Thermal Conductivity of Composites: How Comsol Revealed an Omission in a Classical Paper

Berne Ph.[1*],
[1]Univ. Grenoble Alpes, F-38000, Grenoble, France
* CEA, Liten, DTNM, SEN, LSN 17 rue des Martyrs, F-38054 Grenoble cedex 9, France - philippe.berne@cea.fr

Abstract: Nanofluids/nanocomposites are suspensions of nanoparticles in a fluid/solid matrix. A simple procedure for the numerical prediction of their effective thermal conductivity was devised using Comsol Multiphysics. It was tested against an analytical formula from a classical paper published by C.W. Nan et al. in the Journal of Applied Physics in 1997 taking into account an interfacial thermal resistance. Despite repeated attempts the results were found to differ significantly, which led to question the derivation of the analytical formula. The omission of two contributions, from respectively the shape and the aspect ratio of the particle + interfacial layer system, was detected. The formula could be corrected for the aspect ratio contribution, which led to considerably improved agreement with the numerical predictions.

Keywords: Effective thermal conductivity, Interfacial resistance, Nanofluids.

1. Introduction

"Nanofluids" and "nanocomposites" can be defined as fluids or materials consisting in a matrix in which a certain amount of small-sized particles, for instance with dimensions under 100 nm, is dispersed. They have received a lot of attention in the past few years because they are expected to have much improved properties compared to the initial matrix, without the drawbacks of "conventional" (not nanometric in size) suspensions. Since the possibilities for manufacturing particles with exotic shapes or characteristics are ever growing (see for instance [1]), it was thought useful to devise a way to select which materials and shapes have a potential for better characteristics. One property of particular interest is the thermal conductivity. The initial motivation for the present work was therefore to explore the relationship between the shape and nature of the particles and the thermal conductivity of the nanofluids or composites containing them.

2. Method

Our approach was guided by the "benchmark study on the thermal conductivity of nanofluids" published in 2010 in the Journal of Applied Physics [2], a conclusion of which was that a wide range of experimental data could be correctly reproduced by a standard conduction model including an interfacial resistance between the particles and the matrix.

More specifically, the technique adopted (as presented by Mejdoubi and Brosseau in [3]) consists in solving a heat conduction problem in a cubic cell containing one particle and submitted to a temperature difference on two opposite faces and to a zero-flux condition on the other ones, as illustrated on Figure 1:

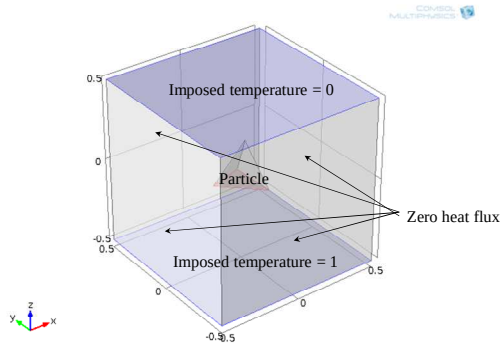

Figure 1. Conduction problem to be solved.

The equations read (T: temperature, K: thermal conductivity, R_{Bd}: interfacial resistance; subscripts m and p denote the matrix and the particle phases; n_i: outward-directed normal to phase i):

$$\nabla \cdot \left(K_i \nabla T_i \right) = 0,\ i = m,\ p$$

$$\frac{\partial T_m}{\partial n_m} = 0\ ,\ T_m = 0 \text{ or } T_m = 1$$

$$-K_m \frac{\partial T_m}{\partial n_m} = \frac{T_m - T_p}{R_{Bd}} = K_p \frac{\partial T_p}{\partial n_p}$$

They express respectively the steady-state conduction of heat, the zero flux and imposed

temperature boundary conditions, and the continuity of heat flux at the particle-matrix interface.

The heat flux through the cell is calculated by integration on one of the imposed-temperature faces and translated into an equivalent conductivity *K*. The calculation is repeated for various cell sizes, corresponding to various (low) particle volume fractions *v*. The *K*-*v* relationship is finally analysed as a series expansion:

$$\frac{K}{K_m} = 1 + [K]v + O(v^2)$$

[*K*] is termed the "intrinsic conductivity". It expresses by how much the equivalent conductivity will be increased by the addition of a given volume fraction of particles, and can therefore be used to compare the efficiency of different particle shapes, materials or sizes.

