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Optimal mass distribution in carbon nanotubes for extreme thermal conductivity: Analytical manipulation of isotope effects

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ABSTRACT

Using a gradient-based optimization method, an optimal mass distribution for a single-walled carbon nanotube (CNT) is determined for extremal thermal conductivity. The variation of atomic mass distribution or the isotope impurity in the CNT could lead to either extremely high or low thermal conductivity. The adjoint variable method is employed for the efficient and accurate design sensitivity analysis of thermal conductivity, which can be obtained from non-equilibrium molecular dynamics (NEMD) approach. The obtained analytical sensitivity can be extensively utilized to determine the optimal distribution of atomic masses, using a density-based topology optimization method. The resulting thermal conductivity is reduced by more than 90% or increased by 70% of the one of the pristine CNT. The density of states (DOS) after the optimization indicates that the optimization process yields the effective and physically meaningful result as we interpret the resulting distribution of mass.

1. Introduction

Ever since Iijima [1] first discovered a carbon nanotube (CNT) in 1991, the CNT has become an important material in thermal sciences as well as other fields. There are immense interests in nanoscale graphitic structures and CNTs for mechanical, electrical, and thermal properties of systems. Current synthetic methods for CNTs include laser ablation, arc discharge, electrolysis, and chemical vapor deposition [2]. Berber et al. [3] reported that the thermal conductivity of a single-walled CNT was as high as 6000 W/m K at room temperature, which is higher than diamond and graphite under the same conditions. Also, the extremely low thermal conductivities of CNTs are discovered in case the CNTs have certain chirality, isotope impurity, and defects. Now, the CNTs possess the versatile capability that can be utilized as thermal insulators as well as heat conductors.

In drug delivery systems, for instance, CNTs are utilized as effective nano-carriers to deliver active drug molecules such as anticancer drugs, antimicrobials, anti-inflammatories, anti-hypertensives, and anti-oxidants [4]. Most interestingly, thermal conductivity properties of CNTs are successfully applied for a photo-thermal therapy to ablate cancer cells. The major merit of near infrared laser (NIR, 700–1100 nm range) used in the photo-thermal therapy is a safe penetration of light on normal cells. However, the cancer cells where CNTs are attached absorb NIR light, which finally leads to destroy cancer cells by heating them [5]. To apply the photo-thermal therapy in practical uses, there are two critical factors to be considered; *the thermal conductivity of CNTs* and *the modification of CNTs for specific targeting* to cancer cells. If the thermal conductivity of CNTs can be increased during synthetic processes, the required amount of NIR light will decrease. This minimizes the NIR light penetration into the normal cells that will further enhance the safety of cancer photo-thermal therapy in nanomedicine.

Zhu and Li [6] discovered that the ultrathin CNT of (2,1) chirality exhibited surprisingly low thermal conductivity by using molecular dynamics (MD) simulations with a non-equilibrium molecular dynamics (NEMD) method. The thermal conductivity of (2,1) CNT was calculated as only 16–30% of those in regular (2,2) and (5,5) CNTs. Examining phonon modes in (2,1) CNT, they found that the acoustic phonon modes in (2,1) CNT were soften and the phonon lifetimes also showed significant reduction compared to (2,2) CNT. They concluded that these two factors accounted for the significant reduction of thermal conductivity of (2,1) CNT.

Thermal conductivity of nanotubes with junctions was reported, using MD simulations, such that they were less than that of straight ones. Cummings et al. [7] investigated that the thermal conductivity of Y-shaped junction CNT was less than that of straight (14,0) CNT. A jump in temperature profile around the Y-shape junction was reported and a similar discontinuity was found when some defects were introduced to the corresponding straight zigzag (14,0) CNT. Meng et al.

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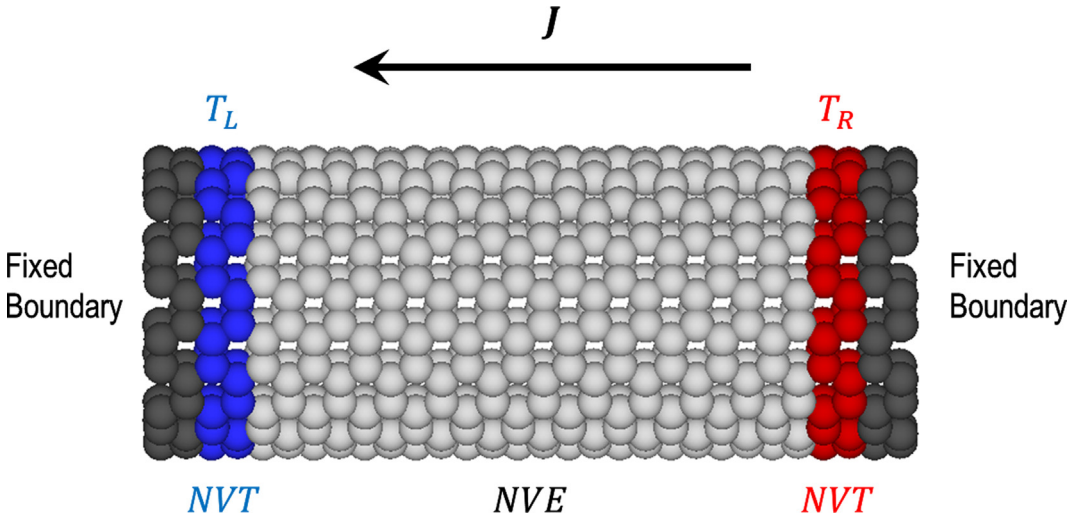

Fig. 1. (10,10) CNT model for MD simulations.

