# Turning Carbon Nanotubes from Exceptional Heat Conductors into Insulators

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Thermal conductivity ($\kappa$) of isolated carbon nanotubes (CNTs) is higher than the $\kappa$ of diamond; however, in this Letter we show that the $\kappa$ of a packed bed of three-dimensional random networks of single and multiwall CNTs is smaller than that of thermally insulating amorphous polymers. The thermoelectric power ($\Sigma$) of the random network of CNTs was also measured. The $\Sigma$ of a single wall nanotube network is very similar to that of isolated nanotubes and, in contrast with $\kappa$, $\Sigma$ shows a strong dependence on the tube diameter.

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The thermal conductivity ($\kappa$) of isolated single wall (SW) and multiwall (MW) carbon nanotubes (CNTs) is ~3000 W/m K or higher at room temperature [1,2] which is higher than the $\kappa$ of diamond. Therefore CNTs are of both fundamental and practical interest [3]. $\kappa$ of CNTs has been measured primarily in two forms: (a) isolated CNTs [1,2] (b) in-plane $\kappa$ of films or mats of CNTs (bulk CNT) [4–6]. In films, $\kappa$ was found to be ~250 W/m K [5] and ~30–75 W/m K [4–6] for aligned samples [one-dimensional (1D) bulk form] and random orientation [two-dimensional (2D) bulk form], respectively. Therefore $\kappa$ of 1D bulk CNTs and 2D bulk CNTs is approximately 1 and 2 orders of magnitude smaller than $\kappa$ of individual CNTs, respectively. Hence the question that we seek to answer in this Letter is whether $\kappa$ of randomly oriented three-dimensional (3D) network of CNTs (3D bulk samples) follows this trend; their $\kappa$ is ~1000 times smaller than that of individual CNT. This would mean that these CNTs assemblies would behave more like thermal insulators than conductors. We report on the experimental, molecular dynamics and atomistic Green's function study of $\kappa$ of random 3D network of SWCNTs and MWCNTs of different diameters forming packed beds as shown schematically in Fig. 1. We found that $\kappa$ of the packed bed of CNTs is smaller than $\kappa$ of typical isotropic polymers. A clear implication of our results is that the $\kappa$ of 3D tube networks is dominated by the contact resistance of the junctions formed between CNTs. Although our primary goal was to study $\kappa$, we also measured the thermoelectric power ($\Sigma$) of the CNT beds. Finally we show that the thermoelectric figure of merit (ZT) of the CNT beds can be ~2 orders of magnitude larger than ZT of isolated CNTs.

Commercially available CNTs (NanoAmor, Inc.) were used with different tube diameters as shown in Table I. The length of the tubes ranged from 5–15 $\mu$m. During the tests, the CNT samples were pressed using two copper rods and the $\kappa$ of the CNT bed was measured using the American Society for Testing and Materials standard [7]. The thickness of the CNT bed ($L$) was measured using a laser extensometer. The thickness of various samples ranged from ~200 to 800 $\mu$m. More details of the measurement setup and methodology have been discussed by the authors elsewhere [8]. Measurement results are summarized in

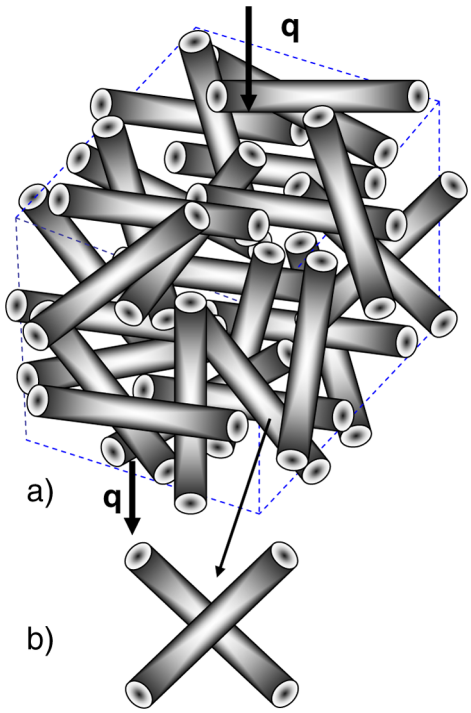


FIG. 1 (color online). (a) Schematic of the 3D random array of CNTs forming a bed. (b) Schematic of the crossed CNT junction.

