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Invited review

Kohn anomaly in Raman spectroscopy of single wall carbon nanotubes

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ABSTRACT

Phonon softening phenomena of the Γ point optical modes including the longitudinal optical mode, transverse optical mode and radial breathing mode in "metallic" single wall carbon nanotubes are reviewed from a theoretical point of view. The effect of the curvature-induced mini-energy gap on the phonon softening which depends on the Fermi energy and chirality of the nanotube is the main subject of this article. We adopt an effective-mass model with a deformation-induced gauge field which provides us with a unified way to discuss the curvature effect and the electron-phonon interaction. © 2010 Elsevier B.V. All rights reserved.

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LOW-DIMENSIONAL SYST A HANDSTRUCTURES

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1. Introduction

The lattice structure of a single wall carbon nanotube (SWNT) can be specified uniquely by the chirality defined by two integers (n,m) [1,2], and the chirality can be determined by Raman spectroscopy [3–5]. A simple tight-binding model shows that a SWNT is primarily metallic if n-m is a multiple of 3 or semiconducting otherwise. A "metallic" SWNT can have a mini-energy band gap due to the curvature of a SWNT which gives rise to a hybridization between the σ and π orbitals. The presence of an energy band gap in a metallic SWNT has attracted much attention since the early stages of nanotube research [6,7]. The present paper deals with the effect of curvature on the Raman spectra for two in-plane Γ point long-itudinal and transverse optical phonon (LO and TO) modes [8,9] and the out-of-plane radial breathing mode (RBM) [10,11].

In the Raman spectra of a SWNT, the LO and TO phonon modes at the Γ point in the two-dimensional Brillouin zone (2D BZ), which are degenerate in graphite and graphene, split into two peaks, denoted by G⁺ and G⁻ peaks, respectively, [4,12,13] because of the curvature effect. The splitting of the two peaks for SWNTs is inversely proportional to the square of the diameter, d_t , of SWNTs due to the curvature effect, in which G⁺ does not change with changing d_t , but the G⁻ frequency decreases with decreasing d_t [14]. In particular, for metallic SWNTs, the G⁻ peaks appear at a lower frequency than the G⁻ peaks for semiconducting SWNTs with a similar diameter [15]. The spectra of G⁻ for metallic SWNTs.

It has been widely accepted that the frequency shift of the G-band in metallic SWNTs is produced by the electron-phonon (el-ph) interaction [16-21]. An optical phonon changes into an electron-hole pair as an intermediate state by the el-ph interaction. This process is responsible for the phonon selfenergy. The phonon self-energy is sensitive to the structure of the Fermi surface [22] or the Fermi energy, $E_{\rm F}$. In the case of graphite intercalation compounds in which the charge transfer of an electron from a dopant to the graphite layer can be controlled by the doping atom and its concentration, Eklund et al. [23] observed a shift of the G-band frequency with an increase of the spectral width. In this case the frequency shifted spectra show that not only the LO mode but also the TO mode is shifted in the same fashion by a dopant. For a graphene mono-layer, Lazzeri et al. calculated the $E_{\rm F}$ dependence of the shift of the G-band frequency [17]. The LO mode softening in metallic SWNTs was shown by Dubay et al. [24,25] on the basis of density functional theory.



Fig. 1. (a) The curvature-induced hybridization between two p_z orbitals of carbon atoms at \mathbf{r}_1 and \mathbf{r}_2 is illustrated. $\mathbf{e}_i(\mathbf{r})$ ($i \in \{x, y, z\}$) denotes the basis of the (x, y, z)-coordinate system whose origin is located at a carbon atom \mathbf{r} . (b) $\mathbf{e}_i^{\parallel}(\mathbf{r}_2)$ and $\mathbf{e}_i^{\parallel}(\mathbf{r}_1)$ induce the hybridization, including σ bonding.

Recently, Nguyen et al. [26] and Farhat et al. [8] observed the phonon softening effect of SWNTs experimentally as a function of E_F by electro-chemical doping, and their results clearly show that the LO phonon modes become soft as a function of E_F . Ando [27] discussed the phonon softening for metallic SWNTs as a function of the E_F position, in which the phonon softening occurs for the LO phonon mode. In this paper, we consider the effect of a curvature-induced mini-energy gap on the frequency of the LO, TO, and RBM in "metallic" SWNTs.

The organization of the paper is as follows. In Section 2 we show that the curvature of a SWNT gives rise to a hybridization between the σ and π orbitals. Then we show our calculated result for the curvature-induced mini-energy gap appearing in "metallic" SWNTs. The current status of the scanning tunneling spectroscopy experimental results is briefly mentioned, confirming the curvature-induced mini-energy gap. In Section 3 we formulate the phonon self-energy which is given by the electron-hole pair creation process. The Fermi energy dependence of the self-energy is shown for graphene with or without an energy gap, as a simple example. In Section 4 we provide a theoretical framework for including a lattice deformation into an effective-mass Hamiltonian. A lattice deformation is represented by a deformation-induced gauge field which is shown to be a useful idea to discuss both the appearance of the curvature-induced mini-energy gap and also the el-ph interaction. Section 5 is a main section in this article in which we discuss the effect of curvature on the phonon self-energy. In Section 6 we discuss and summarize our results.

2. Curvature effect

Let us start to discuss the effect of the curvature of a SWNT on the hybridization between the σ and π orbitals (Section 2.1). We will then show the calculated result of the curvature-induced minienergy gap appearing in "metallic" SWNTs (Section 2.2). The phonon softening phenomena are sensitive to this mini-energy gap.

