Effect of percolation on thermal transport in nanotube composites

S. Kumar
School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907

M. A. Alam
School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47907

J. Y. Murthy
School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907

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The effective thermal conductivity of two-dimensional (2D) nanocomposites composed of carbon nanotubes (CNTs) dispersed in a host substrate is simulated to quantify the role of tube percolation on the thermal transport. The model is in excellent agreement with a 2D effective medium theory for low tube densities, but departs significantly from it when tube-tube interaction becomes significant. It is found that percolation effects may play a role for tube-tube and tube-substrate thermal resistance parameters typical of CNT composites. They are quantified in terms of a conductivity exponent for a range of governing parameters. © 2007 American Institute of Physics.

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In recent years, carbon nanotube (CNT)-based composites have been investigated intensively in diverse applications including macroelectronics, thermal management, and high strength materials. In these applications, CNTs are randomly dispersed in a host substrate and may form a percolating network even at low volume fractions (~0.2%) due to their high aspect ratio. Heat exchange with the substrate through the large lateral contact area has been assumed to diminish the role of percolation in determining composite thermal conductivity. Therefore, most published theoretical research does not account for percolation, including widely used effective medium approximations. However, recent studies of thermal contact resistance have shown that tube-substrate and tube-tube contact resistances are both very high. If the soft contact between the tube and the substrate is resistive enough to dominate the high tube-tube resistance, network percolation may play a role in thermal transport. Though a few recent publications have accounted for percolation in nanotube networks, none have considered the role of these competing effects, and nearly all address three-dimensional (3D) bulk composites.

The focus of this letter is thermal transport in two-dimensional (2D) thin-film CNT composites used in flexible macroelectronics and organic electronics. Our objectives are (i) to establish the limits of the traditional effective medium approximation (EMA) in analyzing the effective thermal conductivity of 2D CNT composites and (ii) to identify the range of contact parameters for which percolation could play a role in thermal transport. We demonstrate that 2D EMA underpredicts effective thermal conductivity (keff) even at tube densities well below the percolation threshold. We show that the role of percolation depends critically on the strength of tube-to-substrate and tube-to-tube contact resistances for large enough tube-to-substrate conductivity ratio, and that percolation could play a role for resistance values that fall within the range of published measurements. We quantify the importance of percolation effects by determining the conductivity exponent as a function of tube density.

We represent the CNT network composite [see inset in Fig. 1(b)] as a 2D random network of nanotubes of length L and diameter d dispersed in a matrix of length L, width H, and thickness t. Since L/d ≫ 1, there are sufficient phonon boundary scattering events at the substrate-tube interface that classical Fourier conduction obtains in both tube and substrate. Assuming one-dimensional diffusive transport along the nondimensional length s of the tube, three-dimensional conduction in the substrate, and heat transfer

![Color online] (a) Comparison of normalized effective thermal conductivity (keff/kT) computed from numerical simulations and analytically derived expressions for different kT/kC ratios. L/ =8 (L=0.5 μm), H/L=4, BiB=10−8, and ρ =0.0–0.3 (ρ=0.1–6.5 μm−2). BiC=0 for simulations unless otherwise stated. (b) Comparison of normalized effective thermal conductivity (keff/kT) computed from numerical simulations and 2D EMA for different values of the interfacial thermal resistance Bi (10−7–10−5) for BiC=0. L/ =8 (L=0.5 μm), H/L=4, kS/kT=10−3, and ρ =0.0–0.3 (ρ=0.1–6.5 μm−2).

