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Austin Minnich and Gang Chen

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Modified effective medium formulation for the thermal conductivity of nanocomposites

Austin Minnich[a] and Gang Chen
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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This letter introduces a modified effective medium formulation for composites where the characteristic length of the inclusion is on the order of or smaller than the phonon mean free path. The formulation takes into account the increased interface scattering in the different phases of the nanocomposite and the thermal boundary resistance between the phases. The interface density of inclusions is introduced and is found to be a primary factor in determining the thermal conductivity. The predictions are in good agreement with results from Monte Carlo simulations and solutions to the Boltzmann equation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2771040]

The thermal properties of composite materials have attracted significant interest in recent years, especially in fields such as thermoelectrics and thermal management of electronics.[1–5] The early research on this topic was the classical work of Rayleigh[6] and Maxwell,[7] who derived expressions for the thermal conductivity of dilute concentrations of spherical particles embedded in a host. Hasselman and Johnson[8] later proposed a theoretical model to account for thermal boundary resistance (TBR); Benveniste[9] also independently derived the same result using a different model. Most recently, Nan *et al.* introduced a general equation for the thermal conductivity of a two-phase composite which is applicable in a wide variety of geometries and includes TBR.[10] These approaches in finding an effective thermal conductivity of a composite are known as the effective medium approximation (EMA).

The EMA accurately predicts the thermal conductivity of macrocomposites, but in nanocomposites, where the inclusion size is smaller than the phonon mean free path (MFP), the results from the EMA do not agree with those from more rigorous solutions.[3,11] This is because the host and particle thermal conductivities in nanocomposites are not equal to their bulk values due to increased interface scattering. In several papers Yang *et al.* were able to calculate the effective thermal conductivity of a nanocomposite using the phonon Boltzmann equation, but this approach can be difficult to implement.[2,3] Monte Carlo (MC) techniques have also been used to calculate the thermal conductivity, giving good results but requiring significant computational time.[11] Prasher has had considerable success obtaining analytical solutions to the Boltzmann equation for simple geometries.[4,5]

In this letter we introduce a modified EMA formulation which gives a closed-form expression for the thermal conductivity of a nanocomposite. The formulation gives results that are in good agreement with more rigorous solutions and allows for a more intuitive understanding of the parameters governing the thermal conductivity of nanocomposites. The principle is to account for size effects in each phase by modifying the bulk MFP, from which modified thermal conductivities can be obtained to use in the usual EMA equations.

We first consider spherical nanoparticles of diameter d embedded in a host geometry with effective cell length a, where a is defined as the average length of a side of a cube that encloses one nanoparticle. From this definition, the density of nanoparticles is $n=1/a^3$. The general EMA equation derived by Nan reduces to the following for spherical particles:

$$\frac{k_e}{k_h} = \frac{k_p(1+2\alpha)+2k_h+2\varphi[k_p(1-\alpha)-k_h]}{k_p(1+2\alpha)+2k_h-\varphi[k_p(1-\alpha)-k_h]}, \tag{1}$$

where k_e is the effective composite thermal conductivity, k_h is the host material thermal conductivity, k_p is the particle thermal conductivity, φ is the volume fraction of nanoparticle inclusions, and α is a dimensionless parameter defined as $\alpha=r_{\mathrm{TBR}}/(d/2)$. Here d is the diameter of the nanoparticle and $r_{\mathrm{TBR}}=Rk_h$, where R is the TBR. We will base our discussion on a kinetic theory expression for the thermal conductivity,

$$k = \frac{1}{3}\int C(\omega)v(\omega)\Lambda(\omega)d\omega \approx \frac{1}{3}Cv\Lambda, \tag{2}$$

where C is the volumetric specific heat, v is phonon group velocity, and Λ is the phonon MFP. Frequency independent properties will first be considered as in the approximate expression since the extension to include frequency dependence is straightforward and will be discussed later in this letter. A nanocomposite can now be defined as a composite where $d/\Lambda \ll 1$. Equation (1) in its current form does not give accurate results for nanocomposites; however, if we could modify this EMA formulation to account for the increased interface scattering we might still be able to use the EMA.

