TRANSPORT INVOLVING CONDUCTING FIBERS IN A NON-CONDUCTING MATRIX

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I. ABSTRACT

Thermal and electrical transport through a low-conductivity matrix containing high-conductivity fibers is important to several applications including flexible thin-film transistors, PEM fuel cells, and direct energy-conversion devices. Nanofibers can limit thermal transport through phonon confinement and boundary scattering while maintaining high electrical conductivity. The substrate will not contribute to electrical performance but may participate in thermal transport. The net result is a material whose Lorenz number can be tuned by loading the matrix with fibers. The purpose of the present work is to investigate the effectiveness of several transport models in the context of two-dimensional fiber composites and to compare the thermal and electrical transport through a given material as a function of the conductivity ratio and the fiber density. Three models will be considered and compared: 1)discretized solutions, 2) equivalent resistance, and 3)effective medium approximation. In the case of electrical transport, where the conductivity of the fiber is presumably many orders of magnitude larger than the matrix, the second model provides a fast and reliable way to predict conductance of the combined system. However, if the two materials are similar in conductivity, the second model fails to accurately capture the conductivity. Thermal transport is predicted using the discretized model because the conductivity ratio is non-negligible. The third model is an analytic approximation based on Maxwell's equation and is used to predict both types of transport through a compound with inclusions of ellipsoidal geometry. This model works well for low fiber densities but predicts lower conductivity for high fiber-densities because the analytic solution fails to account for fiber overlap.

II. INTRODUCTION

Thermal and electrical transport through a low-conductivity matrix containing high-conductivity fibers is important to several applications including flexible thin-film transistors (TFT) [4], proton exchange membranes (PEM)[11], and direct-energy conversion devices [1].

For flexible TFTs, low-temperature processes are required to prevent destruction of the substrate, but most semiconductors with good electrical performance require high-temperature processing[12]. Most research has been directed toward finding compatible high-temperature substrates [6]or high-performance electronic materials with low processing temperatures[5] [8]. Another approach is to combine the good electrical performance of nanofibers into flexible substrates. In fact, Biercuk et al. [2] have shown that nanotube/epoxy composites percolate at 0.1-0.2 wt% loading. This feature suggests that composite materials may retain the flexibility while providing good electrical performance with low processing temperatures. In direct energy conversion devices, particularly Peltier devices, high electrical conductivity and low thermal conductivity are preferred for superior performance[3]. However, most materials do not exhibit both of these properties simultaneously and strategies for tuning the material properties are being sought[9]. For example, composite structures involving high conductivity fibers and a low conductivity matrix could improve the performance of direct energy conversion devices. Nanofibers can limit the thermal transport through phonon confinement and boundary scattering while maintaining high electrical conductivity[1]. The substrate, while not contributing to the electrical performance, will also limit thermal transport. The net result is a material with high electrical conductivity and low thermal conductivity.

If we consider the fiber composite more carefully, we also notice that the conductivity ratio for thermal and electrical performance is different by orders of magnitude. Table I illustrates this feature for a composite composed of fibers (Calcined Needle Coke Fl08) embedded in a thermoplastic copolymer matrix (Vectra A950RX) [7]. Because the transport is a function of the conductivity ratio, we expect that different concentrations of fibers in the matrix will affect the thermal and electrical transport in different ways. In fact, Zimmerman [14] has shown that as the aspect ratio of fibers increases, the transport properties of the compound become more sensitive to the conductivity ratio.

The purpose of the present work is to investigate the effectiveness of several transport models in the context of two-dimensional fiber composites and to compare the thermal and electrical transport through a given material as a function of the conductivity ratio and the fiber density. Because the conductivity ratio of the fiber to the matrix is different when considering thermal transport compared to electrical transport, the rate of conductivity enhancement with fiber density should also be different. If the thermal and electrical properties can be decoupled, then the opportunity for designing improved TFTs and energy conversion devices can be identified.

Our analytic model is an effective medium approximation for a compound with inclusions of ellipsoidal geometries. This approximation works well to predict the total conductivity of a compound material with a low density of inclusions. However, the approximation underestimates the conductivity at higher fiber densities because the model does not account for fiber overlap. Numerical models are well suited for iteratively solving for transport and better approximate for fiber-fiber overlap. Thermal transport is determined using a percolation model. Fibers are placed randomly on the surface of the device. When a direct path of fibers is established between the two contacts, the compound is said to percolate. This model works well to determine thermal transport because the conductivity ratio of matrix/fiber is $\approx 10^2$. Thus, thermal transport is predicted by a discretization model which superimposing a small, square mesh on the device. Conductivity is determined by solving a system of linear equations which obey Kirchoff's law at each node of the network. Electrical transport is predicted by assuming that the matrix does not contribute to transport because the conductivity ratio of matrix/fiber is $\approx 10^{-14}$. A resistor is placed between any two fiber intersections and Ohm's law is used to relate the current through the resistor to the potential across the resistor.

