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Thermal rectifiers from deformed carbon nanohorns

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Abstract
We study thermal rectification in single-walled carbon nanohorns (SWNHs) by using a non-equilibrium molecular dynamics (MD) method. It is found that the horns with the bigger top angles show larger asymmetric heat transport due to the larger structural gradient distribution. This kind of gradient behavior can be further adjusted by applying external strain on the SWNHs. After being carefully elongated along the axial direction, thermal rectification in the elongated SWNHs can become more obvious than that in undeformed SWNHs. The maximum rectification efficiency of SWNHs is much bigger than that of carbon nanotube intramolecular junctions.

(Some figures in this article are in colour only in the electronic version)

Although it is a long time since human beings first mastered the techniques to control electronic flux by using elements such as diodes and/or transistors, how to fabricate such devices to control the heat flux is still an open and challenging question. Given the importance of heat to human beings, thermal controlling devices should also play an important role in our future life, ranging from nanoscale calorimeters, cooling of microelectronic processors, to macroscopic refrigerators and energy-saving buildings.

The extensive study of heat conduction in low-dimensional systems from a microscopic point of view in the past two decades [1–3] has enriched our understanding of heat conduction in finite size systems. In turn, some interesting inventions have been made recently. For example, two interesting solid state thermal diode/rectifier models have been proposed from nonlinear lattices [4–6]. Based on the *negative differential thermal resistance* (NDTR), a thermal transistor model has been constructed [7]. By combining thermal transistors in different ways, elementary thermal logic gates such as NOT, AND/OR gates have been also demonstrated recently [8]. More significantly, the two segment model of the thermal rectifier proposed in [4, 5] has been experimentally realized by using gradual mass-loaded carbon and boron nitride nanotubes [9]. It has been illustrated that the carbon nanotube intramolecular junctions also exhibits a thermal rectifying effect [10]. However, the maximum rectification efficiency of the real materials seems to be no more than 1.5. Therefore, to find more efficient thermal rectifiers is becoming of primary importance for future applications.

Nanocarbon materials [11], such as carbon nanohorn aggregates [12], have recently attracted considerable attention since they are promising nanoscale materials with potential applications in a broad field, for example in catalyst supports in fuel cell electrodes [13], in gas storage devices [14, 15], as well as in drug delivery systems [16].

The nanohorn is composed of a horn-shaped, cap-closed carbon nanotube (CNT) formed out of a single-walled graphene sheet. Several of them are put together to form a flower-like aggregate with a rather uniform diameter of about 100 nm. CNHs have very large surface areas which enable them to support very fine catalyst particles and to entrap drug molecules and even gases.

If the CNH is made of one single graphene sheet, we call it a single-walled carbon nanohorn (SWNH). Two examples are shown in figure 1. The SWNH has an angle of about 19°, a diameter of 2–4 nm, and a length of about 50 nm [12]. The SWNHs come together to form a spherical aggregate, and at their center they coalesce (see figure 6 of [11]).

In this paper, we will demonstrate that SWNHs can be very efficient thermal rectifiers. Moreover, we find that

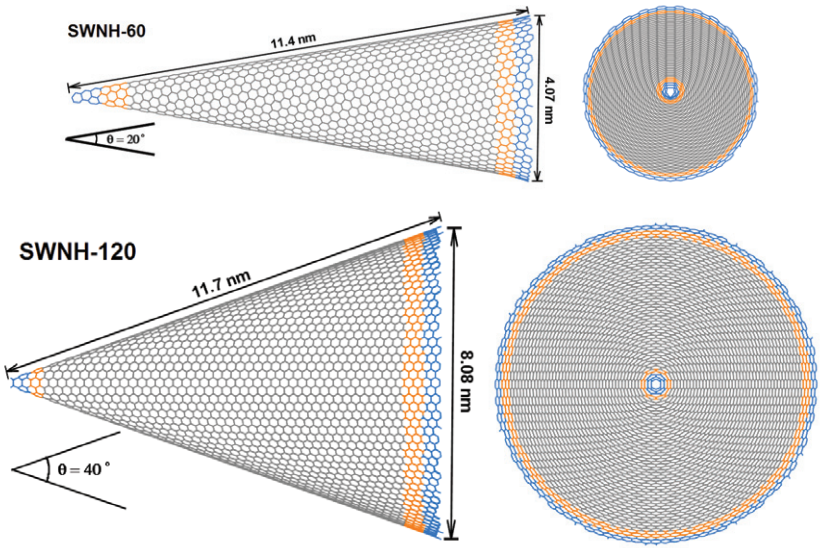

Figure 1. Structures of the two SWNHs in our work. Upper panel shows the side view and top view of the SWNH-60 structure. Lower panel shows the side view and top view of the SWNH-120 structure.

