

Supporting Information

**Enhancement of Heat Conduction in Carbon Nanotubes with Filled
Fullerene Molecules**

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I. Finite-size effect

The simulation length with respect to the phonon mean-free-path can be an important factor affecting the accuracy of thermal conductivity calculation via MD simulations. In this work, the thermal conductivities of CNTs and CNPs with different lengths were calculated by EMD method at 300 K. As the results shown in Fig.1, the values of thermal conductivity change little when the length exceeds 16 nm, which is in the same order as reported data for bare CNTs [1-3]. Therefore, the period length of both CNT and CNP was set to be 19.68 nm in our simulations, which is large enough to overcome the finite-size effect on the thermal conductivity.

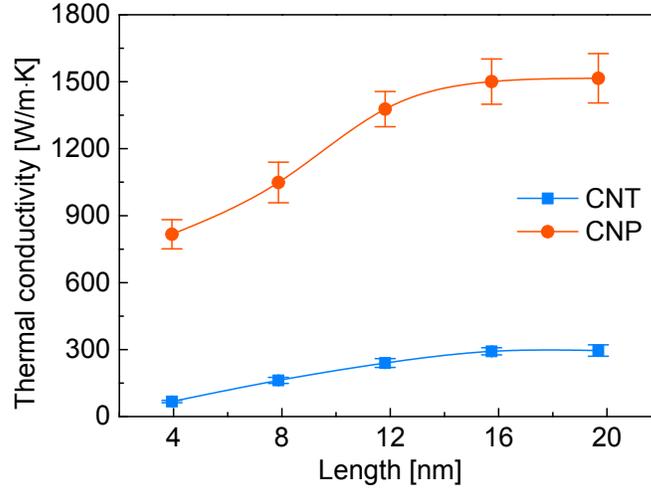


Figure 1. Size effect on the thermal conductivity of CNTs and CNPs.

II. EMD simulation details

The interactions between carbon atoms of CNPs are determined by the adaptive intermolecular reactive empirical bond order (AIREBO) potential [4]

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left[E_{ij}^{\text{REBO}} + E_{ij}^{\text{LJ}} + \sum_{k \neq i, j} \sum_{l \neq i, j, k} E_{kijl}^{\text{TORSION}} \right] \quad (1)$$

where E_{ij}^{REBO} is the REBO potential function, E_{ij}^{LJ} adds longer-ranged interactions, $E_{kijl}^{TORSION}$ is an explicit 4-body potential which represents dihedral angle preferences. It needs to be emphasized that the term of $E_{kijl}^{TORSION}$ has been turned off in this work. The AIREBO potential not only accurately computes the bond–bond interactions for a system of carbon atoms, but also reproduces the Van der Waals interactions precisely in CNPs [5].

Before the simulations, all atoms are subjected to potential energy minimization, during which C_{60} molecules can rotate and translate parallel to the tube axis freely. The free boundary condition was used in the x and y directions, whereas the periodic boundary condition was applied along the z direction. The time step was set to be 0.50 fs. At the beginning of simulation, a time integration on non-Hamiltonian equations of motion [6] was performed, velocities and positions sampled from the thermostatic canonical (NVT) ensemble were generated. The temperature in NVT ensemble was controlled via a Nosé–Hoover thermostat [7]. Then, the system ran under the constant-energy micro-canonical (NVE) ensemble, and the heat current was calculated for every time step. The numbers of simulation time steps for NVT, NVE and heat current vectors integration based on the Green–Kubo’s equation are 2×10^6 , 1×10^7 and 3×10^6 , respectively.

The equilibrium molecular dynamics (EMD) based on the Green–Kubo’s equation was employed to simulate the thermal conductivity. The thermal conductivity λ is the integral of the heat flux autocorrelation function over the correlation time t . The z -direction λ_z is given by,

$$\lambda_z = \frac{V}{k_B T^2} \int_0^\infty \langle J_z(0) J_z(t) \rangle dt \quad (2)$$

where V is the system volume, T is the system temperature, k_B is Boltzmann's constant. Angular brackets indicate the ensemble average. The heat flux $J_z(t)$ can be computed as [8]

$$J_z(t) = \frac{1}{V} \left[\sum_i \mathbf{v}_i \varepsilon_i + \frac{1}{2} \sum_{i,j,i \neq j} r_{ij} \left(\mathbf{f}_{ij} \cdot \mathbf{v}_j \right) + \sum_{i,j,k} r_{ij} \left(\mathbf{f}_j(ijk) \cdot \mathbf{v}_j \right) \right] \quad (3)$$

where v_i is the velocity of atom i , ε_i is the local site energy, $r_{ij,L}$ is the distance between atom i and j , \vec{f}_{ij} and $\vec{f}_j(ijk)$ are the two-body and three-body forces, respectively.

In order to obtain a good convergence for the thermal conductivity of CNTs and CNPs, their final values were computed by averaging the integral of the HCACF functions from six uncorrelated NVE ensembles (1500 ps for each ensemble). This estimation method for thermal conductivity was also used in the previous literatures[9, 10]. The uncertainties were determined from the averaged thermal conductivity curves in the region between 900 and 1500 ps for the correlation time.

Fig. 2 shows the normalized heat current autocorrelation functions (HCACFs) of CNT and CNP under temperature of 300 K. The normalization is relative to the initial value of HCACF, i.e., $\langle J_z(0)J_z(t) \rangle / \langle J_z(0)J_z(0) \rangle$. The HCACF trends of other simulation cases are similar to Fig.2. Generally, the HCACF clearly consists of two stages, a rapid initial decay followed by a gradual exponential decay over a very long time. The initial fast decay corresponds to the contribution from high-frequency optical modes to thermal conductivity, while the gradual decay corresponds to the contribution from low-frequency acoustic modes, which is the dominating part in thermal conductivity [3, 11]. Fig. 2 also shows that HCACF decays to approximately zero within 150 ps, which is much shorter than the total simulation time of 1500 ps. Consequently, the total

simulation time of 1500 ps is adequate for the thermal conductivity calculation.

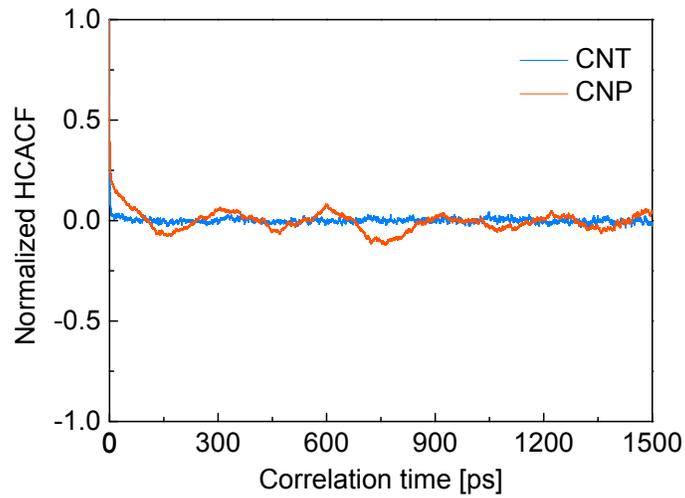


Figure 2. Heat current autocorrelation functions (HCACFs) under temperature of 300 K.

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