Nanoengineering Heat Transfer Performance at Carbon Nanotube Interfaces

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ABSTRACT Carbon nanotubes are superb materials for nanoscale thermal management and phononic devices applications, due to their extremely high thermal conductivity (3000−6600 W/mK) and quasi-one-dimensional geometry. However, the presence of interfaces between individual carbon nanotubes as found widely in nanocomposites, nanoelectronics, and nanodevices severely limits their performance for larger scale applications. Solving this issue requires a deep understanding of the heat transfer mechanism at this nanoscale interface between low-dimensional structures, where conventional models developed for interfaces in bulk materials do not apply. Here we address this challenge through a bottom-up approach based on atomistic simulations. We demonstrate that the huge thermal resistance of carbon nanotube junctions can be significantly improved through modifying the molecular structure at the interface to enhance both the matching of phonon spectra and phonon mode coupling. Specifically, two approaches based on polymer wrapping and metal coatings are investigated here and have shown to improve both the structural stability and interfacial thermal conductivity of carbon nanotube junctions. By properly designing the interface molecular structure between individual carbon nanotubes, significant performance gains up to a factor of 4 can be achieved. These results pave the way for future designs of thermal management networks and phononic devices with thermally transparent and structurally stable interfaces.

KEYWORDS: carbon nanotubes · interfacial thermal conductivity · thermal management · molecular dynamics · mechanical properties

Carbon nanotubes (CNTs) and graphene, low-dimensional materials with single atomic layer thickness, are excellent thermal conductors that also possess outstanding mechanical and electronic properties.[1] Various applications have been proposed from nanoelectromechanical systems,[2] integrated circuits[3] to thermoelectricity devices.[4] In these high power density devices, the heat dissipated during operation (reaching up to 10−50% of the electronic energy[5]) must be efficiently dissipated through the environment or contacts with electrodes. Thus not only the electrical, but also the thermal conductivity in carbon nanotubes and between interfaces with contacts is vital to ensure reliable device performance. Recently, there has also been an increased interest in phononic devices in which heat flow is manipulated and controlled in nanostructures, such as phonon waveguides[6] and thermal rectifiers.[7] The design of such devices also requires the understanding of phononic energy transfer at the atomic level, in particular at the nanoscale interfaces. Because of the high in-plane sound speeds in graphene sheets, experimental measurements have confirmed ultrahigh thermal conductivities for single-walled carbon nanotubes (6000 W K^{-1} m^{-1})[8] and monolayer graphene (5300 W K^{-1} m^{-1}).[9] The nature of their low dimensionality and their single atomic layer thickness provide great advantages over other high thermal conducting materials such as diamond and silicon carbide nanowires. Similar as observed in nanowires, surface scattering effects due to the mismatch between the phonon spectrum of the bulk and surface phase significantly reduce their thermal conductivities, whereas in carbon nanotubes and graphene sheets, the two-dimensional structure ensures an identical phonon spectrum over the entire structure. Thus, carbon nanostructures are excellent candidates for multifunctional thermal management networks. Furthermore, carbon nanomaterials have also been proposed to increase the thermal conductivity of nanocomposites. Recent experiments have shown that by filling organic fluid[10] or polymers[11] with carbon nanotubes can significantly improve their thermal conductivities. However, thus far significant improvements of the thermal conductivity of composites is only achievable when the immersed carbon nanotube network percolates[12] as heat flows through the network, which results in a much higher thermal conductivity than the surrounding oil or polymers.[13] Carbon nanotube fibers and graphite have extremely anisotropic heat

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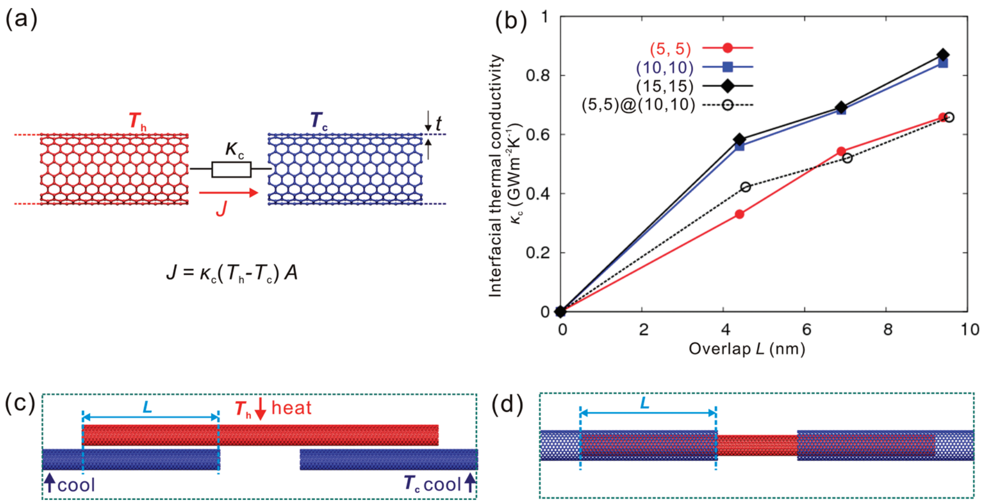