the force constants along the SWNHs' axes can be adjusted in the elongated structure. With suitable tensile stress, the rectification in deformed SWNHs becomes more obvious than that in undeformed ones, which makes the deformed SWNH an ideal candidate for a thermal rectifier.

The SWNHs are obtained by cutting out 60° and 120° sectors from a graphene sheet and then gluing together the two cut sides of the sheet. They are shown in figure 1 and are referred to as SWNH-60 and SWNH-120 in the following text. In addition, we also perform simulation on a smaller SWNH-120 structure, the central axial length of which is only half of the original SWNH-120. This smaller structure is named SWNH-120-SEG. In figure 1, the blue atoms are fixed in the MD process and orange atoms are put in thermostats, which are realized by the Nosé–Hoover thermostat technique [17]. The temperatures of the left and right ends are T_{L} and T_{R}, respectively. When $T_{\mathrm{L}} \neq T_{\mathrm{R}}$, a temperature gradient can be built up in the SWNH. For convenience, we introduce two variables: $\Delta T = \frac{T_{\mathrm{L}}-T_{\mathrm{R}}}{2\langle T\rangle}$ and $\langle T\rangle = \frac{T_{\mathrm{L}}+T_{\mathrm{R}}}{2}$. In this work, $\langle T\rangle$ is always kept at 290 K. The heat flux running from the narrow end to the wide end is defined as positive.

The velocity Verlet method is adopted to integrate the equations of motion with a time step of 0.51 fs. The typical total MD process is 1×10^7 steps which is about 5.1 ns, and the statistic averages of interesting quantities start from half of the MD process, i.e. 5×10^6 steps are used to relax the system to a stationary state.

The instant temperature of atom i is defined as $T_i(t) = \frac{m_i}{3k_{\mathrm{B}}}(v_x(t)^2 + v_y(t)^2 + v_z(t)^2)$, where m_i is the mass, $v(t)$ is the velocity at time t, and k_{B} is the Boltzmann constant. This is a result of the energy equipartition theorem.

The thermal flux is obtained from the thermostats, i.e. the total work from the thermostats can be regarded as the heat flux runs from thermostats to the system. For more detail, please refer to our recent work [10]. The second-generation reactive empirical bond order potential [18] is employed to describe the C–C interactions.

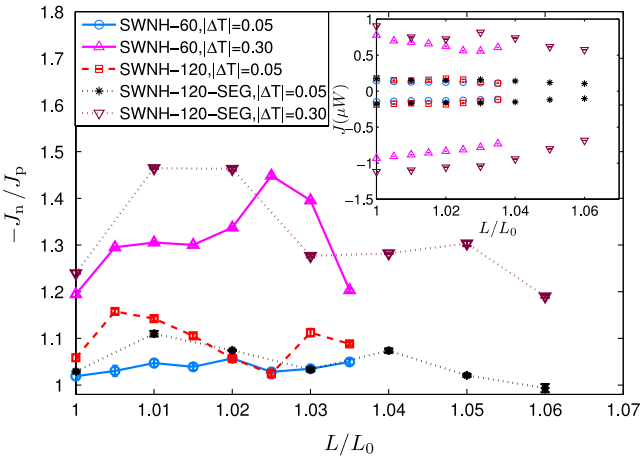

Figure 2. Thermal rectification in SWNHs under different tensile strain versus top angle and temperature difference. The negative heat fluxes correspond to negative temperature differences ΔT. The inset shows the corresponding heat flux. Error bars are also plotted.

We use quantity L/L_0 to describe the strength of the tensile strain, where L and L_0 are the central axial length after and before elongation, respectively. L_0 is obtained after full structural optimization.