FIG. 1. (Color online) (a) Comparison of normalized effective thermal conductivity (keff/kT) computed from numerical simulations and analytically derived expressions for different kT/kC ratios. L/ =8 (L=0.5 μm), H/L=4, BiB=10−8, and ρ =0.0–0.3 (ρ=0.1–6.5 μm−2). BiC=0 for simulations unless otherwise stated. (b) Comparison of normalized effective thermal conductivity (keff/kT) computed from numerical simulations and 2D EMA for different values of the interfacial thermal resistance Bi (10−7–10−5) for BiC=0. L/ =8 (L=0.5 μm), H/L=4, kS/kT=10−3, and ρ =0.0–0.3 (ρ=0.1–6.5 μm−2).
between intersecting tubes as well as to the substrate, the
governing nondimensional energy equations in the tube and
substrate may be written, respectively, as

\[ \frac{d^2 \theta_i}{ds^2} + \sum_{\text{interacting tubes } j} B_{ij}(\theta_i - \theta_j) + B_{ii}(\theta_i - \theta_i) = 0, \]  
(1a)

\[ \nabla^2 \theta_S + \sum_{i=1}^{N_{bhs}} B_i \beta_i \frac{k_i}{k_S} (\theta_i - \theta_S) = 0. \]  
(1b)

Here, \( \theta = (T - T_s)/(T_L - T_R) \), where \( T_L \) and \( T_R \) are the boundary
temperatures [see inset in Fig. 1(b)], and all lengths are
nondimensionalized by the tube diameter \( d \). Here, \( B_{ij} \) re-
presents the dimensionless tube-to-tube contact conductance
and \( B_i \) represents the dimensionless tube-substrate contact
cconductance. \( k_S/k_i \) is the ratio of the substrate and tube con-
ductivities and \( \rho = \rho_L/\rho_{th} \) is the dimensionless tube density,
where \( \rho_{th}(=4.23^2/\pi L_t^2) \) (Refs. 4 and 22) is the density at the
global percolation threshold. Other details are given in Ref.
23. The problem is solved numerically using the finite vol-
ume method.\(^{6,24} \) 100 random realizations are used to obtain a
statistically significant result.

For low-density ellipsoid dispersions, the effective con-
ductivity \( (k_{eff}) \) has been derived in Ref. 16 using a Maxwell-
Garnett EMA. For a planar CNT network, isotropic in the
\( x-y \) plane [see inset in Fig. 1(b)] and embedded in a substrate
of thickness \( d \), the theory in Ref. 16 may be modified to yield
\( k_{eff} \) in the \( x-y \) plane as

\[ k_x = k_y = k_S \frac{2 + f [\beta_{11}(1 - L_L) + \beta_{33}(1 - L_L)]}{2 - f [\beta_{11} + \beta_{33} L_L]}. \]  
(2)

Here \( f \) is the volume fraction, \( L_{ii} \) is the depolarization
factor, and \( \beta_{ij} = (k_i - k_S)/[k_i + L_L(k_i - k_S)] \), \( k_{11} = k_{22} = k_S/(1 + \langle 2a_k k_i/k_i \rangle) \), and \( k_{33} = k_S/(1 + \langle 2a_k k_i/k_i \rangle) \). Here, \( a_k \) is the
Kapitza radius.\(^{9,16} \) \( k \) axis 3 represents the longitudinal axis of
the CNT, and axes 1 and 2 are the other two axes of the
CNT.\(^{16} \)

The finite volume computation of \( k_{eff} \) is compared with
predictions from the 2D EMA in Figs. 1(a) and 1(b). For this
case, the polarization factors are given by \( L_{11} = L_{22} = 0.5, \)
\( L_{33} = 0 \). Equation (2) assumes that \( \rho \) is very low, and that the
tubes do not interact with each other. Consequently, the
tube-tube contact parameter \( B_{ij} \) is set to zero in the finite volume
computations. Since the parameter \( B_{ij} \) is not known \emph{a priori},
it value is adjusted to match the results from EMA for a
previous study.\(^{9} \) A good match with the results of EMA is obtained
for the case of \( B_{ij} = 0.5 \). Calculations were also performed in
Fig. 1(a) for \( B_{ij} = 10 \), representing nearly perfect contact.
For high \( B_{ij} \), the numerically computed \( k_{eff} \) is observed to devi-
ate substantially from the EMA prediction even for densities
below \( \rho_{th} \). This deviation is significant for all but the highest
values \( k_S/k_i \) (\( \sim 10^{-2} \)) and would therefore be significant for
computations of electrical and thermal conductivities in CNT
composites. This suggests that high aspect ratio tubes inter-
act with each other even at tube densities well below \( \rho_{th} \) and
that the EMA may be inadequate for the prediction of \( k_{eff} \) at all
but the very lowest densities if tube-tube contact is suffi-
ciently good.