3. COMSOL Multiphysics calculation

Two "heat transfer in solids" physics modules were used, respectively for the matrix and the particle phases. They were coupled via "heat flux" conditions, using the "inward heat flux" option ("heat transfer coefficient" = $1/R_{Bd}$, "external temperature" equal to the temperature in the other domain).

Alternatively, a single "heat transfer in solids" module was also used with a "thin thermally resistive layer" inserted between the particle and the matrix. But this option was not found quite as reliable as the simple coupling described above.

Default quadratic discretization was used in most cases.

The "finer" element size with a "physics-controlled" mesh generally did a good job (the "extra fine" and "extremely fine" options were also tested, but gave essentially the same results).

Comsol Multiphysics version 4.3 was used on a standard Personal Computer. Convergence was usually obtained within a few tens of seconds with the default solver settings.

4. Validating the procedure: platonic solids

Before attempting the optimisation of nanoparticles, it was thought wise to validate our procedure, first of all in the case of no interfacial resistance.

Abundant data have been published on this subject (for instance in the paper by Mansfield et al. [4]). Among them we selected the results of a study by Sihvola et al. [5]. These authors computed very carefully the polarizabilities (an equivalent of our intrinsic thermal conductivity) of the platonic solids: namely the tetrahedron, cube, octahedron, dodecahedron and icosahedron, to which the sphere was added as a limit case.

The results are shown in Table 1 for an infinite K_p/K_m ratio. Our results do not differ by more than 2% from Sihvola's.

Table 1: Intrinsic conductivity of the platonic solids

Solid	Sihvola [5]	This work
Tetrahedron 	5.0285	5.027
Cube 	3.6442	3.697
Octahedron 	3.5507	3.618
Dodecahedron 	3.1779	3.206
Icosahedron 	3.1304	3.148
Sphere 	3	2.9996

In our opinion these results are astonishingly good. One should keep in mind that the volume fractions used in the calculations are in the 10^{-3}-10^{-2} range. The K/K_m ratio therefore differs from unity by no more than about 1%, which means that a 4 to 5-digit accuracy in the heat flux calculation has to be attained to achieve such precision on [*K*].

5. Validating the procedure: Nan et al.'s classical paper [6]

The case of the effective conductivity with interfacial thermal resistance is clearly more difficult and published data seem much scarcer.

A theoretical paper on the subject was published in 1997 by C.W. Nan and co-workers in the Journal of Applied Physics. It addresses the case of a composite containing ellipsoidal particles, taking into account an interfacial resistance, and derives a reasonably simple analytical solution. This paper is quite popular and has received, as of today, almost 600 citations according to the Scopus bibliographic database. It was used, for instance, in the above-mentioned benchmark study on nanofluids [2] to analyse the experimental data.

The basis of Nan et al.'s paper consists in calculating the equivalent conductivity of the ellipsoidal particle plus the interfacial resistance, actually the equivalent conductivity tensor since this object is not isotropic. The result reads:

$$K_i^c = \frac{K_p}{1+\frac{K_p R_{Bd}}{a_1} L_i \left(2+\frac{1}{p}\right)} \qquad (1)$$

where i = 1,2,3 denotes the 3 principal axes of the ellipsoid, p the aspect ratio (ratio of the dimensions along the axis of revolution and perpendicular to it: p>1, oblate particle, p<1, prolate particle), a_1 the dimension perpendicular to the axis of revolution and the L_i's are functions of p:

$$L_1 = L_2 = \begin{cases} \frac{p^2}{2\left(p^2-1\right)} - \frac{p}{2\left(p^2-1\right)^{3/2}}.\cosh^{-1}(p), & p>1 \\ \frac{p^2}{2\left(p^2-1\right)} - \frac{p}{2\left(1-p^2\right)^{3/2}}.\cos^{-1}(p), & p<1 \end{cases}$$

$$L_3 = 1-2L_1$$

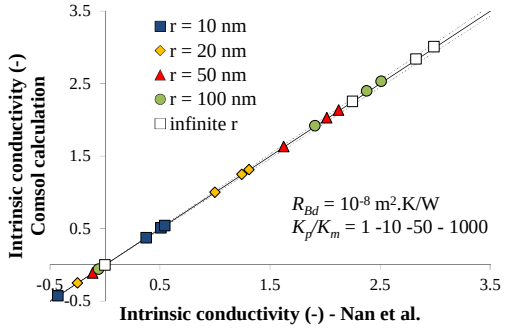

Figure 2. Results of our procedure against Nan et al.'s formulae: sphere with interfacial resistance. r: radius of the sphere.