The *rectification*, which was defined as the heat flux ratio $|J_{\mathrm{n}}/J_{\mathrm{p}}| = -J_{\mathrm{n}}/J_{\mathrm{p}}$ [4, 5], is used to quantify the asymmetric heat conduction. Here J_{n} means that the heat flux runs from the wide end to the narrow end, and J_{p} means that the heat flux runs in the opposite direction.

We first study the heat conduction of SWNHs with different top angles under different temperature difference ($\Delta T = -0.05, 0.05, -0.30$ and 0.30) and/or tensile strains. The results are shown in figure 2.

It is obvious that $|J_{\mathrm{n}}| > |J_{\mathrm{p}}|$ in most cases. That is to say, the heat flux runs preferentially along the direction of decreasing radius and mass. This result is analogous to a

recent experiment [9], which implies that the radius and mass gradients are possible reasons for thermal rectification.

In order to understand the origin of the thermal rectification, we can consider similar phenomena in carbon nanotube intramolecular junctions (IMJs) [10] as a reference. Both of the SWNHs and IMJs can be considered as curved graphene surfaces, so their phonon spectra are similar to those of graphene, with some difference induced by the curvature effect and the Born–von Karman boundary condition along the circumferential direction. For the narrow end of the SWNHs, the curvature effect is very significant and the phonon spectra deviates greatly from that of the graphene; whereas for the wide end, the phonon spectra approaches that of the graphene. Therefore, the phonon spectra along the central axis of the SWNH changes gradually from the narrow to the wide end. As we know, the matching and/or mismatching of the energy spectra along the direction of heat transport is the underlying mechanism of the rectification in nonlinear lattice systems [4–6] and IMJs [10], so we can easily understand the appearance of thermal rectification in SWNHs. Furthermore, it was shown that heat can more easily transport from the wider side to the narrower side in IMJs. This behavior is also consistent with our observation of the thermal rectification in SWNHs. This correspondence also implies the common underlying mechanism of the thermal rectification in both systems.

SWNH-120-SEG can be elongated more than either SWNH-60 or SWNH-120. In figure 2, the maximum possible tensile strain for SWNH-120-SEG is about 1.06, while that for SWNH-60 and SWNH-120 is about 1.03. This is because the largest strain occurs at the narrow end, when the system is elongated, the narrower end of a longer SWNH will endure more strain than that of shorter ones due to the higher structural asymmetry.

It is found from the inset of figure 2 that both the temperature difference ($|\Delta T|$) and the tensile strain (L/L_0) have a large influence on the heat flux J, but their effects are in contrast with each other. Namely, an increase in temperature gradient will cause an increase of heat flux, but when tensile strain becomes stronger, heat flux J decreases. When the system is elongated, the interatomic force constants decrease, which leads to the decrease of the heat flux.

In addition, more interesting are the influences of the temperature difference and the tensile strain on the thermal rectification.

We find that an increase in temperature difference $|\Delta T|$ will result in an increase in rectification. The rectification is found to be mainly controlled by the middle-frequency optical phonon modes [10], which can be further excited when the temperature gradient increases. In fact, these middle-frequency optical phonon modes are most sensitive for the curvature effect in CNT [19], so their participation in the transport process also plays a most important role in the thermal rectification of SWNHs. In other words, these phonon modes at the narrower end are sensitive to temperature change, which makes thermal rectification change when temperature gradient changes.

Under the same $|\Delta T|$, SWNH-60 shows smallest rectification when the strain is weak. This is reasonable because the top angle θ of the horn can be regarded as an indicator of the structural asymmetry and curvature gradient along the central axis. When $\theta = 0$ is considered as an extreme situation, the SWNH will degenerate to SWNT and the phonon spectra gradient disappears. and as we know there is no thermal rectification in SWNTs. Moreover, the rectification in SWNH-120 is even larger than that in SWNH-120-SEG. This is due to the larger structural difference between the two ends of SWNH-120. Therefore, if we want to design a device exhibiting large rectification, the best choice is to find a system with large structural asymmetry. On the other hand, considering that the mass density along the Z direction is not homogeneous, the SWNHs can also be thought of as a mass graded system. A recent study [20] has demonstrated that thermal rectification exists in a mass graded anharmonic system. So the mass gradient system, which is a special case of a structural asymmetry system, will hopefully be a thermal rectifier. In fact, a recent experiment on thermal rectifiers [9] has proven this idea.

