Bipolar thermoelectric effects in semiconducting carbon nanotubes: Description in terms of one-dimensional Dirac electrons

Takahiro Yamamoto\textsuperscript{1} and Hidetoshi Fukuyama\textsuperscript{2}

\textsuperscript{1} Department of Liberal Arts, Faculty of Engineering, Tokyo University of Science, Katsushika, Tokyo 125-8585, Japan
\textsuperscript{2} Department of Applied Physics, Faculty of Science, Tokyo University of Science, Shinjuku, Tokyo 162-8601, Japan

The thermoelectric effects in semiconducting single-walled carbon nanotubes (SWCNTs) are investigated based on the linear response theory combined with the thermal Green’s function method. It is shown that the electronic states near the lowest conduction band minimum and the highest valence band maximum can be effectively described in terms of one-dimensional (1D) Dirac electrons to which a theoretical scheme is developed to describe the thermoelectric responses making it possible to study the effects of inter-band impurity scattering and in-gap states. Using the proposed scheme, the bipolar thermoelectric effects (i.e., the sign inversion of the Seebeck coefficient) in semiconducting SWCNTs observed in recent experiments are explained. Moreover, the temperature dependence of the Seebeck coefficient of semiconducting SWCNTs at low temperature is clarified.

KEYWORDS: Seebeck coefficient, power factor, Dirac electron, carbon nanotube, linear response theory, thermal Green’s function

1. Introduction

The development of high-performance thermoelectric materials is important for sustainable energy production. Hicks and Dresselhaus\textsuperscript{1} proposed that significant enhancements in the thermoelectric performance of materials could be realized by employing one-dimensional (1D) semiconductors. Various 1D materials exhibiting high thermoelectric performance have since been discovered.\textsuperscript{2–6} Single-walled carbon nanotubes (SWCNTs), which are rolled up graphene in a cylindrical form, have received particular interest as high-performance and flexible thermoelectric 1D materials.\textsuperscript{7–24}

At present, the reported maximum power factor of SWCNTs is ∼700 µW m\(^{-1}\) K\(^{-2}\) at 298 K, which is comparable to that of high-performance inorganic thermoelectric materials.\textsuperscript{21}

Recently, the present authors theoretically demonstrated that “band-edge engineering” is crucial for the development of high-performance thermoelectric materials using impurity-doped semiconducting SWCNTs as an example.\textsuperscript{24} For band-edge engineering, the chemical potential \(\mu\) of SWCNTs has been experimentally adjusted via chemical adsorption on the SWCNT surface,\textsuperscript{8,15,19} encapsulation of molecules inside an SWCNT,\textsuperscript{18} and carrier injection into an SWCNT by applying a gate voltage using a field-effect transistor (FET) setup.\textsuperscript{12,13} In view of the FET experiment,\textsuperscript{12,13} which clarified the bipolar thermoelectric effect of SWCNTs (i.e., the sign inversion of the Seebeck coefficient from positive (p-type) to negative (n-type) when the gate voltage is changed), the present study investigates this bipolar effect theoretically based on the conduction and valence bands, described as 1D Dirac electrons in order to treat the effects of disorder induced coupling between the bands in a unified way (see Appendix A).

2. Theory of Thermoelectric Effects of Dirac Electrons in One-Dimensional Solids

2.1 Dirac electrons in one-dimensional solids with disorder

This section gives a brief review of 1D Dirac electrons in solids with disorder. The Hamiltonian of 1D Dirac electrons in an impurity disorder potential is given by

\[ \mathcal{H} = \int_{-\infty}^{\infty} dx \Psi^\dagger(x,t) H(x) \Psi(x,t) \] (1)

with the local Hamiltonian matrix

\[ H(x) = -i\hbar v \sigma_z \frac{\partial}{\partial x} + \Delta \sigma_x + U(x), \] (2)

where \(\hbar\) is the Dirac constant, \(\Delta\) is one half of the band gap, \(v\) is the velocity of a Dirac electron in the high-energy region of \([|E| \gg \Delta]\), and \(\sigma_x\) and \(\sigma_z\) are the \(x\) and \(z\) components of Pauli matrices,

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \] (3)

respectively, and \(U(x)\) is an impurity potential.

In Eq. (1), the field operators \(\Psi(x,t)\) and \(\Psi^\dagger(x,t)\) are defined as the following column and row vectors,

\[ \Psi(x,t) \equiv \begin{pmatrix} \psi_1(x,t) \\ \psi_2(x,t) \end{pmatrix}, \quad \text{and} \quad \Psi^\dagger(x,t) \equiv \begin{pmatrix} \psi_1^\dagger(x,t) & \psi_2^\dagger(x,t) \end{pmatrix}, \] (4)

respectively. Here, \(\psi_1^\dagger(x,t)\) and \(\psi_2^\dagger(x,t)\) are the fermionic creation and annihilation field operators in the Heisenberg picture and satisfy the Heisenberg equations \(i\hbar \frac{d[\psi_1^\dagger(x,t), \mathcal{H}]}{dt} = [\psi_1^\dagger(x,t), \mathcal{H}]\) and \(i\hbar \frac{d[\psi_2^\dagger(x,t), \mathcal{H}]}{dt} = [\psi_2^\dagger(x,t), \mathcal{H}]\), respectively. Thus, it can be easily proven that \(\Psi(x,t)\) and \(\Psi^\dagger(x,t)\) satisfy the Shrödinger equation

\[ i\hbar \frac{d\Psi(x,t)}{dt} = H(x) \Psi(x,t), \] (5)

and its Hermitian conjugate

\[ -i\hbar \frac{d\Psi^\dagger(x,t)}{dt} = (H(x)\Psi(x,t))^\dagger. \] (6)

Performing the Fourier transform of \(\Psi(x,t)\) as

\[ \Psi^\dagger(x,t) = \frac{1}{\sqrt{L}} \sum_k e^{-ikx} \Phi_k^\dagger(t) \] (7)
with \( \Phi_k^*(t) \equiv (c_{1k}^\dagger(t), c_{2k}^\dagger(t)) \) and using

\[
U(x) = \sum_q e^{i\Omega U(q)}, \tag{8}
\]

the 1D Dirac Hamiltonian in Eq. (1) can be rewritten as

\[
\mathcal{H} = \sum_k \Phi_k h_0(k) \Phi_k + \sum_{k\neq k'} \Phi_k^\dagger \chi_{kq}(U(q)) \Phi_{k'}, \tag{9}
\]

where \( h_0(k) \) is the Hamiltonian density of a 1D free Dirac electron in \( k \) space, which is given by

\[
h_0(k) = \hbar v k \sigma_x + \Delta \sigma_z (10)
\]

The eigenvalues of \( h_0(k) \) in Eq. (11) can be easily obtained as

\[
E_{\pm}(k) = \pm \sqrt{\Delta^2 + (\hbar v k)^2}, \tag{12}
\]

where \( \pm \) corresponds the conduction (+) and valence (−) bands, respectively. Thus, the band gap is given by \( E_g \equiv E_{+}(0) - E_{-}(0) = 2\Delta \).

2 General theory of thermoelectric responses

The thermoelectric effect is typically characterized by the Seebeck coefficient, \( S \), which is defined as the voltage induced by a finite temperature gradient along a given direction (herein the \( x \)-direction) under the condition that there is no electrical current (i.e., \( J = 0 \)) along that direction. This can be written as

\[
S = -\left( \frac{AV}{\Delta T} \right)_{J=0}, \tag{13}
\]

where \( AV \) is the induced voltage and \( \Delta T \) is the temperature difference between the two ends of the material.

