Thermal Conductivity of Carbon Nanotubes Embedded in Solids *

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A carbon-nanotube-atom fixed and activated scheme of non-equilibrium molecular dynamics simulations is put forward to extract the thermal conductivity of carbon nanotubes (CNTs) embedded in solid argon. Though a 6.5% volume fraction of CNTs increases the composite thermal conductivity to about twice as much as that of the pure basal material, the thermal conductivity of CNTs embedded in solids is found to be decreased by 1/8-1/5with reference to that of pure ones. The decrease of the intrinsic thermal conductivity of the solid-embedded CNTs and the thermal interface resistance are demonstrated to be responsible for the results.

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Enhancement of the thermal conductivity of composites is often highly desirable in engineering situations, such as thermal management, design and optimization. Filling basal materials with fibres with higher thermal conductivity is a promising way to effectively increase the thermal conductivity of composites.^[1] Higher thermal conductivity of a fibre is always better for improving the thermal conductivity of composites. Carbon nanotubes (CNTs) have attracted ever increasing attention as a potential filler for composites because of their abnormally high thermal conductivity. Measurements of the thermal conductivity of individual multi-walled CNTs at room temperature gave an order of 2000-3000 W/mK.^[2,3] The thermal conductivity of individual single-walled CNTs was measured to have higher values of about 3000-3500 W/mK.^[4-6] Molecular dynamics (MD) simulations reported even higher values, e.g. 200-6600 W/mK at room temperature for single-walled CNTs.^[7–11] Based on these researches, the thermal conductivity of CNT-based composites is rationally expected to be very high.

Though direct experimental measurements show a significant increase in the thermal conductivity of CNT-based composites,^[12–14] the increase is much lower than theoretical expectations. A theoretical consideration predicted that filling 1% volume fraction of CNTs into a low-conductivity material might increase the thermal conductivity of the corresponding composite by 50-fold.^[15] However, with 1% volume fraction of carbon nanotubes filled, polymer composites and oil suspensions exhibit thermal conductivity of about 0.4 W/mK, only twice that of the pure basal material.^[12,13] The discrepancy in the experimental measurements and theoretical expectations is guessed to be attributed to a number of possible reasons, such as distribution of nanotubes in a solid, interaction between nanotubes, the intrinsic thermal conductivity of nanotubes, thermal resistance at nanotube-solid interfaces. Though several theoretical models considering the above factors were put forward,^[16,17] they often terribly underestimate or overestimate the effects of CNTs on the composite thermal conductivity.^[18]

In fact, there is another significant pendent question, i.e. the real thermal conductivity of carbon nanotubes embedded in other basal solids for a CNTbased composite. It is extremely difficult to measure this quantity through experiments since the heat flux and temperature distribution in such carbon nanotubes cannot be directly obtained. The most promising solution points to the particle-based method of MD simulations. In this Letter, we put forward a novel CNT-atom fixed and activated scheme to extract the thermal conductivity of the carbon nanotubes embedded in solid argon. The thermal conductivity of the carbon nanotubes embedded in solids is found to be decreased by 1/8-1/5 with reference to that of pure ones. The mechanism of heat conduction of carbon nanotubes embedded in solids is also demonstrated.

Molecular dynamics simulations of a (5,5) carbon nanotube embedded in solid argon are performed as shown in Fig. 1(a). The lengths of the simulation system are $L_x = 17.7$ nm and $L_y = L_z = 3.4$ nm. Periodic boundary conditions are applied along the three directions. The diameter of the (5,5) nanotube is d = 0.68 nm, which is about 1/5 of the size of the cross section. The simulation system contains 6192 argon atoms and 1440 carbon atoms. The volume (crosssectional area) fraction of the carbon nanotube in the simulated composite is 6.5%.

