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A statistical model for effective thermal conductivity of composite materials

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Thermal interface materials composed of polymers and solid particles of high thermal conductivity have been used widely in electronic cooling industries. However, theoretical prediction of effective thermal conductivity of the composites remains as a crucial research topic. Theoretical modelings of the effective thermal conductivity of composites were based mainly on the analog between electric and thermal fields that satisfy Laplace equation under steady condition. Two approaches were employed, either by solving the Laplace equation or by equating the composite to a circuit network of conductors. In this study, the existing models obtained from these two approaches are first briefly reviewed. However, a close examination of the second approach reveals that there exists a paradox in this approach. To resolve this paradox, a statistical approach is then adopted. To this end, a mesoscopic ensemble that contains microscopic states is first constructed. The thermal conductivities of the microstates are identified by the principle of least action. A statistical parameter for each microstate is identified to characterize the effect of interface resistance on heat flow, as well as the connection between microstates. Effective thermal conductivity of the ensemble was then obtained from the variation principle that minimizes the standard deviation with optimal distribution of the parameter. The predictions by the present statistical model fit to experimental data with excellent agreement.

1. Introduction

As the size of electronic and micromechanical devices decreases continually, how to dissipate heat efficiently has received great concerns. Generally, the methods for effective heat dissipation are by using heat sinks, radiators, fans, thermoelectric devices, heat pipes, convective micro-channels [1–6] and so forth. For electronic components in direct contact, the existence of air interspaces is inevitable since the component surfaces can never be perfectly smooth. As the thermal conductivity of air is merely 0.024 W/m K (at 0 °C), the existence of interspaces creates a thermal barrier, called contact resistance, that greatly lowers the efficiency of heat transfer. To decrease the contact resistance, thermal interface materials (TIMs) to fill the interspaces are commonly used. Polymer-matrix composites (PMCs) used as TIMs are nothing new and are becoming important materials for electronic cooling. A variety of high conductivity materials (such as boron nitride, aluminum nitride, carbon nanotube, graphene, graphite, aluminum, and aluminum oxide [7–14]) are chosen as additive fillers in PMCs to increase the thermal (or electrical) conductivity, while boron nitride nanotubes (BNNTs) [15] were added to polyhedral oligosilsesquioxane (POSS) to further reduce the thermal expansion. Similarly, many kinds of polymers (such as epoxy resin, polyethylene, polybenzoxazine, polypropylene, and silicone rubber [16–20]) are chosen as matrix materials based on different mechanical properties. The determination of the thermal conductivity of composites, either experimentally or theoretically, then becomes a critical issue.

Theoretical treatment of heat conduction in composite materials is based traditionally on the mixture theory. The phase components of the composites are assumed to be locally in thermal equilibrium, so that the heat transfer in the composites can be regarded as equivalent to that of a single phase with an effective thermal

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conductivity. The problem then becomes construction of an appropriate model for effective thermal conductivity of the composites.

Considerable works had been devoted to the determination of effective thermal conductivities of composites, experimentally and theoretically. Although there were many experiments conducted with considerable data collected on the effective thermal conductivities of composites, theoretically modeling of effective thermal conductivities remains as a challenge nowadays, mainly owing to the lack of knowledge of interfacial properties. Most existing models on effective thermal conductivity were based on the analogy between electric conduction and heat conduction under steady condition where electric potential and temperature both satisfy the Laplace equation. Two approaches were generally adopted in the modeling. The first approach, as pioneered by Maxwell [21], examines the far-field spherical harmonic solution of Laplace equation caused by a spherical particle of conductivity different from the ambient. The effective conductivity is then determined by obtaining the equivalent far-field potential if the spherical particle is replaced with a sphere partially filled with many smaller spherical particles. The second approach is to regard the composite as a heterogeneous medium consisting of elements with different thermal conductivities that are connected into a circuit network. The effective thermal conductivity is then obtained by the evaluation of overall conductivity of the network.