III. Transport Models

A. Effective Medium Approximation

Most effective medium approximation (EMA) models predict the effective conductance of a composite material where severe restrictions are placed on the inclusion geometry and material properties. For example, what is considered to be Maxwell's model is valid for circular inclusions that are randomly distributed and non-overlapping. This approach has been shown to be valid only for low concentrations [10]. This model however has been extended to ellipsoidal geometries where the thermal conductivity of the compound k can be found as

TABLE I
Conductivity ratios of the matrix to fiber. Data obtained from King et al. [7]

	Thermal (W/mK)	Electrical $1/\Omega$m
matrix	0.2	$1*10^{-12}$
fiber	600	$1*10^{2}$
ratio	$3.3*10^{-4}$	$1*10^{-14}$

$$\frac{k}{k_0} = \frac{1-\beta c}{1+\beta c} \quad (1)$$

where c is the area fraction of fibers to matrix material, and

$$\beta = \frac{(1-r^2)(1+\alpha)^2}{4(1+\alpha r)(\alpha + r)} \quad (2)$$

In the foregoing expression the matrix material thermal conductivity is k_0, and the ellipse is described by the major axis radius, and α is the aspect ratio. The thermal conductivity ratio $r < 1$ is the conductivity of the matrix divided by the thermal conductivity of the inclusion fiber. This method can be used to approximate an inclusion of arbitrary aspect ratio including fibers ($\alpha \rightarrow 0$). In the limit of extremely narrow fibers compared to their length, the fiber-density parameter na^2 becomes a more meaningful independent variable than the area fraction [13], where a is the fiber length normalized by the device size. Note that a non-trivial limit can only be obtained for a conductivity ratio of $r \rightarrow 0$. In this case, the conductivity of the compound becomes

$$\frac{k}{k_0} = \frac{1-n\pi a^2/4}{1+n\pi a^2/4} \quad (3)$$

This form may be appropriate for the electrical transport, but equation 1 should be used for thermal transport where the conductivity ratio is non-negligible. Zimmerman [14] further provides a comparison between the extended Maxwell's model and the differential method, which gives an implicit form (stated without derivation).

$$\frac{1}{1-c} = (\frac{k}{k_o})^{2\alpha/(1+\alpha)^2}(\frac{k_o-k_i}{k-k_i})(\frac{k+k_i}{k_o+k_i})^{[\frac{1-\alpha}{1+\alpha}]^2} \quad (4)$$

Again, a non-trivial limit for $\alpha \rightarrow 0$ can only be found if the conductivity ratio limit $r \rightarrow 0$ leading to

$$\frac{k_o}{k} = exp(\frac{-\pi n a^2}{2}) \quad (5)$$

Note that Maxwell's model does not account for overlap of the fibers, but the differential method does statistically.

Therefore, Maxwell's method is strictly only valid in the dilute limit, but conceivably the differential method applies for a wider range of fiber densities. In addition, Maxwell's model is for inclusions with ellipsoidal geometry and not for fibers. Because the fibers have a larger area for the same aspect ratio compared to ellipsoids, the fiber density will not be accurate using Maxwell's model. For comparison, we have used two numerical models which will increase the accuracy of the simulation for conducting fibers in a polymer matrix.

B. Thermal Transport

Thermal transport was determined by creating a numerical model where the device is discretized into an equivalent resistor network of uniformly spaced resistors. Fibers are randomly-oriented on the surface and a square mesh is superimposed on the composite device. The mesh size is defined smaller than the width of the fibers so that several nodes lie within each fiber in both directions. Each node is modeled as four resistors having the same R_o or R_i (with R_o/R_i=1/r). A sample device is shown in Figure 1.