 

TABLE I. Thermal conductivity of the CNT bed.

| Sample | Pressure (psi) | $k_{bed}$ (W/m K) | $\phi$ |
|---|---|---|---|
| 1–2 nm | 20 | 0.155 | 17.2% |
| SWCNT | 50 | 0.175 | 18.1% |
| | 90 | 0.194 | 19.4% |
| <8 nm | 20 | 0.154 | 12.7% |
| MWCNT | 50 | 0.171 | 13.7% |
| | 90 | 0.195 | 15.2% |
| 60–100 nm | 20 | 0.134 | 8.9% |
| MWCNT | 50 | 0.154 | 10.4% |
| | 90 | 0.170 | 12.4% |

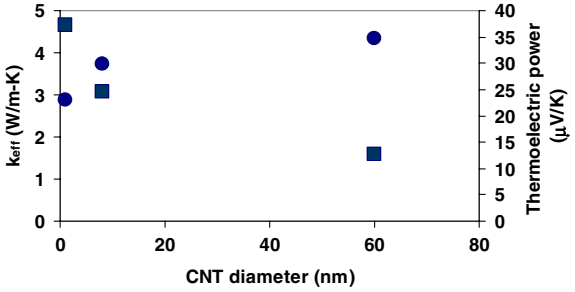


FIG. 2 (color online). Circles are the effective thermal conductivity of the CNTs in the 3D random array obtained from Eq. (1). Squares are the thermoelectric power of the CNT bed. The maximum error in $\kappa$ and $\Sigma$ from all experiments is 5%.

Table I. It shows that all particle beds made of "highly heat conductive" CNTs behave as thermal insulators with $\kappa$ of only 0.13–0.20 W/m K in a pressure range of 20–90 psi (138–621 kPa). The main effect of increased pressure was an increase in the volume fraction of the CNT in the bed as seen from Table I. $\kappa$ increased linearly with packing fraction. $\kappa$ is smaller than that of typical isotropic polymers (~0.2 W/m K). These values are in stark contrast with values expected for a 3D random network of large aspect ratio rods where the theoretical $\kappa$ of the bed ($\kappa_{bed}$) can be estimated as [9]

$$\kappa_{bed} = 1/3\kappa_{CNT}\phi, \quad (1)$$

where $\phi$ is the volume fraction of the CNTs, and $\kappa_{CNT}$ is the $\kappa$ of CNTs. Assuming that intrinsic $\kappa$ of CNT is 3000 W/m K and a $\phi$ of 15% (Table I), Eq. (1) gives $\kappa_{bed} = 150$ W/m K which is ~1000 times larger than experimental $\kappa$. The crucial assumption yielding such large value of the theoretical estimate is that the tube-tube contact resistance is negligible. It is well known that the energy transfer between carbon nanotubes in van der Waals contact is limited by a large contact resistance [10] arising from weak intertube bonding. Similarly, large interfacial resistance between CNT and polymers or liquids has major effects on $\kappa$ of CNT composites [11]. We have estimated the effective $\kappa$ of the CNT from Eq. (1) as shown in Fig. 2. $\kappa_{eff}$ for 3D networks of CNTs is ~1000 times smaller than the $\kappa$ of isolated CNTs, and follows the dimensionality trend hypothesis discussed in the introduction. $\kappa_{eff}$ of CNT is a weak function of diameter, because of two competing effects. The contact resistance for larger diameter CNT is smaller than the smaller diameter CNT due to larger contact area whereas the number of contacts per unit volume will be larger for smaller nanotubes due to large aspect ratio.

To get an accurate estimate of the tube-tube contact conductance ($G$) we independently used both molecular dynamics (MD) and atomistic Green's function (AGF) simulation for a model structure of SWCNT in van der Waals contact at 90°, as shown in Fig. 3(a). In these simulations the junctions are completely isolated from neighboring junctions; i.e., we simulated thermal transport through single junction. In MD the covalent forces between C atoms were described by widely used many-body Tersoff potential [12] and Lenard-Jonnes pair potential was used to model nonbonded interactions between the tubes, involving the bonding energy between two C atoms of 0.003 eV and the equilibrium distance of 3.4 A [13]. Periodic boundary conditions were used in all directions. Therefore both tubes have no ends and there are two contacts between the