[8] reported the thermal conductivity for ultrathin CNT with and without X-shaped junction using NEMD approach. There was also a jump around the junction, where large temperature gradients lead to the significant reduction of thermal conductivity. Prasher et al. [9] showed that the thermal conductivity of random networks bed of single and multiwall CNTs is lower than that of thermally insulating amorphous polymers by an experimental approach. They compared the thermal conductivities of an isolated CNT and two CNTs with a junction by using an equilibrium molecular dynamics (EMD) method. Yang et al. [10] employed the NEMD method to investigate the longitudinal thermal conductivity of non-orthogonally extended X-shaped junctions of CNTs. In the NEMD calculations, there were two distinct jumps in temperature profile around the extended X-shaped junction, which were different from the previously reported standard junctions.

Isotope impurity affects the material behaviors such as thermal, mechanical, and vibrational properties. There are usually three isotopes of carbon atom, denoted by ^{12}C,^{13}C, and ^{14}C, which possess the same electronic structure but different mass. The dependence of thermal conductivity of CNTs on isotope impurity has been studied using MD simulations by many research groups. Zhang and Li [11,12] studied the isotope impurity effects on the thermal conductivity of (5,5) CNTs. In the simulation model, ^{14}C atoms are randomly distributed in ^{12}C CNT. They calculated the thermal conductivity of (5,5) CNT at room temperature 300 K using NEMD approach, where the temperature difference between hot and cold slabs is set to 10 K. With 40–50% ^{14}C, the thermal conductivity was reduced to about 40% of that of a pure ^{12}C CNT. Cheng et al. [13] theoretically investigated the effects of isotope doping with ^{13}C on vibrational, optical, and thermal properties of CNTs. For CNTs of armchair and zigzag types, they investigated the properties of three configurations after isotope doping. Liu et al. [14] investigated the thermal conductivity of silicone nano-sheets (SiNSs) via MD simulations. They found that isotopic doping was an efficient tool in reducing the thermal conductivity of SiNSs. Also, they reported that when the SiNSs were randomly doped with ^{30}Si at 50% doping, a maximum reduction of 20% is achieved. In case of Boron Nitride nanotubes, thermal conductivity was reported to be exceptionally sensitive to isotopic substitution [15]. The isotope doping provides an efficient method to adjust the thermal conductivity of nanomaterials [16]. However, the resulting isotope-doped configurations seem randomly distributed and/or to possess a simple topology of a band structure. *Is there an optimal isotope doping or mass distribution of CNTs for minimal thermal conductivity?* In this paper, we present an optimal design method in molecular level to systematically determine the optimal distribution of masses with the help of gradient-based optimization method, which requires an adjoint design sensitivity analysis (DSA) method to determine the design direction in a very accurate and efficient way.

Generally, a topology optimization method [17] enables designers to find a suitable material layout for the required performances of systems. In this paper, the objective of topology optimization is established to find an optimal mass distribution within the allowed amount of isotopes by varying the mass of each atom, which is regarded as a design variable. Since the design optimization in MD simulations necessarily involves many design variables, the sensitivity of performance measures with respect to design variables should be determined in a very efficient way. Among various DSA methods, the adjoint variable method (AVM) is computationally efficient especially for the problems of many design variables but small number of performance measures because their design sensitivity can be computed in a selective manner. The AVM for transient dynamics was well established in Ref. [18] and the corresponding adjoint system turned out to be a terminal value problem. There was a few literature [19] regarding the DSA methods for the transient dynamics. Kim et al. [20] developed an efficient and accurate analytical DSA method using the AVM for a reduced GLE (Generalized Langevin Equation) system which were non-conservative and time-irreversible. Due to the expensive costs of MD simulations, a gradient-based approach and parallel computation are indispensable to obtain the optimal morphology of molecular structures [21].

In this paper, we determined the optimal distribution of mass in a single-walled CNT for extremal thermal conductivity with the help of a gradient-based optimization algorithm. The AVM provides the efficient and accurate design sensitivity of thermal conductivity with respect to the distribution of atomic mass in the NEMD approach. The obtained analytical design sensitivity can be extensively utilized to determine the optimal distribution of atomic mass. To verify the optimal design process, the density of states (DOS) is compared before and after the optimization.

2. Results and discussions

2.1. Thermal conductivity by NEMD approach

Consider an armchair type (10,10) CNT that is 3.684 nm long and consists of 600 carbon atoms in 15 unit cells as shown in Fig. 1, where the CNT model is composed of two temperature-controlled sections and a body tube section.

A Tersoff bond-order potential is utilized in this simulation to represent the carbon-carbon (C-C) bonded interactions. In the beginning of MD simulations, the CNT is thermally equilibrated at 100 K for 1 ns using the Nose-Hoover thermostat. Periodic boundary conditions are