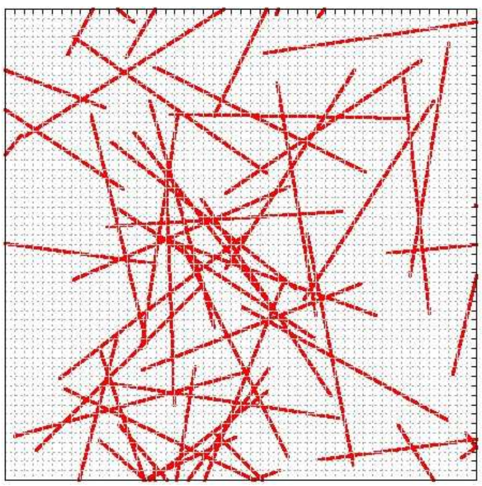

Fig. 1. Discretization of equivalent resistance for $n = 50$ and $L_f = 0.5$

A system of linear equations obeying Kirchoff's law at each node of the network is then generated. These equations can be gathered using matrix notation

$$A\mathbf{v} = \mathbf{0} \tag{6}$$

where A is a square matrix that has the size of the number of sites and the number of resistors placed in each node with equations for Ohm's law and Kirchoff's law, **v** is the vector containing the potential and current at each node.

Finally, the system is solved iteratively. In this way, the value of the potential can be calculated across the network for a known applied field. This leads to the total conductance of the lattice. In both numerical models, the system is treated as being periodic in terms of fiber placement. If a fiber extends beyond the boundary, it is allowed to reenter at the opposite side. Consequently, the fiber density remains constant for each simulation.

C. Electrical Transport

Because the fibers are long compared to their width, a dilute random array of fibers in a matrix could conceivably be arranged such that the fibers provide a direct conduction path between two contacts (either electrical or thermal). When a direct path is established, the network of fibers is said to conduct. As a result, the effective conductivity of the compound may appear more like that of the fiber material despite having low fiber densities. This argument suggests that the fiber laden compound could conduct at significantly lower densities than compounds with circular inclusions. Therefore, we have developed a simple conduction model based on the fiber connectivity. In this model, we assume the matrix does not contribute to the transport. Instead, only when the fibers create a conduction path will the transport be non-zero.

To compute the effective conductivity using the fiber network model, the fibers are placed randomly in the device. Between any two intersections that share a fiber, we create a resistor. A sample device with 4 fibers is shown in Figure 2. The resistance (R) depends on the material resistivity (ρ), length and width (diameter) of the fiber and reduces to

$$R = \frac{2\rho}{\pi a \alpha} \tag{7}$$

where the resistivity is the reciprocal of conductivity. Ohm's law (V=IR) is used to relate the current through the resistor to the potential across the resistor. Furthermore, at each intersection, we balance the currents to produce a linear system with the same number of unknown potentials and currents as equations. The applied voltage divided by the total current through the device gives the effective conductivity of the compound. The resistance network approach is valid when the conductivity ratio is small. This model should approach the percolation model for large fiber density but will predict zero conductivity depending on the network formed by the random placement of fibers. If there is no conductive path, then the conductivity is zero. This model can be used to identify the percolation threshold as well as predict the effective conductivity of the network.

IV. Results

Using the properties in Table I, we have constructed a study on the electrical and thermal transport of a two-terminal planar device that contains a compound material. The compound consists of a matrix with random placed fibers. The number and length of fibers is varied to determine the effects of the fiber-density parameter na^2 on transport. Note that the area density c can be deduced from the density parameter as

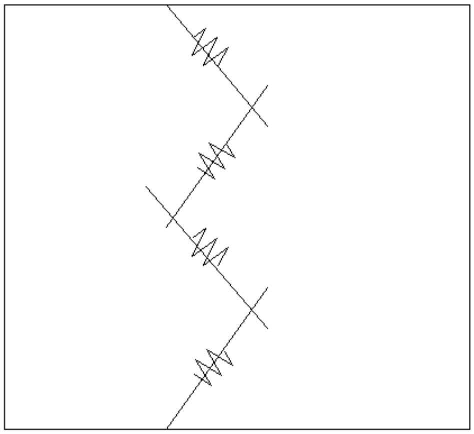

Fig. 2. Fiber network showing resistors

$$c \approx \frac{n\pi(L_f/2)^2}{L^2} = \frac{n\pi a^2 \alpha}{4} \quad (8)$$

where $a = L_f/L$ is the fiber length normalized by the square root of the device area ($L = \sqrt{A}$). In the present case, L is simply the length of a side of the square device. However, because our fibers have finite width, an approximation to the area density is more instructive, such that

$$c \approx \frac{nL_f w}{L^2} \quad (9)$$

where w is the fiber width. Note that neither equation 8 or 9 are exact because they do not consider overlap. Therefore, the approximation becomes worse for large numbers of fibers. Furthermore, the accuracy also depends on the aspect ratio $\alpha = wL_f$; for long thin fibers the overlap area between two intersecting fibers decreases as w^2, but the fiber area decreases as w.