Comparison with the results from our procedure was excellent in two cases, the sphere with interfacial resistance (Figure 2) and the ellipsoid without it (Figure 3). Maximum deviations again never exceeded 2%.

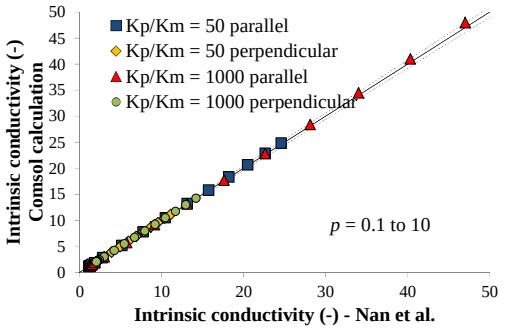

Figure 3. Ellipsoid without interfacial resistance. The "parallel" and "perpendicular" directions are defined with respect to the axis of revolution of the ellipsoid.

On the contrary, agreement was very poor in the case of ellipsoids with interfacial resistance (Figure 4), where differences as large as 100% could be observed.

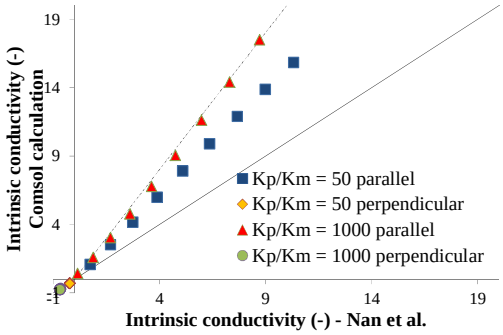

Figure 4. Ellipsoid with interfacial resistance. a_1= 5 nm, R_{Bd} = 10^{-8} m^2.K/W, K_m = 1 W/m.K. Dashed line: +100%.

More specifically, the discrepancy increases when the aspect ratio differs significantly from unity (Figure 5).

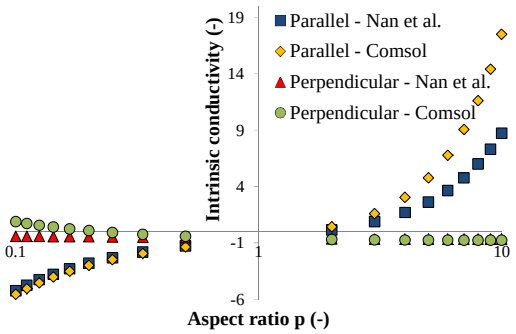

Figure 5. Selected data from Figure 4 (K_p/K_m = 1000), expressed as a function of aspect ratio p.

This observation was found quite disturbing and various classical remedies were tested:

- increase of mesh density,
- use of a more precise discretisation scheme,
- creation of a finite-thickness buffer domain between the matrix and the particle,
- use of the "thin thermally resistive layer" option.

None of them allowed to reduce the gap between numerical and analytical predictions; as a matter of fact, the same results were repeatedly obtained.

6. Analysis of Nan et al.'s model and subsequent modification

It was then decided to trust the numerical simulation and (not without qualms) examine the derivation of Nan et al.'s model.

This derivation is basically composed of two parts. The first one, briefly mentioned in the previous Section, consists in calculating the equivalent conductivity of the particle + interface system. The second one establishes the relationship between the conductivities at the particle and the nanofluid or nanocomposite scales, independently of the existence of the interfacial resistance. Our initial success with the no-interfacial resistance ellipsoids suggests that the problem, if any, lies in the first part of the analytic development.

The technique used by Nan et al. consists in calculating the equivalent conductivity of a unit cell composed of the ellipsoidal particle embedded in an interface layer with constant thickness δ, and passing to the limit that δ tends to zero. We hold that the calculation as developed by Nan et al. implies that i) the overall shape of this cell should be an ellipsoid ii) the aspect ratios of the particle and the surrounding layer should be identical. It so happens that neither is true, as illustrated by Figure 6 (the parameters of which have been deliberately chosen to emphasize the differences).

