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Thermal rectification in inhomogeneous nanotubes

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Heat transfer in axially inhomogeneous nanotubes is known to be asymmetric with respect to the direction of transfer. This phenomenon is known as the thermal rectification. We demonstrate that thermal rectification in such nanotubes arises due to the interference of phonons excited in the different parts of the nanotube. It is shown that the rectification does not vanish when the thickness of nanotube increases, but it vanishes as the external diameter of nanotubes decreases to a few nanometers. The understanding of the origin of thermal rectification opens a way to the design of devices controlling heat flows that could perform as efficiently as their electronic counterparts controlling electric currents. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4971390]

The widespread use of electronic devices such as diodes that have electric conductance depending on the direction of the voltage gradient inspires hopes that similar devices for heat transfer, if fabricated, may improve the thermal management in systems ranging from microelectronics to large refrigerators and even energy-efficient buildings. This hope is based on experimental observations, the first of which, about the asymmetric heat transport between copper and copper oxide, was reported back in 1936.[1] This phenomenon, called the "thermal rectification," was met with interest because the classical theory of heat conduction based on the Fourier law and heat equation does not predict it. Over the years, it has been understood that thermal rectification can be provided by several mechanisms determined by a large number of factors, such as the material properties and geometry of heat exchanging objects, imperfections of material boundaries and interfaces, external conditions, and, especially, the value of the temperature differential.[2] Nevertheless, this phenomenon is still not understood well enough for the development of new technologies.

Some of the mechanisms of thermal rectification are rather expected. Thus, since material properties of all real materials are temperature dependent, some thermal rectification appears in any inhomogeneous structure due to arising nonlinearities.[3] In order to observe the inevitability of thermal rectification in inhomogeneous structures, it suffices to consider the bi-material structures consisting of two parts with different physical properties.[4] Indeed, let $A(T)$ and $B(T)$ denote material bodies A and B at the temperature T. Then for $T_1 \neq T_2$, the rate of heat transport in such two-body structures with interchanged temperatures, denoted as $A(T_1)\rightleftarrows \mathrm{B}(\mathrm{T}_2)$ and $A(T_2)\rightleftarrows \mathrm{B}(\mathrm{T}_1)$, may not coincide because these structures actually involve different pairs of materials.

It is clear that if at least one of the materials undergoes a phase change when the temperatures are interchanged, then even a small temperature differential $\Delta T = |T_1 - T_2|$ may cause such strong asymmetry that the structure may be used as a "thermal switch."[5] If the temperature differential $\Delta T = |T_1 - T_2|$ is large, then a high rate of thermal rectification may occur without phase changes because the temperature differential ΔT generally increases the dissimilarity between the structures $A(T_1)\rightleftarrows \mathrm{B}(\mathrm{T}_2)$ and $A(T_2)\rightleftarrows \mathrm{B}(\mathrm{T}_1)$ with interchanged temperatures. Thus, Ref. 6 reports a strong rectification of the radiative heat transfer between silicon and silicon dioxide at temperature differentials up to $\Delta T = 1200\,\mathrm{K}$. In these cases, materials do not change phases, but Ref. 6 argues that the asymmetry of heat transfer is caused by less visible changes in the structures of electromagnetic resonances affecting thermal radiation. The mechanism of asymmetric heat radiation caused by the temperature dependence of radiation spectra is widely discussed in the literature, e.g., in Refs. 7 and 8. A similar mechanism of thermal rectification in solids, where heat is carried by mechanical waves of lattice vibrations, a.k.a. by phonons, is discussed in Refs. 4 and 9–11. In particular, Refs. 4 and 11 claim that the asymmetry heat transport across heterojunctions in nanostructures increases as the size of the structures decreases. This agrees well with the concept that the rate of heat rectification depends on the temperature dependence of the parts of the structure. Indeed, in objects with dimensions comparable with the wavelength of thermally excited waves, the spectra of such waves are almost discrete, and the interchange of the temperatures in the structure $A(T_1)\rightleftarrows \mathrm{B}(\mathrm{T}_2)$ may significantly change the alignment of spectra in heat exchanging domains.

