RAPID COMMUNICATION

Modeling of thermal conductivity for disordered carbon nanotube networks

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Several theoretical models have been developed so far to predict the thermal conductivities of carbon nanotube (CNT) networks. However, these models overestimated the thermal conductivity significantly. In this paper, we claimed that a CNT network can be considered as a contact thermal resistance network. In the contact thermal resistance network, the temperature of an individual CNT is nonuniform and the intrinsic thermal resistance of CNTs can be ignored. Compared with the previous models, the model we proposed agrees well with the experimental results of single-walled CNT networks.

Keywords: thermal conductivity, carbon nanotube networks, contact thermal resistance

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In 2001, the thermal conductivity of carbon nanotubes (CNTs) was reported to be higher than 3000 W/(m·K) at room temperature.[1] This extremely high thermal conductivity of CNTs has motivated a wealth of research on the applications of CNTs.[2] However, experiments carried out by Prasher *et al.*[3] showed that the thermal conductivity of the three-dimensional (3D) random networks of CNTs can be lower than 0.2 W/(m·K). The unexpectedly low thermal conductivities of CNT networks were verified later by other groups.[4–6] For example, Yang *et al.*[4] demonstrated that the thermal conductivity of single-walled CNT (SWCNT) networks is 0.142 W/(m·K), and can be reduced further to 0.057 W/(m·K) as the density of networks reduces from 0.217 g/cm^3 to 0.097 g/cm^3.

This ultralow thermal conductivity of CNT networks has been attributed to both the large contact thermal resistance between CNTs and the high porosity of CNT networks.[3–5] When only the porosity is considered, the thermal conductivity of a CNT network $k_{\rm net}$ can be written as[3,7]

$$k_{\rm net} = \frac{1}{3} k_{\rm CNT} \phi, \tag{1}$$

where $k_{\rm CNT}$ is the thermal conductivity of an individual CNT, and ϕ is the volume fraction of the CNTs in the network. If $\phi = 15\%$, $k_{\rm net} = k_{\rm CNT}/20$, which is ~ 1000 times larger than the experimental results.[3] This may suggest that the contact thermal resistance between CNTs should be far larger than the intrinsic thermal resistance of CNTs in the network, and we can simplify the thermal transport model of CNT networks by ignoring the intrinsic thermal resistance of CNTs.

Ignoring the intrinsic thermal resistance of CNTs may imply that $k_{\rm CNT}$ is infinitely large and the temperature on each CNT is uniform. Under this assumption, Chalopin *et al.*[8] and Volkov *et al.*[9] proposed models to describe the thermal transport in CNT networks. However, both the two models unexpectedly overestimate the thermal conductivity of CNT networks. For example, if the intertube contact thermal conductance $G_{\rm c} = 50$ pW/K is used,[3] the $k_{\rm net}$ given by Chalopin's model is ~ 30 times larger than the experimental results reported in Ref. [3], the $k_{\rm net}$ given by Volkov's model[9] is even 4 orders of magnitude larger than the experimental results.

It should be emphasized that the high value of $k_{\rm net}$ given by the above models is not due to the larger $G_{\rm c}$ used in the calculations. In fact, $G_{\rm c} = 50$ pW/K was obtained from molecular dynamics and atomistic Green's function simulation on two (10, 10) SWCNTs forming a cross contact,[3] and is lower than the values reported by others.[10,11] It has been verified by experiments[12] and simulations[10] that the contact thermal conductance can be increased by increasing the inter-tube contact area. When the contact form changes from cross contact into aligned contact, $G_{\rm c}$ can be increased by nearly two orders of magnitude.[10–12] For example, the $G_{\rm c}$ between two (10, 10) SWCNTs lies in the range of 10^2–10^4 pW/K due to the different contact configurations.[10]

Later, Volkov and Zhigilei attributed the overestimation of the thermal conductivity of CNT networks to the absence of the intrinsic thermal resistance of CNTs from the models,[13] and they proposed a revised model to include the intrinsic thermal resistance of CNTs. A similar model was also proposed by Zhao *et al.*[7] to predict the thermal conductivity of nanofiber

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networks. However, the k_{net} given by the revised model is still more than 400 times larger than the experimental results. Meanwhile, the strong effect of the k_{CNT} on the k_{net} is also counter-intuitive, since the thermal resistance of one inter-tube contact is averagely equivalent to the thermal resistance of a CNT segment of 59 μm in length.[13]

In this paper, a simple model is proposed to describe the thermal conductivity of CNT networks. In the proposed model, the temperature of an individual CNT is nonuniform, but the intrinsic thermal resistance of CNT can be ignored. The thermal conductivities of some 3D random CNT networks with various densities are evaluated with the proposed model and compared with the experimental results. The calculated results agree well with the experiment values.