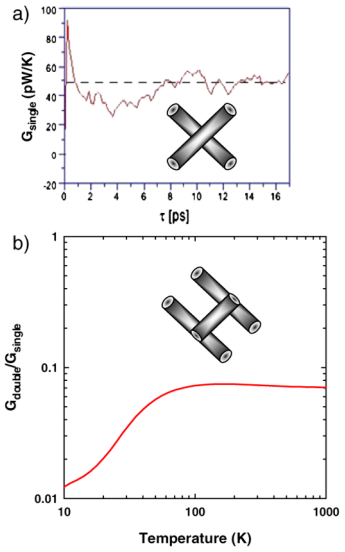


FIG. 3 (color online). (a) The running integral of the power auto correlation function converging to the contact conductance between the two (10, 10) SWCNT obtained by MD simulation for a single isolated junction. Atomistic Green's function simulation independently gives similar value of the contact conductance (see text for details). The error in conductance obtained from MD is ~5 pW/$K$ (b) The lower data show the *ratio* of the conductance of a double junction and a single junction obtained by AGF simulations. The two junctions in the double junction are separated by a distance much smaller than the mean free path. The conductance of the double junction is ~1 order of magnitude smaller than a single junction (see text for details).

tubes, one as shown in Fig. 3 and the second across the boundary of the simulation cell. We determined the exact dimensions of the simulation cell by relaxing the system at low temperature and zero pressure. In the next step of the simulations the whole system was evolved at constant volume and temperature = 300 K for 15 000 MD steps of $1.8 \times 10^{-16}$ s. With this time step, using 5th order predictor-corrector integrator in microcanonical ensemble the total energy was conserved within 0.01% over $1 \times 10^6$ MD steps. Finally we followed with $2 \times 10^6$ MD simulations at constant volume and energy. $G$ was calculated using the equilibrium simulations and the Green-Kubo formula [14], $G = 1/(k_b T^2) \int_0^\infty \langle P(t)P(0)\rangle dt$ where $P(t)$ is the thermal power exerted by one tube on the other. Since the power autocorrelation function $\langle P(t)P(0)\rangle$ decays to zero as a function of time the upper integral can be performed to a finite time $\tau$. In evaluation of the power autocorrelation function we used the last $1 \times 10^6$ of MD steps of our simulations. The running integral of $G$ as shown in Fig. 2 converges to about 50 pW/K. The details of the AGF are described elsewhere [15]. Our AGF simulation also shows a conductance ~50 pW/K for ~1 nm SWCNT. The match between MD and AGF for single junction shows that we are correctly capturing the physics of thermal transport at single isolated junctions.

To evaluate the significance of the contact resistance we can compare it with the conductance of 1 $\mu$m long (10, 10) CNT. Assuming tube $\kappa$ of 3000 W/m K and cross section of $\pi \times 1.4$ nm $\times$ 0.36 nm (0.36 nm = spacing between graphene sheets in graphite) one obtains axial tube conductance of 4747 pW/K which is 94 times larger than the contact conductance. This estimate clearly shows that the resistance of the tube between contacts is far lower than the contact resistance; thus, the $\kappa$ of the CNT network is controlled by $G$, and not by intrinsic axial $\kappa$ of the tubes. For tube-tube contact dominated $\kappa$ of random 3D network of large aspect ratio SWCNTs, Chalopin *et al.* [15] derived the following relation:

$$k_{\text{bed}} = G \frac{0.18l}{2\pi d \rho_{\text{graphene}}} \rho, \tag{2}$$

where $\rho_{\text{graphene}} = 7.6 \times 10^{-7}$ kg/m$^2$ is the surface mass density of graphene, $\rho$ the volume mass density of the network ($\rho = 2260\phi$), $d$ the diameter, and $l$ the length of the CNT. Assuming $l = 5$ $\mu$m and using $G =$ 50 pW/K obtained from MD results, for $\phi = 15\%$, $\kappa_{\text{bed}} \sim$ 2.25 W/m K which is an order of magnitude larger than the experimental $\kappa$. To match the experimental data, $G$ needs to be ~3 pW/K, i.e., an order of magnitude smaller than that obtained from MD simulations.

We believe that the main reason for the overprediction of contact conductance lies in the fact that we have simulated a single isolated junction. Our MD and AGF simulation of individual junctions is directly relevant to heat flow via multiple junctions (e.g., two junctions) when the junctions are separated by a distance larger than the coherence lengths of phonons which are of the order of microns in CNTs for frequencies below 50 THz [16]. In reality the distance between adjacent junctions is much smaller than the coherence length in the CNT bed. Therefore interference effects and coherent transport of phonons may play a significant role. However, single junction results do not provide information about multiple junction heat flow. It is possible that the effective resistance of two junctions is much larger than twice the single junction resistance due to these effects. Therefore more realistic large-scale simulations should be those of heat flow across two junctions separated by a distance comparable to or smaller than the coherence length. Such simulations are rather challenging due to very large number of atoms involved and long simulation time for MD. Therefore to validate this hypothesis we performed AGF simulations for a double junction between two parallel infinite nanotubes joined by a finite length nanotube segment perpendicular to them, as shown in Fig. 3(b). The ratio of the conductance of double and single junctions are plotted in Fig. 3(b). The junctions are separated by 8.16 Å. The conductance of the double junction is approximately one order of magnitude smaller than that of the single junction at room temperature, which is consistent with the experimental results.