Let us first consider the host phase. We expect the effective thermal conductivity to be a function of the bulk MFP and a characteristic length that accounts for the nanoparticle density. The appropriate length scale for the host phase is not immediately obvious, but it has recently been shown that the interface density, defined as the surface area of the nanoparticles per unit volume of composite, is a primary factor in determining the effective thermal conductivity,[11] and so we form a length scale from this parameter. The interface density for spherical particles is defined as

$$\Phi = \frac{4\pi(d/2)^2}{a^3} = \frac{6\varphi}{d}, \tag{3}$$

where φ is the volume fraction of nanoparticles,

[a]Electronic mail: aminnich@mit.edu

$$\varphi = \frac{(4/3)\pi(d/2)^3}{a^3} = \frac{(1/6)\pi d^3}{a^3}, \tag{4}$$

where a is the unit cell effective length defined before. The effective area of collision for a phonon and a spherical nanoparticle is $\pi d^2/4$; thus if a phonon travels a distance L it will encounter $N=\pi d^2 Ln/4$ inclusions. The MFP is the distance traveled divided by the number of collisions,

$$\Lambda_{\text{coll}} = \frac{L}{n(\pi d^2 L/4)} = \frac{4a^3}{\pi d^2} = \frac{2d}{3\varphi}. \tag{5}$$

We can now relate the collision MFP and Φ,

$$\Lambda_{\text{coll}} = \frac{4}{\Phi}. \tag{6}$$

Applying Matthiessen's rule, the effective MFP of the host phase is

$$\frac{1}{\Lambda_{\text{eff},h}} = \frac{1}{\Lambda_{b,h}} + \frac{1}{\Lambda_{\text{coll}}} = \frac{1}{\Lambda_{b,h}} + \frac{\Phi}{4}, \tag{7}$$

where $\Lambda_{\text{eff},h}$ and $\Lambda_{b,h}$ are the effective and bulk MFPs of the host phase, respectively. Inserting the effective MFP into Eq. (2) gives the effective thermal conductivity.

We next consider the inclusion phase. With diffuse scattering the MFP of the particle phase should only be a function of the bulk MFP and the characteristic length of the particle phase, which we set to d. Again using Matthiessen's rule, we get an effective MFP,

$$\frac{1}{\Lambda_{\text{eff},p}} = \frac{1}{\Lambda_{b,p}} + \frac{1}{d}. \tag{8}$$

We can use this MFP to get the effective thermal conductivity of the particle phase. The remaining parameter to be determined is the TBR R. Assuming diffuse scattering we can use the result from Chen,[12]

$$R \approx 4\left(\frac{C_1 v_1 + C_2 v_2}{C_1 v_1 C_2 v_2}\right), \tag{9}$$

where v_1 and v_2 are the phonon group velocities, and we have assumed that the volumetric specific heats C_1 and C_2 are independent of temperature.

We now have an expression for the effective thermal conductivity of a nanocomposite as a function of the interface density Φ and nanoparticle diameter d,

$$k_{\text{eff}}(\Phi;d) = \frac{1}{3} C_h v_h \frac{1}{(1/\Lambda_h) + (\Phi/4)} \times \frac{k_p(d)(1+2\alpha(\Phi,d)) + 2k_h(\Phi) + 2(\Phi d/6)[k_p(d)(1-\alpha(\Phi,d)) - k_h(\Phi)]}{k_p(d)(1+2\alpha(\Phi,d)) + 2k_h(\Phi) - (\Phi d/6)[k_p(d)(1-\alpha(\Phi,d)) - k_h(\Phi)]}. \tag{10}$$

This equation can be decomposed into two terms. The first term, the host phase thermal conductivity, scales the entire solution as it decreases with increasing interface density. Since $\Phi=6\varphi/d$, for large particle diameters the interface density term is negligible, but for $d/\Lambda \ll 1$ this term causes the host phase thermal conductivity to drop as $1/\varphi$. The second term, from the unmodified EMA, accounts for the shape of the particles and includes the traditional TBR parameter α. Thus in the modified EMA formulation the total TBR is dependent on both α and Φ. α is a macroscale term which accounts for the TBR in macrocomposites, while Φ accounts for increased interface scattering due to size effects. Note that α depends on Φ and d as $\alpha=k_h(\Phi)/(d/2)$.

