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Interface effect on thermal conductivity of carbon nanotube composites

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A simple formula for the thermal conductivity enhancement in carbon nanotube composites is presented by incorporating the interface thermal resistance with an effective medium approach. This model well describes the thermal conductivity enhancement observed recently in nanotube suspensions. In particular, this simple formula predicts that a large interface thermal resistance across the nanotube-matrix interface causes a significant degradation in the thermal conductivity enhancement, even for the case with ultrahigh intrinsic thermal conductivity and aspect ratio of the carbon nanotubes embedded. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1808874]

Carbon nanotube composites in which the carbon nanotubes are used as fillers to employ their unique physical properties have attracted ever increasing attention and is a promising direction in nanotechnology. For example, carbon nanotubes are used to reinforce polymers,[1–4] since the carbon nanotubes are much stronger and have larger aspect ratio than conventional carbon fibers. Recently, the carbon nanotubes were embedded into polymers or other media to get materials with good electrical and thermal transport properties.[5–7] Experiments show a significant increase in the thermal conductivity of organic fluids or polymers as filled with relatively low concentration of carbon nanotubes,[6,7] since the carbon nanotubes have unusually high thermal conductivity (e.g., 3000 W/mK for multiwalled carbon nanotubes[8] or even higher for single-walled nanotubes[9]). This is very technologically important for thermal management. In these carbon nanotube filled organic fluids or polymers, the nanotube-matrix interface is of particular interest. More importantly, one very recent experiment on interfacial heat flow in carbon nanotube suspensions by the Cahill and Keblinski group[10] reports the first measurement on the interface thermal conductance (or interface thermal resistance) across the nanotube-matrix interface, and the heat transport in the nanotube composites will be limited by the small interface thermal conductance. Thermal transport behavior in such carbon nanotube suspensions/composites is theoretically intriguing, and a complete theoretical analysis of the thermal transport behavior of these carbon nanotube media is still missing. In this letter, we present understanding of the interface effect in the thermal behavior of the nanotube composites.

The interface thermal resistance (i.e., the reciprocal of the interface thermal conductance) is now known as the Kapitza resistance, R_K, and defined by the heat flux, Q, and the temperature drop, ΔT, across the interface, as $Q \approx \Delta T/R_K$. The interface thermal resistance across the carbon nanotube matrix reported by the Cahill and Keblinski group[10] is about 8.3×10^{-8} m^2 K/W. This R_K value is of the same order of magnitude as those in other composite materials[11] and polycrystals.[12] Thus the interface thermal resistance can also dramatically alter the effective thermal conductivity of the nanotube composites.

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For the nanotube composites with very small loading of nanotubes, the Maxwell–Garnett-type effective medium approach (EMA) is valid.[13] In the nanotube composites, the thermal conductivity K_c of the carbon nanotubes is much larger than that K_m of the matrix (e.g., organic fluids or polymers), and the aspect ratio p of the nanotubes is quite high, i.e., $p>1000$. According to the EMA,[11] the resultant effective thermal conductivity K_e of the nanotube composite with carbon nanotubes randomly dispersed in a matrix can be derived as

$$\frac{K_e}{K_m} = \frac{3 + f(\beta_x + \beta_z)}{3 - f\beta_x} \tag{1}$$

with

$$\beta_x = \frac{2(K_{11}^c - K_m)}{K_{11}^c + K_m}, \quad \beta_z = K_{33}^c/K_m - 1, \tag{2}$$

where f is the volume fraction of the nanotubes; K_{11}^c and K_{33}^c are, respectively, the equivalent thermal conductivities along transverse and longitudinal axes of a composite unit cell, i.e., a nanotube coated with a very thin interfacial thermal barrier layer (see Fig. 1), and can be expressed as[14]

$$K_{11}^c = \frac{K_c}{1 + \dfrac{2a_K}{d}\dfrac{K_c}{K_m}}, \quad K_{33}^c = \frac{K_c}{1 + \dfrac{2a_K}{L}\dfrac{K_c}{K_m}}, \tag{3}$$

where d and L $(p=L/d)$ are the diameter and length of the nanotubes, respectively; and a_K is a so-called Kapitza radius defined by

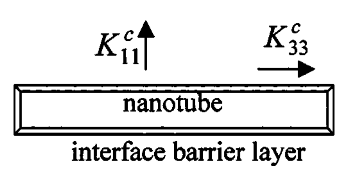

FIG. 1. Schematic illustration of a composite unit cell of a nanotube coated with a very thin interfacial thermal barrier layer. The transverse and longitudinal equivalent thermal conductivities, K_{11}^c and K_{33}^c, of this composite unit cell can be directly obtained from the mixture rule for a simple series model of this interface-barrier/nanotube/interface barrier, i.e., $1/K_{11}^c = 2R_K/d + 1/K_c$, and $1/K_{33}^c = 2R_K/L + 1/K_c$.

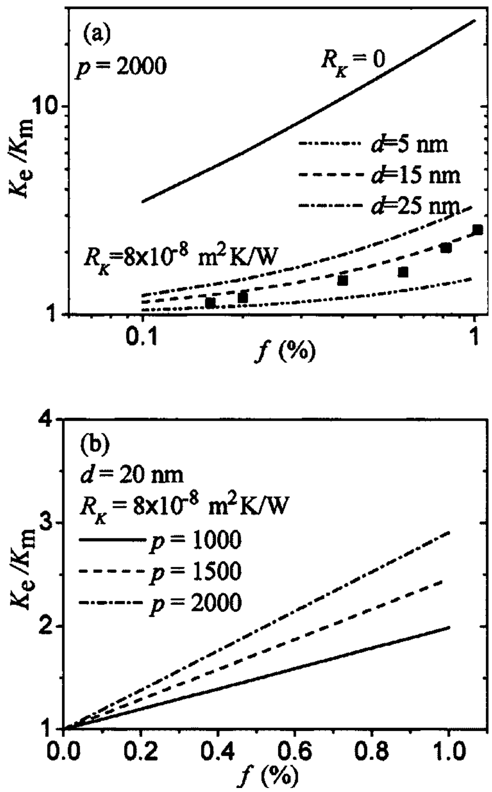

FIG. 2. The thermal conductivity enhancement in the carbon nanotube composites filled with a very small amount of nanotubes with different (a) diameters and (b) aspect ratios. Solid line in (a) is for the ideal case without the interface thermal resistance. K_c=3000 W/mK and K_m=0.4 W/mK. For comparison, the recent experimental results for the nanotube suspensions (see Ref. 7) (solid dots) are also shown.

$$a_K = R_K K_m. \tag{4}$$

For the nanotube composites, $a_K \sim 16$–40 nm when $K_m \sim 0.2$–0.5 W/mK and $R_K \sim 8 \times 10^{-8}$ m^2 K/W. Equation (1) is a desired EMA formulation for the thermal conductivity enhancement of the carbon nanotube composites, which contains the effects of the diameter, aspect ratio, and volume fraction of the nanotubes, interface thermal resistance, and thermal conductivity ratio K_c/K_m, on the effective thermal conductivity of the nanotube composites. In the dilute limit as in the carbon nanotube composites reported in the literature, e.g., $f < 0.01$, Eq. (1) for the thermal conductivity enhancement is simplified as

$$\frac{K_e}{K_m} = 1 + \frac{fp}{3} \frac{K_c/K_m}{p + \dfrac{2a_K}{d}\dfrac{K_c}{K_m}}. \tag{5}$$

This simple relation more clearly demonstrates that the interface thermal resistance degrades the thermal conductivity enhancement induced by the carbon nanotubes with high thermal conductivity.

For calculations and without loss of generality, we take K_c=3000 W/mK and K_m=0.4 W/mK. Figures 2 and 3 show some calculations. For comparison, a recent experiment on suspensions with carbon nanotubes ($d \sim 25$ nm and $p \sim 2000$) in an oil[7] is also shown in Fig. 2(a). The comparison shows good agreement between the calculated and observed thermal conductivity enhancement. The thermal conductivity enhancement decreases with decreasing diameter [Fig. 2(a)] and aspect ratio [Fig. 2(b)] of the nanotubes. As seen, the thermal conductivity enhancement induced by the carbon nanotubes without the interface thermal resistance would be much larger than that in the case with the interface thermal resistance [Fig. 2(a)]. In the case of both perfect interface without any interface thermal resistance and $p \gg 1$ as for the carbon nanotubes, the thermal conductivity enhancement is further expressed as[13]

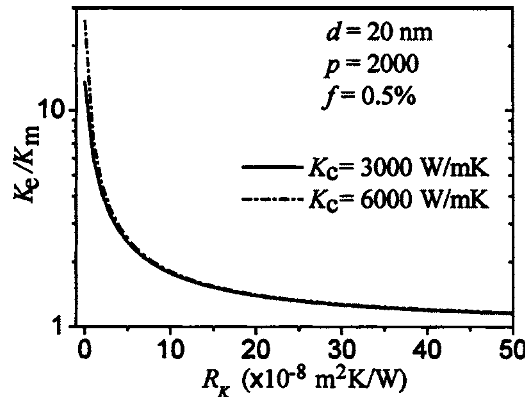

FIG. 3. Effect of the interface thermal resistance on the thermal conductivity enhancement in the carbon nanotube composites.

$$\frac{K_c}{K_m} = 1 + \frac{f}{3}\frac{K_c}{K_m}, \tag{6}$$

which is independent of geometric parameters (d and p) of the nanotubes and simply proportional to the thermal conductivity ratio K_o/K_m. Thus large K_o/K_m ($\sim 10^4$) should have led to much larger thermal conductivity enhancement than observed in experiments. However, the presence of a large interface thermal resistance across the nanotube-matrix interface causes a significant decrease in the thermal conductivity enhancement as observed in experiments.

Figure 3 more clearly shows this dramatic degradation in the thermal conductivity enhancement induced by the interface thermal resistance. This dramatic degradation in the thermal conductivity enhancement occurs mainly within the region of $R_K < 10^{-7}$ m^2 K/W. As $R_K > 10^{-7}$ m^2 K/W, the thermal conductivity enhancement is quite low. The calculations show that the thermal conductivity enhancement is already very insensitive to high thermal conductivity K_c when $R_K \geqslant 10^{-8}$ m^2 K/W. This means that the single-walled nanotubes with high thermal conductivity (e.g., K_c =6000 W/mK[9]) do not induce larger thermal conductivity enhancement in the nanotube composites than the multiwalled nanotubes with a bit low thermal conductivity (e.g., K_c=3000 W/mK or lower[8]) when $R_K \sim 8 \times 10^{-8}$ m^2 K/W as reported. By contrast, the single-walled nanotubes would induce even lower thermal conductivity enhancement in the nanotube composites than the multiwalled nanotubes, due to smaller diameters of the single-walled nanotubes than the multiwalled nanotubes [Fig. 2(a)]. In comparison with the nanotube suspensions, solid nanotube composites could exhibit more lower thermal conductivity enhancement due to processing challenges and poor nanotube dispersion.

In summary, a simple equation for predicting the effective thermal conductivity of the nanotube composites has been developed in terms of an effective medium approach incorporated with the interface thermal contact resistance. Comparison with recently reported experiment for the nanotube suspensions illustrates good validity of the simple model for the thermal conductivity enhancement in the nanotube composites. In particular, the model shows that the thermal conductivity enhancement in the nanotube composites is mainly limited by the interface thermal resistance. A large interface thermal resistance across the nanotube-matrix interface causes a significant degradation in the thermal conductivity enhancement, and in this case, the single-walled nanotubes with even higher intrinsic thermal conductivity would induce even lower thermal conductivity enhancement in the nanotube composites than the multiwalled nanotubes.

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[14]The transverse equivalent conductivity K_{11}^c was given in Ref. 11, which is just the result of the mixture rule for a simple series model of the interface-barrier/nanotube/interface barrier along the transverse axis of the composite unit cell (Fig. 1). Similarly, the longitudinal equivalent conductivity K_{33}^c can be given also by the mixture rule for the simple series model of the interface-barrier/nanotube/interface barrier along the longitudinal axis of the composite unit cell (see Fig. 1). This K_{33}^c is a little different from that given previously in Ref. 11, but is more reasonable than that in Ref. 11, especially more valid for the very long (e.g., $p \gg 1$) cylinder-shaped unit cell randomly dispersed in a matrix as in the present case. That K_{33}^c in Ref. 11 is valid for the ellipsoidal composite unit cell with not much large p or long cylinder-shaped unit cell continuously aligned in a matrix.