Figure 1. Interface thermal conductivity between carbon nanotubes. (a) Interfacial thermal resistance model to connect two carbon nanotubes. The interface as considered in this work is represented as a resistor with thermal conductivity κ_c, which can be calculated from the heat flux J flowing through and temperature jump $\Delta T = T_h - T_c$ across the interface. The contact area between the carbon nanotube is calculated as for a shell with thickness $t = 0.142$ nm. (b) The interface thermal conductivity κ_c calculated from the heat flux and temperature difference at interfaces of different junctions. For both types of junctions, κ_c depends linearly on the overlap length L between the carbon nanotubes, with values on the order of 0.1−1 GW m^{-2} K^{-1} for overlap length less than 10 nm. The interfacial thermal conductivity of parallel carbon nanotubes increases with increasing contact area, but saturates for (15,15) nanotubes with diameter of 2 nm, as shown by our simulations up to (20,20) nanotube junctions. The double-walled carbon nanotubes, although having mismatched phonon spectra at each side of interface, have a larger contact area and a comparable κ_c. (c) Parallel (10,10) single-walled carbon nanotubes junction model for thermal conductivity calculation. (d) Coaxial double-walled carbon nanotube (5,5)@(10,10) junction. The dash box represents the periodic boundary condition utilized in the heat transfer direction (along the carbon nanotube axis). Heat flux is introduced by kinetic energy exchange between atoms in the heat and cool region (as marked in red and blue colors, respectively, see Methods section for details) to reach a steady temperature distribution in the system.

conductivities. Moreover, the heat conductivity within graphene layers is 2 orders of magnitude higher than in the transverse direction,[14,15] because the intertube van der Waals interaction is much weaker than sp^2 bonding force. Moreover, the nanosized constriction of the interface limits heat transfer across the cross-linking between carbon nanotubes significantly.[16,17] The distinct difference between intertube and intratube thermal conductivity critically restricts the overall thermal performance of carbon-nanotubes-based composites. To address the challenges summarized above, an in-depth fundamental understanding of the interfacial heat transfer in one-dimensional nanostructures is needed, which lays the foundation for further engineering and improvements of the interfacial thermal transfer among carbon nanostructures. However, current models developed for interfaces in bulk materials[18,19] cannot be directly applied to a nanoscale interface, specifically to interfaces between similar materials bonded through weak interactions (*i.e.*, van der Waals forces) and can therefore not be used to engineer the performance of nanostructured junctions between carbon nanotubes.

In carbon nanotube junctions or percolated carbon nanotube networks, individual nanotubes interact and entangle through intertube van der Waals forces. Locally, carbon nanotubes tend to bind and form energetically stable bundles.[1] For such a parallel junction as illustrated in Figure 1a, the thermal conductivity κ_c of the interface can be defined from the temperature difference ΔT and the heat current density J flowing through the structure; that is, $J = \kappa_c \Delta T$. The ballistic phonon propagation within each nanotube is scattered at the interface, which results in a notably large interfacial resistance.[17,20] Such a system of two nanotubes can be modeled by two harmonic oscillators coupled through a low-order interacting terms.[21] The performance of heat transfer is then determined by two primary factors: (1) by the matching of phonon spectra of the nanotubes that determines resonant energy transfer events. In random networks of carbon nanotubes or carbon nanotube mats, nanotubes do not align well but may form point-contacts at intersection points. The limited contact area at these junctions results in thermal conductivities that are even lower than those of thermally insulating polymers.[16,17] (2) By the coupling between carbon nanotubes, that is, the geometrical overlap between the phonon modes in individual nanotubes, which directly depends on the contact area and the coupling strength. Conventional theories for interfacial thermal conductivity such as acoustic mismatch model (AMM) or diffusive mismatch model (DMM)[18,19] are constructed for dissimilar materials with mismatch phonon spectra, and the thermal conductivity is derived from the transmission coefficients of phonon modes. In contrast, at the interface between parallel carbon nanotubes, the phonon spectra are identical, so that the transmission coefficient of phonon modes across the interface is incorrectly predicted to be one, without taking into account the scattering at the interface. To address this issue, the effects of geometrical overlap of phonon modes in different nanotubes and the associated coupling strength must be considered. Atomistic simulation provides a promising approach for the analysis to enable a bottom-up description of this phenomenon. This strategy is pursued in this paper.