2.1. Curvature-induced hybridization

At each carbon atom located at **r** on the surface of a SWNT, we define the atom-specific (*x*, *y*, *z*)-coordinate axes and the unit vector for each axis by $\mathbf{e}_i(\mathbf{r})$ ($i \in \{x,y,z\}$), where $\mathbf{e}_z(\mathbf{r})$ is taken as the unit normal vector to the cylindrical surface, and $\mathbf{e}_x(\mathbf{r})$ and $\mathbf{e}_y(\mathbf{r})$ are unit vectors in the tangent plane [see Fig. 1(a)]. Here, $\mathbf{e}_x(\mathbf{r})$ is taken to be parallel to the axis of a SWNT. In the case of a flat graphene sheet, we can set the common axis vector for all carbon atoms and thus a unit vector \mathbf{e}_i at \mathbf{r}_1 can be taken orthogonal to the orthogonal conditions are not satisfied because of the atom specific coordinate, that is, $\mathbf{e}_z(\mathbf{r}_1) \cdot \mathbf{e}_z(\mathbf{r}_2) \neq 1$, $\mathbf{e}_z(\mathbf{r}_1) \cdot \mathbf{e}_y(\mathbf{r}_2) \neq 0$, etc. To see the curvature effect more clearly, it is useful to project

$$\mathbf{e}_i(\mathbf{r}_1)$$
 and $\mathbf{e}_j(\mathbf{r}_2)$ onto

$$\mathbf{e}_i(\mathbf{r}_1) = \mathbf{e}_i^{\perp}(\mathbf{r}_1) + \mathbf{e}_i^{\parallel}(\mathbf{r}_1), \quad \mathbf{e}_j(\mathbf{r}_2) = \mathbf{e}_i^{\perp}(\mathbf{r}_2) + \mathbf{e}_i^{\parallel}(\mathbf{r}_2), \tag{1}$$

where $\parallel (\perp)$ denotes the vector which is parallel (perpendicular) to the displacement vector $\mathbf{r}_2 - \mathbf{r}_1$ [see Fig. 1(b)]. Let $|p_i(\mathbf{r})\rangle$ ($i \in \{x,y,z\}$) be the $2p_i$ -orbital of a carbon atom located at \mathbf{r} . Then, the transfer integral from $|p_i(\mathbf{r}_1)\rangle$ to $|p_j(\mathbf{r}_2)\rangle$ may be written as

$$\langle p_j(\mathbf{r}_2)|\hat{\mathcal{H}}|p_i(\mathbf{r}_1)\rangle = \mathcal{H}_{pp\pi}\mathbf{e}_j^{\perp}(\mathbf{r}_2)\cdot\mathbf{e}_i^{\perp}(\mathbf{r}_1) + \mathcal{H}_{pp\sigma}\mathbf{e}_j^{\parallel}(\mathbf{r}_2)\cdot\mathbf{e}_i^{\parallel}(\mathbf{r}_1), \qquad (2)$$

where $\mathcal{H}_{pp\pi}$ and $\mathcal{H}_{pp\sigma}$ are the transfer integrals for π and σ bonds, respectively. According to a first-principles calculation with the

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local density approximation obtained by Porezag et al. [28], $\mathcal{H}_{pp\pi} \approx -3 \text{ eV}$ and $\mathcal{H}_{pp\sigma} \approx 8 \text{ eV}$ for nearest-neighbor carbon sites. Using Eq. (1), we eliminate $\mathbf{e}_{i}^{\perp}(\mathbf{r}_{1})$ and $\mathbf{e}_{i}^{\perp}(\mathbf{r}_{2})$ from Eq. (2), and get

$$\langle p_j(\mathbf{r}_2)|\mathcal{H}|p_i(\mathbf{r}_1)\rangle = \mathcal{H}_{pp\pi}\mathbf{e}_j(\mathbf{r}_2)\cdot\mathbf{e}_i(\mathbf{r}_1) + (\mathcal{H}_{pp\sigma} - \mathcal{H}_{pp\pi})\mathbf{e}_j^{\mathbb{I}}(\mathbf{r}_2)\cdot\mathbf{e}_i^{\mathbb{I}}(\mathbf{r}_1), \quad (3)$$

where we have used $\mathbf{e}_i^{\perp}(\mathbf{r}_1) \cdot \mathbf{e}_j^{\parallel}(\mathbf{r}_2) = 0$ and $\mathbf{e}_i^{\parallel}(\mathbf{r}_1) \cdot \mathbf{e}_j^{\perp}(\mathbf{r}_2) = 0$. The last term of Eq. (3) corresponds to the curvature effect of a SWNT. Note that the coefficient of the last term includes $\mathcal{H}_{pp\sigma}$ showing that the σ bond is partially incorporated by the curvature-induced hybridization (see Ref. [29] for more details).

In the case of a flat graphene, we have $\mathbf{e}_z^{\parallel}(\mathbf{r}_1) = 0$ and $\mathbf{e}_z^{\parallel}(\mathbf{r}_2) = 0$. Then, the last term of Eq. (3) disappears and the theoretical model taking only the $2p_z$ orbital (or π - orbital) into account becomes a good approximation. The curvature of a SWNT results in $\mathbf{e}_z^{\parallel}(\mathbf{r}_2) \cdot \mathbf{e}_z^{\parallel}(\mathbf{r}_1) \neq 0$, $\mathbf{e}_z^{\parallel}(\mathbf{r}_2) \cdot \mathbf{e}_y^{\parallel}(\mathbf{r}_1) \neq 0$, etc., and the last term of Eq. (3) is non-vanishing and consequently the curvature-induced hybridization occurs. The curvature-induced hybridization is relevant to the following two physical properties. First, the hybridization can open a mini-gap (up to ~ 100 meV) near the Fermi energy in metallic SWNTs. Second, the curvature-induced gap depends on the SWNT (*n*,*m*) chirality. For example, the gap is zero for armchair SWNTs, while it is about 70 meV for a (12,0)



Fig. 2. (a) The dependence of the curvature-induced energy gap, E_{gap} , on the chiral angle θ and tube diameter d_t . The surface is a plot of Eq. (4) which reproduces well the calculated results. (inset) Due to the nanotube curvature, the cutting line which was exactly crossing the Dirac point in the absence of curvature can miss the Dirac point when curvature is included. This curvature gives rise to an energy gap E_{gap} in "metallic" SWNTs. (b) The d_t dependence of E_{gap} is given as a one-dimensional projection of (a) onto the d_t axis. The points on the dashed, and dotted curves satisfy n-m=3, 6, 9, respectively. We plot the energy of the RBM, $\hbar \omega_{\text{RBM}}$ of Eq. (5), as a solid curve for comparison.

metallic zigzag SWNT. The chirality dependent curvature-induced energy gap will be analytically given in the next subsection.