Because fibers are placed randomly, several simulations were performed, results were averaged to obtain a representative conductivity. In the case of a compound whose conductivity ratio is large (fiber conductance is much larger than the matrix), the variation in predicted compound conductance can be orders of magnitude. A simple average will prefer values at the high end of the range and mask the fact that many orientations will result in nearly zero conductance.

The effective thermal conductivity as predicted by the discretized model is shown in Figure 3 and 4. The results are shown for $L_f = 1.0$ and 0.50. The horizontal error bars represent the variance in the fiber density which results from the amount of overlap due to the random placement of the fibers and the vertical error bars represent the variance in the calculated thermal conductivity. The blue line represents Maxwell's approximation for ellipsoidal geometry (eq 1) with an additional factor of $4/\pi$

$$\frac{k}{k_0} = \frac{1 - \beta c 4/\pi}{1 + \beta c 4/\pi} \quad (10)$$

which accounts for the difference in area between fibers with $r \to 0$ and inclusions with ellipsoidal geometry.

Both the numerical and analytic model are in very good agreement at low fiber density. However, it is interesting to note that Maxwell's model predicts lower conductivity at higher pixel densities. The reason for the discrepancy is Maxwell's model does not account for fiber overlap. This result corresponds well with observed low percolation thresholds observed in CNT/epoxy compounds [2].

The electrical conductivity is shown in Figure 5 and 6. Higher conductivity is predicted for longer fibers and the device percolates at c≈0.10 for $L_f = 1$. In contrast, the compound did not percolate until $c \approx 0.18$ for $L_f = 0.5$ (Figure 5). The numerical models agree well with Eq 5 but predict lower conductivities for higher fiber densities.

The results of this model correlates well with the analytical model, however, fibers with shorter length and systems with low fiber density are often problematic due to the fact low density systems often yield non-invertible singular matrices. Consequently, solutions are difficult to obtain for dilute systems. The fiber network model could not be used to predict thermal transport because the matrix/fiber conductivity ratio is only a few orders of magnitude. Therefore, thermal transport was predicted using a discretized model which superimposes a square mesh on top of the device and placed a resistor between every two nodes. The conductivity is calculated using a system of linear equations which obey Kirchoff's law. The discretized model correlates well with the analytical model for low fiber densities, but underestimated the conductivity at higher fiber densities.

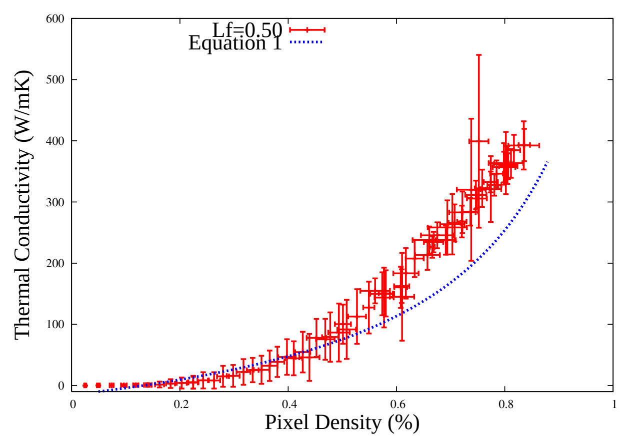

Fig. 3. Thermal Conductivity for Lf=0.5

The Lorenz number (L) is the ratio of thermal to electrical conductivity and a plot of L vs. pixel density is shown in