RESULTS AND DISCUSSION

Following the discussion above, to improve the thermal conductivity of carbon nanotube junctions in nanodevices and materials, approaches that can improve both the structural stability and thermal coupling between carbon nanotubes must be developed. We begin our analysis with a study of carbon nanotube interfaces based on native van der Waals interactions. We then propose two solutions to enhance the thermal performance of these junctions. The first approach is based on wrapping polymer chains with dimension close to the size of the intertube gap. The second one is to coat the carbon nanotubes with a metal layer. Both methods can be easily implemented on the basis of current experimental techniques. To investigate the effectiveness of these approaches on the interfacial thermal transfer between carbon nanotubes, we perform molecular dynamics simulations to calculate the thermal conductivity at the interfaces and provide a comparison with native van der Waals interactions.

Carbon Nanotube Interface through van der Waals Interaction. We begin with a discussion of the reference case where two carbon nanotubes are bonded *via* van der Waals interactions (Figure 1c,d). The interfacial thermal conductivities κ_c of native carbon nanotube junctions calculated from molecular dynamics simulations, which can be represented as a thermal resistor as sketched in Figure 1a, are summarized in Figure 1b. The results show that the interfacial thermal conductivities are on the order of 0.1 to 1 GW K^{-1} m^{-2}. This value is close to the interfacial thermal conductivity at various symmetric tilt grain boundaries in bulk silicon,[19] but is much higher than those at dissimilar materials interface such as carbon-nanotube−silicon junctions as investigated previously (0−500 MW K^{-1} m^{-2})[22] or carbon-nanotube−surfactant junctions,[13] where the phonon spectra in carbon nanotubes and the other material are highly mismatched (in these cases, phonon modes with high population in one material can hardly be transmitted into the other material). From the aspect of geometrical overlap between phonon modes in different carbon nanotubes, our molecular dynamics simulations show that the modes with lower frequencies such as bending, waving, and radial breathing have a much larger amplitude and thus contribute more to the intertube coupling than the higher frequency phonon modes such as in-plane distortions. In the extreme case, the vibrational energy of the radial breathing modes excited in one tube can be transmitted into the other ones with negligible loss through the resonant coupling.[23] Furthermore, κ_c is found to be enhanced as the contact length L increases, which enlarges the contact area and geometrical overlap between the intratube vibrational modes (Figure 1c). The dependence is almost linear, and a value of 1 GW K^{-1} m^{-2} is reached for a contact length of 10 nm. The κ_c is expected to be even higher for longer contact lengths (which is currently not accessible by atomistic simulation because of limitations in system size). To analyze the significance of the interfacial thermal resistance in terms of the equivalent length of a perfect carbon nanotube that provides the same thermal resistance, we define the Kapitza length[19] as $L_c = \kappa/\kappa_c$, where $\kappa = 6000$ W K^{-1} m^{-1} is the thermal conductivity of single-walled carbon nanotubes. Thus $\kappa_c = 1$ GW K^{-1} m^{-2}, gives $L_c = 6$ μm as the length of carbon nanotubes that should be used to substitute the junctions. The large Kapitza length clearly shows the limitation of carbon nanotube junctions on the overall thermal transfer performance. The interfacial thermal conductivity between carbon nanotubes is found to increase as the diameters of carbon nanotubes increases as well, which eventually saturates when the carbon nanotubes has a diameter larger than 1.4 nm (corresponding to a (10,10) nanotube). The van der Waals interaction is only effective in the range of approximately 1 nm, and κ_c only depends on the interacting parts in the nanotubes. When the radius of carbon nanotube increases, the contact area defined by the van der Waals forces increases very slowly, and κ_c does not change much for larger radius nanotubes exceeding (10,10) tubes.

To obtain a fundamental understanding of the effect of intertube coupling strength on the energy transfer, we investigate the thermal conductivity κ between graphene layers, along the *c*-axis direction. The coupling strength between graphene layers can be easily tuned by adjusting the intertube van der Waals parameter ε in the Lennard-Jones formula (see inset in Figure 2). Our results shown in Figure 2 display a strong dependence of the interface conductivity (defined here as $\kappa_c = \kappa/d$, where d is the interlayer distance) on ε. This result shows that the thermal conductivity at interfaces between carbon nanotubes, graphene sheets, or in multiwalled carbon nanotubes can be tuned by modifying the intergraphene layer interaction strength. Experimentally, this can be achieved by applying pressure[24] or prestress through electron irradiation and annealing approaches.[25]

Thermal interfaces between carbon nanotubes are also present in multiwalled carbon nanotubes, where concentric nanotubes aligned coaxially (Figure 1d). In multiwalled carbon nanotubes carbon nanotube junctions are typically more stable due to the cylindrical constraints. Similarly as for the single wall case, the interfacial thermal conductivity shows a linear dependence on the contact length L. The results shown in Figure 1b also illustrate that although in the multiwalled

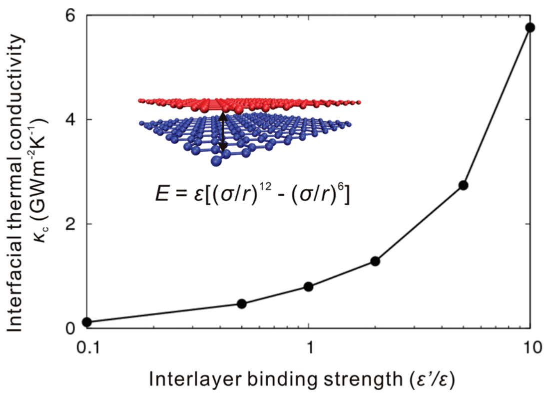

Figure 2. Interlayer thermal conductivity between graphene sheets. The interfacial thermal conductivity in graphite depends on the van der Waals interaction strength between adjacent graphene layers, which is modeled by tuning the interaction strength factor ε' in the Lennard-Jones expression for the van der Waals binding energy. The resulting κ_c presents a remarkable change that shows that the interfacial thermal conductivity can be tuned by the coupling strength at the interface. This can be realized by applying pressure[24] or prestress through electron irradiation and annealing approaches.[25]

carbon nanotubes there is a much larger contact area between two neighboring carbon nanotubes in comparison with the parallel junction, there is not a significant improvement of the overall interfacial conductivity. One of the reasons for this is that the phonon spectra of the inner and outer nanotube differ, so that the transmission coefficient of the phonon modes through the carbon nanotubes is lowered. Furthermore from an application point of view, the contact length *L* between the inner and outer carbon nanotubes can be tuned easily through external control such as mechanical manipulation or the application of an electrical field,[26,27] while in parallel carbon nanotube junctions, in particular with small contact length, the carbon nanotubes can easily misalign and form crossed junction, as widely observed in the random networks.[17] This instability significantly reduces the intertube heat transfer efficiency and removes the tunability of interfacial thermal conductivity through contact lengths. Therefore, coaxial multiwalled carbon nanotubes that are structurally stable provide a structural basis for novel phononic devices applications such as mechanotunable thermal links.[28] This could be important for the development of devices in which thermal transfer through intertube links can be tuned by external displacement control. In addition, this mechanism might also be useful for high precision displacement measurements. Although parallel carbon nanotube junctions also feature a length dependence, instabilities such as misalignment of carbon nanotubes, or inclusions at the interface may limit the robustness of the quantitative dependence between thermal conductivity and contact length. Thus, other approaches must be developed to increase the thermal coupling between individual carbon nanotubes.

Polymer-Wrapped Carbon Nanotube Interface. The micrometer order Kapitza length as discussed above results in the weak performance of the carbon nanotubes interfaces for heat transfer. Furthermore, the weak van der Waals interaction cannot reliably hold parallel nanotubes together under thermal fluctuations or due to elastic deformation of the material, leading to inferior mechanical stability of such arrangements. These limitations have to be overcome for applications in higher performance thermal management applications, such as hierarchical networks to mitigate ultrasmall thermal point loads[29] that contain a large number of such interfaces. The mechanism of heat transfer through van der Waals interaction dominated interface suggests that in addition to directly increasing the intertube interaction, another efficient way to enhance their performance is to increase the intertube interaction beyond the intrinsic van der Waals interaction through interfacial modification, for example by enhancing the coupling between phonon modes in different nanotubes. One experimentally feasible approach is to wrap the carbon nanotube junctions using polymer chains as has been suggested earlier.[30,31] Here we probe the effect of this strategy under varying polymer wrapping densities. In our simulations we model polyethylene chains to wrap the interface. The polyethylene chains feature a linear conformation and overall dimensions comparable with the intertube gap. Equilibrium molecular dynamics simulations are performed at 300 K using an NVT ensemble after the polyethylene chains are introduced close to the interface. Various initial configurations of the polymer chains such as vertical, perpendicular, and random orientations are used in the simulations. The results show that the final arrangements of the polymer chains at the carbon nanotube junctions do not depend on the initial pattern. In the equilibrated structure, polymer chains are found to reside on both surfaces of carbon nanotubes and in the grooves between them (see snapshots shown in Figure 3), depending on the density of polymer chains. The registry between polyethylene and carbon nanotube and the elasticity of polyethylene help to stabilize the carbon nanotube junctions. Pulling load is applied to investigate the mechanical properties of the interface using steered molecular dynamics simulation. The result (shown in Figure 3) shows that polyethylene wrapping significantly enhances the structural stability and toughness of parallel carbon nanotube junctions. The thermal conductivity through this interface is calculated on the basis of the equilibrium configuration (without mechanical deformation applied). We find that a small fraction of polymer wrapping can improve the interfacial thermal conductivity from κ_{c0} (for pure van der Waals interface between carbon nanotubes, without any polymer wrapping) by 40%, up to 1.4 κ_{c0}. The phonon spectrum of the hybrid structure (Figure 4b) shows that vibrational modes in polyethylene and car-