2.2. Curvature-induced mini-energy gap

In Fig. 2(a) we plot the calculated curvature-induced energy gap, E_{gap} , for each (n,m) for metallic SWNTs as a function of the chiral angle $\theta(\)$ and tube diameter $d_t(\text{nm})$. We performed the energy band structure calculation in an extended tight-binding (ETB) framework developed by Samsonidze et al. [30] to obtain E_{gap} . In the ETB framework, 2s and 2p orbitals, and their transfer and overlap integrals up to fourth nearest neighbor atoms are taken into account (see Ref. [30,31] for more details).¹ We have adopted the values of the transfer and overlap integrals as a function of the carbon-carbon inter-atomic distance that were derived by Porezag et al. [28].²

Fig. 2(a) shows that, for a fixed diameter of a metallic SWNT d_t , a zigzag SWNT ($\theta = 0^\circ$) has the largest value of E_{gap} and an armchair SWNT ($\theta = 30^\circ$) has no energy gap. The calculated results are well reproduced by

$$E_{\rm gap} = \frac{c}{d_t^2} \cos 3\theta,\tag{4}$$

with $c = 60 (\text{meV} \text{nm}^2)$ [11]. The chirality and diameter dependence of E_{gap} is consistent with the results by Refs. [29,32]. The value of *c* is about two times larger than the result by Ref. [32]. This difference may come from the inclusion of $\mathcal{H}_{pp\sigma}$ in our calculation. As we will explain in detail in Section 4.2, the curvature moves the Dirac point in *k*-space away from the hexagonal corner of the first BZ [2]. As a result, the curvature can cause the quantized transverse electron wave vector (the cutting line) to miss the Dirac point and make a gap [see the inset in Fig. 2(a)].

When we discuss the phonon softening of the RBM, the relationship between the mini-energy gap and the RBM phonon energy will be important. In Fig. 2(b), we plot the energy of the RBM,

$$\hbar \omega_{\rm RBM} = \frac{c_1}{d_t} + c_2,\tag{5}$$

as a solid curve for comparison. Here $\hbar \omega_{\text{RBM}}$ is a monotonic function of the tube diameter (d_t nm) and is modeled as being linear in the inverse diameter, with an offset c_2 which is known as the effect of the substrate. We assume that $c_1 = 223.5 \text{ cm}^{-1}$ and $c_2 = 12.5 \text{ cm}^{-1}$ which are experimentally derived parameters as obtained by Refs. [33,34]. Using Eqs. (5) and (4) for zigzag SWNTs ($\theta = 0^\circ$), we see that E_{gap} is smaller than $\hbar \omega_{\text{RBM}}$ when $d_t > 2 \text{ nm}$ (see Fig. 2(b)).

The presence (absence) of a curvature-induced mini-energy gap in "metallic" zigzag (armchair) SWNTs was confirmed experimentally by Ref. [35]. The chirality was measured experimentally for (9,0), (12,0), and (15,0) zigzag SWNTs by these authors. The observed energy gap can be fitted by $4A_0/d_t^2$ which has the same d_t dependence in Eq. (4). Note that the coefficient is given by $A_0 = 3\gamma_0 a_{cc}^2/16$, and $4A_0 \approx 40 \text{ meV nm}^2$ is smaller than the value of $c = 60 \text{ meV nm}^2$ in Eq. (4).³ This discrepancy may be

¹ In the ETB program, we numerically solve the energy eigenequation, $\hat{\mathcal{H}}|\Psi\rangle = E|\Psi\rangle$, in the basis of $|s(\mathbf{r})\rangle$ and $|p_i(\mathbf{r})\rangle$ for two carbon atoms (A and B). The basis orbitals for the A-atom are non-orthogonal to those for the B-atom due to the curvature effect, and the Hamiltonian and overlap matrices are 8×8 matrices. We assumed the on-site energies E(2p) = -4.882 eV and E(2s) = -13.573 eV. E(2s) = -6.7 eV is close to the value (-8.868 eV) shown in Ref. [2].

² Although the energy gap at the Fermi level has little to do with the overlap integral, we shall note that the overlap integrals $S_{pp\sigma}^{CC}$ and $S_{pp\pi}^{CC}$ are switched in Table I of Ref. [28].



Fig. 3. (a) In time-dependent second-order perturbation theory, we consider an intermediate state including only electron-hole pairs (the case of t < t'), and an intermediate state including two phonons and electron-hole pairs (the case of t > t'). The former process corresponds to $h_+(E^{eh})$, while the latter one corresponds to $h_-(E^{eh})$. (b) The energy correction to the phonon energy by an intermediate electron-hole pair, especially the sign of $\text{Re}(h_+(E^{eh}))$ (solid curve), that corresponds to frequency hardening or softening, depends on the energy of the intermediate state E^{eh} . The contribution to $\Pi(\omega, E_F)$ of a low energy electron-hole pair satisfying $0 \le E^{eh} \le E_{gap}$ is forbidden. $\text{Im}(h_+(E^{eh}))$ (dashed curve) is non-zero only when E^{eh} is very close to $\hbar\omega$, which shows that a phonon mode can resonantly decay into an electron-hole pair with the same energy.

attributed to (1) uniaxial and torsional strain which is unintentionally applied to a SWNT [36–38],⁴ or (2) renormalization of the value of *c* due to the el–ph interaction, or (3) a SWNT-substrate interaction effect. (1) and (2) are intrinsic to SWNTs, while (3) is extrinsic. Since there are various factors which can affect the energy gap, it is not easy to predict the precise value of the energy gap, although the curvature-induced gap has been examined within the framework of first principles calculations including the effect of structure optimization [39]. It is noted that the chirality dependence of $\cos 3\theta$ in Eq. (4) has not been tested experimentally so far, except for $\theta = 0$ (zigzag SWNTs) and $\theta = 30^{\circ}$ (armchair SWNTs). Study of a chiral SWNT is left for future experiments.

$$E_{\text{gap}} = \left\{\frac{c}{d_r^2} - a\right\} \cos 3\theta,\tag{6}$$

3. Effect of curvature on the phonon energy

In this section we formulate the self-energy of a phonon mode (Section 3.1), and explain qualitatively the effect of the curvature on the self-energy (Section 3.2). The relationship between our formulation and that of others is referred to in Section 3.3.