In the presence of both an electric field \( \mathcal{E} \) and a temperature gradient \( dT/dx \) along the \( x \)-direction, the current density \( J \) is generally given by

\[
J = L_{11} \mathcal{E} - L_{12} \frac{dT}{dx}, \tag{14}
\]

within the linear response regime with respect to \( \mathcal{E} \) and \( dT/dx \). Here, \( L_{11} \) and \( L_{12} \) are the electrical conductivity and the thermoelectric conductivity, respectively. The zero-current condition \( (J = 0) \) leads to \( L_{11} \mathcal{E} = L_{12} \frac{dT}{dx} \). Because the electric field and the temperature gradient can be written as \( \mathcal{E} = -AV/L \) and \( dT/dx = \Delta T/L \), respectively, for a spatially uniform system with length \( L \) (assumed here), \( S \) as defined in Eq. (13) can be expressed in terms of the response functions \( L_{11} \) and \( L_{12} \) as

\[
S = \frac{1}{L_{11}} \frac{L_{12}}{L_{11}}. \tag{15}
\]

One of the figures of merit for thermoelectric materials is the power factor, \( PF \), defined as

\[
PF \equiv \sigma S^2 = \frac{1}{T^2} \frac{L_{12}^2}{L_{11}}. \tag{16}
\]

It should be noted that the basic quantities used for the thermoelectric responses of materials are \( L_{11} \) and \( L_{12} \) rather than \( S \) and \( PF \).

2.3 Microscopic representation of \( L_{11} \) and \( L_{12} \)

\( L_{11} \) and \( L_{12} \) are expressed in terms of the \( J_e-J_q \) correlation function and the \( J_e-J_q \) correlation function, respectively, where \( J_e \) and \( J_q \) are the electronic current and the thermal current, respectively.\(^{2,6,7} \) Microscopic justification for calculating \( L_{11} \) based on the \( J_e-J_q \) correlation function and \( L_{12} \) based on the \( J_e-J_q \) correlation function was first given by Kubo in 1957\(^{26} \) and Luttinger in 1964\(^{39} \), respectively. This subsection presents the explicit expressions of \( L_{11} \) and \( L_{12} \) for 1D Dirac electrons with an impurity potential based on the thermal Green’s function formalism.

According to the linear response theory, the thermosteal conductivity \( L_{12} \) can be obtained as

\[
L_{12} = -\lim_{\omega \to 0} \frac{\chi_{12}(\omega) - \chi_{12}(0)}{i\omega}, \tag{17}
\]

where \( \chi_{12}(i\omega) \) is the correlation function between the electrical current \( J_e \) and the thermal current \( J_q \), expressed as

\[
\chi_{12}(i\omega) = \frac{1}{V} \int_0^\infty dt \langle \mathcal{T}_x [J_e(t)J_q(0)] \rangle e^{i\omega t}, \tag{18}
\]

with \( \beta \equiv 1/(k_BT) \) the inverse temperature, \( \tau_x \) is the imaginary-time-ordering operator, \( \langle \cdots \rangle \) denotes the thermal average, and \( V \) is the volume of a system.

Now, \( J_e(t) \) and \( J_q(t) \) for 1D Dirac electrons with a disorder potential are needed. The electric current carried by 1D Dirac electrons is given by

\[
J_e(t) = -e \sum_k \Phi_k^*(t)v(k)\Phi_k(t), \tag{19}
\]

where \( e(>0) \) is the elementary charge and \( v(k) \) is a \( 2 \times 2 \) velocity matrix, which is given by

\[
v(k) = \begin{pmatrix} \hbar & \frac{\partial H_0(k)}{\partial k} \end{pmatrix} = v \sigma_x = \begin{pmatrix} 0 & v \\ v & 0 \end{pmatrix}. \tag{20}
\]

The thermal current \( J_q(t) \) is expressed as \( J_q(t) = J_{qL}(t) + \frac{\tau_x}{2} J_{qL}(t) \), where the energy current \( J_{qL}(t) \) is defined as

\[
J_{qL}(t) = \frac{d\omega(t)}{dt} \tag{21}
\]

with energy polarization

\[
\omega(t) = \frac{1}{2} \int_{-\infty}^{\infty} \Psi^\dagger(x,t) \begin{pmatrix} \sin Qx & QH(x) + H(x) \sin Qx/Q \end{pmatrix} \Psi(x,t). \tag{22}
\]

Here, \( Q \) is a parameter used to control the effects of the unbounded variable \( x \) and should be set to zero in the final step of a calculation.\(^{30} \) Using Eqs. (5) and (6), Eq. (22) is calculated by

\[
J_{qL}(t) = \frac{\tau_x}{2} \int_{-\infty}^{\infty} \Psi^\dagger(x,t) \begin{pmatrix} \sigma_x H(x) + H(x) \sigma_x \end{pmatrix} \Psi(x,t). \tag{23}
\]

The derivation of Eq. (24) is given in Appendix B. Substituting Eqs. (7) and (8) into Eq. (24) yields

\[
J_{qL}(t) = \frac{1}{2} \sum_k \Phi_k^*(t) \begin{pmatrix} \langle v(k)H_0(k) + H_0(k)v(k) \rangle \Phi_k(t) \\ \sum_q \langle \Phi_k^*(t) v(k + q)U(q) + U(q)v(k) \rangle \Phi_k(t) \end{pmatrix}, \tag{24}
\]

where \( H_0(k) \) is the Hamiltonian density of 1D free Dirac elec-
trons in Eq. (11).

In the imaginary-time Heisenberg picture \((t \rightarrow -it)\), the electric current is expressed as

\[ J_e(t) = -e \int_{-i\infty}^{i\infty} dx \tilde{\Phi}_e(t) \nu(k) \Phi_e(t), \]

where \( \tilde{\Phi}_e(t) \equiv (\tilde{c}_e(t), \tilde{c}_e^\dagger(t)) = (e^{iHt}c_e^\dagger e^{-iHt}, e^{iHt}c_e^\dagger e^{-iHt}) \).

Similarly, the energy current is given by

\[ J_{E}(\tau) = -\frac{1}{2e} \sum_{\sigma} \left\{ \Phi_{\sigma}(\tau) H_0(k) + \sum_{q} U(q) \Phi_{\sigma-k-q}(\tau) J_e \Phi_{\sigma}(\tau) \right\}, \]

\[ + \Phi_{\sigma}(\tau) J_e \left\{ H_0(k) \Phi_{\sigma}(\tau) + \sum_{q} U(q) \Phi_{\sigma-k-q}(\tau) \right\}, \]

where the current matrix \( J_e = -e\sigma_y \). As first noted by Johnson and Mahan,\(^{31}\) Eq. (27) can be rewritten as

\[ J_{E}(\tau) = -\frac{1}{2e} \sum_{\sigma} \left[ \frac{d\Phi_{\sigma}(\tau)}{d\tau} J_e \Phi_{\sigma}(\tau) - \Phi_{\sigma}(\tau) J_e \frac{d\Phi_{\sigma}(\tau)}{d\tau} \right], \]

by using the relations

\[ \frac{d\Phi_{\sigma}(\tau)}{d\tau} = -H_0(k) \Phi_{\sigma}(\tau) - \sum_{q} U(q) \Phi_{\sigma-k-q}(\tau), \]

\[ \frac{d\Phi_{\sigma-k}(\tau)}{d\tau} = \Phi_{\sigma}(\tau) H_0(k) + \sum_{q} \Phi_{\sigma-k+q}(\tau) U(q), \]

