論 文 の 内 容 の 要 旨

Abstract of dissertation:

Title of dissertation:

Theoretical study of thermoelectric properties of conical carbon nanofibers

（コニカルカーボンナノファイバーの熱電特性の理論解析）

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1. Introduction

Thermoelectric (TE) materials have the ability to generate usable electric power from waste heat or to act as solid-state refrigeration and heat pumps without the need for moving parts. While TE devices can meet these goals in principle, it is critical to develop high performance materials with the goal to improve efficiency (both thermodynamically and cost-effectively) and power output. Carbon nanostructures are promising candidates for next generation TE applications because of their unique thermal and electrical transport properties as well as stability in low-dimensional nanostructures. Among carbon nanostructures there exist structures whose effect on thermal and electrical properties are not well established, for example, the conical-helix nanofiber (CHNF). CHNF is an annular structure formed by a helically wound GNR and has been observed in both carbon and boron-nitride nanostructures. The nanostructure of CHNF and CSNF are shown in figure 1. The nanostructures are similar except that CSNF is made of discrete graphitic cones and CHNF is a continuous covalent network.

In this dissertation, I explore the thermal and electrical transport properties of carbon nanofibers using both classical non-equilibrium molecular dynamics (MD) and tight-binding (TB) simulations. Despite similarities in structure, CSNF and CHNF have differences in thermal conduction mechanisms [1,2], which are explored here. To accomplish this study I have also developed a simplified naming convention for CNF that contains complete geometrical information for a constant radius nanofiber with axial periodicity [3].

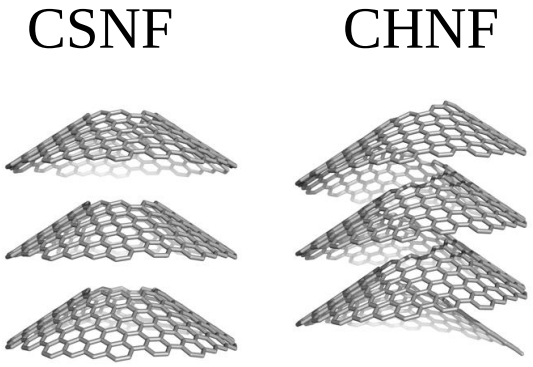

Fig 1. Conical nanofiber natnostructures investigated in this dissertation. The structures are the cup-stacked nanofiber (CSNF) and the conical-helix nanofiber (CHNF).

2. Nanofiber geometry

To aid in the research of conical nanofibers I have developed a novel naming convention, which will help in communication and research of these nanostructures. This naming convention simplifies the geometry to 3 independent variables (n, m, k) such that n describes the outer radius, m describes the inner radius, and k describes the apex-angle. This naming convention is consistent with but does not necessitate periodic boundary conditions, which allows for simulation of nanostructures that have properties independent of distance from the boundary. Classical

molecular dynamics (MD) revealed that the CHNF structure expresses a wide range of stable apex angles above 110˚, which agrees qualitatively well experimental observations.

2. Lattice contribution to thermal conductivity

The thermoelectric figure of merit *ZT* describes the efficiency of a system. *ZT* approaches infinity as the efficiency approaches the Carnot efficiency. G is electrical conductance, S is thermopower, T is temperature, and the total thermal conductance is the sum of phonon κ_p and κ_e components.

$$ZT = T\frac{GS^2}{\kappa_p + \kappa_e} \quad (1)$$

Good thermoelectric materials will have a value of *ZT* greater than one and are typically highly doped semiconductors with large carrier concentrations and low thermal conductivity. Maximum efficiency of a TE device is inversely proportional to the material thermal conductivity. Therefore, it is important to study the thermal conductivity of novel materials to better evaluate their applicability. To estimate the thermoelectric figure of merit ZT of the nanofibers, we want to incorporate both phonon and electron contributions to thermal conductivity. Classical, non-equilibrium MD is adopted for lattice contribution to thermal transport simulations. I use the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) open-source classical MD simulation package. Axial length dependence of thermal conductivity is shown in figure 2(a) for a variety of one-dimensional carbon nanostructures shown in figure 2(b).