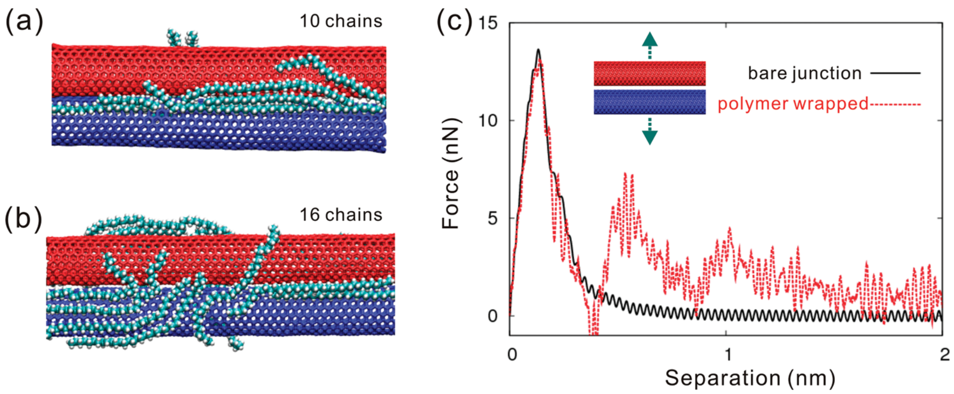

Figure 3. Polyethylene wrapping at interface between carbon nanotubes packed in parallel. (a) At a relatively low polymer chain density (10 chains for each junction), the polyethylene chains $(CH_2)_{20}$ align at the groove between nanotubes. (b) As the density increases to 16 chains per junction, the interaction between polyethylene chains and their binding registry with the graphene lattice results in a considerable number of chains adsorbed on the side of the carbon nanotubes instead of the groove. (c) Polymer wrapping enhances the stability of parallel carbon nanotube junctions, which is investigated through steered molecular dynamics used to mechanically separate the interface. A junction wrapped with 10 polyethylene chains (red dash line) has a much larger binding range than the bare junction, and thus more work needs to be done to break the junction (this effect is similar to role of sacrificial bonds in improving energy dissipation in bone fracture[48]).

bon nanotubes overlap significantly at the low frequency range (in particular below 70 THz), which indicates that the energy transfer between carbon nanotube and polyethylene is effective. Furthermore, the enhancement of κ_c increases with wrapping density at small wrapping densities. However, as the wrapping density increases beyond 10 polyethylene chains per junction, the enhancement of the interfacial thermal conductivity decreases. This result suggests that the optimum wrapping density is ≈10 chains per junction for our (10,10) carbon nanotube case. From the simulation trajectory we observe that at small polymer wrapping densities, the polymer chains align at the groove (Figure 3a) and help by assisting the energy transfer between carbon nanotubes, whereas at larger wrapping densities, the polymer chains themselves form networks and wrap around the carbon nanotube surfaces (Figure 3b). These surface adsorptions perturb the heat flow within carbon nanotubes and thus reduce the overall thermal conductivity. As the randomly arranged polyethylene network has a lower thermal conductivity, the overall enhancement is reduced. These results suggest that an improvement of thermal transfer at an interface between identical structures can be achieved through enhancing the coupling strength, that is, by introducing bridging molecules and by increasing the mechanical coupling. In addition, κ_c for the wrapped carbon nanotube junction is also improved as the overlap length increases, and reaches the highest value at the optimum wrapping density.

Carbon Nanotube Coated by Metal Layers. Another feasible approach to connect carbon nanotubes is through metal coating.[32] Metals like Au, Cu, and Ni can form stable and electrically transparent junctions with carbon nanostructures.[33,34] The strong mechanical binding and electronic coupling between metal and graphene layers[35] suggests promising applications. In carbon nanotube interfaces through van der Waals in-