As shown in figure 2, when tensile strain becomes stronger, the rectification does not change monotonically. However, the trend of the rectification versus strain seems similar for all the horns. Under weak strain, the rectification increases with increasing strain; nevertheless, the rectification will decrease if the strain becomes large. We can understand this qualitatively as follows.

When the system is elongated, the interatomic force constants do not decrease at the same rate along the Z direction. Actually, the end with large radius can hardly be elongated. As a result, high local strain occurs near the narrow end and the force constants along the Z direction will change gradually. Consequently, the nanohorn becomes a force constant graded system. Therefore, the asymmetry in curvature and mass distribution needs to compete (or cooperate) with the asymmetry in the force constant distribution. Furthermore, the force constants are not linearly dependent on the bond length when the strain is strong, so the gradient in force constants does not always increase with the increase of strain. The above reasons finally lead to a complicated change of the phonon spectra gradient, and in turn to a complicated trend of the rectification. Some additional details of the trend of the curves should be due to the different responses of the horns to tensile stress.

So far, we have found that the deformed SWNH-120-SEG exhibits obvious thermal rectification, and its dependence on strain seems similar to the other two nanohorns in the paper. Thus we can take SWNH-120-SEG as a typical example in the following text. In order to find the maximum performance of SWNH-120-SEG, we adjust only the temperature difference of the two ends by fixing L/L_0 to 1.015. The results are presented in figure 3. For comparison, the temperature difference dependence of undeformed SWNH-120-SEG is also shown.

In the inset of figure 3, the heat flux appears obviously asymmetric in both structures, but the elongated structure shows larger asymmetry. It can be found that the dependence of heat flux on temperature difference rapidly deviates from a linear relationship when $|\Delta T|$ is larger than about 0.1. When $|\Delta T|$ is larger than 0.5, the rectification can be as large

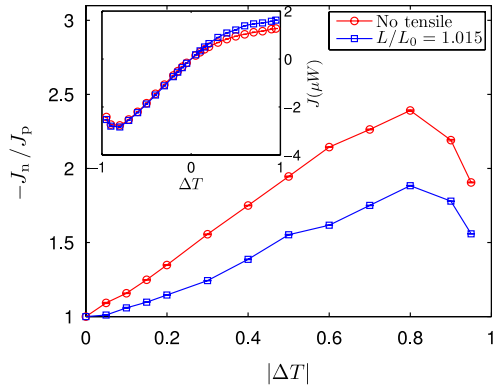

Figure 3. Thermal rectification of SWNH-120-SEG under different temperature difference. The inset shows the corresponding heat flux. Error bars are also plotted.

as 2 in deformed SWNH-120-SEG. The overall maximum rectification is about 2.4 when $|\Delta T| \approx 0.8$. This behavior seems very similar to the junction situation [10], but the rectification in SWNH is more obvious. This result is due to more distinct structural asymmetry in SWNHs.

A more significant fact is that a larger temperature difference can induce a smaller heat flux when $|\Delta T| > 0.8$. This phenomenon is called *negative differential thermal resistance* (NDTR) [7], which is essential for thermal transistors. This indicates that the SWNH might be used to construct thermal transistors and other thermal devices such as thermal logic gates.

In summary, thermal rectification, i.e. asymmetric heat conduction, has been studied in SWNHs by the MD method. The structural asymmetry is shown to have a great effect on the asymmetric heat transport. The horns with bigger top angle can show larger thermal rectification. Our results also show that SWNHs behave like mass graded systems.

Furthermore, force constants can be adjusted by external stress to influence the structure's uniformity. The competition between the radius gradient and force constant gradient makes the system show a complicated response to the tensile strain. After choosing suitable tensile strain, thermal rectification in the SWNHs may become more obvious than that in undeformed SWNHs.

Our work suggests a possible efficient heat control device, and the efficiency of this device can be controlled by simply applying external stress. In this system, on-site potential is not necessary to achieve asymmetric heat conduction. Because SWNHs have been fabricated experimentally, we believe that thermal controlling devices will be made in the near future.

Acknowledgments

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