In this study, we first give a brief review of the first approach and then focus on the second approach. For the second approach, the existing models that macroscopically simplify the circuit networks to layers in-parallel and in-series based on specific particle-matrix geometry are first examined. This also leads to a paradox on this second approach, where the predictions of effective thermal conductivity for a composite depend entirely on how many conductors are used and how they are connected. Hence, a statistical approach is adopted for modeling the effective thermal conductivity. To this end, an ensemble of mesoscale volume containing microstate volumes is firstly constructed. The conductivity of each microstate is then identified as the maximal conductivity based on the principle of least action. Corresponding to this maximal conductivity is a generalized interface parameter that characterizes the effect of interface on heat flow and the connection of the microstate to its neighbors. The effective thermal conductivity of the ensemble is then obtained by optimizing the distribution of the generalized interface parameter over the mesoscale volume based on the variation principle to minimize the standard deviation. It is found that the expression of the present statistical model of effective thermal conductivity bears some similarities to that of Agari and Uno [22] obtained unphysically from a macroscopic approach. However, the physical implications between the two are quite different. The predictions by present statistical model were fitted to the experimental data obtained recently by Gao et al. [23] with excellent agreement.

2. Review of models on effective thermal conductivity

In this section, existing models on effective thermal conductivity are reviewed. Those based on the first approach that solves directly the Laplace equation are only reviewed briefly. A slightly more detailed review is given to those of the second approach with networks, as they are closely related to the present study.

2.1. Maxwell's model and its extensions

Maxwell [21] derived the effective electric resistivity of a sphere containing N spherical particles based on theory of electric potential that satisfies the Laplace equation using the resistivity of continuum phase as the far field resistivity. By regarding the electric resistivity of the system of N spheres as having an equivalent resistivity of the single sphere, and from the analogy between electric potential and temperature of steady conduction, the effective thermal conductivity of composites was obtained as given by:

$$k_e = \frac{2k_f + k_s + 2\phi_s \cdot \left(k_s - k_f\right)}{2k_f + k_s - \phi_s \cdot \left(k_s - k_f\right)} \cdot k_f \tag{1}$$

where ϕ_s is the volume fraction of N particles, and k_e, k_f, k_s the thermal conductivities of composite, polymer matrix, particle fillers, respectively.

The predictions by Eq. (1) are found to be considerably lower than the experimental results of the effective thermal conductivities of composites, except at very low particle concentration [16,24].

Since the model was firstly proposed by Maxwell, there were several extensions to Maxwell model, to include the effects of particle concentration at high order [25], of interfacial resistance [26], and of nanoscale transfer [27]. These extended results recover Eq. (1) when the corresponding effects were removed. Most recently, Xu and Gao [28] revealed that there are several deficiencies in Maxwell model, namely, the non-uniqueness and the lack of phase-symmetry. Following the same procedure of Maxwell's in deriving Eq. (1) but using the effective thermal conductivity as the far field conductivity based on mean-field potential theory, they reconstructed the Maxwell model that circumvent these deficiencies. By further including thermal contact resistance between particles, the newly reconstructed Maxwell model becomes:

$$\frac{1}{k_{se}} = \frac{1}{k_s} + R_c \tag{2}$$

$$\frac{k_e - k_f}{2k_e + k_f}\phi + \frac{k_e - k_{se}}{2k_e + k_{se}}\phi_s = 0 \tag{3}$$

where R_c is contact thermal resistance between particles, k_{se} is the effective thermal conductivity of particles, and $\phi = 1 - \phi_s$. Eq. (3) bears the similarity to that of a self-consistent model. In other word, if the Maxwell approach is followed properly to construct the effective thermal conductivity of composites, the results of effective thermal conductivity will recover that of the self-consistent model.

2.2. Models based on circuit networks of conductors

There were considerable models for the effective thermal conductivity of composites based on circuit networks approach [22,29–35]. The models that are more relevant to the present work are reviewed in the followings.

(1) Models of layers in-series and in-parallel

The calculation of the effective thermal conductivity of composites based on the thermal-electric analog of circuit network of many conductors is complicated. Simplification of the network was usually employed. Deissler and Boegli [29] were among the first to simplify composites by disaggregating two phases into two layers with the interfaces being either in parallel or in perpendicular to heat flux direction. The effective thermal conductivities are given respectively by: