Thermal conductivity enhancement of carbon nanotube composites: A simple model containing the anisotropy, aspect ratio and non-straightness of carbon nanotubes

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ABSTRACT

Simple and analytical models for thermal conductivity for randomly oriented distribution CNT composites were presented as analytical functions of volume fraction, anisotropic thermal conductivities, aspect ratio, non-straightness, and interfacial thermal resistance of the CNTs. Moreover, using the interaction direct derivative (IDD) micromechanics scheme, we have incorporated interactions between included CNTs and gained non-linear volume fraction dependence of thermal conductivity enhancement which agreed quite well with the observed data. Based on the analysis, it is an efficient means using CNTs as straight as possible with aspect ratio high enough to get much higher thermal conductivity enhancement of CNT composites.

Keywords: thermal conductivity, carbon nanotube composites, anisotropy, aspect ratio, non-straightness

1 INTRODUCTION

Shrinking size of electronic and micromechanical devices has raised increasing interest in superb material such as carbon nanotubes (CNTs). As a kind of carbon-based material, CNTs display a supreme measured thermal conductivity than many known materials at moderate temperatures. For example, the axial thermal conductivity of CNTs observed was extremely high, about 2000W/mK [1] or more than 3000W/mK [2] for multi-walled CNTs and even higher for single walled CNTs [3], [4]. Recently, CNTs have been embedded into polymers or other medium to get much better thermal conductivity materials, such as CNT-in-oil suspensions and CNT-in-polymer composites, whose thermal conductivities were found to be significantly improved [5], [6] up to, for example, a 150% increase at 1% volume fraction of CNTs [6]. A good and overall understanding of this issue is essential in management of thermal conductivity of CNT composites.

Several theoretical predictions on the thermal conductive enhancements of CNT composites have been proposed in the literatures, as summarized in Table 1 with detailed explanations to be gradually given later. Compared with the experimentally observed data [6], the Model-I predictions [6], [7] based on the thermal isotropy and spherical inclusion assumptions for the CNTs terribly underestimated the thermal conductivity enhancements, while the Model-II predictions [8] by taking account of thermal isotropy and very large aspect ratios of CNTs exaggerated too much the enhancements. Further, some improved predictions (e.g. Model-III [9], typically) were proposed incorporating with an interfacial thermal resistance [10]-[12].

Model	CNTs	$\frac{k}{k_\mathrm{m}}$
I [6],[7]	isotropic, spherical	$1+3f$
II [8]	isotropic, $L/d\to\infty$	$1+\frac{f}{3}\frac{k_\mathrm{c}}{k_\mathrm{m}}$
III [9]	isotropic, $L/d\to\infty$, with interface	$1+\frac{f}{3}\frac{k_{33}^{\mathrm{cs}}}{k_\mathrm{m}}$
Our	anisotropic, finite $L/d=p$, Non-straightness η with interface	$1+\frac{\eta f/3}{(k_{33}^{\mathrm{cs}}/\eta k_m-1)^{-1}+H(\eta p)}$

Table 1. Predictions of thermal conductive enhancements in CNT composites.

However, we know of no studies that agree well enough with the observations. Not only the previous studies mostly give underestimated [6] or overestimated [8] predictions of the overall thermal conductivity of CNT composites, but also the predicted linear dependence of thermal conductivity enhancement on volume concentration does not agree with the observed nonlinear relationship. To understand these inconsistencies and give a much better prediction for this important issue, we note that several important factors have been neglected in the previous predictions.

Firstly, it is noted that all the models proposed so far were based on the isotropy assumption for the thermal conductivity of CNTs, while the thermal conductivity of graphite is known to be highly anisotropic. The measured thermal conductivities of graphite in the basal plane,

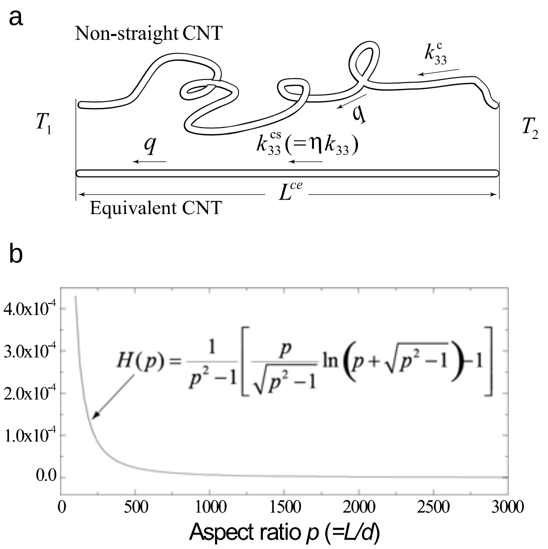

Figure 1. (a)A schematic illustration of the non-straight CNT and its straight equivalent. (b) Dependence of $H(p)$ on the aspect ratio p (= L/d).

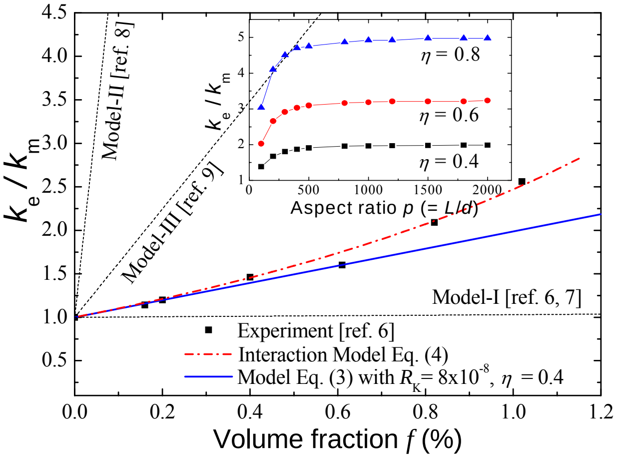

Figure 2. The measured and predicted thermal conductivity enhancements of the composites filled with low loadings of CNTs. The same parameters (k_c = 2000 W/mK, k_m = 0.1448 W/mK and p = 2000) in the experiments are used in the predictions with R_K = 8×10^{-8} m^2 K/W and η = 0.4. The insert depicts the effects of aspect ratio p and straightness ratio η on thermal conductivity enhancement based on the model Eq. (3).

ranging from 940 to 2000 W/mK, is about 2 orders larger than those normal to the basal plane (between 5 and 20 W/mK [13]). For highly oriented pyrolytic graphite, the ratios of the basal to the normal thermal conductivities can be even larger [14]. Since MWNTs have a curled graphite structure, it is expected that their axial and transverse thermal conductivities would be similar to those of the graphite basal and normal ones and thus be quite different, because of the very weak van der Waals interwall interaction. Indeed, there have been molecular simulations [15] that predicted the axial and transverse thermal conductivities of CNT bundles to be very closed to the basal and normal ones of graphite, although there have been no measurements of the radial thermal conductivity of CNTs. Regarding to the thermal anisotropy, we may need to further claim an exception that the radial thermal conductivity of individual single-walled carbon nanotubes may be much larger than those of MWNTs because the former have no wall-to-wall interaction. Anyway, the effect of thermal-conductivity anisotropy of CNTs on the thermal conductivity enhancement of CNT-composites, which is often neglected or simplified in previous predictions, should be examined.

Secondly, microscopic observations show that well-dispersed and lowly loaded CNTs in composites are often far from being straight due to their high aspect ratio. For a non-straight CNT as schematically illustrated in Fig. 1(a), the high thermal anisotropy ($k_{11}^{c}/k_{33}^{c} \ll 1$, where k_{33}^{c} and k_{11}^{c} denote the axial and transverse thermal conductivities of the CNTs separately) of CNTs induces a unique property that individual CNTs are nearly perfect one-dimensional thermal cables with negligibly small thermal flux losses during long distance thermal conductions. For a non-straight CNT with length L under a two-end temperature difference, ΔT = T_2 − T_1, as illustrated in Fig. 1(a), the thermal flux q is equal to $k_{33}^{c}\,\Delta T/L$ because of the thermal cable property of the CNT. We can further regard this CNT as an equivalent straight thermal cable such that the same thermal flux q is conducted (Fig. 1(a)) between the two ends of the CNT in the distance L^{ce} instead of L, and η = L^{ce}/L is used to denote the non-straightness ratio.

Furthermore, very recently the Cahill and Keblinski group [10] reported the first measurement on the interface thermal conductance (or interface thermal resistance) across the nanotube-matrix interface, and found that the heat transport in the nanotube composites is limited by the interface thermal resistance. While, a recent theoretical study [16] further showed that the effective thermal conductivity is affected much by the tube-end heat transport property, rather than the thermal contact resistance on the lateral surfaces of the CNTs. We note that an interesting and important function of the lateral interfacial thermal resistance is to further reduce the transverse thermal conductivity to a lower level k_{11}^{cs} than the k_{11}^{c}, thus improve the thermal cable property of CNTs. The influence of the tube-end thermal resistance can be reflected by modifying the k_{33}^{c} with the effective $k_{33}^{cs}=k_{33}^{c}/(1+2R_K k_{33}^{c}/L)$, where the Kaptiza resistance R_K = 8×10^{-8} m^2 K/W [10]-[12].

The above analyses raise the need to systematically examine the effects of the thermal- conductivity anisotropy, aspect ratio, non-straightness and thermal resistance of CNTs on the effective thermal conductivities of CNT-composites, and also indicate reasonable methods to deal with these issues.

2 THEORETIC PREDICTION AND ANALYSIS

Based on the above analysis, we first give an analytical model of thermal conductivity for CNT-composites with low densities of randomly distributed CNTs. Because of no measured transverse thermal conductivities available for CNTs, we use the data for graphite in our model [13]. For CNT composites with low loadings of randomly oriented straight CNTs of average length L and diameter d, an analytical estimate for the effective thermal conductivity, k_{e}, of the CNT composites can be given in the following form [17], [18]:

$$\frac{k_{\mathrm{e}}}{k_{\mathrm{m}}} = 1 + \frac{\eta f}{3}\left(\frac{1}{(\eta k_{33}^{\mathrm{cs}}/k_{\mathrm{m}} - 1)^{-1} + H(\eta p)} + \frac{2}{(k_{11}^{\mathrm{cs}}/k_{\mathrm{m}} - 1)^{-1} + (1 - H(\eta p))/2}\right), \quad (1)$$

where f denotes the volume fraction of the CNTs, k_{m} denotes the thermal conductivity of the isotropic matrix, and H reflects the influence of the effective aspect ratio, $\eta p = \eta L/d$, in the form

$$H(\eta p) = \frac{1}{(\eta p)^2 - 1}\left[\frac{\eta p}{\sqrt{(\eta p)^2 - 1}}\ln\left(\eta p + \sqrt{(\eta p)^2 - 1}\right) - 1\right]. \quad (2)$$

It is important to note that the analytical expression Eq. (1) is precise up to the first order of f as $f \to 0$, and it takes account of the thermal conductivity anisotropy, aspect ratio, non-straightness and thermal resistance of the CNTs through the effective thermal conductivity anisotropy (dimensionless parameters $\eta k_{33}^{\mathrm{cs}}/k_{\mathrm{m}}$ and $k_{11}^{\mathrm{cs}}/k_{\mathrm{m}}$) and effective aspect ratio (ηp). We note that the non-straightness, represented by the ratio η, contribute to both the effective thermal conductivity anisotropy ($\eta k_{33}^{\mathrm{cs}}/k_{\mathrm{m}}$ and $k_{11}^{\mathrm{cs}}/k_{\mathrm{m}}$) and the effective aspect ratio (ηp) of CNTs.

The function $H(\eta p)$ monotonously decreases from 1/3 to 0 as effective aspect ratio ηp changes from 1 (for regarding effective CNTS as spherical inclusions) to ∞ (for modelling effective CNTs as infinitely long fibres). In fact, typical CNTs have aspect ratios in the order of 1000 or even larger. We note that the values of k_{m} = 0.1448 W/mK and k_{33}^{c} = 2000 W/mK estimated in the experiments [6] lead to a very small quantity of $(\eta k_{33}^{\mathrm{cs}}/k_{\mathrm{m}} - 1)^{-1}$ about 10^{-5} in the order. Meanwhile, the values of H can be similar small, with ranging from 1.0×10^{-4} to 1.0×10^{-6} as increasing p from 230 to 2800, as shown in Fig. 1(b). Therefore, the H in the denominator of the first term in the square bracket in Eq. (1) can have notably contribution while the whole second term in the square bracket is 4 orders smaller than the first term and thus negligible. The above analyses yield the following excellent approximation of Eq. (1)

$$\frac{k_{\mathrm{e}}}{k_{\mathrm{m}}} = 1 + \frac{\eta f/3}{k_{\mathrm{m}}/\eta k_{33}^{\mathrm{cs}} + H(\eta p)}. \quad (3)$$

Interestingly, the Eq. (3) becomes the so-called Model-III prediction [9] ($k_{\mathrm{e}}/k_{\mathrm{m}} = 1 + (f/3)(k_{33}^{\mathrm{cs}}/k_{\mathrm{m}})$) by assuming the thermal isotropy and ideal CNTs (ηp =1 and H = 1/3). Further assuming no thermal resistance, we obtain the so-called Model-II prediction [8] ($k_{\mathrm{e}}/k_{\mathrm{m}} = 1 + (f/3)(k_{33}^{\mathrm{c}}/k_{\mathrm{m}})$). The Model-I [6], [7] ($k_{\mathrm{e}}/k_{\mathrm{m}} = 1 + 3f$) can even be deduced from the Eq. (3) with the spherical inclusions supposition.