which are obtained from \( dc_{\sigma\lambda}(\tau)/dt = [H, c_{\sigma\lambda}(\tau)] \) and \( dc_{\sigma-k}(\tau)/dt = [H, \tilde{c}_{\sigma-k}(\tau)] \). Using Eq. (28), the correlation function \( \chi_{12}(i\omega_n) \) is expressed in terms of the impurity-averaged thermal Green's function \( G(k, i\omega_n) \equiv \langle \eta(k', i\omega_n) \rangle_{\text{imp}} \) as

\[ \chi_{12}(i\omega_n) = \frac{-e^2}{V_B} \sum_{\sigma} \left( \frac{i\epsilon_n + i\epsilon_{n+1}}{2} - \mu \right) \]

\[ \times \sum_{k} \text{Tr} \left[ \sigma_z \eta(k, i\epsilon_n) \tilde{\sigma}_z(k) \eta(k, i\epsilon_{n+1}) \right], \]

with \( \epsilon_n \equiv \epsilon_n + \omega \Lambda \) and \( \tilde{\sigma}_z(k) \) is given as \( \tilde{\sigma}_z(k) = \sigma_z + \sigma'_z(k) \) with

\[ \sigma'_z(k) = \sum_{k' \neq k} \langle U(k-k') \eta(k', i\epsilon_n) \tilde{\sigma}_z(k'') U(k'') - k) \rangle_{\text{imp}} \]

(32)

gives the vertex correction for the current operator. In the following discussion, we assume that the vertex correction is neglected, i.e., \( \tilde{\sigma}_z \rightarrow \sigma_z \). In Eq. (31), \( G(k, i\epsilon_n) \) is given by a 2\times2 matrix as

\[ G(k, i\epsilon_n) = \begin{pmatrix} G_{11}(k, i\epsilon_n) & G_{12}(k, i\epsilon_n) \\ G_{21}(k, i\epsilon_n) & G_{22}(k, i\epsilon_n) \end{pmatrix}, \]

where \( G(k, i\epsilon_n) \) is defined by the Fourier transform of \( g_{\text{imp}}(k, \tau) \equiv -\langle T_\tau [c_{\sigma\lambda}(\tau) \tilde{c}_{\sigma\lambda}(0)] \rangle \).

\[ g_{\text{imp}}(k, \tau) = \int_0^\infty d\tau' g_{\text{imp}}(k, \tau) e^{i\omega_n \tau}. \]

The summation over \( n \) in Eq. (31) can be transformed into a contour integral in the complex energy space. Taking the limit of \( \omega \rightarrow 0 \) after the analytic continuation \( i\omega_n \rightarrow \hbar \omega + i\delta \) yields the expression of \( L_{12} \) as

\[ L_{12} = -\frac{1}{e} \int_{-i\infty}^{i\infty} dE \left\langle \frac{\partial f(E - \mu)}{\partial E} \right\rangle (E - \mu) \eta(E), \]

(35)

where \( f(E) = [1 + \exp((E - \mu)/k_B T)]^{-1} \) is the Fermi-Dirac distribution function and \( \eta(E) \) is often called the spectral conductivity, which is expressed as

\[ \eta(E) = \frac{\hbar e^2}{2}\int_{-i\infty}^{i\infty} dE \sum_{k} \text{Tr} \left[ \sigma_z G(k, E) \sigma_z G(k, E) \right] - \text{Re} \left[ \sigma_z G(k, E) \sigma_z G(k, E) \right] \]

(36)

by use of the retarded/advanced Green's function,

\[ G^{R/A}(E, k) = \left[ E - H_0(k) \mp \Sigma^{R/A}(E, k) \right]^{-1}, \]

(37)

where \( I \) is the 2\times2 identity matrix. The expression of \( L_{12} \) in Eq. (35) was first proposed for general cases by Sommerfeld and Bethe\(^{32}\) in 1933, and subsequently by Mott and Jones\(^{33}\) and by Wilson\(^{34}\) based on Boltzmann transport theory. Recently, Ogata and Fukuyama clarified the range of validity of the Sommerfeld and Bethe relation expressed as Eq. (35) for single-band systems with a disorder potential, electron-phonon coupling, and electron correlations as well as for multi-band disorder systems based on the Luttinger-Kohn representation.\(^{36}\)

Using the expression of \( \eta(E) \) in Eq. (36), the electrical conductivity \( \sigma_{11} \) of 1D Dirac electrons in a disorder potential is given by

\[ \sigma_{11} = \int_{-i\infty}^{i\infty} dE \left\langle \frac{\partial f(E - \mu)}{\partial E} \right\rangle \eta(E). \]

(38)

3. Electronic States and Thermoelectric Responses of 1D Dirac Electrons

In this section, the thermoelectric effects of 1D Dirac electrons in a disorder potential are studied based on the thermal Green's function formalism using the self-energy corrections of Green's functions. The following subsections present two methods for treating self-energy correction: the constant-\( \tau \) approximation and the self-consistent Born approximation.

3.1 Constant-\( \tau \) approximation

As the simplest treatment of self-energy correction for a disorder potential, the constant-\( \tau \) approximation (i.e., \( \Sigma^{R/A} = \pm i\hbar/(2\tau)I \)) is employed here and vertex correction is neglected. Here, \( \tau \) is the relaxation time of a Dirac electron scattered by a disorder potential, which is assumed to be independent of the energy \( E \) and the wavenumber \( k \). Although this constant-\( \tau \) approximation is simple, the approximation is very useful for obtaining an overview of the thermoelectric response of 1D Dirac electrons in a disorder potential.

3.1.1 Density of states and spectral conductivity

In the constant-\( \tau \) approximation, the retarded and advanced Green's functions for a 1D Dirac electron are given by

\[ G^{R/A}(E, k) = \left( E \mp i\frac{\hbar}{2\tau} \right) \left[ 1 - \langle \hbar v k \sigma_x + \Delta \sigma_z \rangle \right]^{-1}, \]

(39)

which leads to the following expressions for the density of states (DOS) \( \rho(E) \) per unit cell of the system and spectral con-
The electrical conductivity $\alpha(E)$ is given by

$$\rho(E) = -\frac{1}{\pi N} \text{Tr} \sum_k \text{Im} G^R(k, E),$$

where $N$ is the total number of unit cells, $n$ is the length of a unit cell, $A$ is the cross-sectional area of the system, and

$$\alpha(E) = \frac{e^2}{\hbar} \frac{1}{\pi A k_+ - k_-} \left( 1 - \frac{E^2 + \gamma^2 - \Delta^2}{\hbar^2} \right),$$

for an SWCNT $A$ is conventionally taken to be $A \equiv \pi d_0 \delta$, where $\delta = 0.34$ nm is the van der Waals diameter of carbon.