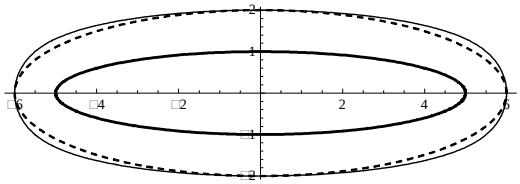

Figure 6. Ellipsoidal particle, aspect ratio p=5, a_1=1 (thick line); interfacial zone with thickness δ=a_1=1 (thin line). Dashed line is the ellipse with aspect ratio $\left(p+\delta/a_1\right)/\left(1+\delta/a_1\right)$ = 3.

It appears clearly that the interfacial zone (thin line) does not coincide with the only possible ellipse (dashed line) and that the latter also has a much smaller aspect ratio than the original particle. These differences obviously become vanishingly small when thickness δ tends to zero, but that does not mean that they do not contribute to the overall result.

We therefore feel entitled to claim that Nan et al.'s derivation omits a *shape* contribution and an *aspect ratio* contribution. The former is unfortunately rather complicated and at any rate beyond our mathematical abilities. We found the latter more tractable. Our approach consisted in using a classical effective medium "mixing law", described for instance in another paper by C.W. Nan [7], with the correct aspect ratios in the expressions of the L_i functions of the particle and the surrounding layer. The details are of little interest here. It was then straightforward (if rather tedious) to derive a corrected equivalent of equation (1):

$$K_i^c = \frac{K_p}{1+\dfrac{K_p R_{Bd}}{a_1}\left[L_i\left(2+\dfrac{1}{p}\right)-A_i\right]} \qquad (2)$$

where the additional term A_i is given by:

$$A_i = \frac{\partial L_i}{\partial \delta} = \frac{\partial L_i}{\partial p}\frac{\partial p}{\partial \delta} \qquad (3)$$

7. Comparison of the modified model with the numerical results

The analytical data of Figures 4 and 5 were re-calculated using equations (2) and (3). The results are shown in Figures 7 and 8 below.

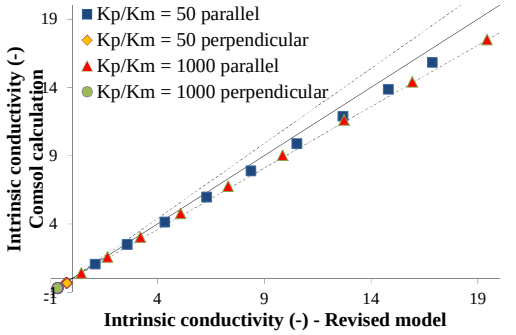

Figure 7. Same calculations as in Figure 4, revised model.

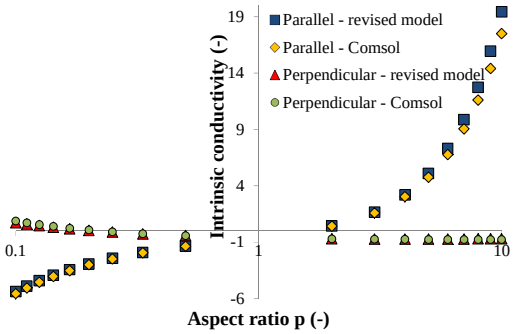

Figure 8. Same calculations as in Figure 5, revised model.

Agreement is still not perfect but much improved since maximum deviation is now less than 10%. The remaining difference might come from neglecting the shape contribution mentioned in the previous section.

8. Conclusions

Two questions can now be raised. Firstly, it is disturbing that a scientific paper with hundreds of cites should lead to erroneous results. Is it plausible that none has ever done the simple simulation reported here, or done it and reached similar conclusions? More generally, can we trust a numerical simulation against an analytical development? In our opinion, the coincidence of the numerical results and the revised model can hardly be explained by chance or artefact and gives some confidence in the present developments. We should however be happy to see our numerical and analytical calculations checked by someone else.

Secondly, what would the consequences be, if our conclusions are correct? We believe that they should remain quite modest, in the case of nanofluids/nanocomposites, because interfacial resistance R_{Bd} is not well known and often treated as an adjustable parameter. The new formulae would only result in other, probably not very different, values. But again we should be very pleased to see other (and hopefully better) people address this question.

9. References

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