Since the properties of all real materials are temperature dependent, the mechanisms of thermal rectification discussed above are universally applicable to any system. However, in many cases, including, but not limited to, the first reported case of thermal rectification of a junction between the copper and copper oxide,[1] the observed asymmetry of heat transfer is considerably greater than what can be explained by the temperature dependence of the material parameters. Correspondingly, special attention is needed for the understanding of thermal rectification in cases when the temperature differential is not sufficiently large enough to play a dominant role.

Recent advances in the fabrication of nanotubes have led to the conclusion that nanotubes "*are ideal materials for exploring thermal rectification effects*."[12] This is largely due to a simple and nearly perfect molecular structure of nanotubes that allows one to ignore such side effects as those caused by microscopic irregularities and defects of the

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materials. Previous to Ref. 12, other studies have demonstrated that the thermal conductivity of carbon nanotubes is dominated by phonons,[13,14] and that of the uniform nanotubes, the thermal conductance is symmetric. However, Ref. 12 reports that modified nanotubes with non-uniform axial mass distribution, obtained by depositing heavy molecules on part of the nanotube's lattice, demonstrate a thermal rectification. This effect could not be explained by either the geometric asymmetry of the modified nanotubes or by the ordinary theory of heat transport by phonons, and it was conjectured as being due to solitons that might arise due to nonlinearities in the nanotubes.[12]

Although solitons and other non-linear effects may arise in realistic structures, our analysis reveals that the rectification of thermal transport arises in all structures that include interfaces between dissimilar materials across which heat is carried by waves, e.g., by photons or phonons, such as nanotubes with non-uniform axial mass distribution mentioned above. This kind of rectification arises due to the distortion of the spectra of thermally excited wave in the presence of a heat flux.[15] Such distortion causes an interference of heat carrying waves that is neglected in usual macro-scale wave theories of heat transport, but is shown to be important in low micro and nano-scale heat transfer systems.[16,17]

The approach presented here provides a better understanding of this phenomenon. Consider a composite nanotube with different material parameters in the domains $x<0$ and $x>0$, referred to hereafter as A and B, as shown in Fig. 1. The heat transfer in such structures is carried by phonons, i.e., waves of mechanical vibrations. We assume that the outer diameter of nanotubes is in the range of 10–40 nm and that their temperatures are about 300° K, as in Ref. 12. Since the wall thickness of carbon nanotubes is comparable to or smaller than one nanometer,[18] and the wavelengths of phonons at room temperature are about 1–2 nm, i.e., at least 15 times less that the circumference of a tube, the phonons in such nanotubes may be treated as waves propagating in a x–y plane that is tangent to a surface of the nanotube. In a two dimensional elastic body, there are longitudinal and shear waves propagating with different speeds c_p and c_S. However, for transparency, we adopt here the Debye model convention that waves of both polarizations propagate with the speed $c = 1/\sqrt{1/c_p^2 + 1/c_s^2}$.

Let c_A and c_B be the average wave speeds in the domains A and B of the tube. Then, the wave field at frequency ω in the domain A consists of elementary waves propagating in the opposite directions

$$U_A^+ = a_+ \mathrm{e}^{\mathrm{i}(x\cos\theta_A + y\sin\theta_A)\omega/c_A + \mathrm{i}\alpha_+},$$
$$U_A^- = a_- \mathrm{e}^{\mathrm{i}(-x\cos\theta_A + y\sin\theta_A)\omega/c_A + \mathrm{i}\alpha_-}, \tag{1}$$

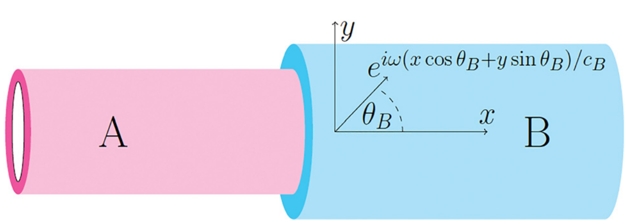

FIG. 1. Composite nanotube.