In order to figure out the reasons why all the models mentioned above[8,9,13] overestimate the thermal conductivity of CNT networks, and find a clue to revise the models, we first evaluate the number density of the inter-tube contacts $n_{c/V}$. $n_{c/V}$ is the contact number per volume. The value of $n_{c/V}$ can be estimated via 3D x-ray scanning,[14] electron tomography technique,[15] Monte Carlo simulations,[16] or the excluded volume approach.[9,17] In this paper, we use the excluded volume approach to evaluate $n_{c/V}$. Comparing with experimental and simulation methods, the excluded volume approach can give us an analytical expression of $n_{c/V}$ which can be used to construct the theoretical model. The excluded volume approach has also been proved as a robust method for predicting fiber-to-fiber contacts in high-aspect-ratio fiber networks.[18]

The excluded volume of an object is defined as the volume around the object into which the center of another similar object is not allowed to enter if overlapping of the two objects is to be avoided.[17] In the excluded volume method, we consider CNTs as capped cylinders of length L and diameter D, as shown in Fig. 1(a). To simplify the calculation, the "soft-core" assumption is adopted,[9] i.e., the capped cylinders can freely intersect with each other. Under this assumption, the excluded volume is a capped parallelepiped, as shown in Fig. 1(b).[17] The base area of the parallelepiped is $L^2 \sin\gamma$ when the angle between two capped cylinders is γ. The height of the parallelepiped is $2D$. The parallelepiped is capped by four half-cylinders of radius D and length L, and by four spherical sectors of radius D. The four spherical sectors add up to a full sphere, and the total volume of the four spherical sectors is $4\pi D^3/3$. Therefore, the excluded volume $V_{ex,\gamma}$ is given by[17]

$$V_{ex,\gamma} = 2DL^2 \sin\gamma + 2\pi D^2 L + \frac{4}{3}\pi D^3. \tag{2}$$

If we assume that the CNT networks are homogenous and isotropic, the average of the excluded volume $V_{ex,\gamma}$ over γ can be written as

$$V_{ex} = \frac{1}{2}\pi DL^2 + 2\pi D^2 L + \frac{4}{3}\pi D^3. \tag{3}$$

In general, the last two terms on the right-hand side of Eq. (3) are far smaller than the first term for CNTs, due to that $D \ll L$. Therefore, $V_{ex} \approx \frac{1}{2}\pi DL^2$.

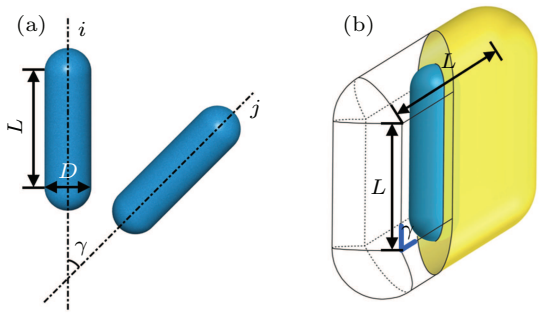


Fig. 1. (a) Schematic of the capped cylinders. (b) The shape of the excluded volume when the angle between two capped cylinders is γ.

In CNT networks, if the number density of CNTs is $n_{t/V}$, the number of CNTs being in the excluded volume of each CNT is $n_{t/V}V_{ex}$. Therefore, the average number of contacts on a CNT, $n_{c/t}$, is

$$n_{c/t} = n_{t/V}V_{ex}. \tag{4}$$

Since there are $n_{t/V}$ CNTs per volume, the number density of the inter-tube contacts can be written as

$$n_{c/V} = \frac{n_{t/V}n_{c/t}}{n_{t/c}}, \tag{5}$$

where $n_{t/c}$ is the number of CNTs forming one contact, and $n_{t/c} = 2$ for most cases. Substitute Eq. (4) into Eq. (5), we get

$$n_{c/V} = \frac{n_{t/V}^2 V_{ex}}{2}. \tag{6}$$

In this paper, we focus on SWCNT networks. In SWCNT networks, $n_{t/V}$ can be evaluated from

$$n_{t/V} = \frac{\rho_{net}}{\pi DL\rho_g}, \tag{7}$$

where ρ_{net} is the mass density of the SWCNT network, ρ_g is the surface mass density of graphene, and $\rho_g = 7.6 \times 10^{-7}$ kg/m^2.[8]