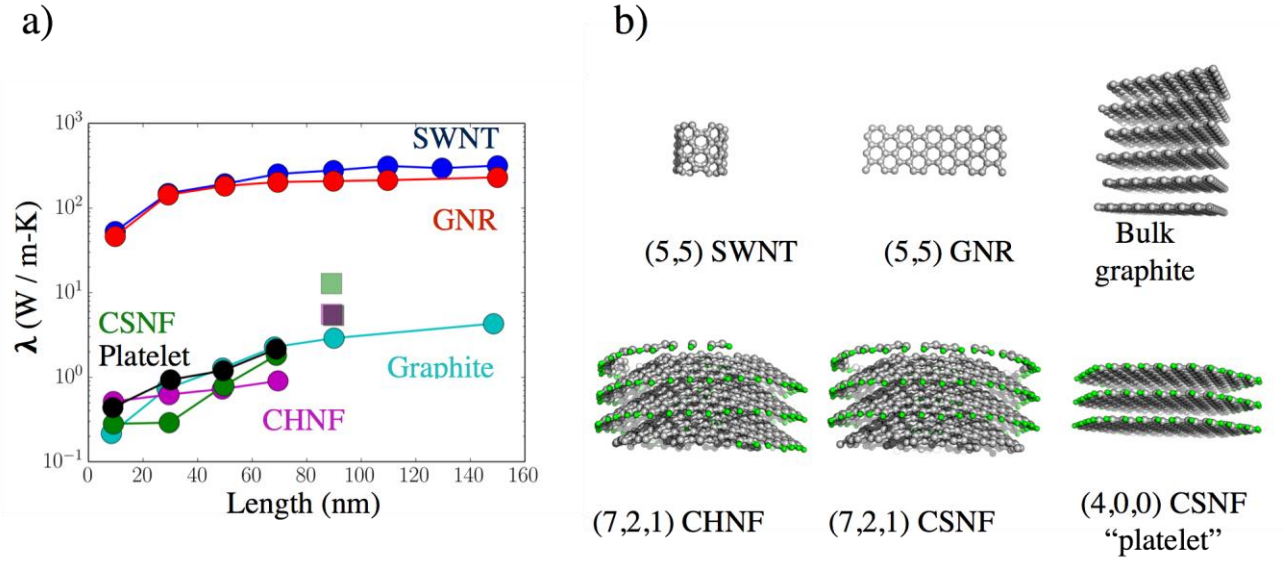

Fig. 2. Thermal conductivity calculated (a) for a variety of carbon nanostructures (b). The nanofiber thermal conductivity is two orders of magnitude lower than SWNT and GNR.

(7,2,1) CSNF and CHNF were simulated for 10.2, 30.0, 50.0 nm, 70.0 nm, and 90.0 nm. These nanofiber structures were chosen to have a wide radius of up to 5 hexagons at the widest point in the disc, while also being computationally feasible to simulate. The system size used here ranges from 25 to 221 cups as opposed to previous studies that were limited to 10 cups. The thermal conductivity of CHNF and CSNF is two orders of magnitude lower than SWNT and GNR. The thermal conductivities of platelet nanofiber and bulk graphite with out of plane restriction are one order of magnitude lower than SWNT and GNR.

The CHNF and CSNF thermal conductivity also show significantly different length dependence. CHNF shows very little length dependence of thermal conductivity, but CSNF, graphite, and platelet structures show strong length dependence. This may suggest diffusive thermal transport in CHNF. To study this further, we investigate the phonon band structure and estimate thermal conductivity from phonons. Analysis suggests that the CSNF length dependence results from very weak, low velocity modes. Conduction is primarily concentrated in a single mode, the longitudinal acoustic (LA) mode. In comparison, the CHNF structure is far more complex and has a

significantly higher number of intersecting modes with larger group-velocity. The larger number of intersecting modes and several modes that avoid crossing the LA branch may indicate a large degree of forward and back scattering in this frequency range. Comparison of CHNF thermal conduction with in-plane GNR and out of plane graphite does not completely explain the low thermal conductivity phenomena for CHNF. However, the phonon structure suggests strong phonon scattering may be the cause. Understanding this will help us better apply this unique nanostructures to TE.

2. Tight binding calculation of thermoelectric figure of merit

Investigation of electrical transport in carbon nanofiber structures is performed with the nonequilibrium Green's function method using Atomistix Toolkit (ATK). This method only considers coherent electron transport. Here I have performed calculations using the semi-empirical TB extended Hückel method as parameterized for bulk materials. It is convenient to use semi-empirical methods to study the electrical transport prior to using more complex algorithms such as the local-density-approximation (LDA) because they are still accurate within the scope of their applicability. Thermoelectric properties are calculated using the Landauer-Buttiker formula. In this study, I am only considering bulk, undoped fibers under a bias voltage. First, I estimate a range of *ZT* based on experimental nanofiber and graphene data, which I use to compare to theoretical simulations.

The band gaps for (4,1,1) and (5,1,1) CSNF are -1.04 eV and 0.85 eV respectively. These results underestimate the 0.44 eV band gap of CSNF determined experimentally [4]. This may be a size effect. CHNF was found to behave metallically. I estimated the transmission spectra for (4,1,1) and (5,1,1) CNFs over the range of chemical potential for the range of ±4 eV. Figure 3(a) show the calculated estimated *ZT* for (4,1,1) and (5,1,1) CSNF using the thermal conductance calculated with MD simulations of 50 nm nanofibers. Maximum values of ZT are located for chemical potential associated with the quantized step in transmission. The maximum calculated *ZT* are 4.1 and 2.6 for (5,1,1) CSNF and (4,1,1) CHNF respectively. CSNF shows peaks near the Fermi level corresponding to chemical potentials that exhibit high electrical conductivity.