Results are presented for a SiGe nanocomposite with Si nanoparticles embedded in a Ge host as these are the material systems that have been analyzed previously with MC simulations and the Boltzmann equation.[2,11] The parameters used in the calculation are shown in Table I. Figure 1(a) compares the modified EMA formulation with the unmodified EMA for particle diameter $d=10$, 50, and 200 nm. Data from MC simulations are also included. The unmodified EMA is in extremely poor agreement with the MC simulation results for $d=10$ and 50 nm, which is expected since $d/\Lambda_b \ll 1$ and the unmodified EMA neglects the increased interface scattering due to size effects.

TABLE I. Material parameters used in calculation.

Material	Bulk thermal conductivity (W/m K)	Heat capacity ($\times 10^6$ J/m^3 K)	Phonon group velocity (m/s)	Bulk MFP (nm)
Si	150	0.93[a]	1804[a]	268
Ge	51.7	0.87[a]	1042[a]	171

[a]Reference 12.

Figure 1(b) shows the predicted effective thermal conductivity for $\alpha=r_{\text{TBR}}/(d/2)$ and $\alpha=0$, along with data from MC simulations. The modified EMA formulation with macroscale term $\alpha=r_{\text{TBR}}/(d/2)$ is in good agreement with the MC simulation results over the entire nanoparticle diameter range. However, if we set $\alpha=0$ the modified EMA formulation is not accurate. At low volume fraction the second term in the product in the right-hand side of Eq. (10) is approximately unity and the thermal conductivity scales with k_h, but at higher volume fraction this term grows quickly if the TBR is not included, producing the parabolic curves. Thus to obtain good agreement it is important to be consistent and include both factors arising from interface scattering.

We can derive a similar expression for the effective thermal conductivity for cylindrical inclusions and compare the results to numerical solutions of the Boltzmann equation.[2] Here the heat flux is perpendicular to the side walls of the cylinders. If we define the interface density as $\Phi=L\pi d/a^2 L$, use Nan's EMA result for cylindrical inclusions, and follow a similar calculation as before, we find that $\Lambda_{\text{coll}}=\pi/\Phi$. Figures 2(a) and 2(b) show that the modified EMA theory is again in good agreement with numerical solutions to the Boltzmann equation.

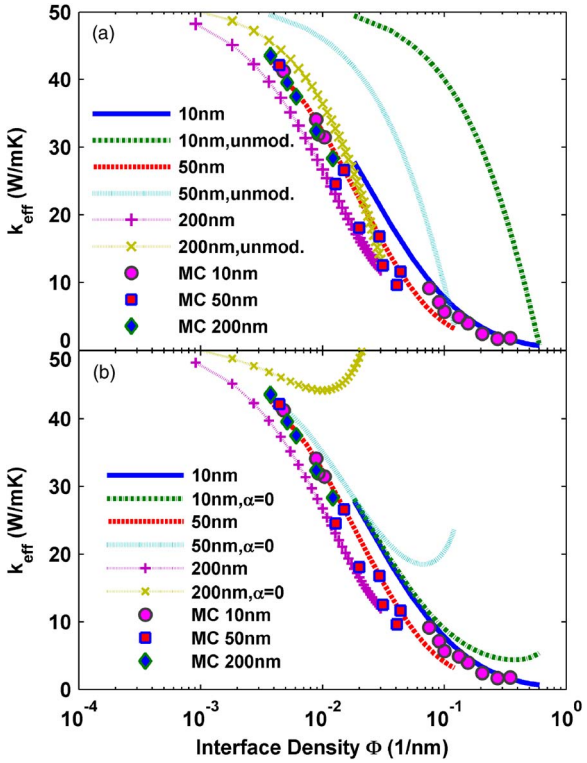

FIG. 1. (Color online) (a) Thermal conductivity of a SiGe nanocomposite with spherical inclusions predicted by the modified and unmodified EMA formulations, along with data from Monte Carlo simulations, and (b) thermal conductivity predicted by the modified EMA formulation for $\alpha = r_{TBR}/(d/2)$ and $\alpha=0$, along with data from Monte Carlo simulations (simulation results from Ref. 11).