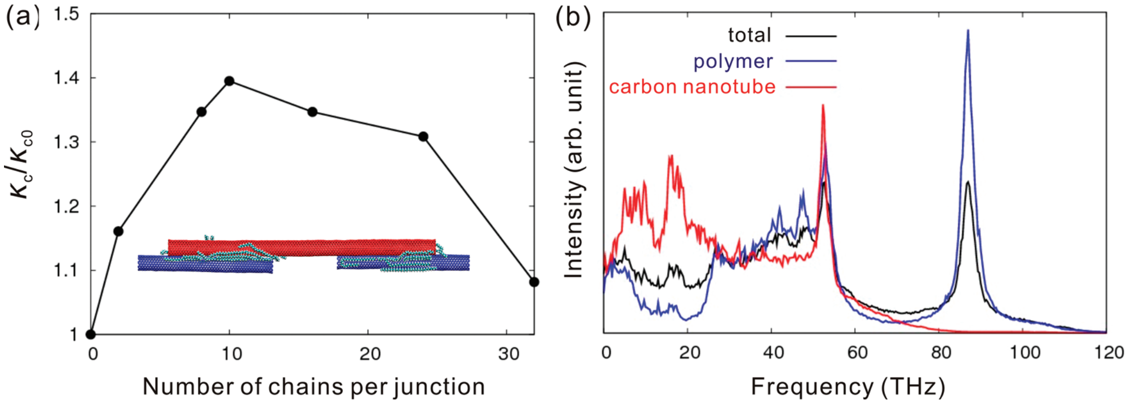

Figure 4. Interfacial heat transfer improved by polymer wrapping. (a) Enhancement factor (κ_c/κ_{c0}) of the interfacial thermal conductivity by polyethylene chain wrapping at different densities, where κ_{c0} is the conductivity in absence of polymer chains. The improvement reaches a maximum of 140% with 10 chains wrapping for each junction, and decreases for larger polyethylene wrapping densities. Inset: snapshot of the (10,10) carbon nanotubes wrapped by 10 polyethylene chains $(CH_2)_{20}$. The overlap length used here is 9.4 nm. (b) Phonon spectrum of the hybrid system containing carbon nanotubes and polyethylene chains. There is a notably larger overlap at frequencies below 70 THz, which results in a more efficient energy transfer between the nanotubes.

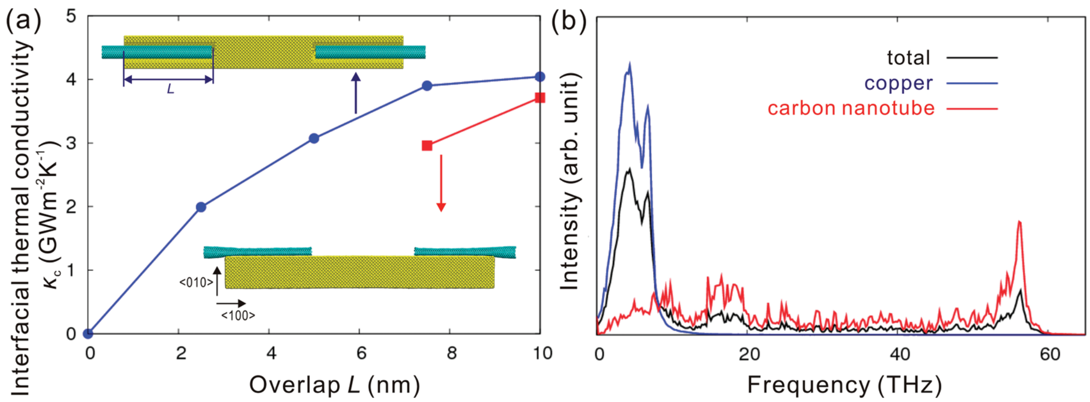

Figure 5. Enhanced heat transfer through metal layer coating. (a) The interfacial thermal conductivity between a (10,10) single-walled carbon nanotube and copper layers is calculated using the two models depicted as insets. The carbon nanotube is embedded in bulk copper along ⟨100⟩ direction (blue dot-line) or deposited on (010) surface (red square-line). The interfacial thermal conductivity increases with overlap length *L*, and is remarkably larger than the bare carbon nanotube junctions with the same overlap *L*. (b) Phonon spectrum of copper, carbon nanotube, and the hybrid system where the carbon nanotube is embedded inside bulk copper. The result clearly shows the mismatch between the phonon spectra.

teraction and polymer wrapping as discussed above, phonons dominate the thermal conductivity. While for the metal–carbon nanotube interface, the electronic transport may help to transfer heat as well, since carbon nanotubes can also be metallic. The electronic contribution to thermal conductivity κ_{ce} can be calculated through the Wiedemann–Franz law that has been extended from bulk materials to their interfaces,[36] that is, $\kappa_{ce} = (\pi^2/3)\sigma_c T(k_B/e)$ where σ_c is the interfacial electronic conductivity, T is temperature, k_B is the Boltzman consant, and e is the electron charge. However, measurements for bulk SWNT samples show that the thermal conductance is still dominated by phonon contributions in the range below or around 300 K,[8] that is, the electronic contribution to the thermal conductance is 2 orders of magnitude lower.[37] Thus, specifically at the metal–carbon nanotube interface, molecular dynamics simulations solving the lattice dynamics at atomistic level can recover all relevant physics for the lattice heat transfer process. We model an interface between face-centered cubic bulk copper and single walled carbon nanotubes in two possible configurations. In the first case, a (10,10) single walled carbon nanotube is embedded inside the bulk copper and the nanotube axis is aligned along the ⟨100⟩ direction of the copper crystal (see upper inset in Figure 5a). Our results show that the interfacial thermal conductivity between the embedded carbon nanotube and surrounding bulk copper surface is on the order of 1 GW K^{-1} m^{-2} (Figure 5a), which is several times higher than the native junction between parallel carbon nanotubes or in multiwalled carbon nanotubes. This result can not be explained by acoustic or diffusive mismatching models, specifically because the phonon spectrum of carbon nanotubes mismatches with the copper layers (Figure 5b), and because phonon transmission between phonon modes should be less efficient than at the interface between carbon nanotubes. This remarkable enhancement of interfacial thermal conductivity in comparison with carbon nanotube junctions could result from the large contact area, good structural stability, and relatively high coupling strength between carbon atoms in the nanotube and in copper. In the second setup of interfaces between carbon nanotube and copper layers, carbon nanotubes are adsorbed on a copper (010) surface. In the equilibrium state at 300 K, the single walled carbon nanotube collapse radially at the interface due to the attractive force (see the lower inset shown in Figure 5a). The simulation result shows that this interface has a slightly lower thermal conductivity than the embedded configuration, as a result of the reduced contact area and the collapse induced structural distortions inside carbon nanotubes. Nevertheless, this value is still significantly higher than the bare junctions between carbon nanotubes. Therefore, coating with metal layers with strong interaction with graphene layers is an effective approach to enhance the interfacial thermal transfer performance.

