ISSN 1674-1056
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Citation: Chin. Phys. B . 2018, 27(2): 026501. **doi:** 10.1088/1674-1056/27/2/026501

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Thermal conductivity of carbon nanotube superlattices: Comparative study with defective carbon nanotubes*

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(Received 26 September 2017; revised manuscript received 8 November 2017; published online 5 January 2018)

We use molecular dynamics simulation to calculate the thermal conductivities of (5, 5) carbon nanotube superlattices (CNTSLs) and defective carbon nanotubes (DCNTs), where CNTSLs and DCNTs have the same size. It is found that the thermal conductivity of DCNT is lower than that of CNTSL at the same concentration of Stone–Wales (SW) defects. We perform the analysis of heat current autocorrelation functions and observe the phonon coherent resonance in CNTSLs, but do not observe the same effect in DCNTs. The phonon vibrational eigen-mode analysis reveals that all modes of phonons are strongly localized by SW defects. The degree of localization of CNTSLs is lower than that of DCNTs, because the phonon coherent resonance results in the phonon tunneling effect in the longitudinal phonon mode. The results are helpful in understanding and tuning the thermal conductivity of carbon nanotubes by defect engineering.

Keywords: thermal conductivity, carbon nanotube superlattices, defective carbon nanotubes, phonon coherent resonance

PACS: 65.80.–g, 63.22.–m **DOI:** 10.1088/1674-1056/27/2/026501

1. Introduction

Since carbon nanotube (CNT) was discovered by Iijima in 1991,[1] it has attracted more and more researchers to study its simple structure, and excellent electrical and thermal properties in the fields of science and engineering. Bulk CNT powders can be used in rechargeable batteries.[2] Single-walled carbon nanotubes (SWCNTs) will be a candidate for transistors or interconnects in integrated circuits.[3] The experimental measurements by Pop *et al.* showed that SWCNTs have a greater thermal conductivity than diamond and graphite.[4] SWCNTs have been widely regarded as one of the best thermal conductor materials, which can be filled with nanofluids or composite materials,[5,6] and designed as thermal interface materials in heat management.[7,8]

The thermal transport properties of CNTs have aroused great interest over the past decade. The phonon transport mechanisms in CNTs have been studied theoretically and experimentally.[9–19] Defect engineering is an effective approach to tuning the thermal conductivity of nanostructures.[20–28] Che *et al.*[20] compared the effects of Stone–Wales (SW) defects and vacancies on the thermal conductivity of CNTs. A prediction from Kondo *et al.*[21] has stated that 1% vacancies would reduce 30% thermal conductivity of CNTs. Feng *et al.*[22] simulated the influences of the concentration of SW defects on the thermal conductivity of CNTs. The results showed that defect type, chirality, radius and length of CNTs have significant influences on thermal conductivity. Li *et al.*[23] analyzed the defect effects from two aspects, i.e., the temperature profile and local thermal resistance of the CNTs. It was shown that a sharp jump in the temperature profile occurs at defect position due to a higher local thermal resistance, thus dramatically reducing the thermal conductivity of CNTs.

In this paper, in order to investigate the effects of periodically collective SW defects and randomly distributed SW defects on phonon transport in CNTs, the thermal conductivities of nanotube superlattices (CNTSLs) and defective carbon nanotubes (DCNTs) are comparatively studied by molecular dynamics simulation at room temperature. Here, SW defects with periodic distribution and random distribution in CNTs are defined as CNTSLs and DCNTs, respectively. A remarkable oscillation effect in heat current autocorrelation function (HCACF) is observed in CNTSLs, while the same effect is absent in DCNTs, which indicates that the underlying mechanisms of phonon transport in these two structures are quite different.

2. Models and simulation methods

Figure 1(a) shows the structure of CNTSLs. The model of an SWCNT (5, 5) has a diameter of 6.78 Å, with a C–C bond length of 1.42 Å. A ring area of van der Waals thickness of 3.4 Å is employed as the cross-sectional area of the nanotubes. The structure with SW defects is located in the blue region and the normal hexagonal structure is located in the gray region. Comparing with pristine CNTs, neither of the total numbers of atoms of CNTSLs and DCNTs is changed.

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11404278 and 11275163) and the Science Foundation of Hunan Province, China (Grant No. 2016JJ2131).