C–C bonding interactions are simulated by the Tersoff–Brenner bond order potential in the form of

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$$\phi(r) = \sum_{i} \sum_{j(j>i)} [V_R(r_{ij}) - \boldsymbol{B}_{ij} V_A(r_{ij})], \quad (1)$$

where $V_R(r)$ and $V_A(r)$ are repulsive and attractive force terms which take the Morse type form with a certain cut-off function. B_{ij} represents the effect of the bonding order parameters. More details about the potential model can consult Refs. [19,20]. Ar–Ar and C–Ar interactions are modelled by the Lennard–Jones potential

$$\phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \qquad (2)$$

where r is the intermolecular distance, ε and σ are, respectively, the energy and molecular distance parameters. We use $\sigma_{Ar-Ar} = 3.405 \times 10^{-10}$ m, $\varepsilon_{Ar-Ar} =$ 1.67×10^{-21} J for the Ar–Ar interactions, and $\sigma_{C-Ar} =$ 0.357×10^{-10} m, $\varepsilon_{C-Ar} = 1.97 \times 10^{-21}$ J for the C–Ar interactions,^[21] respectively.



Fig. 1. (a) Simulation system, a quarter of the simulated solid is cut away for eye guidance. (b) Schematic diagram of computation method.

To simulate heat flow from a hot to a cold region, the simulation system is divided into N equal segments, as shown in Fig. 1(b). The left end segment, i.e. No 1, is set at a low temperature T_l through extracting some energy ε every calculation step. The middle segment, i.e. No N/2+1, is kept at a high temperature T_h by adding some energy ε every step. The mean temperature of the system is $T_0 = (T_l + T_h)/2$. The hot and cold regions are respectively controlled at constant temperatures by a velocity rescaling method expressed as

$$v_i = v_{it} \sqrt{T/T_t}.$$
 (3)

In our simulations, they obey $T_0 = T_l + 10 \text{ K} = T_h - 10 \text{ K}$.

In order to extract the thermal conductivity of the CNTs embedded in solid argon, we simulate two types of system configurations, which is called a CNT-atom fixed and activated scheme. One is to fix all the carbon atoms and leave only argon atoms to transport energy. The CNT-atom fixed simulations give the thermal properties of the basal material affected by the embedded CNTs, and the heat flux Q_f through the solid with a designated temperature difference of 20 K. The other is to activate the carbon atoms, i.e. to simulate a real composite. The CNT-activated simulations can present the thermal properties of the same temperature difference. Then, the thermal conductivity of the CNTs embedded in the solid can be extracted according to

$$k_c = (Q_a - Q_f)\Delta T / (AL_x). \tag{4}$$

The atoms move according to Newton's second law. The equations of motion are integrated using a leapfrog Verlet algorithm^[22] with a time step of dt =0.5 fs. To decrease the time-consuming part of the calculation of interparticle interactions, we mainly take two measures: (a) Typical potential cutoffs, 0.2 nm for C–C and 0.77 nm for C–Ar and Ar–Ar interactions, are respectively used. (b) The combination of cell-linked-list and neighbour-list methods is adopted. Reaching a steady state for the simulated one-dimensional heat conduction often costs about 1000000 time steps. Then the temperature profiles can be collected through an averaging method over 4000000 time steps.



Fig. 2. Temperature profiles at three different mean temperatures based on a CNT-atom fixed and activated scheme.

The temperature profiles at three different mean temperatures obtained by our MD simulations are

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shown in Fig. 2. It is seen from the figures that the temperature distributions on the left and right halves are nearly linear. This ascertains our thermal conductivity calculation based on Fourier's law of heat conduction. Figure 3 depicts the calculated thermal conductivities of the CNTs-argon composite and solid argon at three temperatures. The thermal conductivities of solid argon at 100, 200 and 300 K are respectively 0.52, 0.49 and $0.45 \,\mathrm{W/mK}$. The thermal properties is nearly not affected by the existing of CNTs when compared with bulk argon. The composite thermal conductivity is increased by 1.77 times at 100 K, 1.53 times at 200 K and 1.78 times at 300 K with reference to the basal material. This thermal property enhancement arises from the nanotube filling with a volume fraction of 6.5%, which even quantitatively agrees with the experimental results reported in Refs. [13,14]. A theoretical estimate for the thermal conductivity of composite can be obtained from the volume fraction of CNTs

$$k_c = \langle \cos^2 \theta \rangle f_{\rm CNTs} k_{\rm CNTs}.$$
 (5)

