1969. The prediction of the thermal conductivity of two and three phase solid heterogeneous mixtures. *Int. J. Heat Mass Transfer* 12, 249–264.
- Choi, S.U.S., 1995. Enhancing thermal conductivity of fluids with nanoparticles. In: Siginer, D.A. and Wang, H.P. eds. *Developments and Applications of Non-Newtonian Flows*, ASME, New York, FED – Vol. 231/MD – Vol. 66, pp. 99–105.
- Choi, S.U.S., Z.G. Zhang, W. Yu, F.E. Lockwood & E.A. Grulke, 2001. Anomalous thermal conductivity enhancement in nanotube suspension. *Appl. Phys. Lett.* 79(14), 2252–2254.
- Davis, L.C. & B.E. Artz, 1995. Thermal conductivity of metal-matrix composites. *J. Appl. Phys.* 77(10), 4954–4960.
- Devpura, A., P.E. Phelan & R.S. Prasher, 2001. Size effect on the thermal conductivity of polymers laden with highly conductive filler particles. *Microscale Thermophys. Eng.* 5, 177–189.
- Eastman, J.A., S.U.S. Choi, S. Li, W. Yu & L.J. Thompson, 2001. Anomalous increased effective thermal conductivity of ethylene glycol-based nanofluids containing copper nanoparticles. *Appl. Phys. Lett.* 78(6), 718–720.
- Every, A.G., Y. Tzou, D.P.H. Hasselman & R. Raj, 1992. The effect of particle size on the thermal conductivity of ZnS/diamond composites. *Acta Metall. Mater.* 40(1), 123–129.
- Hamilton, R. L. & O.K. Crosser, 1962. Thermal conductivity of heterogeneous two-component systems. I & EC Fundamentals 1, 187–191.
- Henderson, J.R. & F. van Swol, 1984. On the interface between a fluid and a planar wall: Theory and simulations of a hard sphere fluid at a hard wall. *Mol. Phys.* 51, 991–1010.
- Jeffrey, D.J., 1973. Conduction through a random suspension of spheres. *Proc. R. Soc. London, Ser. A* 335, 355–367.
- Lee, S., S.U.S. Choi, S. Li & J.A. Eastman, 1999. Measuring thermal conductivity of fluids containing oxide nanoparticles. *J. Heat Transfer* 121, 280–289.
- Maxwell, J.C., 1873. *Electricity and Magnetism*. Clarendon Press, Oxford, UK.
- Schwartz, L.M., E.J. Garboczi & D.P. Bentz, 1995. Interfacial transport in porous media: Application to DC electrical conductivity of mortars. *J. Appl. Phys.* 78(10), 5898–5908.
- Torquato, S. & M.D. Rintoul, 1995. Effect of the interface on the properties of composite media. *Phys. Rev. Lett.* 75(22), 4067–4070.
- Yu, C.-J., A.G. Richter, A. Datta, M.K. Durbin & P. Dutta, 2000. Molecular layering in a liquid on a solid substrate: An X-ray reflectivity study. *Physica B* 283, 27–31.