In this study, we will compare our calculation with the experiments results on SWCNT networks reported in Refs. [3,4]. Parameters of the SWCNT networks measured in Refs. [3,4] are listed in Table 1. The diameter D and length L of SWCNTs listed in Table 1 are the average values. For example, the diameter of SWCNT is 1–2 nm and the length is 5–15 μm in Ref. [3]. Therefore, $D = 1.5$ nm and $L = 10$ μm are used in our calculations. Taking sample 7 as an example and substituting the parameters of the sample 7 into the above equations, we get $n_{t/V} = 1.14 \times 10^{22}$ m^{-3}, $V_{ex} = 2.36 \times 10^{-19}$ m^3, $n_{c/t} = 2692$, and $n_{c/V} = 1.54 \times 10^{25}$ m^{-3}. Since there are 2692 contacts on each CNT, the distance between two neighboring contacts along a CNT is only 3.7 nm.

Table 1. Parameters of SWCNT networks.[3,4]

Sample	Ref.	D (nm)	L (μm)	$\rho_{\rm net}$ (kg/m^3)	$k^{\rm e}_{\rm net}$ (W/(m·K))
1	[4]	1.5	2	97	0.057
2	[4]	1.5	2	127	0.077
3	[4]	1.5	2	157	0.096
4	[4]	1.5	2	187	0.120
5	[4]	1.5	2	217	0.142
6	[3]	1.5	10	389	0.155
7	[3]	1.5	10	409	0.175
8	[3]	1.5	10	438	0.194

Many studies have been carried out to determine $G_{\rm c}$ between CNTs.[10–12] The reported values of $G_{\rm c}$ between two (10, 10) SWCNTs are in the range of 10^2–10^4 pW/K due to the different contact configurations.[10] Volkov and Zhigilei calculated the probability density function of $G_{\rm c}$ of (10, 10) SWCNT networks using mesoscopic simulations.[13] Based on the probability density function, the average $G_{\rm c}$ obtained is $\sim$ 900 pW/K. Since the diameter of (10, 10) SWCNT is 1.357 nm, slightly smaller than the average diameter $D =$ 1.5 nm listed in Table 1, and $G_{\rm c}$ increases with the tube diameter, we use $G_{\rm c} = 1000$ pW/K in the following calculations. We will prove later that $G_{\rm c} = 1000$ pW/K is a very good approximation.

Let us still take sample 7 as an example. The total contact thermal conductance on an individual CNT can be estimated as $G_{\rm tc/t} = n_{\rm c/t} \times G_{\rm c} = 2692$ nW/K. If $k_{\rm CNT} = 2000$ W/(m·K),[13] the intrinsic thermal conductance of an individual SWCNT is $G_{\rm t} = 0.32$ nW/K. $G_{\rm tc/t}$ is more than 8000 times $G_{\rm t}$. Even if an ultralow $G_{\rm c} = 50$ pW/K is used, $G_{\rm tc/t}$ is still 400 times larger than $G_{\rm t}$. That $G_{\rm tc/t}$ is far larger than $G_{\rm t}$ implies the temperature on each CNT in CNT networks is nonuniform. As mentioned above, uniform temperature assumption has been adopted in the models previously proposed.[8,9] In these models, the temperature of each CNT was assumed to be determined by the position of its center of mass. The temperature difference on the contact between CNT i and j was overestimated as $\Delta T_{ij} = \left|T_i - T_j\right|$, where T_i and T_j are temperatures of CNT i and j, respectively. Since the heat flux through the contact between CNT i and j is equal to $Q_{ij} = G_{\rm c}\Delta T_{ij}$, the overestimated ΔT_{ij} results in an overestimated Q_{ij}. As a result, the $k_{\rm net}$ given by these models are far larger than experimental results.