Here $f_{\rm CNTs}$ is the volume fraction of CNTs, $k_{\rm CNTs}$ is the thermal conductivity of CNTs, θ is the angle between the CNT axis and a given heat flux direction, and the thermal resistance is not considered.^[12] For the present simulations, the direction of the CNT axis is parallel to the heat flux direction, i.e. $\theta = 0$ $(\cos \theta = 1)$. Thus we have $k_c = f_{\rm CNTs} \cdot k_{\rm CNTs}$. The thermal conductivity of pure CNTs is about 40 W/mK by our MD simulations. The thermal conductivity predicted by the above theory is about 2.4 W/mK, which is about three time larger than the real thermal conductivity of the composite. Therefore, we can conclude that the thermal conductivity of the CNTs embedded in a solid may be greatly decreased by their surrounding materials.



Fig. 3. Thermal conductivities of CNTs-argon composite and solid argon.

Based on Eq. (4), compared the results between the CNT-fixed and CNT-activated simulations produces

the thermal conductivity of the CNTs embedded in solid argon. The thermal conductivities of the CNTs embedded in solid argon and pure CNTs are shown in Fig. 4. A pure carbon nanotube is surely with a high thermal conductivity of about 40 W/mK. The present value seems smaller than the results in some literature. The reason is because the nanotube length is shorter than those in these literature, which decreases the thermal conductivity in a exponent law.^[7-11] Considering the effect of tube length, our results on the pure CNTs agree with the data in Refs. [9,11] very well. However, when the CNTs embedded in argon solid, the apparent thermal conductivity is only about 5 W/mK. The thermal conductivity of CNTs embedded in solids at $100-300 \,\mathrm{K}$ is decreased by 1/8-1/5with reference to that of pure ones.



Fig. 4. Thermal conductivities of CNTs embedded in solids and pure CNTs.

Therefore, the thermal conductivity of CNTs embedded in solids is much smaller than that of pure ones. This can be attributed to the following possible reasons. First, the intrinsic thermal conductivity of nanotubes embedded in a solid is lowered. Coupling interactions between the CNT and basal solid atoms enhance phonon scattering and decrease the mean free path of phonons. In Refs. [23,24], the MD simulations show that the interactions between carbon nanotubes and the surrounding materials lead to a reduced thermal conductivity by a factor of two or three. However, this effect alone can not produce our simulation results. The second possible reason is the thermal resistance at the boundary between CNTs and surrounding materials. Taking the intrinsic thermal conductivity to be $10-20 \,\mathrm{W/mK}$, the thermal boundary resistance in our simulations is estimated to be $2 \times 10^{-9} - 5 \times 10^{-9} \,\mathrm{Km^2/W}$, which is comparable to the MD-calculated results by Shenogin *et al.*^[1] Another possibility from the effect of the CNTs on the thermal properties of the basal material is found to be very small. We can draw a conclusion that the inNo. 4

trinsic thermal conductivity decrease of the CNTs embedded in solids and the thermal interface resistance are two main factors to be responsible for the thermal properties of composites. Therefore, it is unscientific for theoretical predictions on the thermal conductivity of CNT-based composites according to the thermal property of pure CNTs. How to control the intrinsic thermal conductivity by varying the surrounding-CNTs and the thermal interface resistance is quite important for the composite engineering. Accurate predictions of the intrinsic thermal conductivity of the solid-embedded CNTs and the thermal interface resistance in the future are highly desired for the design and optimization of composites.

In summary, we have carried out MD simulations to calculate the thermal conductivity of the CNTbased composite and to extract the thermal property of the composite-embedded CNTs by a CNT-atom fixed and activated scheme. It is shown that a 6.5%volume fraction of CNTs is found to increase the composite thermal conductivity by about twice larger than that of the pure basal material. However, the increase is much smaller than theoretical predictions based on the thermal conductivity of pure CNTs. The reason is that the thermal conductivity of CNTs embedded in solids is decreased by 1/8-1/5 with reference to that of pure ones. We demonstrate that the intrinsic thermal conductivity decrease of the CNTs embedded in solids and the thermal interface resistance are two main factors to be responsible for the thermal properties of composites. Therefore, accurately predicting and even controlling the intrinsic thermal conductivity of the solid-embedded CNTs and the thermal interface resistance are highly desired for the design and optimization of composites.

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