3.1. Phonon self-energy

A renormalized phonon energy is written as a sum of the unrenormalized energy, $\hbar \omega$, and the real part of the self-energy, $\Pi(\omega, E_F)$. The imaginary part of $\Pi(\omega, E_F)$ gives the spectrum width. Throughout this paper, we assume a constant value for $\hbar \omega$ for each phonon mode. The self-energy is given by time-dependent second-order perturbation theory as

$$\Pi(\omega, E_{\rm F}) = 2\sum_{\mathbf{k}} \left(\frac{|V_{\mathbf{k}}|^2}{\hbar \omega - E_{\mathbf{k}}^{\rm eh} + i\Gamma/2} - \frac{|V_{\mathbf{k}}|^2}{\hbar \omega + E_{\mathbf{k}}^{\rm eh} + i\Gamma/2} \right) \times (f_{\rm h} - f_{\rm e}), \quad (7)$$

where the pre-factor 2 comes from spin degeneracy, $f_{h,e} = (1 + \exp(\beta(E^{h,e} - E_F)))^{-1}$ is the Fermi distribution function, $E^{e}_{\mathbf{k}}$ ($E^{h}_{\mathbf{k}}$) is the energy of an electron (a hole) with momentum \mathbf{k} , and $E^{eh}_{\mathbf{k}} = E^{e}_{\mathbf{k}} - E^{h}_{\mathbf{k}} (\geq 0)$ is the energy of an electron-hole pair. $V_{\mathbf{k}}$ is the el-ph matrix element that a phonon with momentum $\mathbf{q} = 0$ changes into an electron-hole pair [see the left diagram of Fig. 3(a)] which will be derived in Section 4. Note that the momentum of an electron \mathbf{k} is the same as that of a hole due to momentum conservation, and therefore pair creation involves a vertical transition. In Eq. (7), the energy shift is given by the real part of the self-energy, $\text{Re}[\Pi(\omega, E_F)]$, and the decay width Γ is determined self-consistently by $\Gamma/2 = -\text{Im}[\Pi(\omega, E_F)]$.⁵ The decay width relates to the average life-time τ via $\tau = \hbar/\Gamma$. It is noted that we use T = 300 K although the self-energy is also a function of temperature [$\beta^{-1} = k_B T$ where k_B is Boltzmann's constant].

3.2. Phonon softening and hardening

By defining the denominators of Eq. (7) as $h_{\pm}(E^{\text{eh}}) \equiv \pm 1/(\hbar\omega \mp E^{\text{eh}} + i\Gamma/2)$, Eq. (7) may be rewritten as

$$\Pi(\omega, E_{\rm F}) = 2\sum_{\bf k} |V_{\bf k}|^2 [h_+(E_{\bf k}^{\rm eh}) + h_-(E_{\bf k}^{\rm eh})] \times (f_{\rm h} - f_{\rm e}).$$
(8)

When we assume that $|V_{\mathbf{k}}|^2$ does not depend on **k**, the E^{eh} dependence of $\text{Re}[\Pi(\omega, E^{\text{eh}})]$ is determined by those of $\text{Re}[h_+(E^{\text{eh}})]$ and $\operatorname{Re}[h_{-}(E^{\operatorname{eh}})]$. It should be noted that $\operatorname{Re}[h_{+}(E^{\operatorname{eh}})]$ (solid curve in Fig. 3(b)) has a positive (negative) value when $E^{\rm eh} < \hbar \omega$ $(E^{\rm eh} > \hbar \omega)$, and the lower (higher) energy electron-hole pair makes a positive (negative) contribution to $\text{Re}[\Pi(\omega, E_F)]$. Therefore, the sign of the contribution to $\text{Re}[\Pi(\omega, E_F)]$, i.e., frequency hardening or softening, depends on its electron-hole virtual state energy, E^{eh} . In contrast, $\text{Re}[h_{-}(E^{\text{eh}})]$ (dashed curve in Fig. 3(b)) always has a negative value, that is, it only contributes to a phonon softening. Note, however, that the contribution of $\text{Re}[h_{-}(E^{\text{eh}})]$ is small compared with $\operatorname{Re}[h_+(E^{\operatorname{eh}})]$ since $-1/\hbar\omega \leq \operatorname{Re}[h_-(E^{\operatorname{eh}})] < 0$. Physically speaking, the $h_{-}(E^{eh})$ term represents an intermediate state including two phonons and an electron-hole pair (see the right hand diagram in Fig. 3(a)), while the $h_+(E^{eh})$ term represents the intermediate state that includes only electron-hole pairs.⁶ Even though the contribution of $h_{-}(E^{\text{eh}})$ is relatively small, $h_{-}(E_{\text{eh}})$ is important to get a symmetric response of $\Pi(\omega, E_{\text{F}})$ relative to the

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³ Putting $\gamma_0 = 2.60 \text{ eV}$ and $a_{cc} = 0.142 \text{ nm}$ into the definition of A_0 , we get the result $4A_0 \approx 40 \text{ meV} \text{ nm}^2$.

 $^{^{\}rm 4}$ We expect that the curvature-induced gap follows (see Section 4.2 for the derivation)

when a uniaxial strain is applied to SWNTs. The value of *a* depends on the model used, but it is probably not dependent on d_t . Considering the fact that the observed energy gap scales as d_t^{-2} , the effect of strain is not so relevant.

⁵ The self-consistent calculation begins by putting $\Gamma/2 = \gamma_0$ into the righthand side of Eq. (7). By summing the right-hand side, we get a new $\Gamma/2$ via $\Gamma/2 = -\text{Im}[\Pi(\omega, E_F)]$ and we then put the new $\Gamma/2$ into the right-hand side again, iteratively. This calculation is repeated until $\Pi(\omega, E_F)$ is converged.

⁶ In fact, we have $h_{-}(E^{\text{eh}}) = h_{+}(2(\hbar\omega + i\Gamma/2) + E^{\text{eh}}).$

Fermi energy. In fact, due to the $h_{-}(E^{\text{eh}})$ term, the electron–hole pair at the Dirac point $(E^{\text{eh}}=0)$ cannot contribute to the self-energy, since $\text{Re}[h_{+}(E^{\text{eh}})+h_{-}(E^{\text{eh}})]=0$ when $E^{\text{eh}}=0$. For high energy electron–hole pairs, the $h_{\pm}(E^{\text{eh}})$ terms contribute equally since $\text{Re}[h_{+}(E^{\text{eh}})] \approx \text{Re}[h_{-}(E^{\text{eh}})] \approx -1/E^{\text{eh}}$.