CONCLUSION

In summary, here we investigated fundamental aspects of heat transfer performance between carbon nanotubes by studying different scenarios of designing intertube junctions. The bare interface interacting through van der Waals forces is shown to be quite inefficient and equivalent to micrometer long (Kapitza length) single-walled carbon nanotubes in terms of the identical effective thermal resistance. Our comparison between parallel, multiwalled nanotubes and graphite based on extensive molecular dynamics simulation results show that in addition to the phonon spectrum matching, interfacial coupling (in terms of both geometrical overlap of the phonon modes and coupling strength) has a strong impact on the thermal transfer process and must also be taken into account.

Guided by these observations, we proposed possible improvements through nanoengineering the interfaces between carbon nanotubes (as summa-

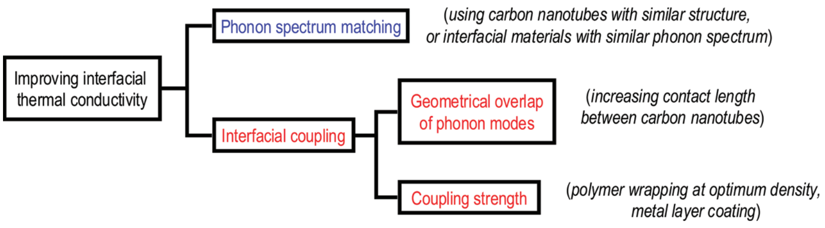

Figure 6. Overview over the approaches to improve the heat transfer performance at carbon nanotubes interfaces. In parentheses are those methods that have been discussed in this work.

rized in Figure 6). Effective approaches include the concept to select carbon nanotubes with similar structure or interfacial materials with a similar phonon spectrum, as reflected by our comparison between parallel identical nanotubes and multiwalled carbon nanotubes with different radius. Furthermore, the performance can be improved by increasing the overlap length between carbon nanotubes, introducing polymer wrapping, or coating by metal with strong interaction with graphene layers. These approaches have been confirmed by our simulation results that show that in addition to stabilizing the interface mechanically, the interfacial thermal conductivity of the carbon nanotube interfaces can be significantly improved. Polymer wrapping gives an optimum performance when the wrapping density assures the polymer chains are lying along the groove between nanotubes and thus assist the heat transfer process. The heat transfer performance of metal coated interfaces, accessible to experimental investigations, can increase by up to a factor of 4. Furthermore, by improving the electronic transfer and electron−phonon coupling between carbon nanotubes and metal layers may result in an even better thermal transfer performance, with great potential for nanoscale devices applications in order to migrate or manage energy and information.

Our results may also be important to better understand thermal properties in biological materials. In biological systems constituted by biological macromolecules such as proteins and DNA, there exists a remarkable number of interfaces formed through noncovalent forces such as van der Waals forces, hydrogen bonds, and hydrophobic and electrostatic forces.[38] Knowledge of the fundamental energy transfer processes at these nanointerfaces is essential for understanding the mechanism in important processes such as heat tolerance,[39,40] protein folding, and photosynthesis.[41] The results reported here and future work in this direction may help to unveil fundamental mechanisms associated with these complex biochemical processes.

TABLE 1. Parameters for the Lennard-Jones Potential $V(r) = 4\varepsilon((\sigma/r)^{12} - (\sigma/r)^6)$, Characterizing the Interatomic Interaction between Carbon and Copper Atoms, Which Is Calculated Using the Mixing Rule from Parameters for Graphite and Face Centered Crystal Copper as Indicated in the Table[45]

	ε (eV)	σ (nm)
C−C	0.004555	0.3851
Cu−Cu	0.167	0.2314
C−Cu	0.02578 ($= (\varepsilon_C\varepsilon_{Cu})^{1/2}$)	0.30825 ($= (\sigma_C+\sigma_{Cu})/2$)

