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Molecular dynamics study on thermal transport at carbon nanotube interface junctions: Effects of mechanical force and chemical functionalization

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ABSTRACT

Classical molecular dynamics (MD) simulations are performed in this work to investigate the interfacial thermal transport across stacked carbon nanotube (CNT) junctions. Various approaches are implemented to increase the thermal conductance (G) between CNTs. Effects of crossing angle, contact area, bonding strength, external force and hydrocarbon functionalization on G are investigated. A remarkably increase of thermal conductance is achieved by connecting two CNTs with hydrocarbon chain linkers CH_2. The predicted G changes from 229 pW/K without linkers to 4901 pW/K with an optimized linker number, which increases by a factor of 20. Meanwhile, thermal conductance is found to increase monotonically with contact area but decrease inversely with crossing angle. The van der Waals (*vdW*) bonding strength has similar effects with applied external force on thermal conductance, both of which facilitate the interfacial thermal transport by enhancing the contact pressures. Synthesized relationship of internal coupling strength, external force and final separation distance between CNTs is explored to illustrate the variation of thermal conductance and intermolecular potential energy.

1. Introduction

Carbon nanotubes (CNTs) have been regarded as one of the perfect materials for improving heat transfer performance since their first discovery [1]. The axial thermal conductivity (κ) of individual CNT can reach a very high level beyond 3000 W/m·K from previous work [2]. The remarkable thermal conductivity is partially attributed to the intrinsic well-organized geometric construction and highly stiff C–C sp^2 atomic bonds. With ever-increasing applications in thermal management due to their superb thermal properties [3–5], studies on the heat transfer processes of CNT-based composite materials are urgently needed. Although κ of single CNT is extremely high, significant decreases of κ are reported in CNT-based composite materials and CNT bulk materials [6–8]. The high thermal resistance at CNT interfaces is one of the major factors hindering its thermal performance [9–11]. To facilitate thermal transport between CNTs, the heat transfer mechanism across CNT-CNT interfaces needs to be comprehensively explored.

The Kapitza conductance, known as Kapitza resistance or interfacial thermal resistance [12], is defined as $G = q/\Delta T$, where G, q and ΔT correspond to Kapitza conductance, heat flux rate and temperature drop, respectively. There have been various methods for investigating the CNT-CNT interfacial thermal conductance. Zhong et al. [13] modeled a non-stationary heat transfer process between two parallel 5 nm long (10,10) carbon nanotubes with 2.5 nm overlap and 6 Å separation distance using molecular dynamics (MD) simulations. The predicted G between the two carbon nanotubes was around 13 pW/K. Xu et al. [14] studied the parallel single wall carbon nanotubes (SWCNTs) by making a nanotube overlapped with two other nanotubes at both ends and obtained the thermal conductance around 100–1000 pW/K based on different overlap length. Two approaches, *i.e.*, phonon spectrum matching and interfacial coupling, were developed to improve the interfacial thermal conductance. A method for phonon spectrum matching is using materials with similar phonon spectrum at interface. It was reported that the increase of contact length between CNTs, polymer-wrapped CNT interface and a metal layer coating on CNTs can enhance the coupling strength by Xu et al. [14]. Chalopin et al. [15] calculated the partial thermal conductance at the junction and their dependence with chirality at different temperatures using the Green's function. The calculated G varied from 10 pW/K to 100 pW/K at temperature 300 K. Yang et al. [16] measured G in two cases. One is about the cross junction between two

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Nomenclature

G	thermal conductance, pW/K
q	heat flux rate, W
ΔT	temperature drop, K
T	temperature, K
n	number of atoms
k_B	Boltzmann constant, J/K
m	mass, kg
E	potential energy, J
V	potential energy, J
r	interatomic distance, Å
L	length, mm
D	diameter, nm
G'	actual thermal conductance, pW/K
d	interlayer distance, Å

Greek symbols

v	velocity, m/s
χ	scaling parameter
ε	energy parameter, eV
θ	angle, degree
σ	van der Waals diameter, Å
λ	ratio of thermal conductance

Subscripts

k,i,j,l	serial number of atom

multiwalled CNTs with diameters of 74 nm and 121 nm, and the thermal conductance was in the order of 10^4 pW/K; the other one is parallel aligned with 2.6 μm in contact length between two multiwalled CNTs with diameters of 170 nm and 165–185 nm, and the thermal conductance was about 10^6 pW/K which was two orders of magnitude higher than that in the former case. Foygel et al. [17] theoretically predicted the thermal conductance in the order of 10^4–10^5 pW/K.