Figures 1(a) and 1(b) show $\rho(E)$ near the band gap of (10,0) SWCNTs per spin and orbital for $\tau = 10$, 30, 50, and 100 fs (green curve) calculated using Eq. (41) and the corresponding semi-log plots, respectively. Two sharp peaks of $\rho(E)$ appear around $E = \pm \Delta = \pm 0.475 \text{ eV}$, corresponding to the van Hove singularity points of pristine (10,0) SWCNTs without disorder. The maximum value of $\rho(E)$ decreases with decreasing $\tau$ (increasing $\gamma$) due to disorder scattering. In the high-energy region of $|E| \gg \Delta$, the $\rho(E)$ data in Figs. 1(a) and 1(b) converge to the constant value of $\rho(\infty) = \alpha \pi \hbar v = 0.206 \text{ eV}$, which is independent of $\tau$, where the unit cell length $a$ of a (10,0) SWCNT is $a = 0.426 \text{ nm}$ and the velocity $v$ of a Dirac electron in the (10,0) SWCNT is given by $v = 1.027 \times 10^6 \text{ m/s}$. In addition, a (10,0) SWCNT with finite $\tau$ exhibits a finite DOS even in its band gap ($|E| < \Delta$), which increases with decreasing $\tau$ (increasing $\gamma$), as shown in Fig. 1(b). As shown below, the in-gap states have a crucial consequence in the thermoelectric effects of SWCNTs.

Figures 2(a) and 2(b) show the spectral conductivities of (10,0) SWCNTs for $\tau = 10$, 30, 50, and 100 fs calculated using Eq. (42) and the corresponding semi-log plots, respectively. Here, $\alpha(E)$ in Eq. (42) was multiplied by a factor of 4 for the (10,0) SWCNTs because their lowest-conduction (LC) and highest-valence (HV) bands both have two-fold orbital degeneracy and two-fold spin degeneracy (see Appendix A). It can be seen that $\alpha(E)$ in $|E| > \Delta$ decreases with decreasing $\tau$, whereas that in $|E| < \Delta$ increases with decreasing $\tau$ (Fig. 2(b)) because the DOS of the in-gap states increases with increasing $\tau$, as shown in Fig. 1(b). Once $\alpha(E)$ is obtained, the electrical conductivity $\sigma_{11}$ and thermoelectric conductivity $\sigma_{12}$ can be respectively calculated using Eqs. (38) and (39), and then the Seebeck coefficient $S$ and the power factor $PF$ can be respectively obtained using Eqs. (15) and (16).
3.1.3 Chemical potential dependence of \( S \) and \( PF \) at 300 K

Inspired by recent experiments regarding the bipolar thermoelectric effects of SWCNTs using the FET setup,\( ^{12} \) we study the \( \mu \) dependence of \( L_{11} \) and \( L_{12} \) of SWCNTs at \( T = 300 \) K. Figure 3(a) shows the \( \mu \) dependence of the \( L_{11} \) of (10,0) SWCNTs for \( \tau = 10, 30, 50, \) and 100 fs at \( T = 300 \) K. As expected from Eq. (38), the \( \mu \) dependence of \( L_{11} \) for each \( \tau \) value shows features similar to those of the spectral conductivity \( \alpha(E) \) in Fig. 2(a). As shown in Fig. 3(b), the \( L_{12} \) values of (10,0) SWCNTs for \( \tau = 10, 30, 50, \) and 100 fs at \( T = 300 \) K have a sharp dip or peak near the conduction and valence band edges \( (E = \pm \Delta) \), respectively.

3.2 Self-consistent Born approximation

In this subsection, another refined approximation, \( i.e., \) the self-consistent Born approximation (SCBA), is adopted for self-energy corrections due to a disorder potential. For the disorder potential, a short-range random impurity potential is calculated using the constant-\( \tau \) approximation.

\[ \mu_{\text{opt}} \] is independent of \( \tau \) using the Boltzmann transport theory combined with a model of two independent bands (TIBs) under the constant-\( \tau \) approximation.\( ^{14} \) The \( \tau \)-dependent shift of \( \mu_{\text{opt}} \) results from the in-gap states (see Fig. 1(b)), which are not taken into account in the framework of the TIB model.

The power factor \( PF \) of (10,0) SWCNTs can also be calculated by substituting the \( L_{11} \) and \( L_{12} \) data in Fig. 3 into Eq. (15). Figure 4(b) shows the \( \mu \) dependence of the \( PF \) of (10,0) SWCNTs for \( \tau = 10, 30, 50, \) and 100 fs at \( T = 300 \) K. \( PF \) has its maximum value near the conduction and valence band edges \( E = \pm \Delta(= \pm 0.475 \) eV) of a pristine (10,0) SWCNT, and decreases with decreasing \( \tau \). The high \( PF \), on the order of 100 mW/mK\(^2 \), at the energy band edges is consistent with our previous theoretical work on the \( \mu \) dependence of the \( PF \) of impurity-doped SWCNTs using a single-band approximation.\( ^{24} \)

Here, we show \( S \) and \( PF \) as a function of \( L_{11} \) (\( i.e., \) the \( S-L_{11} \) plot and the \( PF-L_{11} \) plot) for (10,0) SWCNTs at \( T = 300 \) K for \( \tau = 10 \) (black curve), 30 (blue curve), 50 (red curve), and 100 fs (green curve) in Fig. 5(a) and 5(b).
The impurity potential in the momentum space is given by

\[ \Sigma_{ii}^R(E) = \Sigma_{ii}^R(E) = c_1 u_{11} + c_2 u_{12} X_{11}(E) \]

and the self-consistency equations are

\[ \Sigma_{11}^R(E) = c_1 u_{11} + c_2 u_{12} X_{11}(E) \]
\[ \Sigma_{22}^R(E) = c_1 u_{11} + c_2 u_{12} X_{12}(E) \]

with \( \Sigma_{ii}^R(E) \equiv \frac{1}{\Sigma} \sum_j G_{jj}^R(k, E) \) \( (j = 1, 2) \). In Eqs. (49) and (50), \( c_1 \equiv N_1/N \) and \( c_2 \equiv N_2/N \) are the concentrations of impurities (i.e., the impurity density per unit cell) with potential strengths \( u_{11} \) and \( u_{22} \), respectively (see Fig. 6). Moreover, \( X_{11}(E) \) and \( X_{22}(E) \) can be analytically calculated for the 1D Dirac electrons as

\[ X_{11}(E) = -\frac{1}{2} \frac{a}{h} \frac{k_2}{\sqrt{\kappa k_2}} \]
\[ X_{22}(E) = -\frac{1}{2} \frac{a}{h} \frac{k_1}{\sqrt{\kappa k_2}} \]

where \( \tau_1 \) and \( \tau_2 \) are the relaxation times related to \( u_{11} \) and \( u_{22} \) in the limit \(|E| \to \infty\), which are defined as \( \tau_1 = \frac{\hbar}{\kappa k_2} \) and \( \tau_2 = \frac{\hbar}{\kappa k_2} \), respectively.

The simultaneous equations in Eqs. (53) and (54) can be rewritten as the following equations with respect to \( \sigma_1 \equiv (\Sigma_{11}^R(E) - c_1 u_{11})/\Delta \) and \( \sigma_2 \equiv (\Sigma_{22}^R(E) - c_1 u_{22})/\Delta \).

\[ \sigma_1 = (\epsilon - 1 - c_1 u_{11}) \sigma_1 - \eta_1^2 = 0 \]
\[ \sigma_1 = (\epsilon - 1 - c_1 u_{11}) \sigma_1 - \eta_1^2 = 0 \]

and \( \sigma_2 = -\eta_1 \eta_2 \) with \( \epsilon \equiv E/\Delta \), \( \eta_1 \equiv \hbar/(2\Delta \tau_1) \), \( \eta_2 \equiv \hbar/(2\Delta \tau_2) \), \( \bar{u}_{11} \equiv u_{11}/\Delta \), and \( \bar{u}_{22} \equiv u_{22}/\Delta \). Equation (55) indicates that for each \( \epsilon \), there are four solutions of \( \sigma_1(\epsilon) \), respectively: four real ones or two real and two complex ones, the latter leading to finite DOS. In order to clearly show the difference between the two cases, Eq. (55) is rewritten as

\[ \eta_1 x_1^3 + 1 + c_1 \bar{u}_{11} x_1^2 (1 - c_1 \bar{u}_{22}) x_1 + 1 = 0 \]

with \( x_1 \equiv \sigma_1/\eta_1 \).