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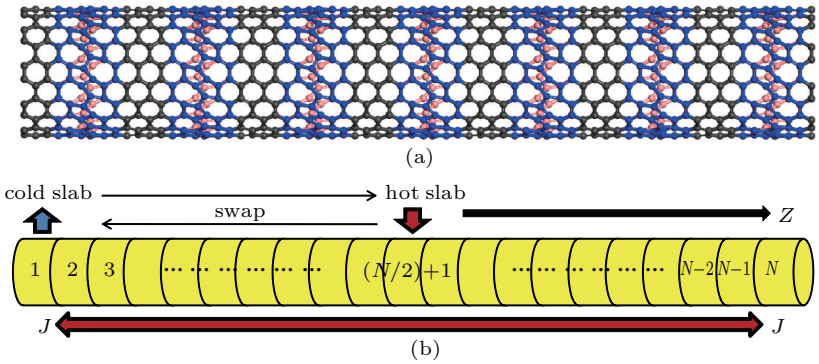


Fig. 1. (color online) (a) Model of CNTSLs and (b) the schematic illustration of the simulation model in the Müller–Plathe method.

In this work, the thermal conductivity is calculated by the Müller–Plathe (MP) method[29] in non-equilibrium molecular dynamics (NEMD) simulations. We adopt periodic boundary conditions in the longitudinal directions of CNTSLs and DCNTs, respectively. As shown in Fig. 1(b), we divide the simulation box into N (N must be an even number) slabs along the longitudinal direction (z axis). Slab 1 and slab $N/2+1$ are defined as the cold and hot slab, respectively. Based on MP method, the energy transferring from the cold to the hot slab is achieved by exchanging the velocity of coldest atoms in the hot slab with the velocity of hottest atoms in the cold slab. Temperature gradient is established in the longitudinal direction. The values of thermal conductivity (k) of CNTSLs and DCNTs can be calculated from the following equation:

$$k = \frac{Q}{2At(\partial T/\partial z)}, \tag{1}$$

where A is the cross-sectional area of CNTs, Q is the summation of energy interchanged in the simulation, and $\partial T/\partial z$ is the temperature gradient along the longitudinal direction, t is the time of the simulation. The factor 2 arises from the periodic boundary condition of the system in the longitudinal direction. In our MD simulation, the AIREBO potential developed by Stuart *et al.*[30] is used. This potential is an extension of the REBO potential[31] and includes non-bonding (intermolecular) atomic interactions and torsional potential. This potential model has achieved great success in predicting the thermal properties of CNTs.[32–35]

The MD code LAMMPS[36] is adopted to calculate the thermal conductivities of CNTSLs and DCNTs along the longitudinal direction (z axis). Firstly, we equilibrate this system in the isothermal-isobaric ensemble (NPT) for 2 ns. After the NPT relaxation, the system continues to relax in the microcanonical ensemble (NVE) for 1 ns. In order to establish a temperature gradient along the longitudinal direction, the NEMD is performed for 3 ns. The simulation of final 2 ns is to calculate the thermal conductivities of CNTSLs and DCNTs by Eq. (1) in time steps of 0.1 fs.

3. Simulation results and discussion

It is shown in Fig. 2 that the thermal conductivities of the CNTSLs and DCNTs decrease with the increase of density of SW defects. Both periodically and randomly distributed SW defects can significantly reduce the thermal conductivity of the CNTs, but the suppression of thermal conductivity in DCNTs is stronger than that in CNTSLs. For example, when the SW defect density is 20%, the reductions of thermal conductivity in CNTSLs and DCNTs are 57.1% and 64.7%, respectively. The thermal conductivities of CNTSLs and DCNTs drop sharply when the SW defect density is less than 15%, but decrease slightly when the SW defect density is higher than 15%.

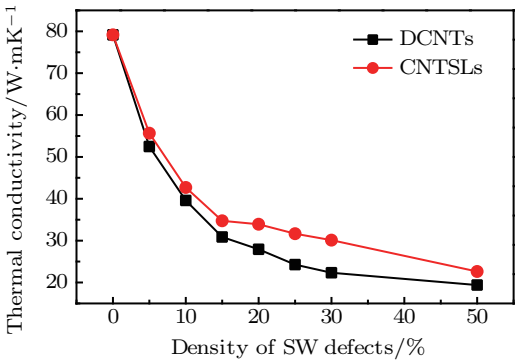


Fig. 2. (color online) Thermal conductivities of DCNTs and CNTSLs versus the density of SW defects.