where $\alpha_\pm$ is the arbitrary phase and $a_\pm = a_\pm(\omega, \theta_A)$ is the amplitude determined by statistical mechanics. Similarly, the wave field in $x>0$ consists of the waves

$$U_B^+ = b_+ \mathrm{e}^{\mathrm{i}(x\cos\theta_B + y\sin\theta_B)\omega/c_B + \mathrm{i}\beta_+},$$
$$U_B^- = b_- \mathrm{e}^{\mathrm{i}(-x\cos\theta_B + y\sin\theta_B)\omega/c_B + \mathrm{i}\beta_-}, \tag{2}$$

where $b_\pm = b_\pm(\omega, \theta_B)$ are amplitudes determined by statistical mechanics, θ_B is related to θ_A by the Snell law $c_B \sin\theta_A = c_A \sin\theta_B$, and $\beta_\pm$ are random phase shifts.

If there is no heat flux in the tube, then the system is in thermal equilibrium, and the amplitudes of these waves are described by the classical Planck's law. If, however, there is a heat flux Q, then these amplitudes are described by the generalization of Planck's law to systems with a steady heat flux,[15] which provides the determinations

$$\begin{aligned}
|a_+|^2 &= \gamma_A p^2(\omega(1 - q_A\cos\theta_A), T_A),\\
|b_+|^2 &= \gamma_B p^2(\omega(1 - q_B\cos\theta_B), T_B),\\
|a_-|^2 &= \gamma_A p^2(\omega(1 + q_A\cos\theta_A), T_A),\\
|b_-|^2 &= \gamma_B p^2(\omega(1 + q_B\cos\theta_B), T_B),
\end{aligned} \tag{3}$$

where γ_ν, with $\nu = A$, B, are constants determined by the nature of the waves, $p^2(\omega, T) = \hbar\omega/(\mathrm{e}^{\hbar\omega/\kappa T} - 1)$ is the average energy of an oscillator at frequency ω in equilibrium at temperature T, and

$$q_\nu = \frac{Q}{c_\nu E_\nu}, \quad \nu = A, B, \tag{4}$$

where E_ν is the energy density of heat carrying waves in the ν-th part of the nanotube. Since $c_\nu E_\nu$ represents the maximal possible fluxes in the corresponding domains, it seems natural to refer to q_ν as relative fluxes.

Waves $U_A^\pm$ and $U_B^\pm$ are defined, so far, independently of each other. However, unless the domains A and B together form a homogeneous tube, none of these waves can exist without interactions with the other waves. Thus, a wave U_A^+ propagating in A towards B generates reflected and transmitted waves U_{refl}^- and U_{tran}^+ propagating in A and B, as illustrated in Fig. 2. Similarly, a wave U_B^- propagating in B towards A generates secondary waves U_{refl}^+ and U_{tran}^- propagating in B and A, respectively. Therefore, the ensembles of waves U_A^+ and U_B^- uniquely define the ensembles of waves U_A^- and U_B^+, which implies that since all four of these ensembles are determined by (3) in terms of T_A, T_B, and Q, these thermodynamical parameters must be connected.

In order for the wave fields to be compatible, their amplitudes must satisfy the relations

$$\begin{aligned}
a_- + R\, a_+ \mathrm{e}^{\mathrm{i}\eta_-} &= \sqrt{1-R^2}\, b_- \mathrm{e}^{\mathrm{i}\chi_-},\\
b_+ + R\, b_- \mathrm{e}^{\mathrm{i}\eta_+} &= \sqrt{1-R^2}\, a_+ \mathrm{e}^{\mathrm{i}\chi_+},
\end{aligned} \tag{5}$$

where $\chi_\pm$ and $\eta_\pm$ are arbitrary phases,

$$R = \left| \frac{\mu_A \cos\theta_B - \mu_B \cos\theta_A}{\mu_A \cos\theta_B + \mu_B \cos\theta_A} \right| \tag{6}$$