The curvature-induced energy gap, E_{gap} , affects the frequency shift since an electron-hole pair creation event is possible only when $E^{\rm eh} \ge E_{\rm gap}$. When $0 < E_{\rm gap} \le \hbar \omega$, the contribution to frequency hardening in Eq. (7) is suppressed. When $E_{gap} > \hbar \omega$, not only are all the positive contributions to the self-energy suppressed, but some negative contributions are also suppressed. Further, Im($h_+(E^{eh})$) is non-zero only when E^{eh} is very close to $\hbar \omega$, which shows that a phonon can resonantly decay into an electron–hole pair with the same energy. Thus, when $E_{gap} > \hbar \omega$, we have $\Gamma \simeq 0$ because no resonant electron-hole pair excitation is allowed near $E = \hbar \omega$. It is therefore important to compare the values of E_{gap} and $\hbar \omega$ for each (n,m) SWNT. For the LO and TO modes, $\hbar \omega$ is about 0.2[eV] and therefore we get $E_{gap} < \hbar \omega$ (see Fig. 2) for most of the SWNTs except for a SWNT with a small diameter.7 Thus, those LO and TO modes can resonantly decay into an electron-hole pair. The RBM mode in some SWNTs (for example, a (12,0) zigzag SWNT) cannot resonantly decay into an electron-hole pair, which results in a long life-time for the RBM in that particular SWNT [11].

At T=0, the Fermi distribution factor, namely f_h-f_e in Eq. (7), plays a very similar role as the curvature-induced gap, E_{gap} . In fact, all the excitations of electron-hole pairs with $E^{eh} \leq 2|E_F|$ are forbidden due to the Pauli exclusion principle. A difference between the energy gap and the Fermi energy arises at a finite temperature. Some electron-hole pairs with $E_{gap} \leq E^{eh} \leq 2|E_F|$ can contribute to the self-energy, while states $E^{eh} < E_{gap}$ do not exist even at a finite temperature. It should be noted that $V_{\mathbf{k}}$ in Eq. (7) depends on the value of E_{gap} since the position of the cutting line depends on E_{gap} , while $V_{\mathbf{k}}$ does not change by changing E_F . This is also a crucial difference between the roles of E_{gap} and E_F in the self-energy.

3.3. Other formulas

Here, we refer to the relationship between our formula and other formulas. First, replacing $\Gamma/2$ in Eq. (7) with a positive infinitesimal 0_+ gives the standard formula for the Fermi Golden rule. In this case, using $1/(x+i0_+) = P(1/x)-i\pi\delta(x)$ with P denoting the principal value of integration and $\delta(x)$ the Dirac deltafunction, $\Gamma/2$ can be calculated directly, i.e., without using the self-consistent way, by performing the summation (or integral) of the right-hand side of Eq. (7). We calculate $\Gamma/2$ self-consistently by taking care of the finite energy level spacing originating from a finite length of a nanotube where $E_{\mathbf{k}}^{\text{eh}}$ now takes a discrete value, and is not a continuous variable. Roughly speaking, the broadening is suppressed when the energy level spacing, $\Delta E = 2\pi\hbar v_F/L$, exceeds Γ . For example, the critical length where the broadening becomes negligible for a (10,10) SWNT is about 700 nm.

Second, the summation index $\sum_{\mathbf{k}}$ in Eq. (7) is not restricted to only inter-band ($E^{eh} \neq 0$) processes but includes also intra-band ($E^{eh} = 0$) processes.⁸ Then, the self-energy can be decomposed into two parts, as $\Pi(\omega, E_F) = \Pi^{inter}(\omega, E_F) + \Pi^{intra}(\omega, E_F)$ where $\Pi^{inter}(\omega, E_F)$ includes only inter-band processes satisfying $E^{eh} \neq 0$. In the adiabatic limit, i.e., when $\omega = 0$ and $\Gamma = 0$ in Eq. (7), it is straightforward to get the following relations, for a single Dirac

cone at T=0:

$$\Pi^{\text{intra}}(0, E_{\text{F}}) = -2\sum_{\mathbf{k}} |V_{\mathbf{k}}|^{2} \begin{cases} f'(E_{\mathbf{k}}^{\text{e}}) & (E_{\text{F}} > 0) \\ f'(E_{\mathbf{k}}^{\text{h}}) & (E_{\text{F}} < 0) \end{cases} = -\frac{\alpha}{2} |E_{\text{F}}|,$$

$$\Pi^{\text{inter}}(0, E_{\text{F}}) = -4\sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^{2}}{E_{\mathbf{k}}^{\text{h}}} = -\frac{\alpha}{2} (E_{c} - |E_{\text{F}}|), \qquad (9)$$

where $\alpha \equiv S|v|^2/\pi(\hbar v_F)^2$, *S* is the area (volume) of the system, and E_c is some cut-off energy. Here, we have assumed that $V_{\mathbf{k}} = v \cos \Theta(\mathbf{k})$.⁹ Note that $\Pi^{intra}(0, E_F)$ does not vanish because $(f_h - f_e)/E_{\mathbf{k}}^{h} \neq 0$ in this limit, while in the non-adiabatic case, $\Pi^{intra}(\omega, E_F)$ vanishes since $(f_h - f_e)/\hbar \omega = 0$. It is only the interband process that contributes to the self-energy in the non-adiabatic case.¹⁰ In the non-adiabatic limit at T=0, it is a straightforward calculation to get

$$\operatorname{Re}[\Pi(\omega, E_{\rm F})] = -\frac{\alpha}{2} \left[E_{\rm c} - |E_{\rm F}| - \frac{\hbar\omega}{4} \ln \left| \frac{|E_{\rm F}| - \frac{\hbar\omega}{2}}{|E_{\rm F}| + \frac{\hbar\omega}{2}} \right| \right], \quad (E_{\rm c} \gg \hbar\omega), \tag{10}$$

where $E_{\mathbf{k}}^{\text{eh}} = 2\hbar v_F k$, $\sum_{\mathbf{k}} \rightarrow V/(2\pi)^2 \int_0^{k_c} k \, dk \int_0^{2\pi} d\Theta$, and $\int x/(x+a) \, dx = x-a \ln|x+a|$ have been used in Eq. (7) to get the right-hand side. The Fermi energy dependence is given by the last two terms for the case of a massless Dirac cone spectrum. The first term is linear with respect to E_F and the second term produces a singularity at $|E_F| = \hbar \omega/2$. This singularity is useful in identifying the actual Fermi energy of a graphene sample.