To analyze in more details the effects of aspect ratio and non-straightness, we plot in Figure 2 the predicted values $k_{\mathrm{e}}/k_{\mathrm{m}}$ by the refined model (Eq.3) versus the volume fractions f of the CNTs in comparison with the recent experimental data [6] as well as the predictions by Models I-III. In these predictions, the same values of k_{m} = 0.1448 W/mK, k_{33}^{c} = 2000 W/mK and $p \approx 2000$ (corresponding to the average CNT length of 50 μm and diameter of 25 nm) as the measured ones in the experiments [6] are adopted. The results shown in Figure 2 indicate that the prediction from the present model Eq. (3) with η = 0.4 and the Kaptiza resistance $R_{\mathrm{K}} = 8\times10^{-8}$ m^2 K/W can agree well with the measured thermal conductivity enhancements. The further results shown in the insert of Figure 2 indicate that both larger straightness ratios η and larger aspect ratios p lead to better thermal enhancement effects, and the enhancement effects tend to be saturated for larger p than 500.

Finally, using the interaction direct derivative (IDD) micromechanics scheme [18], we take account of the interactions between included CNTs and obtain the non-linear volume fraction dependence of thermal conductivity enhancement, which agrees quite well with the observed data [6] (Fig. 2):

$$\frac{k^{\mathrm{IDD}}}{k_{\mathrm{m}}} = 1 + \left[1 - H(q)\left(\frac{k_{\mathrm{e}}}{k_{\mathrm{m}}} - 1\right)\right]^{-1}\left(\frac{k_{\mathrm{e}}}{k_{\mathrm{m}}} - 1\right), \quad (4)$$

where $k_{\mathrm{e}}/k_{\mathrm{m}}$ is the non-interaction estimate given by Eq. (3), $H(q)$ is the function of q in the form Eq. (2), with q = 1 [18], [19] corresponding to the random or isotropic distribution. The very good nonlinear enhancement prediction shown in Figure 2 indicates that the interaction effect among CNTs can be notable even though for very low loadings of CNTs.

With our model, the corresponding analytical formulae for the axial and transverse thermal conductivity enhancements for CNT composites with aligned straight CNTs in unique direction (x_3-axis) distribution can also be induced as follows,

$$\frac{k_{33}}{k_{\mathrm{m}}}=1+\frac{f}{k_{\mathrm{m}}/k_{33}^{\mathrm{c}}+H},\frac{k_{11}}{k_{\mathrm{m}}}=1+\frac{f}{(k_{11}^{\mathrm{c}}/k_{\mathrm{m}}-1)^{-1}+(1-H)/2}. \quad (5)$$

The axial enhancement, $k_{33}^{\mathrm{e}}/k_{\mathrm{m}}-1$, with the aligned CNTs is three times of that with the randomly oriented CNTs, while the transverse enhancement, $k_{11}^{\mathrm{e}}/k_{\mathrm{m}}-1$, is 4 orders in magnitude smaller than $k_{33}^{\mathrm{e}}/k_{\mathrm{m}}-1$.

3 CONCLUSIONS

In conclusion, we have presented simple analytical formulae for predicting the effective thermal conductivity of CNT composites with relatively low loadings and analysis factors that affects the enhanced thermal conductivity by taking into account of anisotropy, aspect ratio, non-straightness, and thermal resistance of the CNT. The excellent agreements between the measured data and the predicted ones using these formulae indicate that the finite aspect ratios and non-straight geometries of the CNTs as well as the tube-end thermal resistance have the dominant influences to the effective thermal conductivity properties of CNT composites, rather than the lateral interfacial thermal resistance. It is further shown that the previously observed nonlinear behavior on the enhancements versus low loadings of CNTs is attributed to an interaction effect among CNTs. Based on the analysis, it is an efficient means using CNTs as straight as possible with aspect ratio high enough to get much higher thermal conductivity enhancement of CNT composites.

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