A defective (4,1,1) CHNF structure was also investigated. For the discontinuous CHNF structure we observe significant decrease in electrical conductivity, which leads to over 75% reduction in ZT for negative chemical potential. However, it is seen that the maxima in the positive chemical potential range is mostly unchanged. This leave the CHNF with a maximum ZT of 1.04.

These estimates of *ZT* are very high and were calculated using the maximum estimated thermal conductance from MD. This value is considered an overestimate because ATK only accounts for coherent electron transport here. That being said, the results are promising and clearly show the feasibility of CNFs for thermoelectric applications. The effect of doping is still not yet investigated.

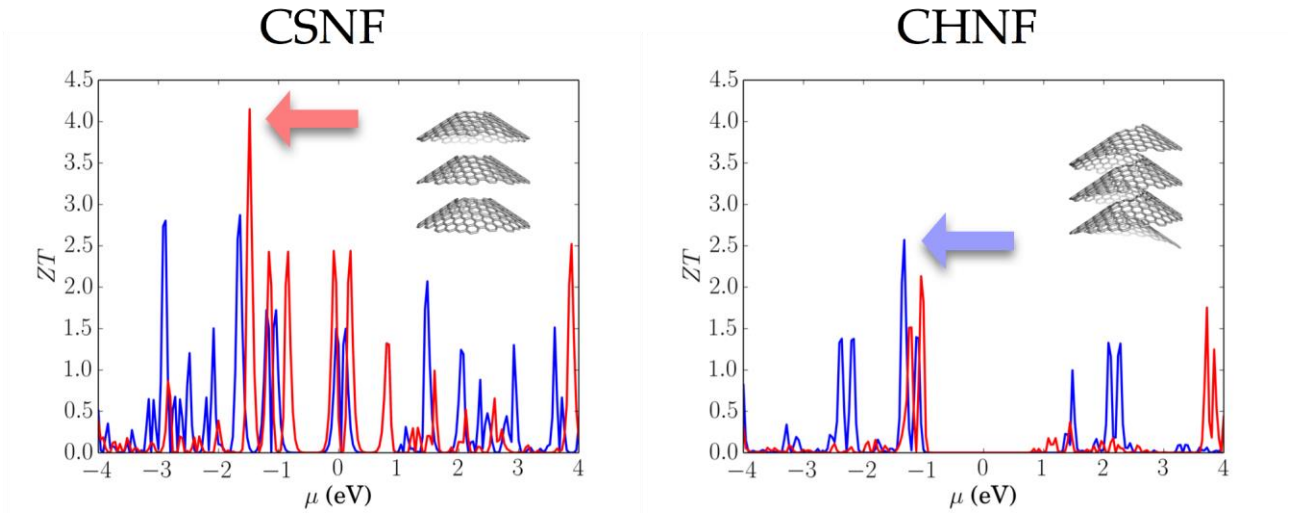

Fig. 3. Estimated thermoelectric figure of merit ZT for CSNF (left) and CHNF (right) nanostructures for (4,1,1) (blue) and wider radius (5,1,1) (red) configurations.

5. Conclusions

Thermal and electrical transport properties and thermoelectric properties of conical carbon nanofibers (CNF) were investigated using MD and TB techniques. The nanofiber structures show two orders of magnitude reduced thermal conductivity compared to single walled nanotubes and graphene nanoribbons. This makes them promising materials for use in low-conductivity applications. Investigation of the cause of reduced thermal conductivity showed that the mechanics of cup-stacked nanofibers (CSNF) and conical-helix nanofibers (CHNF) differ greatly. The CSNF nanostructure has only one primary thermal conducting mode. In CHNF, forward and back scattering appear to be the dominant factor in low thermal conductivity.

Using tight-binding and non-equilibrium Green's function method techniques I estimated *ZT* dependence on structure from a purely theoretical standard to be up to 4.1 for CSNF and 2.6 for CHNF. This shows the conical carbon nanofibers may have efficient and strong usability in the thermoelectric applications including TE generators and TE heating and cooling.

References:

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Peer Reviewed Paper:

1. D.A. Thomas, T. Yamamoto, T. Tada, S. Watanabe, "Non-equilibrium thermal transport simulation of conical carbon nanofibers," *Trans. Mat. Res. Soc. Jpn.* **38**, 183 (2013).

Papers currently in preparation

2. D.A. Thomas, T. Yamamoto, T. Tada, S. Watanabe, "Phonon structure and low thermal conductivity of conical carbon nanofibers."

3. D.A. Thomas, T. Yamamoto, T. Tada, S. Watanabe, "Calculation of high ZT in conical carbon nanofibers."