It is also interesting to consider the case of a massive Dirac cone spectrum, $E = \pm \sqrt{m^2 + (\hbar v_F k)^2}$, where the mass m is in unit of energy. In the non-adiabatic limit at T=0, we get

$$\operatorname{Re}[\Pi(\omega, E_{\mathrm{F}})] = -\frac{\alpha}{2} \left[E_{\mathrm{c}} - |E_{\mathrm{F}}| - \left\{ \frac{(\hbar\omega)^2 - (2m)^2}{4\hbar\omega} \right\} \ln \left| \frac{|E_{\mathrm{F}}| - \frac{\hbar\omega}{2}}{|E_{\mathrm{F}}| + \frac{\hbar\omega}{2}} \right| \right], \quad (11)$$

where $E_c \gg \hbar \omega$ and $V_{\mathbf{k}} = v(\hbar v_F k/E) \cos\Theta(\mathbf{k})$ are assumed. Eq. (11) is for $|E_F| \ge m$. For $|E_F| < m$, the self-energy shift is given by replacing $|E_F|$ with m in Eq. (11). The logarithmic singularity for the last term disappears when $m = \hbar \omega/2$, and its overall sign is interchanged when $2m > \hbar \omega$. Broadening is possible only when $2m < \hbar \omega$, which may be useful for knowing whether the graphene sample has an energy gap or not.

4. The electron-phonon interaction

In this section we provide a framework to obtain the el-ph (electron-phonon) interaction in the effective-mass theory, and show how to calculate the el-ph matrix elements. The main results are Eqs. (22) and (47). Those who are not interested in the details of the derivation can skip this section.

4.1. Unperturbed Hamiltonian

The unperturbed Hamiltonian in the effective-mass model for π - electrons near the K point of a graphene sheet is given by

$$\mathcal{H}_{0}^{K} = \nu_{\mathrm{F}} \boldsymbol{\sigma} \cdot \hat{\mathbf{p}},\tag{12}$$

where $v_{\rm F}$ is the Fermi velocity, $\hat{\mathbf{p}} = -i\hbar\nabla$ is the momentum operator, and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y)$ is the Pauli matrix.¹¹ The *x*, *y*, and *z* coordinate system is taken as shown in Fig. 4. $\mathcal{H}_{\rm K}^{\rm K}$ is a 2 × 2 matrix

⁷ For very small diameter SWNTs, the energy gap disappears because of the lowering of the interlayer energy bonds.

⁸ It may be appropriate to denote an intra-band process by an *E*^{ee}=0 or *E*^{hh}=0 process.

⁹ $\Theta(\mathbf{k})$ is the angle between the vector \mathbf{k} and the k_x -axis [see Eq. (14)].

¹⁰ Ref. [17] showed that $\Pi(0,E_F)$ does not depend on E_F in the adiabatic limit due to the cancellation between $\Pi^{\text{intra}}(0,E_F)$ and $\Pi^{\text{inter}}(0,E_F)$. This shows that the adiabatic approximation is not appropriate for discussing the E_F dependence of the self-energy.

self-energy. ¹¹ We use the Pauli matrices of the form of $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$, and $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. The 2 × 2 identity matrix σ_0 is given by $\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$.



Fig. 4. A hexagonal unit cell of graphene consists of A (closed circle) and B (open circle) sublattices. **a**₁ and **a**₂ are lattice vectors. **R**_a(a=1,2,3) are vectors pointing to the nearest-neighbor B sites from an A site (**R**₁= $a_{cc}\mathbf{e}_{y}$, **R**₂ = $-(\sqrt{3}/2)a_{cc}\mathbf{e}_{x}-(1/2)a_{cc}\mathbf{e}_{y}$, and **R**₃ = $(\sqrt{3}/2)a_{cc}\mathbf{e}_{x}-(1/2)a_{cc}\mathbf{e}_{y})$ where $\mathbf{e}_{x}(\mathbf{e}_{y})$ is the dimensionless unit vector for the *x*-axis (*y*-axis). Local modulations of the hopping integral are defined by $\delta_{\gamma_{0}^{\alpha}}(\mathbf{r}_{i})$ (a=1, 2, 3) where \mathbf{r}_{i} is the position of an A-atom.

which operates on the two-component wavefunction:

$$\psi^{\mathrm{K}}(\mathbf{r}) = \begin{pmatrix} \psi^{\mathrm{K}}_{\mathrm{A}}(\mathbf{r}) \\ \psi^{\mathrm{K}}_{\mathrm{B}}(\mathbf{r}) \end{pmatrix},\tag{13}$$

where $\psi_A^K(\mathbf{r})$ and $\psi_B^K(\mathbf{r})$ are the wavefunctions of π -electrons for the sublattices A and B, respectively, around the K point. The energy eigenvalue of Eq. (12) is given by $\pm v_F |\mathbf{p}|$ and the energy dispersion relation shows a linear dependence at the Fermi point, which forms what is known as the Dirac cone.

The energy eigenstate with wave vector **k** in the conduction energy band is written by a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ with the Bloch function $\psi_{c,\mathbf{k}}^{K}$ as $\psi_{c,\mathbf{k}}^{K}(\mathbf{r}) = Ne^{i\mathbf{k}\cdot\mathbf{r}}\psi_{c,\mathbf{k}}^{K}$ where *N* is a normalization constant satisfying $N^{2}S = 1$, *S* is the area (volume) of the system, and

$$\psi_{\mathbf{c},\mathbf{k}}^{\mathrm{K}} \equiv \frac{1}{\sqrt{2}} \begin{pmatrix} 1\\ e^{i\Theta(\mathbf{k})} \end{pmatrix}.$$
 (14)

Here **k** is measured from the K point, and $\Theta(\mathbf{k})$ is defined by an angle of $\mathbf{k} = (k_x, k_y)$ measured from the k_x -axis as $(k_x, k_y) \equiv |\mathbf{k}| (\cos\Theta(\mathbf{k}), \sin\Theta(\mathbf{k}))$. The eigenvalue of this state is $E = +v_F |\mathbf{p}|$. The energy eigenstate with the energy eigenvalue $E = -v_F |\mathbf{p}|$ in the valence energy band is written by

$$\psi_{\nu,\mathbf{k}}^{\mathbf{K}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{2S}} \begin{pmatrix} 1\\ -e^{+i\Theta(\mathbf{k})} \end{pmatrix}.$$
(15)

The energy eigenstate for the valence band, $\psi_{v,\mathbf{k}}^{\mathsf{K}}(\mathbf{r})$ is given by $\sigma_z \psi_{c,\mathbf{k}}^{\mathsf{K}}(\mathbf{r})$. This results from the particle–hole symmetry of the Hamiltonian: $\sigma_z \mathcal{H}_0^{\mathsf{K}} \sigma_z = -\mathcal{H}_0^{\mathsf{K}}$.