Generally, there are two contrast pictures to describe phonon transport in nanostructures, one is the particle-like incoherent phonons, and the other is the wave-like coherent phonons. Phonon coherent resonances have been observed in GaAs/AlAs superlattices[37] and core–shell nanowires, respectively.[38] The coherence of phonons can be described by the HCACF. Figure 3(a) shows the typical time dependence of HCACF at 300 K among pristine CNTs, CNTSLs, and DCNTs. The SW defect concentrations are 50% in CNTSLs and DCNTs respectively. For comparison, the HCACFs of DCNTs with different concentrations of SW defects are also shown in Figs. 3(c) and 3(d). At the beginning, each of the HCACFs drops sharply, and then there is a long-time tail with a much

slower decay. In some studies of various single-component materials we can observe this two-stage decaying characteristic of HCACF.[39–41] However, the HCACFs of CNTSLs each have a nontrivial oscillation that lasts a long time (see Fig. 3(a)) and does not exist in the pristine CNTs nor DCNTs. The nontrivial oscillation exists in the HCACF for a long time, indicating that the oscillation is periodic and not random (See Fig. 3(b)).

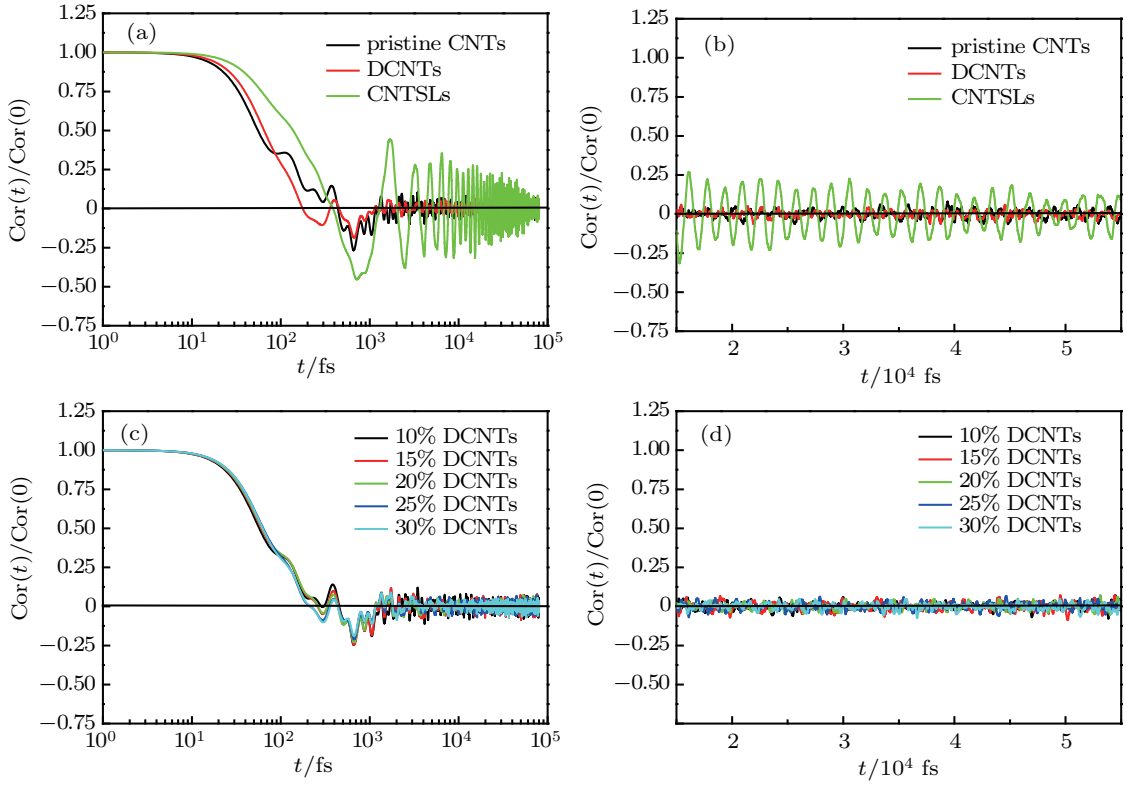


Fig. 3. (color online) Time dependence of normalized heat current autocorrelation functions (HCACF). (a) Normalized HCACF for pristine CNTs (black line), DCNTs with 50% SW defects (red line), and CNTSLs with 50% SW defects (green line). (b) Long-time region of panel (a). (c) Normalized HCACF for DCNTs with different concentration SW defects. (d) Long-time region of panel (c). The black lines in all figures draw the zero axis for reference.