Since $G_{\rm tc/t}$ is far larger than $G_{\rm t}$, it may seem as though the intrinsic thermal resistance of CNTs dominates $k_{\rm net}$. Volkov and Zhigilei proposed a revised model to include the contribution of the intrinsic thermal resistance of CNTs to $k_{\rm net}$.[13] In this model, $k_{\rm CNT}$ is considered finite, and the uniform temperature assumption is abandoned. It is assumed that heat flows in a CNT from one end of the CNT, and flows out through the other end.[7] Under this assumption, the average temperature gradient along a CNT is

$$\frac{{\rm d}T}{{\rm d}l} = \frac{|Q_{\rm CNT}|}{k_{\rm CNT}A_{\rm CNT}}, \tag{8}$$

where $|Q_{\rm CNT}|$ is the averaged net heat flow through a CNT, $A_{\rm CNT}$ is the cross-sectional area of a CNT, $A_{\rm CNT} = \pi D\delta$, and $\delta = 0.34$ nm is the interlayer spacing in graphite.[13] As demonstrated above, there are 2692 contacts on each CNT in sample 7, and the distance between two neighboring contacts along a CNT is only 3.7 nm. Since heat may randomly flow in or out the CNT at each contact, the assumption that the heat flows in CNT from one end and out through the other end exaggerates the temperature gradient along a CNT. The exaggerated temperature gradient further results in an overestimation of the effect of $k_{\rm CNT}$ on $k_{\rm net}$. It is worth pointing out that, although the contribution of the intrinsic thermal resistance of CNTs to $k_{\rm net}$ is overestimated, $k_{\rm net}$ given by the revised model[13] is still more than 400 times larger than the experimental results.

Here, we use $G_{\rm seg}$ to denote the thermal conductance of a CNT segment between two neighboring contacts along a CNT. We claim that whether the contribution of the intrinsic thermal resistance of CNTs to $k_{\rm net}$ can be ignored or not depends on the relative magnitudes of $G_{\rm seg}$ and $G_{\rm c}$. In sample 7, the distance between two neighboring contacts along a CNT is 3.7 nm. We get $G_{\rm seg} = 866$ nW/K when $k_{\rm CNT} = 2000$ W/(m·K). $G_{\rm seg}$ is about 800 times larger than $G_{\rm c} = 1000$ pW/K. The fact that $G_{\rm seg} \gg G_{\rm c}$ indicates that the effect of the intrinsic thermal resistance of CNTs on $k_{\rm net}$ can be ignored, although $G_{\rm tc/t}$ can be far larger than $G_{\rm t}$.

So far, we have argued that the temperature of an individual CNT in CNT networks is nonuniform and the intrinsic thermal resistance of CNT can be ignored in modeling $k_{\rm net}$. In this paper, we consider a CNT network as a contact thermal resistance network. In isotropic CNT networks, heat can be channeled in x, y, or z directions with equal probability. Only the contacts that channel heat along x direction (or x-contacts, for short) contribute to the thermal resistance in the x direction of a CNT network. Therefore, the CNT network can be simplified as a network of x-contacts when the heat flows along x direction. As shown in Fig. 2, these x-contacts can be viewed as a pack of parallel chains of contacts. Since there are $n_{\rm c/V}$ contacts per volume, the number of x-contacts per volume is $n_{\rm c/V}/3$, and the distance between two neighboring x-contacts is $a = \left(n_{\rm c/V}/3\right)^{-1/3}$. The number of the chains in parallel is S_{yz}/a^2, and S_{yz} is the cross-sectional area. The number of contacts in each chain is L_x/a. Thus, the conductivity of the CNT network can be written as

$$k_{\rm net} = \left(\frac{n_{\rm c/V}}{3}\right)^{1/3} G_{\rm c}. \tag{9}$$

This equation is the same as that proposed by Zhou *et al.* for liquid and amorphous solids.[16,19] Substituting the expression of $n_{\rm c/V}$ for SWCNT in Eq. (9), we get

$$k_{\rm net} = \left(\frac{\rho^2_{\rm net}}{12\pi D\rho^2_{\rm g}}\right)^{1/3} G_{\rm c}. \tag{10}$$

In the above model given by Eqs. (9) and (10), the temperature difference on a contact is estimated to be $\nabla T_x a$, where ∇T_x is the temperature gradient of the CNT network along the x direction.