Strengthening the interactions between two CNTs is an effective way to facilitate the CNT-CNT interfacial thermal transport. It can be achieved by increasing thermal contact area (A) [18], applying external force [19] or using chemical organic linkers to connect two individual CNTs [20]. Varying thermal contact angle between two CNTs is feasible to regulate thermal contact area, and thus modulate interfacial thermal transport. Hu et al. [18] simulated two (6,6) single-walled CNTs with different crossing angles from 0° to 90° for different tube lengths of 90 nm and 120 nm using MD simulations. They found that G had an inverse dependence of crossing angle. Smaller thermal contact angle corresponds to a larger A which means better thermal interaction and larger interfacial thermal conductance. Evans et al. [19] also investigated the effect of junction area on interfacial thermal conductance by varying the crossing angles from 0° to 90° and the effect of force applied in the cross-plane direction which is perpendicular to the tube axes on thermal conductance with two limiting crossing angles (0° and 90°) using MD simulations. The effect of junction area/crossing angle on thermal conductance had the same tendency as shown in the work by Hu et al. [18]. The effect of applied force on thermal conductance is twofold reported by Evans et al. [19]. On the one hand, applied force reinforces the CNT-CNT van der Waals (*vdW*) bonding to increase interfacial thermal conductance; on the other hand, applied force deforms the CNTs to alter the junction area between CNTs which may increase or decrease thermal conductance according to different crossing angles. Varshney et al. [20] developed a range of two-nanotube-linked models which consist of two CNTs linked with different chemical organic molecules immersed in the epoxy matrix using MD simulations. The effects of linker type and linker number on thermal conductance were explored [20]. It was reported that there was a positive correlation between G and the number of linkers and an inverse dependence of G on the length of linkers between CNTs in their work. The increased number of covalent bonds due to condensed linkers would reinforce thermal transport between CNTs. They found that longer linkers would increase the separation distance between CNTs, which would weaken the *vdW* interaction and reduce the G values. However, the increasing trend of G with linker amount was only confirmed at very small scales, and whether the trend will continue as the number of linker increases is an unknown problem.

Despite of the existing studies on the thermal conductance across CNT interfaces, the heat transfer mechanisms in aspects of contact angle/area, internal/external pressures and large amount of chemical linkers are still unclear. In this work, effects of crossing angle on CNT-CNT thermal conductance are comparatively studied with thermal contact area. Besides, modulations of interfacial thermal conductance by different interaction types, such as the internal coupling strength, external exerted force and the covalent hydrocarbon functionalization, are systematically investigated. In addition, the size effect of CNTs on G is significant and there have been works about the size effect on G between CNTs. Evans et al. [19] investigated effect of CNT length on contact conductance and found a positive dependence of thermal conductance on CNT length. In their work, thermal conductance reached saturation of 91 pW/K for CNT length of 20 nm. Hu et al. [18] and Salaway et al. [21] both explored CNT length effect on thermal conductance between two perpendicular CNTs with lengths ranging from 20 to 200 nm. The trends of thermal conductance varied with CNT length are coincident with that in the work by Evans et al. [19], whereas thermal conductance neither seemed to be saturated even CNT length reached 200 nm.

2. Models, physical basis, and computational approach

In this work, non-equilibrium molecular dynamics (NEMD) [22] is applied to investigate the CNT-CNT interfacial thermal conductance. Two 10 nm length (10,10) CNTs are used in all simulations. Atomic configuration of the hybrid system is shown in Fig. 1. To build a constant temperature gradient, 200 atoms at each end of one CNT are grouped as hot reservoirs with a heat flux rate q by velocity rescaling, and 200 atoms at each end of the other CNT are treated as the cold reservoirs with negative q. The amount of thermal energies added/subtracted to/from the hot/cold reservoirs are equivalent, which ensures the overall temperature of the system remains constant. Only non-translational kinetic energies are applied in the thermal reservoirs so the system's aggregate momentum is conserved. The outermost 20 carbon atoms at each end of both CNTs are fixed to prevent the CNTs from moving and rotating [23]. The remaining regions are divided into 10 slabs along the transverse direction. The temperature of each slab is calculated as

$$T = \frac{1}{3nk_B}\sum_{k=1}^{n} m_k v_k^2 \tag{1}$$