METHODS

Calculation of the Interfacial Thermal Conductivity. Thermal conductivities of carbon nanotubes and their interfaces are calculated through nonequilibrium molecular dynamics (MD) simulation.[42] The interatomic (carbon and hydrogen) interactions in carbon nanotubes and polyethylene are described using adaptive intermolecular reactive empirical bond-order (AIREBO) potential function.[43] Copper nanowires are described using the embedded atom method (EAM).[44] An additional Lennard-Jones form-based pairwise interaction is introduced to model the carbon−copper interactions. The parameters are mixed from those for carbon (in graphite form) and copper (in face-centered crystal) (see Table 1).[45] The thermal conductivities are calculated using the Muller-Plathe algorithm[46] where a heat flux (energy flow rate, in units of W) is applied through momentum exchanges between atoms in the heat source and sink. All the MD simulations in this work are performed using the LAMMPS simulation package.[47]

In the simulations of carbon nanotube junctions, two parallel single-walled carbon nanotubes with the same length and overlap length L are embedded in a periodic boundary condition (Figure 1), creating two interfaces. The unit cell is partitioned axially into $N_{\text{slab}} = 50$ slabs for temperature recording and Muller-Plathe momentum exchange processes. Before the nonequilibrium thermal conductivity calculation, a Nose−Hoover thermal bath (coupling time constant $\tau = 0.1$ ps, time step $\Delta t = 0.5$ fs) is coupled for 1 ns to equilibrate the system. All simulations are carried out at room temperature (300 K). In the Muller-Plathe nonequilibrium simulation, two slabs separated by half of the nanotube length are selected as heat source and sink slabs, that is, at the edge and center of the simulation box as shown in Figure 1c. A heat flux J (energy flow rate, in units of W) is then injected/released in these two slabs by introducing elastic collision between the "hottest" atom (with kinetic energy $mv_h^2/2$) in heat sink slab and the "coldest" atom in the heat source slab (with kinetic energy $mv_c^2/2$) in the NVE ensemble (see inset in Figure 1 for illustration of the model). The collision process is elastic and conserves both total momentum and energy of the system. The momentum exchanging is performed every 20 fs. The heat flux J is collected during an interval of temperature profile evaluation t_{transfer}, where N_{transfer} exchanging has been performed; that is,

$$J = \frac{\sum_{N_{\text{transfers}}} \frac{1}{2}(mv_h^2 - mv_c^2)}{t_{\text{transfer}}} \qquad (1)$$

where the summation is carried out over all momentum-exchanging events, and t_{transfer} is the time period for the summation. Simultaneously the temperature profile $T(x)$ of the carbon nanotube is obtained after averaging over a 50 ps time interval. The interfacial thermal conductivity of carbon nanotubes is evaluated as

$$k_c = \frac{J}{2A\Delta T} \tag{2}$$

where ΔT is the temperature difference at different sides of the interface. The factor two in eq 2 accounts for two interfaces present in the system with periodic boundary condition. Because we are studying the interfacial thermal conductivity between carbon nanotube in comparison with intratube thermal transfer, we consider the cross section of carbon nanotube as the contact area A between carbon nanotubes and their junction. A is calculated by considering the carbon nanotubes as thin shell with thickness of a single carbon−carbon bond-length 0.142 nm, as used in the study of thermal conductivity of single-walled carbon nanotubes.[42] In calculating the interfacial thermal conductivity between concentric nanotubes (5,5)@(10,10) or between (10,10) nanotube and metal layer, we use the cross-sectional area of (10,10) nanotubes as A in order to compare with pristine (10,10) carbon nanotube junctions to quantify the influence of interfacial effects.

Although the system size used in our simulation is far shorter than the mean free path (which is on the order of micrometers[1]), the interfacial thermal transfer at carbon nanotube junctions can be correctly predicted from our model because the thermal resistance of carbon nanotubes is negligible compared with the interfacial resistance, as reflected by the long Kapitza length. Thus, the parts in carbon nanotubes that are not in contact with other nanotubes can be considered as thermally transparent leads and κ_c is independent of them. To validate this, we perform simulations with carbon nanotube lengths ranging from 25 to 75 nm, with the overlap length L kept fixed. The interfacial thermal conductivities thereby obtained show only a very small dependence on the carbon nanotube length. Therefore, the model gives a reasonable consideration of the carbon nanotube junctions with contact length from ten to hundreds of nanometers.

Calculation of the Binding Strength between Carbon Nanotubes. To calculate the interfacial binding strength between carbon nanotubes, in the case with or without polymer wrapping, steered molecular dynamics simulation was performed. One of the carbon nanotube is pulled along the direction perpendicular to the interface at a constant speed of 0.1 m/s while the center of mass of the other nanotube is constrained by a spring to its original position. The elastic constant for the spring connect between the constant tether point and center of mass of the carbon nanotubes is $k = 1.6$ kN/m. The force exerted by the spring and displacement of the carbon nanotube is recorded and the data is used for plotting in Figure 3c.

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