Clearly, the underlying mechanisms of thermal conduction reduction in DCNTs and CNTSLs are quite different. In CNTSLs, as SW defects are periodically and collectively distributed, the wave nature of phonons affects the thermal transport dominantly, and phonon coherent resonance takes place. In DCNTs, SW defects are randomly distributed. Suffering phonon-defect scattering, phonons cannot preserve their phases, the wave nature of phonons is destroyed, and phonon transport is incoherent. Although both coherent and incoherent mechanism can significantly reduce thermal conductivity of CNTs, the thermal conductivity of DCNTs is lower than that of CNTSLs. In order to explain the stronger suppression of thermal conductivity in DCNTs than in CNTSLs, we study the localization effect of the phonon modes in CNTSLs and DCNTs. Phonon localization effect can be described by phonon vibration mode participation ratio P_λ, which is defined for each eigen-mode λ as[42]

$$P_\lambda^{-1} = N\sum_i \left(\sum_\alpha \varepsilon_{i\alpha,\lambda}^* \varepsilon_{i\alpha,\lambda}\right)^2, \qquad (2)$$

here, N is the total number of atoms, $\sum_i$ is the summation over all the atoms, and $\varepsilon_{i\alpha,\lambda}$ is the α-th vibrational eigenvector component of the normal eigen-mode λ for the ith atom, α is the Cartesian direction and summation over X, Y, Z, respectively.

The fraction of atoms participating is expressed by the participation ratio in a particular mode. The participation ratio varies between O$(1/N)$ (for localized states) and O(1) (for delocalized states). We can determine the degree of localization through the participation ratio.[43,44] The participation ratios of vibrational eigen-modes of pristine CNTs, DCNTS with 50% SW defects and CNTSLs with 50% SW defects are all presented in Fig. 4. It is obvious that the participation ratios of the CNTSLs and DCNTs are much lower than that of the pristine CNTs. The localization of phonons of all modes by SW defects scattering sharply reduces the phonon vibrational mode participation ratio, which results in the much lower thermal conductivity of CNTSLs and DCNTs than that of pristine CNTs shown in Fig. 2. The mean values of participation ratios of all modes versus density of SW defects for CNTSLs and DCNTs are presented in Fig. 5, respectively. Because the phonon coherent resonances in the SW defect regions in CNTSLs cause the tunneling effects,[45] the mean participation ratio of CNTSLs is higher, which indicates that the localization effect of phonons in CNTSLs is weaker than in DC-

NTs. As a result, the thermal conductivity of DCNTs is lower than that of CNTSLs.

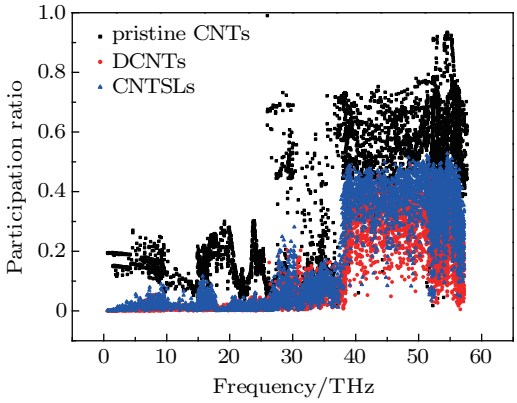


Fig. 4. (color online) Participation ratios of vibrational eigen-modes of pristine CNTs, DCNTs, and CNTSLs.

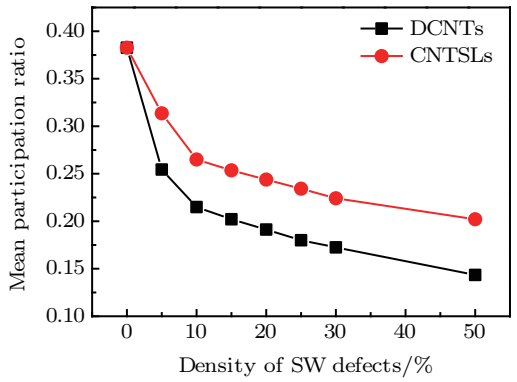


Fig. 5. (color online) Mean values of participation ratios of all modes versus density of SW defects for DCNTs, and CNTSLs.

4. Conclusions

In summary, by performing the NEMD simulations, we demonstrate that the thermal conductivity of CNTs can be reduced remarkably by SW defects, and DCNTs have lower thermal conductivity than CNTSLs in the case of the same defect density. Equilibrium molecular dynamics simulations show that a remarkable oscillation effect in HCACF occurs in CNTSLs, while the same effect does not exist in DCNTs, therefore the underlying mechanisms of phonon transport in these two structures are quite different. Phonon transport in CNTSLs is wave-like, but phonon transport in DCNTs is particle-like. The analysis of phonon spectra indicates that the SW defects can cause the phonons of all modes to be localized, resulting in the severe reduction of thermal conductivity of CNTs. The DCNTs have lower participation ratio than CNTSLs, especially for high-frequency modes, because the randomly distributed SW defects scatter high-frequency phonons more severely. The phonon localization effect in CNTSLs is weaker than in DCNTs, therefore the thermal conductivity of CNTSL is higher than that of DCNT with the same concentration of SW defects. Our study is helpful in understanding and tuning the thermal conductivity of carbon nanotubes by defect engineering.

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