The unperturbed Hamiltonian near the K' point is given by

$$\mathcal{H}_{0}^{\mathrm{K}'} = \nu_{\mathrm{F}} \boldsymbol{\sigma}' \cdot \hat{\mathbf{p}},\tag{16}$$

where $\sigma' = (-\sigma_x, \sigma_y)$. The dynamics of π -electrons near the K' point relates to the electrons near the K point by time-reversal symmetry, $\psi^K \rightarrow (\psi^K)^*$ [40]. Because lattice vibrations do not break time-reversal symmetry, we mainly consider electrons near the K point in this paper.

4.2. Deformation-induced gauge field

Lattice deformation modifies the nearest-neighbor hopping integral locally as $-\gamma_0 \rightarrow -\gamma_0 + \delta \gamma_{0,a}(\mathbf{r}_i)$ (*a*=1,2,3) (see Fig. 4). The corresponding perturbation of the lattice deformation is

given by

$$\mathcal{H}_{1} \equiv \sum_{i \in A} \sum_{a = 1,2,3} \delta \gamma_{0,a}(\mathbf{r}_{i}) [(c_{i+a}^{B})^{\dagger} c_{i}^{A} + (c_{i}^{A})^{\dagger} c_{i+a}^{B}],$$
(17)

where c_i^A is the annihilation operator of a π electron of an A-atom at position \mathbf{r}_i , and $(c_{i+a}^B)^{\dagger}$ is a creation operator at position \mathbf{r}_{i+a} ($=\mathbf{r}_i+\mathbf{R}_a$) of a B-atom where $\mathbf{R}_a(a=1,2,3)$ are vectors pointing to the three nearest-neighbor B sites from an A site.

The perturbation of Eq. (17) gives rise to scattering within a region near the K point (intra-valley scattering) whose interaction is given by a deformation-induced gauge field $\mathbf{A}^{q}(\mathbf{r}) = (A_{x}^{q}(\mathbf{r}), A_{y}^{q}(\mathbf{r}))$ in Eq. (12) as

$$\mathcal{H}_{0}^{K} + \mathcal{H}_{1}^{K} = \nu_{F} \boldsymbol{\sigma} \cdot [\hat{\boldsymbol{p}} + \boldsymbol{A}^{q}(\boldsymbol{r})], \qquad (18)$$

where **A**^q(**r**) is defined from $\delta \gamma_{0,a}(\mathbf{r})$ (*a*=1,2,3) as [41–43]

$$v_{F}A_{x}^{q}(\mathbf{r}) = \delta\gamma_{0,1}(\mathbf{r}) - \frac{1}{2}[\delta\gamma_{0,2}(\mathbf{r}) + \delta\gamma_{0,3}(\mathbf{r})],$$

$$v_{F}A_{y}^{q}(\mathbf{r}) = \frac{\sqrt{3}}{2}[\delta\gamma_{0,2}(\mathbf{r}) - \delta\gamma_{0,3}(\mathbf{r})].$$
(19)

When $\delta \gamma_{0,2} = \delta \gamma_{0,3} = 0$, then $\mathbf{A}^{q}(\mathbf{r}) = (A_{x}(\mathbf{r}), 0)$ and $\mathbf{A}^{q}(\mathbf{r}) \cdot \mathbf{R}_{1} = 0$. Similarly, when $\delta \gamma_{0,1} = \delta \gamma_{0,3} = 0$, we have $\mathbf{A}^{q}(\mathbf{r}) \cdot \mathbf{R}_{2} = 0$. Generally, the direction of $\mathbf{A}^{q}(\mathbf{r})$ is pointing perpendicular to the bond whose hopping integral is changed from γ_{0} . For the K' point, we obtain

$$\mathcal{H}_{0}^{K'} + \mathcal{H}_{1}^{K'} = \nu_{\mathrm{F}} \boldsymbol{\sigma}' \cdot [\hat{\mathbf{p}} - \mathbf{A}^{\mathrm{q}}(\mathbf{r})].$$
(20)

Even though the $\mathbf{A}^{q}(\mathbf{r})$ appears as a gauge field, it does not break time-reversal symmetry because the sign in front of $\mathbf{A}^{q}(\mathbf{r})$ is opposite to each other for the K and K' points. This is in contrast with the fact that $\mathbf{A}(\mathbf{r})$ (vector potential) violates time-reversal symmetry because the signs in front of $\mathbf{A}(\mathbf{r})$ are the same for the K and K' points since $\hat{\mathbf{p}} \rightarrow \hat{\mathbf{p}} - e\mathbf{A}(\mathbf{r})$ in the presence of a magnetic field.

The gauge field description for the lattice deformation (Eq. (19)) is useful to show the appearance of the curvatureinduced mini-energy gap in metallic carbon nanotubes. For a zigzag nanotube, we have $\delta\gamma_{0,1} = 0$ and $\delta\gamma_{0,2} = \delta\gamma_{0,3} \neq 0$ from the rotational symmetry around the tube axis (see Fig. 4). Then, Eq. (19) shows that for $A_x^q \neq 0$ and $A_y^q = 0$, the cutting line of $k_x=0$ for the metallic zigzag nanotube is shifted by a finite constant value of A_x^q because of the Aharanov–Bohm effect for the lattice distortion–induced gauge field \mathbf{A}^q . For an armchair nanotube, we have $\delta\gamma_{0,1} \neq 0$ and $\delta\gamma_{0,2} = \delta\gamma_{0,3}$. Then, Eq. (19) shows that for $A_x^q \neq 0$ and $\delta\gamma_{0,2} = \delta\gamma_{0,3}$. Then, Eq. (19) shows that for $A_x^q \neq 0$ and $\delta\gamma_{0,2} = \delta\gamma_{0,3}$. Then, Eq. (19) shows that for $p_x = 0$ for the armchair nanotube is not shifted by a vanishing A_y^q . This explains the presence (absence) of the curvature–induced mini–energy gap in metallic zigzag (armchair) carbon nanotubes [32].