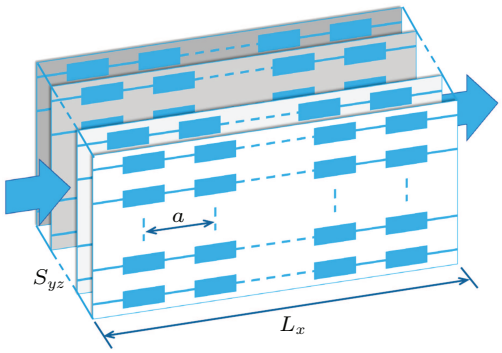


Fig. 2. Schematic of the contact thermal resistance network along the x direction.

To verify the proposed model given by Eq. (10), we fit the model to experimental results with G_c as the only fitting parameter. As shown in Fig. 3, Eq. (10) can fit the experimental results very well. Here, we define the relative error between the calculated thermal conductivity k_{net}^c and the experimental values k_{net}^e as

$$e_k = \frac{|k_{net}^c - k_{net}^e|}{k_{net}^e} \times 100\%. \tag{11}$$

The maximum and average e_k of Eq. (10) are only 21.0% and 9.5%, respectively. The value of G_c given by fitting is $G_c = 1043$ pW/K, which is very close to the 1000 pW/K we used in the above discussion. Thus, the conclusions we obtained in the above discussion based on $G_c = 1000$ pW/K still hold.

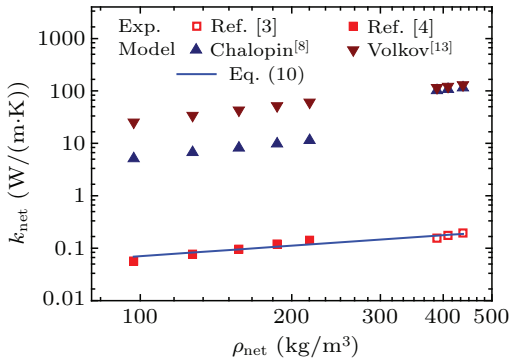


Fig. 3. The calculated thermal conductivities of SWCNT networks versus the experimental values at 300 K.

For comparison, the predictions of Chalopin's model [8] and Volkov's model [13] are also given in Fig. 3. The G_c used in these calculations is also 1043 pW/K. The predictions given by Chalopin's model[8] and Volkov's model [13] are more than 70 and 400 times larger than the experimental results, respectively. Therefore, Eq. (10) agrees better with the experimental results than Chalopin's model and Volkov's model.

Equation (10) shows that k_{net} is independent of the CNT length L. This coincides with Volkov's model.[13] In Chalopin's model,[8] k_{net} is linearly proportional to L. Therefore, there is a jump between the predictions given by Chalopin's model, because $L = 10$ μm and 2 μm in Refs. [3,4], respectively.

Additionally, Eq. (10) successfully captures the dependence of k_{net} on ρ_{net}. If both G_c and exponent of ρ_{net} in Eq. (10) are used as fitting parameters, we can get $k_{net} \propto \rho_{net}^{0.63}$. In Eq. (10), k_{net} is proportional to $\rho_{net}^{2/3}$, which is very close to the fitting result. Meanwhile, k_{net} is proportional to ρ_{net} in both Chalopin's model[8] and Volkov's model.[13]

Equation (10) also provides ways of improving the thermal conductivity of CNT networks. We can increase k_{net} by increasing G_c and ρ_{net}. The contact thermal conductance G_c can be increased by ion irradiation[20] or high-temperature annealing treatment.[21] For example, Mu *et al.*[21] experimentally demonstrated that thermal conductivity of buckypapers can be improved from 2.4 W/(m·K) to 5.4 W/(m·K) after annealed at 2800 °C. They attributed the enhanced thermal conductivity to the increased G_c. The spark plasma sintering (SPS) method[4,22] can densify the CNT network and bond CNTs together, so that ρ_{net} and G_c can be improved simultaneously. For example, the density of the CNT blocks is 1450 kg/m^3 after sintered at 2000 °C, and k_{net} is as high as 4.2 W/(m·K).[22]

In summary, number density of contacts in CNT networks was evaluated using the exclude volume method. Based on the number density of contacts, we claimed that a CNT network can be considered as a network of contact thermal resistance. In the contact thermal resistance network, the temperature of an individual CNT is nonuniform and the intrinsic thermal resistance of CNT can be ignored. Compared with the previous models, the model we proposed agrees well with the experimental results of SWCNT networks.

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