is the reflection coefficient, and

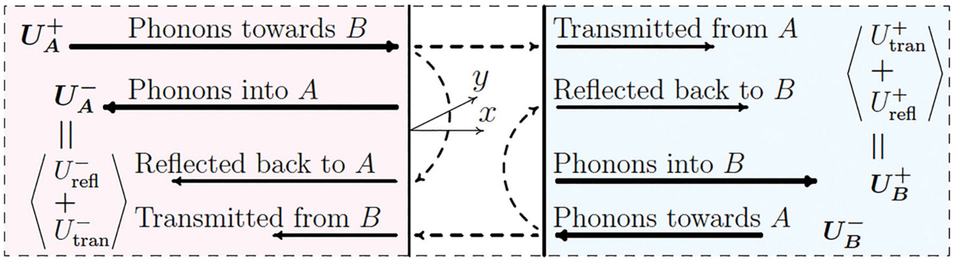

FIG. 2. Connections between the phonon spectra in A and B. Phonons U_A^+ and U_B^- radiated from the domains A and B towards their boundaries, completely determine fields U_A^- and U_B^+ propagating into the interiors of these domains. However, the Planck law determines the spectra of waves $U_A^\pm$ and $U_B^\pm$ propagating in all directions. Therefore, the spectra of U_A^- and U_B^+ are determined twice: directly by the Planck law, and indirectly, through the spectra of U_A^+ and U_B^-. The comparison of two results makes it possible to compute the heat transport between A and B.

$$\mu_A = \rho_A c_A \quad \text{and}\ \mu_B = \rho_B c_B, \tag{7}$$

are the acoustic impedances of the parts of the tube, defined as the products of the mass densities ρ_A, ρ_B and the wave speeds c_A, c_B.

Observing that Equation (5) has the form $X + Ye^{i\eta} = Ze^{i\chi}$, we conclude that thetriangle inequality (5) can be satisfied if and only if the frequency and the incidence angle satisfy the inequalities

$$F_-(q_A\cos\theta_A, T_A;\omega) \le f(q_B\cos\theta_B, T_B;\omega) \le F_+(q_A\cos\theta_A, T_A;\omega), \tag{8}$$

and

$$F_-(-q_B\cos\theta_B, T_B;\omega) \le f(-q_A\cos\theta_A, T_A;\omega) \le F_+(-q_B\cos\theta_B, T_B;\omega), \tag{9}$$

where

$$F_\pm(q,T;\omega) = |p(\omega(1+q),T) \pm R\,p(\omega(1-q),T)|, \tag{10}$$

$$f_\pm(q,T;\omega) = \sqrt{1-R^2}\,p(\omega(1+q),T). \tag{11}$$

These inequalities together with the expression $q_\nu = Q/c_\nu E_\nu$, where $E_\nu = E_\nu(T_\nu)$ is the energy density of the heat carrying waves in the ν-th part of the nanotube, connect the two temperatures T_A, T_B, and the heat flux Q, so that if two of these parameters are known, the third can be computed.

Since a frequency-angle pair determines a wave vector, the inequalities (8) and (9) may be considered as the definition of the bands of wave vectors of waves that carry energy from A to B and from B to A, respectively. If $Q = 0$ and $T_A = T_B$, then $q_A = q_B = 0$ and these bands coincide, implying that there are equal numbers of waves carrying heat in each direction. If the heat flux Q deviates from zero, or the temperatures T_A and T_B deviate from each other, the bands of the wave vectors (8) and (9) become different, which thereby create a difference between the numbers of waves carrying energy in the different directions. This appears as an analog of a conduction band of electrons. The analogy between heat transport by phonons and that by electric current is not surprising because the Helmholtz equation describing mechanical waves carrying heat is similar to the Schrödinger equation describing the dynamics of electric charges. The similarity of the mathematical models suggests that there may be similarities between heat transport in layered structures by waves and the electric conductance across material junctions. In particular, it suggests that the heat transport across interfaces and layered structures may be asymmetric, as is the case with electric transport in solid-state junction diodes.