In the special case of \( \eta_2 = 0 \), Eq. (55) gives a cubic equation with respect to real \( x_1(= \sigma_1/\eta_1) \). Figure 7(a) shows Eq. (56) as a function of real \( x_1 \) for \( \eta_1 = 0.07 \) and \( \eta_2 = 0 \) for

Fig. 6. Self-consistent Born approximation for the retarded self-energy \( \Sigma_{ii}^R(E) \) \( (i = 1, 2) \) of a one-particle retarded Green’s function. The \( \times \) marks, dotted lines, and solid double lines with an arrow denote the impurity sites, impurity potential, and \( k \)-averaged retarded Green’s function \( X_{ii}(E) \) to be determined self-consistently, respectively.
(10,0) SWCNTs with $2\Delta = 0.95$ eV. In the shaded regions in Fig. 7(a), Eq. (55) has two complex and one real solutions of $x_1$. DOS is finite in these energy regions. The boundaries between the finite- and zero-DOS regions ($\epsilon_c$ and $\epsilon_v$ in Fig. 7(a)), which are band edges, can be determined using the condition $d\rho(E)/dx_1 = 0$. In coherent potential approximation (CPA) methods, including the present SCBA, the spectral conductivity $\sigma(E)$ becomes finite once DOS becomes finite (see §3.2.1), since CPA ignores the effects of Anderson localization due to the interference effects of scattered waves, which can lead to finite DOS even in the energy region where the conductivity is zero. It is known that every state is localized in one and two dimensions in the presence of finite scattering.\footnote{J. Phys. Soc. Jpn.} However, once the system size or temperature becomes finite, the effects of Anderson localization are greatly reduced. This situation is assumed in the present study and hence the band edges in the CPA are used to represent the effective mobility edges. For the case of $\eta_2 = 0$, one of the mobility edges is always $\epsilon_v = -1$ (i.e., $E_v = -\Delta$), as shown in Fig. 7(a).

The case of $c_1 = c_2 (\equiv c_0)$ which we call symmetric case, $\bar{u}_{11} = \bar{u}_{22} (\equiv \bar{u}_0)$ (i.e., $\eta_1 = \eta_2 (\equiv \eta_0)$) is also considered. For this case, Eq. (56) becomes

$$\tilde{\epsilon} = \frac{\eta_0 x_1^3 + x_1^2 - 1}{x_1^2 + 1} - \frac{\eta_0}{x_1(x_1^2 + 1)},$$

with $\tilde{\epsilon} = \epsilon - c_0\bar{u}_0$. Figure 7(b) shows $\tilde{\epsilon}$ in Eq. (57) as a function of real $x_1$ for $\eta_1 = \eta_2 = 0.07$, corresponding to (10,0) SWCNTs with $2\Delta = 0.95$ eV, and $\tau_1 = \tau_2 = 10$ fs. In the shaded regions in Fig. 7(b), Eq. (55) has two complex and two real solutions of $x_1$. These regions have finite DOS. The two mobility edges ($\epsilon_c$ and $\epsilon_v$) satisfy $\epsilon_c = -\epsilon_v$, as shown in Fig. 7(b).

The following discussion mainly focuses on thermoelectric properties of SWCNTs for the symmetric case of $\eta_1 = \eta_2$ (i.e., $\eta_1 = \eta_2$). The thermoelectric properties for the asymmetric case of $\eta_1 \neq \eta_2$ will be reported elsewhere.

### 3.2.1 Density of states and spectral conductivity

Once the self energy $\Sigma^R(E)$ is obtained via the above procedure, the DOS can be calculated using

$$\rho(E) = -\frac{1}{\pi} \sum_{j=1,2} \text{Im} X_{jj}(E)$$

$$= \frac{a}{2\pi\hbar v} \text{Re} \left\{ \frac{\kappa_1 + \kappa_2}{\sqrt{\kappa_1\kappa_2}} \right\}. \quad (58)$$

Figure 8(a) shows the calculated DOS values near the band gap of (10,0) SWCNTs per spin and orbital for $\tau(\equiv \tau_1 = \tau_2) = 10$ (black curve), 30 (blue curve), 50 (red curve), and 100 fs (green curve) and Fig. 8(b) shows the corresponding semi-log plots. In contrast to the DOS values calculated using the constant-$\tau$ approximation (see Fig. 1), clear mobility edges (i.e., $E_c$ and $E_v = -|E_c|$) exist, as shown in Fig. 8. As
\( \tau \) decreases, the band gap becomes small and the value of the DOS peak decreases. It can also be seen that the DOS near the mobility edges shows the behaviors \( \rho(E) \propto \sqrt{E-E_c}\) for \( E \geq E_c(>0) \) and \( \rho(E) \propto E_v-E \) for \( E \leq E_v(<0) \), respectively.

When the self-energy matrix is given in a diagonal and \( k \)-independent form, as shown in Eq. (48), the spectral conductivity \( \alpha(E) \) in Eq. (36) can be analytically calculated as

\[
\alpha(E) = \frac{1}{\hbar A} \frac{1}{E_{\text{Im}}(\kappa_1 \kappa_2)} \text{Re} \left( \frac{2 \kappa_1 \kappa_2 + \kappa_1^* \kappa_2^* + \kappa_1 \kappa_2^*}{\sqrt{\kappa_1 \kappa_2}} \right) \tag{59}
\]

with \( \text{Im} \sqrt{\kappa_1 \kappa_2} > 0 \). Note that Eq. (59) reduces to Eq. (42) in the constant-\( \tau \) approximation (i.e., \( \Sigma = -i\hbar/2\tau \)). Figure 9(a) shows the spectral conductivity \( \alpha(E) \) of (10,0) SWCNTs for \( \tau(=\tau_1=\tau_2)=10 \) (black curve), 30 (blue curve), 50 (red curve), and 100 fs (green curve) and Fig. 9(b) shows the corresponding semi-log plots. Here, \( \alpha(E) \) in Eq. (59) was multiplied by a factor of 4. In contrast to the results obtained with the constant-\( \tau \) approximation (see Fig. 2), \( \alpha(E) \) has a clear gap, as shown in Figs. 9(a) and 9(b). It can also be seen that \( \alpha(E) \) near the mobility edges \( E = E_c(>0) \) and \( E = E_v(<0) \) shows the behaviors \( \alpha(E) \propto (E-E_c) \) for \( E \geq E_c \) and \( \alpha(E) \propto (E_v-E) \) for \( E \leq E_v \), respectively (see Appendix D for details).

3.2.2 Chemical potential dependence of \( L_{11} \) and \( L_{12} \) at 300 K

Figure 10(a) shows the \( \mu \) dependence of the \( L_{11} \) of (10,0) SWCNTs at 300 K for \( \tau(=\tau_1=\tau_2)=10 \) (black curve), 30 (blue curve), 50 (red curve), and 100 fs (green curve). As expected from Eq. (38), the \( \mu \) dependence of \( L_{11} \) for each \( \tau \) shows features similar to those for the \( E \) dependence of the spectral conductivity \( \alpha(E) \) in Fig. (8). As shown in Fig. 10(b), the \( L_{12} \) values of (10,0) SWCNTs for \( \tau = 10, 30, 50, \) and 100 fs at \( T = 300 \) K have peaks and dips near the mobility edges \((E = E_c)\) and \((E = E_v)\), respectively. These characteristics of \( L_{11} \) and \( L_{12} \) are essentially the same as those obtained using the constant-\( \tau \) approximation in the previous section.