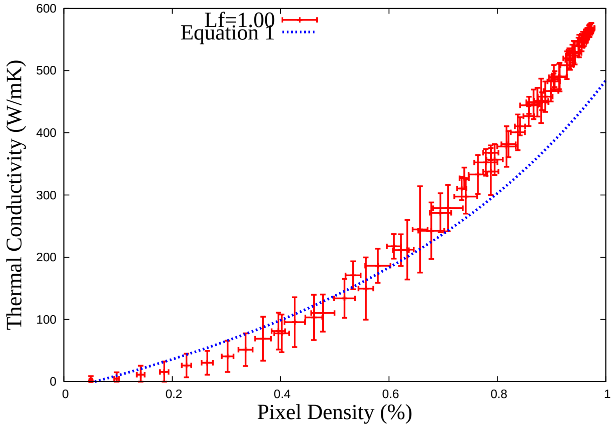

Fig. 4. Thermal Conductivity for Lf=1

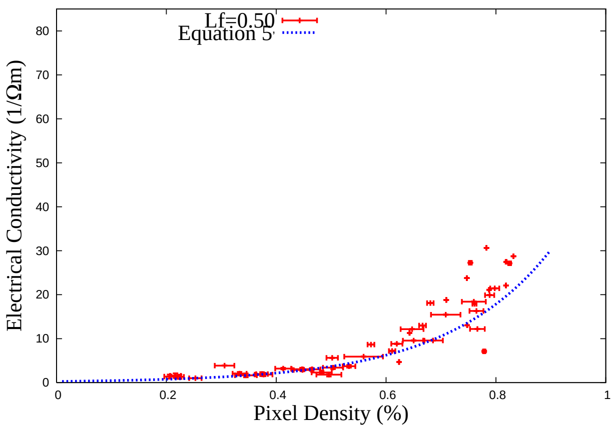

Fig. 5. Electrical Conductivity for Lf=0.5

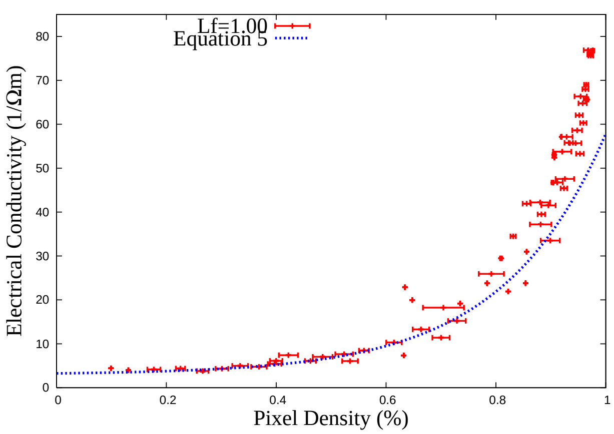

Fig. 6. Electrical Conductivity for Lf=1

Figure 7. Since L is not constant, the models presented in this work show that thermal and electrical properties can be predicted and decoupled for the design of electronic devices.

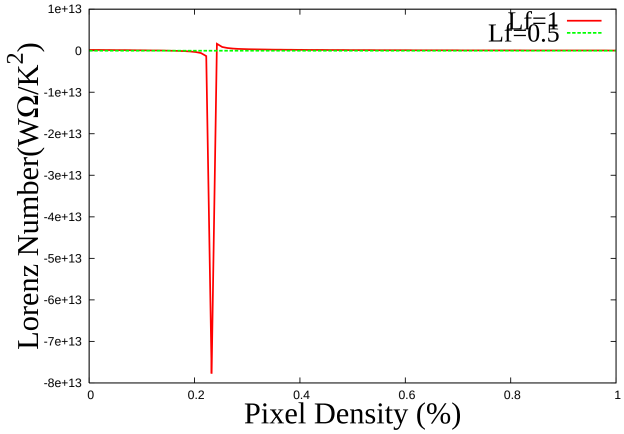

Fig. 7. Lorenz number as a function of pixel density

V. Conclusion

Effective thermal and electrical transport through randomly-oriented conducting fibers in a non-conducting matrix was predicted using analytical and numerical methods. Analytical solutions were obtained by calculating the effective conductivity of a matrix with ellipsoidal geometry using an effective medium approximation. This model works well for dilute systems with low fiber density. However, this model does not account for fiber-fiber overlap and therefore under-predicts the conductivity for systems with high fiber density. Numerical methods must be used in order to determine conductivity for non-dilute systems. Electrical transport was predicted by assuming that the matrix does not contribute to transport and that the system will conduct when a direct path fibers is established between contacts. The conductivity is calculated by placing a resistor between two fiber-fiber intersections and using a system of linear equation which obey Ohm's law to predict the resistance of the system. The results of this work show that thermal and electrical properties can be decoupled to predict material properties for fiber-polymer thin film devices and thermoelectric devices. For example, thin-film transistors require high thermal conductivity and high electrical conductivity. However, the device must be designed with maximum flexibility. Our results can be used to predict an optimum thermal and electrical transport without sacrificing the flexibility of the TFT. Decoupling transport properties would also be advantageous for the design of thermoelectric devices which require low thermal conductivity and high electrical transport without increasing the value of the Seebeck coefficient.

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