The hypothesis that the structure of the bands (8) and (9) implies the asymmetry of heat transfer by phonons in a composite nanotube can be straightforwardly verified by analysis of the inequalities (8) and (9).

Since $q_\nu = Q/c_\nu E_\nu$, where E_ν is the energy density of heat carrying waves in the ν-th domain, it is clear that these inequalities are invariant under the interchange of the indices A and B, accompanied by the reversal of the heat flux $Q \to -Q$ and the interchange of the temperatures $T_A \leftrightarrow T_B$. This invariance corresponds to a trivial fact that if the parts A and B of the tube are interchanged without changing their temperatures, then the heat flux changes its direction. However, if the reversal of the flux Q and the interchange of the temperatures $T_A \leftrightarrow T_B$ are not accompanied by the interchange of the parts A and B of the tube, then the band determined by the conditions (8) and (9) is not preserved, unless $q_A\cos\theta_A = q_B\cos\theta_B$ for all θ_A and θ_B connected by the Snell law, which can only happen if $c_A = c_B$. Indeed, the energy density of two-dimensional waves in the ν-th part of the nanotube is determined by the integrals

$$E_\nu(T_\nu) = \frac{1}{2\pi}\int\!\!\int p^2(\omega, T_\nu) D_2(\omega, c_\nu)\,d\omega\, d\theta, \tag{12}$$

where

$$D_2(\omega, c_\nu) = \frac{\omega}{\pi c_\nu^2}, \tag{13}$$

is the density of states of two-dimensional sound waves propagating with the speed c. Therefore, the relative heat fluxes $q_\nu = Q/c_\nu E_\nu$ have the structure $q_\nu = c_\nu Q Y_2(T_\nu)$, where $Y_2(T)$ is some function of the temperature, which implies that if $c_A \neq c_B$, then $q_A \neq q_B$.

The structure of the conduction bands and their dependence on the direction of heat transfer are illustrated in Fig. 3. In these figures, the upper and lower boundaries of the shadowed areas correspond to the right-hand and left-hand sides of the inequalities (8) and (9), respectively. The dashed lines correspond to the middle parts of these inequalities. For definiteness, the incidence angle is fixed as $\theta = 0$, so that the horizontal axes correspond to the frequency.

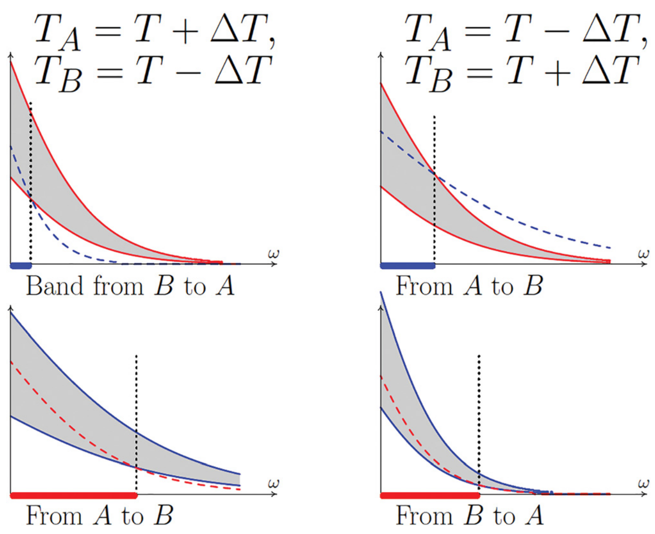

FIG. 3. Conductance bands for different directions of the heat differential.

In the equilibrium case with $T_A = T_B$ and $Q = 0$, the inequalities (8) coincide with (9), which means that the conduction bands in the opposite directions also coincide, resulting in a vanished net heat flux. The situation changes when $T_A \neq T_B$. In this case, the inequalities (8) and (9) that determine the conduction bands in the opposite directions do not coincide, resulting in a non-vanishing net heat flux.