3.2.3 Chemical potential dependence of \( S \) and \( \text{PF} \) at 300 K

Figure 11(a) shows the \( \mu \) dependence of the Seebeck coefficient \( S \) of (10,0) SWCNTs for \( \tau = 10, 30, 50, \) and 100 fs at 300 K, which was obtained by substituting the \( L_{11} \) and \( L_{12} \) data in Fig. 10 into Eq. (15). As shown in Fig. 11(a), the absolute value of \( S \) decreases with decreasing \( \tau \), and \( S \) exhibits bipolar effects as a function of \( \mu \) (i.e., a bipolar thermoelectric effect).\(^{12,13}\) In contrast to the results shown in Fig. 4(a), the optimal chemical potentials \( \mu = \mu_{\text{opt}} \) are almost independent of \( \tau \). Figure 11(b) shows the power factor \( \text{PF} \) of (10,0) SWCNTs for \( \tau = 10, 30, 50, \) and 100 fs at \( T = 300 \) K, which was calculated by substituting the \( L_{11} \) and \( L_{12} \) data in Fig. 10 into Eq. (16). Similar to the results obtained using the constant-\( \tau \)
approximation, $PF$ has a maximum value near the conduction and valence band edges of pristine (10,0) SWCNTs.

Here, we show $S$ and $PF$ as a function of $L_{11}$ (i.e., the $S$-$L_{11}$ plot and the $PF$-$L_{11}$ plot) for (10,0) SWCNTs at $T = 300$ K for $\tau = 10$ (black curve), 30 (blue curve), 50 (red curve), and 100 fs (green curve) calculated using the SCBA.

3.3 Low-temperature behavior of Seebeck coefficient

In this section, we discuss the low-temperature behavior of $S$ for SWCNTs within SCBA. Since a clear band gap exists, as shown in Fig. 9, the spectral conductivity $\alpha(E)$ can be divided into two parts as

$$\alpha(E) = \alpha_c(E)\theta(E - E_c) + \alpha_h(E)\theta(E - E_v), \tag{60}$$

where $\alpha_{e(h)}(E)$ is the conduction-electron (valence-hole) spectral conductivity and $\theta(x)$ is the Heaviside step function. For this case, the Seebeck coefficient $S$ can be rewritten as

$$S(E) = \frac{1}{T} \frac{L_{12}^c + L_{12}^h}{L_{11}^c + L_{11}^h} = \frac{L_{11}^c S^c + L_{11}^h S^h}{L_{11}^c + L_{11}^h}, \tag{61}$$

with

$$L_{11}^c \equiv \int_{E_c}^{\infty} dE \left[-\frac{\partial f(E - \mu)}{\partial E}\right] \alpha_c(E),$$

$$L_{11}^h \equiv \int_{-\infty}^{E_v} dE \left[-\frac{\partial f(E - \mu)}{\partial E}\right] \alpha_h(E). \tag{63}$$

$S^c \equiv L_{12}^c / T L_{11}^c$. Here, the superscripts $c$ and $h$ represent electrons and holes, respectively. Note that although Eq. (61) is formally the same as the TIB model for the Seebeck coefficient based on the Boltzmann transport theory, Eqs. (63)-(65) include the effects of inter-band scattering between the conduction and valence bands, which is not taken into account in TIB model.

The temperature dependence of the Seebeck coefficient for a symmetric case satisfying $E_c = -E_v = \Delta$ is now discussed. For the case of $\mu > E_c$ and $2\Delta \gg k_B T$, $L_{11}^c$ and $L_{11}^h$ can be neglected and $S \approx S^c$. For this case, $S^c$ in the low-temperature limit can be easily obtained as

$$S^c \approx -\frac{\pi^2 k_B^2 T}{3e} \left(\frac{d \ln \alpha_c(E)}{dE}\right)_{E=E_c}, \quad (\mu > E_c) \tag{66}$$

by performing the Sommerfeld expansion of Eqs. (63)-(65). The $T$-linear behavior of $S$, known as Mott’s formula, \cite{39} can be seen for the (10,0) SWCNTs when $\mu$ is larger than $E_c = 0.30$ eV, as shown in Fig. 13. The $T$-linear region becomes smaller as $\mu$ approaches the mobility edge $E_c$.

When $\mu = E_c$, the above-mentioned $T$-linear region van-
Fig. 13. (Color online) Temperature dependence of the Seebeck coefficient of (10,0) SWCNTs with $\tau = 10$ fs for $\mu = 0.28$ eV (black curve), 0.29 eV (blue curve), 0.30 eV ($E_c$, red curve), 0.31 eV (green curve), and 0.32 eV (purple curve). Here, $E_c$ is the mobility edge.

The Seebeck coefficient $S^c$ becomes constant as

$$S^c = \frac{k_B}{e} \int_0^{E_c} dx \left( \frac{-\partial f(x)}{\partial x} \right) x^2 \approx \frac{k_B}{e} \times 2.37, \quad (\mu = E_c),$$

where $f(x) = 1/(1 + e^x)$ with $x \equiv E - E_c$. For $\mu = E_c (=0.30$ eV), the Seebeck coefficient $S$ of (10,0) SWCNTs with $\tau = 10$ fs is constant with respect to $T$, as shown in Fig. 13. When $\mu < E_c$, but as far as $E_c - \mu < 2\Delta$ together with low temperature $k_B T \ll E_c - \mu$, the valence holes are frozen out (i.e., $L_{11}^0 = 0$ and $L_{12}^1 = 0$) and the Seebeck coefficient $S \approx S^c$, which is inversely proportional to $T$ as

$$S^c \approx -S_0 = \frac{E_c - \mu}{eT}, \quad (\mu < E_c; k_B T \ll E_c - \mu \ll 2\Delta).$$

The Seebeck coefficient $S$ can be seen for (10,0) SWCNTs with $\tau = 10$ fs for $\mu = 0.28$ eV and 0.29 eV ($E_c = 0.30$ eV) in Fig. 13.

5. Conclusion

The present study based on 1D Dirac electrons has developed a theoretical framework of bipolar thermoelectric effects in SWCNT described as 1d Dirac electrons under disorder. Based on the thermal Green’s functions, effects of disorder have been treated within self-consistent Born approximation (SCBA), which is the simplest version of coherent potential approximation (CPA). The results has led to prediction of characteristic behaviors of Seebeck coefficient and power factor of semiconducting SWCNT, including the sign change of Seebeck coefficient as a function of chemical potential (gate voltage) as observed in recent experiments. It is to be noted that effects of Anderson localization, which will play important roles at low temperatures, are totally ignored in the present study since our interest here in mainly at elevated temperatures, e.g., room temperature. We have also studied the crossover from $T$-linear to $T$-inverse behavior of the Seebeck coefficient of semiconducting SWCNTs at low $T$ when the chemical potential changes from $\mu > E_c$ to $\mu < E_c$. The $S \approx 1/T$ behavior for $\mu < E_c$, which is commonly seen in texts, should be taken with care for the temperature range of its observability because the present linear response theory breaks down in the limit of $T \to 0$, which needs separate and detailed studies.