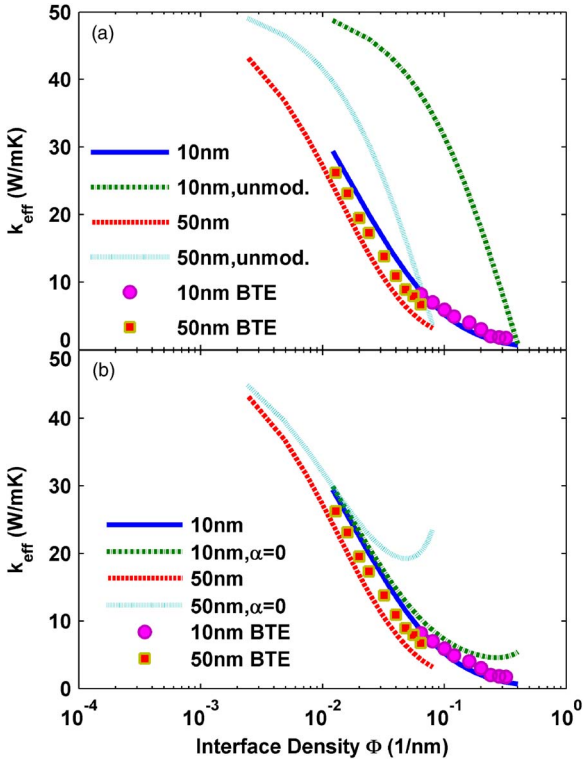

FIG. 2. (Color online) (a) Thermal conductivity of a SiGe nanocomposite with cylindrical inclusions predicted by the modified and unmodified EMA formulations, along with numerical solutions to the Boltzmann equation, and (b) thermal conductivity predicted by the modified EMA formulation for $\alpha=r_{TBR}/(d/2)$ and $\alpha=0$, along with numerical solutions to the Boltzmann equation (numerical solutions from Ref. 2).

These results illustrate the major difference between the thermal properties of macrocomposites and nanocomposites. In macrocomposites the TBR from interface scattering is negligible and the effective thermal conductivity is primarily determined by the host and inclusion thermal conductivity and α. In nanocomposites, however, the effective thermal conductivity is strongly dependent on the interface density. The inclusions primarily serve as phonon scattering sites, increasing the interface scattering and reducing the host thermal conductivity. This interface scattering is well characterized by the interface density term. Previous works have arrived at this result but with far more complex methods of solution,[11,12] and it is encouraging that this fundamental aspect of the thermal properties of nanocomposites can be predicted from this simple formulation.

It is also worthwhile to note that frequency-dependent properties, such as a frequency-dependent MFP, can easily be incorporated into the formulation such as Eq. (10). One need only insert the frequency-dependent bulk MFP of each phase into Eqs. (7) and (8) and use the integral expression in Eq. (2). Incorporating frequency dependence should be beneficial; the phonon MFP distribution function, for example, is not uniform, with certain phonon frequencies contributing significantly more to the thermal conductivity than other frequencies.

In summary, we have introduced a modified EMA formulation for nanocomposites. Our results are in good agreement with results from MC simulations and solutions to the Boltzmann equation. We find that the thermal conductivity in nanocomposites is governed by the interface density and that TBR plays a critical role in determining the effective thermal conductivity. The modified EMA formulation provides a simpler method of estimating the thermal conductivity of nanocomposites and allows for a more intuitive understanding of the parameters governing thermal conductivity on the nanoscale.

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