Thus, if $T_A = T + \Delta T > T_B = T - \Delta T$, as shown in the left-hand side of Fig. 3, the conduction band of phonons traveling from A to B is larger than in the opposite direction, and the heat flows towards B. In the opposite case $T_A = T - \Delta T < T_B = T + \Delta T$, illustrated in the right-hand side of Fig. 3, the conduction band in the direction $B \to A$ is larger than that in the direction $A \to B$, but this difference is not equal in the two cases. This asymmetric response of conductance bands on the interchange of the temperatures translates into the asymmetry of heat transport known as the thermal rectification.

It is instructive to observe that the conclusion about the asymmetry of the heat conduction bands (8) and (9) that causes a thermal rectification remains valid in cases when heat is carried by three dimensional waves, when the density of states $D_3(\omega, c) = 3\omega^2/\pi^2 c^3$, but it fails in the one-dimensional case with the density of states $D_1(\omega, c) = 1/2\pi c$. Indeed, the relative fluxes $q_\nu = Q/(c_\nu E_\nu)$ with E_ν from (12), have the structure

$$q_\nu \equiv q_\nu(Q, T) = c_\nu^{d-1} Q\, Y(T_\nu), \tag{14}$$

where d is the dimension of the space and $Y(T)$ is a function of T. Therefore, in the two and three dimensional cases $q_A(Q, T_A) \neq q_B$ but in the one-dimensional case $q_\nu = QY\,(T)$ and the bands (8) and (9) interchange when ΔT and Q simultaneously change signs, which means the thermal rectification vanishes. This shows that the thermal rectification effect in nanotubes decreases as their circumference becomes comparable to the dominant wavelength of heat carrying phonons, i.e., about 1–2 nanometers at room temperature.

The above analysis also shows that the rate of thermal rectification of composite nanotubes of sufficiently large diameter depends on the contrasts between the material parameters of the different parts of the nanotube. Thus, if the wave speeds in the parts A and B are equal, then it follows from (14) that the conduction domain defined by (8) and (9) does not change when $Q \to -Q$ and $T_A \leftrightarrow T_B$, which means that there is no thermal rectification. As the ratio of the wave speeds $\gamma = c_A/c_B$ deviates from unity, then the interchanges $Q \to -Q$ and $T_A \leftrightarrow T_B$ modify the conduction domain (8) and (9), which results in the emergence of thermal rectification.

However, the bands (8) and (9) depend not only on the relative heat fluxes q_A and q_B but also on the reflection coefficient R defined by (6) in terms of the acoustic impedances μ_A and μ_B from (7). If the impedances are very dissimilar, i.e., their ratio μ_A/μ_B approaches either zero or infinity, then $R \to 1$ and the conduction domain (8) and (9) narrows, implying that the heat conduction vanishes. On the other hand, of the impedances come closer to each other, then $R \to 0$ and the heat conduction increases in either direction.

The comparison of the dependencies of heat transport on the ratio of sound speeds and of the ratio of impedances shows that in order to increase thermal rectification but still maintain thermal conductance, it is desirable to increase the contrast between sound speeds but to keep the acoustic impedances close to each other. Since the sound speed in a solid is usually defined by the formula $c = \sqrt{K/\rho}$, where K is an elastic modulus and the acoustic impedance (7) admits the representation $\mu = \sqrt{K\rho}$. Therefore, in order to make a better thermal rectifier from a bi-material structure, it is desirable to have the ratio of impedances $\mu_A/\mu_B = \sqrt{K_A\rho_B/K_B\rho_A}$ as close to unity as possible and the same time to have the ratio of wave speeds $c_A/c_B = \sqrt{K_A\rho_A/K_B\rho_B}$ as far from unity as possible. This means that the stiffer material must be lighter and the weaker material must be heavier, but not vice versa.

The understanding of the origin of thermal rectification opens a way to design applications of this phenomenon, which may play a key role in modern technology. The similarity between the sources of thermal and electronic rectifications suggests that thermal rectifiers may eventually make their way into devices controlling heat flow as efficiently as their electronic counterparts control electric currents.

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