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Appendix A: 1D Dirac electrons in semiconducting carbon nanotubes

Figures A.1(a) and A.1(b) show the real and reciprocal lattices of graphene, respectively. The two-dimensional principal lattice vectors are $a_1 = (\sqrt{3}a/2, a/2)$ and $a_2 = (\sqrt{3}a/2, a/2)$ with $\alpha = |a_1| = |a_2| = 0.246nm$. The unit cell contains two carbon atoms, A and B. The reciprocal lattice vectors are $b_1 = (2\pi/\sqrt{3}a, 2\pi/a)$ and $b_2 = (2\pi/\sqrt{3}a, 2\pi/a)$, respectively. In particular, the $\Gamma$, $K$, and $K'$ points of the Brillouin zone are given by $\Gamma = (0,0)$, $K = (4\pi/\sqrt{3}a, 0)$, and $K' = (2\pi/\sqrt{3}a, 2\pi/a)$, respectively.

The $\pi$-orbital tight-binding Hamiltonian of graphene is given by

$$H(k) = \begin{pmatrix} 0 & H_{AB}(k) \\ H_{BA}(k) & 0 \end{pmatrix},$$

with the matrix elements $H_{AB}(k) = (H_{BA}(k))^\dagger$, which are given by

$$H_{AB}(k) \equiv -\gamma_0 \sum_{l=1}^3 e^{-ik \cdot R_l},$$

where

$$H_{AB}(k) = -\gamma_0 \left( e^{ik_a/\sqrt{3}} + 2e^{-ik_a/2\sqrt{3}} \cos \frac{k_a}{2} \right).$$

Here, $R_1 = (a/\sqrt{3}, 0)$, $R_2 = (a/2, 0)$, and $R_3 = (\sqrt{3}a/2, a/2)$ are the vectors going from a $B$ lattice point to three neighboring $A$ lattice points, as shown in Fig. A.1. $\gamma_0$ is

behavior of the Seebeck coefficient at low temperature in Fig. 13 will also be an interesting experimental challenge.
the hopping integral between nearest-neighbor carbon atoms \((\pi \text{ orbitals}, \text{ set to } \gamma_0 = 2.7 \text{ eV in the present study})\). By diagonalizing the Hamiltonian in Eq. (A-5), the energy dispersion relation of graphene can be obtained as
\[
E_{\pm}(k) = \pm \gamma_0 \sqrt{1 + 4 \cos \frac{\sqrt{3}ak_x}{2} \cos \frac{ak_y}{2} + 4 \cos^2 \frac{ak_y}{2}} \quad (A-4)
\]
with the gapless points (so-called Dirac points) at the K and K' points. In Eq. (A-4), the sign \(\pm\) represents the conduction (+) and valence (−) bands, respectively. As is well known, graphene has the linear dispersion relation \(E_{\pm}(k) \approx \pm \hbar v_F |k|\) with \(v = \sqrt{3} \gamma_0 / 2 \hbar \) around the K and K' points.

Here, zigzag-edged SWCNTs (z-SWCNTs) are considered as an example of pure 1D semiconductors. The Hamiltonian of a z-SWCNT can be obtained by imposing the periodic boundary condition along the y axis to the graphene as follows.
\[
H_q(k) = \begin{pmatrix} 0 & H_{AB}^{(q)}(k) \\ H_{BA}^{(q)}(k) & 0 \end{pmatrix} \quad (A-5)
\]
with the matrix elements
\[
H_{AB}^{(q)}(k) = (H_{BA}^{(q)}(k))^T,
\]
\[
H_{AB}^{(q)}(k) = -\gamma_0 (ka)^2 \sqrt{1 + 2e^{-i \sqrt{3}ak_2/2} \cos \frac{\pi a}{n}}, \quad (A-6)
\]
where \(k\) is the wavenumber along the tube-axial direction, \(q = 0, 1, \cdots, 2n - 1\) is the discrete wavenumber along the circumferential direction, and \(n\) is a natural number \((n = 1, 2, \cdots, \infty)\) specifying the unique structure of a particular z-SWCNT. Herein, a z-SWCNT with index \(n\) is represented as \((n, 0)\) CNT in accordance with customary practice.

The energy dispersion relations \(E_{\pm}^{(q)}(k)\) of the conduction (+) and valence (−) bands can be expressed as\(^{37,38}\)
\[
E_{\pm}^{(q)}(k) = \pm \gamma_0 \sqrt{1 + 4 \cos \frac{ka}{2} \cos \frac{\pi at_n}{n} + 4 \cos^2 \frac{\pi at_n}{n}} \quad (A-7)
\]
\( (q = 0, 1, \cdots, 2n - 1 \text{ and } -\pi/a; < k < \pi/a). \)

Here, \(a_c = 0.426 \text{ nm}\) is the unit cell length of the z-CNTs. A \((n, 0)\) CNT includes \(4n\) carbon atoms in the unit cell and its diameter \(d_1\) is given by \(d_1 = \frac{na_c}{\sqrt{\pi}}\).

z-SWCNTs can be either metallic or semiconducting depending on whether or not \(n\) is a multiple of 3, respectively.

For the case of metallic \(z\)-SWCNTs \((n \text{ mod } 3 = 0)\), two pairs of lowest-conduction (LC) and highest-valence (HV) bands \(E_{\pm}^{(q)}(k)\) are specified by the following two values of \(q\), respectively.
\[
q = \begin{cases} q_1 \equiv 2n/3 & \text{ for } n \text{ mod } 3 = 0 \quad (A-8) \\
q_2 \equiv 4n/3 & \text{ for } n \text{ mod } 3 = 1 \quad (A-9) \\
q_3 \equiv 6n/3 & \text{ for } n \text{ mod } 3 = 2 \quad (A-10)
\end{cases}
\]
As can be seen in Eqs. (A-8)-(A-10), both the LC and HV bands will have two-fold degeneracy \((q_1, q_2)\) for a given \(n\).

In the long-wavelength limit \((k \to 0)\), the Hamiltonian matrix of \(z\)-SWCNT in Eq. (A-6) can be approximately expressed as
\[
H_{AB}^{(q)}(k) = e^{i\theta_k} \left( \Delta_q + \frac{\hbar^2 k_z^2}{2m_q} + i\hbar v_q k \right) \quad (A-11)
\]
with \(\theta_k = ka/\sqrt{3}\) and
\[
\Delta_q = -\gamma_0 \left( 1 + 2 \cos \frac{\pi q}{n} \right) \quad (A-12)
\]
\[
m_q^{-1} = \frac{a_c^2 \gamma_0}{2\hbar^2} \cos \frac{\pi q}{n} \quad (A-13)
\]
\[
v_q = \frac{a_c \gamma_0}{\hbar} \cos \frac{\pi q}{n} \quad (A-14)
\]
The unitary transform of the Hamiltonian in Eq. (A-17) can
now be performed as
\[
\tilde{H}_g(k) = U_k^\dagger H_g(k) U_k \equiv \left( \Delta_q + \frac{\hbar^2 k^2}{2m} \right) \frac{\hbar v_F k}{v_F k - \Delta_q - \frac{\hbar^2 k^2}{2m}}
\]
(A-15)
using the unitary matrix
\[
U_k = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta_k} & e^{-i\theta_k} \\ e^{i\theta_k} & -e^{i\theta_k} \end{pmatrix}.
\] (A-17)

For the case of \(k | h| \approx 2 \sqrt{m q y} \) (small wavenumber) and \(\Delta_q / m q y^2 \ll 1\) (small band gap), the effective Hamiltonian in Eq. (A-16) can be approximately described by
\[
\tilde{H}_g(k) \approx \left( \Delta_q - \frac{\hbar^2 k^2}{2m} \right) \frac{\hbar v_F k}{v_F k - \Delta_q - \frac{\hbar^2 k^2}{2m}}.
\] (A-18)