We also measured thermoelectric power ($\Sigma$) of these CNT beds as shown in Fig. 2 by measuring the electrical voltage between the copper/CNT bed/Copper sandwiches for a given temperature gradient using the same setup that was used for measuring $\kappa$ [17]. $\Sigma$ was not found to be sensitive to the applied pressure. $\Sigma$ is positive indicating $p$-type behavior which might be due to oxygen absorption [18] as the experiments were conducted in ambient conditions. The data show a strong dependence of thermoelectric power on the diameter of the CNT. One possible reason is that CNT samples contain tubes (in the SWNT case) or shells (in the MWNT case) of both metallic and semiconducting chiralities. For the semiconducting ones, the band gap becomes smaller for larger diameters. This means that the ''metallic'' character of the bed should increase with the diameter, so $\Sigma$ should decrease with increasing diameters. $\Sigma$ of the 3D bulk SWCNT sample is comparable to that of isolated SWCNT (~42 $\mu$V/K) [2]. The key to explaining why $\Sigma$ is comparable to that of isolated tubes, despite the strong thermal conductivity reduction, can be found in Ref. [19]. As explained there, $\Sigma$ will be completely determined by the junction's $\Sigma$, since the thermal resistance of the junction is so large. From Sec. III-F of Ref. [19], it is also clear that the nanocomposite's $\Sigma$ will be of the same order as the $\Sigma$ of the single junction, regardless of the density of junctions. The junction's $\Sigma$, on the other hand, can be of comparable magnitude to that of isolated nanotubes, because it does not depend on the coupling strength between the tubes [19].

Very low $\kappa$ of the CNT bed suggests that CNT-based materials can be used for low $\kappa$ applications such as thermal insulation and thermoelectrics. We could not measure the electrical conductivity ($\sigma$) of the CNT bed in our test setup; however, we provide an estimate of a $\sigma$. We expect that $\sigma$ of the bed will be also dominated by the conductance of the junction [20]. $\sigma$ of the bed can be estimated as $\sigma_{\text{bed}} = \kappa_{\text{bed}} G_{\text{electrical}}/G_{\text{thermal}}$, where $G_{\text{electrical}}$ is the electrical contact conductance. Experimental measurement on crossed SWCNT junctions [21] have shown that for semiconducting ($S$)/semiconducting $S$ and metal ($M$)/metal ($M$) junctions $G_{\text{electrical}} = 0.1e^2/h$ where $e$ is the electron charge and $h$ is the Planck's constant whereas for $M/S$ junction $G_{\text{electrical}} \sim 0$ due to the formation of Schottky barrier. In SWCNT network of different chiralities, $1/3$ of the SWCNTs will be metallic and $2/3$ will be semiconducting [22]. Therefore probabilities of $M/M$, $S/S$, and $S/M$ junctions are $1/9$, $4/9$, and $4/9$, respectively. Hence effective $G_{\text{electrical}} = 0.1e^2/h \times 5/9$. Assuming $G_{\text{thermal}} = 5$ PW/K as discussed earlier, $\sigma_{\text{bed}} \approx 0.64 \times 10^3$ S/cm which is comparable to the experimentally obtained $\sigma$ ($\sim 1.3 \times 10^3$ S/cm) in the thickness direction of thick films [5] and $\sigma$ ($\sim 3$–$5 \times 10^3$ S/cm) of soft sinter of bulk CNTs [23]. The estimated thermoelectric figure-of-merit ($\text{ZT} = \Sigma^2 \sigma T/\kappa$) of the SWCNT bed at room temperature is $\sim 0.2$. ZT of isolated SWCNT [24] is $\sim 0.0047$. Therefore ZT of the CNT bed is $\sim 2$ orders of magnitude larger than the ZT of isolated CNTs. The main reason for this is the dramatic decrease in the thermal conductivity as compared with other properties.

Experimental and theoretical results presented here can also have a bearing on other types of one-dimensional nanostructures. For example, 3D network of nanotubes of other materials such as Bismuth telluride [25] can be explored to increase ZT. The key physics will be the control of electrical and thermal contact resistances of the junction.

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