Figure 1(b) presents the variation of \( k_{eff} \) with tube den-
sity with \( B_{ij} \) as a parameter for \( B_{ij} = 0 \); the ratio \((1/a_k)/B_{ij}\)

![FIG. 2. (Color online) Variation of normalized effective thermal conductivity \( k_{eff}/k_S \) against normalized tube density \( \rho^* \) for different \( k_S/k_i \).](image)
indicate the broad order of magnitude. Nevertheless, for the type of soft contact encountered in these composites, with $B_{iS}$ in the range of $10^{-5} - 10^{-7}$ and $B_{iC}$ in the range of $10^{-4} - 10^{-5}$. Fig. 2 indicates that percolation could play a role. However, the value of $k_f/k_s$ is critical. For CNTs in polymer, $k_f/k_s \sim 10^{-8}$ if $\rho_x \sim 0.1 \text{W/mK}$ and $k_f \sim 10^3 \text{W/mK}$, commensurate with freestanding CNT values. However, if $k_f$ is significantly reduced because of phonon scattering at the tube-substrate boundary, Fig. 2 indicates that percolation effects would not be visible, and that predicted $k_{eff}/k_s$ would be low. Effective thermal conductivity values reported in the literature for 3D composites all have $k_{eff}/k_s < 3$ or so, in contrast to some of the high values seen in Fig. 2, indicating that $k_f$ reduction due to interface scattering could play a significant role.

Electrical transport in the linear regime in CNT organic composites may be analyzed using a model similar to that for thermal transport. Figure 2 indicates that strong nonlinear behavior near the percolation threshold would be observed for electrical (charge) transport in CNT-polymer composites due to very low $k_f/k_s(<10^{-8})$. low $B_{iS}$, and high $B_{iC}$.

The effect of $B_{iS}$ and $k_f/k_s$ on percolation behavior is quantified by computing the conductivity exponent $n$, given by $k_{eff} = A(\rho_0 - \rho)^n$ in Fig. 3; it is computed for $(\rho_0 < \rho < 2 \rho_0)$. For high tube-substrate thermal resistance ($B_{iS} \sim 10^{-8}$), $n$ is nearly constant at a value of 1.2, close to the 2D exponent of 1.3. The boundaries for the pure network. The value of this exponent depends on $L_c/L_s$ and is expected to tend to 1.3 when $L_c/L_s$ is sufficiently large. With increasing $B_{iS}$, the variation in $n$ with $k_f/k_s$ becomes significant. For high $B_{iS}$ and high $k_f/k_s$, $n$ is close to 1.0, so that the medium behaves like a linear resistor and percolation effects are completely suppressed. When $k_f/k_s$ is decreased at high $B_{iS}$, $n$ increases until $k_f/k_s \sim 10^{-6}$, but attains a constant value for $k_f/k_s < 10^{-8}$, indicating that percolation effects are becoming more pronounced. This muting of the effects of network percolation at high $B_{iS}$ has been observed in electrical measurements of current-voltage characteristics ($I_{PD}/V_G$ curves) in CNT-organic transistors. However, the conductivity exponents in Fig. 3 are not universal and are sensitive to many factors including $d/L_{m}, L_c/L_s$, and $B_{iC}$.

In summary, a computational diffusive transport model is used to explore the thermal conductivity of 2D nanotube composites and the dependence of percolation behavior on $B_{iC}$, $B_{iS}$, and $k_f/k_s$. Numerical predictions are in excellent agreement with theoretical EMA-based results in the extremely low volume fraction limit, but depart from EMA for higher volume fractions below the percolation limit because of tube-tube interaction. The effective thermal conductivity varies linearly with $\rho$ in the low and high density regimes (explained by the average $L_{PD}$), while nonlinear behavior near $\rho_\Delta$ is found for low $k_f/k_s$, low $B_{iS}$, and high enough $B_{iC}$. This analysis of percolation effects will help interpret and guide the future experiments on nanocomposites for a wide range of practical applications.