By diagonalizing the Hamiltonian \(\tilde{H}_g(k)\) in Eq. (A-18), the energy dispersion relations \(E^{(q)}_{\pm}\) of the conduction (+) and valence (−) bands of 1D Dirac electrons can be obtained as
\[
E^{(q)}_{\pm}(k) = \pm \sqrt{\Delta_q^2 + (\hbar v_F k)^2}.
\] (A-19)

As an example, Fig. A-2 shows the energy bands \(E^{(q)}_{\pm}\) of the (10,0) z-SWCNT calculated using the \(\pi\)-orbital tight-binding model (solid curves) and the 1D Dirac electron model (dashed curves). The dashed curves are in excellent agreement with the solid curve in the vicinity of \(k = 0\). For a (10, 0) z-SWCNT, the energy difference \(\Delta E\) between the bottom of the LC band and the second-lowest conduction band is \(\Delta E = 0.557\) eV. Herein, the focus is on the low-energy excitation regime, in which the thermal energy \(k_B T\) is much lower than \(\Delta E\). In the low-energy excitation regime, the thermoelastic properties of z-SWCNTs can be explained in terms of single-band 1D Dirac electrons in the LC and HV bands denoted as \(q = q_1, q_2\) in Eqs. (A-9) and (A-10). Here, it is assumed that the effects of possible mixing between the two LC bands due to impurity scattering can be ignored. This assumption is valid under the condition that the characteristic momentum contributing to the formation of the bound state due to impurity potential is much smaller than the momentum difference between the two LC (HV) bands with \(q = q_1\) and \(q_2\), as discussed in our previous work.24 Thus, in the main text of the present study, the focus is only on the LC and HV bands and the subscript or subscript \(q = q_1\) and \(q_2\) is dropped from the 1D Dirac Hamiltonian \(h_0(k)\) in Eq. (11).

**Appendix B: Derivation of Eq. (24)**

This appendix derives Eq. (24). By substituting Eq. (23) into Eq. (22), the energy current \(J_Q\) can be rewritten as
\[
J_Q = \int_{-\infty}^{\infty} dx \left\{ \frac{\partial \Psi^\dagger (x,t)}{\partial t} \left( \sin \frac{Qx}{2Q} H(x) \right) \Psi(x,t) + \Psi^\dagger (x,t) \left( \sin \frac{Qx}{2Q} H(x) \right) \frac{\partial \Psi(x,t)}{\partial t} \right\} + \text{H.c. (B-1)}
\]
Applying Eqs. (5) and (6) to Eq. (B-1), \(J_Q\) becomes
\[
J_Q = \frac{i}{\hbar} \int_{-\infty}^{\infty} dx \sin \frac{Qx}{2Q} \left\{ (H(x) \Psi(x,t)) (H(x) \Psi(x,t)) - (\Psi^\dagger (x,t) H(x) \Psi(x,t)) \right\} + \text{H.c. (B-2)}
\]
As the 1D Dirac Hamiltonian with a disorder potential \(U(x)\) is given by \(H(x) = -i\hbar \sigma_y \partial x + \Delta \sigma_x + U(x)\) in Eq. (2), Eq. (B-2) can be rewritten as
\[
J_Q = \frac{v}{2} \int_{-\infty}^{\infty} dx \sin \frac{Qx}{2Q} (\Psi^\dagger (x,t) \sigma_y H(x) \Psi(x,t) + H^\dagger \Delta B - 3) + \text{H.c. (B-3)}
\]
In the limit of \(Q \rightarrow 0\), Eq. (24) in the main text can be obtained as
\[
J_Q = \int_{-\infty}^{\infty} dx \Psi^\dagger (x,t) (\sigma_y H(x) + H^\dagger \Delta B - 3) \sigma_x + \text{H.c. (B-4)}
\]
Recently, Ogata and Fukuyama gave a general expression of Eq. (24) for multi-band disorder systems based on the Lüttinger-Kohn representation.29

**Appendix C: Absence of vertex correction**

In this appendix, a vertex correction for the current operator. Up to the lowest order of \(U, \sigma_q^z(k)\) in Eq. (32) is expressed as
\[
\sigma_{q'}^z(k) = \langle U(k - k') \sigma_q^z(k, i\epsilon_0) \sigma_{q'}^z(k', i\epsilon_0) U(k' - k) \rangle_{\text{imp}} \quad (C-1)
\]
where we used \(\mathcal{G}(k', i\epsilon_0) \approx \delta_{k,k'} \mathcal{G}(k, i\epsilon_0)\). We now assume that the impurity potential is a short range and diagonal, that is, \(U(q)\) is given by
\[
U(q) = \frac{U_0}{N} \sum_{i,j} e^{-iq\delta_{ij}} \quad (C-2)
\]
with \(U_0 = (u_0 I + u_k \sigma_z)\), where \(I\) is the 2x2 identity matrix. In this case, \(\sigma_{q'}^z(k)\) is rewritten as
\[
\sigma_{q'}^z(k) = \sum_k (U_0 \mathcal{G}_0(k, i\epsilon_0) \sigma_q^z(k, i\epsilon_0) U_0) f(k - k') \quad (C-3)
\]
where \(f(q) \equiv \left( \frac{1}{N} \sum_{i,j} e^{iq\delta_{ij}} \right) \left( \frac{1}{N} \sum_{i,j} e^{-iq\delta_{ij}} \right)_{\text{imp}}\). Thus, the vertex correction \(\Gamma\) for the correlation function in Eq. (31) is given by
\[
\Gamma \propto \sum_{k,k'} \mathcal{G}_0(k, i\epsilon_0) \mathcal{G}_0(k', i\epsilon_0) \frac{A(k) \sigma_z - iu_0 \Delta x \sigma_z}{D(k, i\epsilon_0)} U_0 \mathcal{G}_0(k', i\epsilon_0) \sigma_q^z(k', i\epsilon_0) U_0 = \frac{1}{D(k, i\epsilon_0)} \left( \frac{1}{N} \sum_{i,j} e^{-iq\delta_{ij}} \right)_{\text{imp}}
\]
\[
\mathcal{J}(k') \approx \frac{\beta k}{\sqrt{\kappa k_2}} \left( 1 - \frac{z}{2} - \frac{z^2}{8} \right). \tag{D-9}
\]

Substituting Eqs. (D-4), (D-5) and (D-9) into Eq. (D-1), we can straightforwardly obtain
\[
\alpha(E) \propto \frac{2}{(k'^2_1 k^2_2)^{1/2}} k^2_1 k^2_2 \tag{D-10}
\]

near the mobility edge \( E = E_c \). As can be seen in Fig. 8(a) and can be analytically verified from Eq. (56) and Fig. 7 as \( \text{Im} \sigma_1 \propto \sqrt{E - E_c} \) together with \( \sigma_1 \sigma_2 = \eta_1 \eta_2 \), the DOS is proportional to \( \sqrt{E - E_c} \) in the vicinity of \( E = E_c \) and \( k^2_1 \) and \( k^2_2 \) near \( E = E_c \) show the behaviors \( k^2_1 \propto k^2_2 \propto \sqrt{E - E_c} \). Therefore, \( \alpha(E) \) behaves as
\[
\alpha(E) \propto (E - E_c) \tag{D-11}
\]

near the mobility edge \( E = E_c \).

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