The gauge field description is also useful to discuss the effect of a uniaxial strain on the gap. Let us consider applying a strain along the axis of a zigzag SWNT. Then, due to the symmetry, we have $\delta\gamma_{0,1} = a$ and $\delta\gamma_{0,2} = \delta\gamma_{0,3} = a/2$ where *a* is a constant. Putting these perturbations into Eq. (19) we see that $v_F A_x^q = a/2$, which means that the curvature-induced gap in a zigzag nanotube can change a little by the strain along the axis. For an armchair SWNT, instead, we have $\delta\gamma_{0,1} = 0$ and $\delta\gamma_{0,2} = \delta\gamma_{0,3} = b$, which results in $v_F A_y^q = 0$. This shows that the absence of the gap in armchair SWNT is robust against a strain applied along the nanotube axis.

4.3. Deformation-induced gauge fields for LO and TO modes

Here, we derive $\mathbf{A}^{q}(\mathbf{r})$ for the LO and TO modes. Let $\mathbf{u}(\mathbf{r})$ be the relative displacement vector of a B site from an A site $(\mathbf{u}(\mathbf{r})=\mathbf{u}_{B}(\mathbf{r})-\mathbf{u}_{A}(\mathbf{r}))$ and let g be the el-ph coupling constant, then $\delta \gamma_{0,a}(\mathbf{r})$ for the LO and TO modes is given by

$$\delta \gamma_{0,a}(\mathbf{r}) = \frac{g}{\rho} \mathbf{u}(\mathbf{r}) \cdot \mathbf{R}_a, \tag{21}$$

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where \mathbf{R}_a denotes the nearest-neighbor vectors (Figs. 4 and 5(a)) and $g=6.4 \text{ eV}/\text{\AA}$ is the off-site el-ph matrix element [28]. We rewrite Eq. (19) as

$$v_{\mathrm{F}}(A_{\mathrm{x}}^{\mathrm{q}}(\mathbf{r}), A_{\mathrm{y}}^{\mathrm{q}}(\mathbf{r})) = g(u_{\mathrm{y}}(\mathbf{r}), -u_{\mathrm{x}}(\mathbf{r})), \qquad (22)$$

where $u_i(\mathbf{r}) \equiv \mathbf{u}(\mathbf{r}) \cdot \mathbf{e}_i$, (i=x,y), and $\mathbf{R}_1 - (\mathbf{R}_2 + \mathbf{R}_3)/2 = \ell \mathbf{e}_y$ and $\sqrt{3}/2(\mathbf{R}_2 - \mathbf{R}_3) = -\ell \mathbf{e}_x$ ($\ell \equiv 3a_{cc}/2$) have been used (see the caption of Fig. 4). Then, the el-ph interaction for an in-plane lattice distortion $\mathbf{u}(\mathbf{r})$ can be rewritten in terms of the vector product of $\boldsymbol{\sigma}$ and $\mathbf{u}(\mathbf{r})$ [18] as

$$\mathcal{H}_{G} \equiv v_{F} \boldsymbol{\sigma} \cdot \mathbf{A}^{q}(\mathbf{r}) = g(\boldsymbol{\sigma} \times \mathbf{u}(\mathbf{r})) \cdot \mathbf{e}_{z}.$$
(23)

The gauge field description for the el-ph interaction of the LO and TO modes (Eq. (22)) is useful to show the absence of the el-ph interaction for the TO mode with a finite wavevector, as shown below. The TO phonon mode with $\mathbf{q} \neq 0$ does not change the area of the hexagonal lattice but instead gives rise to a shear deformation. Thus, the TO mode ($\mathbf{u}_{TO}(\mathbf{r})$) satisfies

$$\nabla \cdot \mathbf{u}_{\text{TO}}(\mathbf{r}) = \mathbf{0}, \quad \nabla \times \mathbf{u}_{\text{TO}}(\mathbf{r}) \neq \mathbf{0}. \tag{24}$$

Using Eqs. (22) and (24), we see that the TO mode does not yield a deformation-induced magnetic field,

$$\mathbf{B}^{\mathbf{q}}(\mathbf{r}) \equiv \nabla \times \mathbf{A}^{\mathbf{q}}(\mathbf{r}),\tag{25}$$

but the divergence of $\mathbf{A}^{q}(\mathbf{r})$ instead does not vanish because

$$B_{z}^{q}(\mathbf{r}) = -\frac{g}{v_{F}} \nabla \cdot \mathbf{u}_{TO}(\mathbf{r}) = 0,$$

and
$$\nabla \cdot \mathbf{A}^{q}(\mathbf{r}) = \frac{g}{v_{F}} (\nabla \times \mathbf{u}_{TO}(\mathbf{r})) \cdot \mathbf{e}_{z} \neq 0.$$
 (26)

Thus, we can define a scalar function $\varphi(\mathbf{r})$ which satisfies $\mathbf{A}^{q}(\mathbf{r}) = \nabla \varphi(\mathbf{r})$. Since we can set $\mathbf{A}^{q}(\mathbf{r}) = 0$ in Eq. (18) by selecting the gauge as $\psi^{K}(\mathbf{r}) \rightarrow \exp(-i\varphi(\mathbf{r})/\hbar)\psi^{K}(\mathbf{r})$ [41] and thus the $\mathbf{A}^{q}(\mathbf{r})$ in Eq. (18) disappears for the TO mode with $\mathbf{q} \neq 0$. This explains why the TO mode with $\mathbf{q} \neq 0$ is completely decoupled from the electrons, and that only the TO mode with $\mathbf{q} = 0$ couples with electrons. This conclusion is valid even when the graphene sheet has a static surface deformation. In this sense, the TO phonon mode at the Γ - point is anomalous since the el-ph interaction for the TO mode cannot be eliminated by a phase of the wavefunction. In contrast, the LO phonon mode with $\mathbf{q} \neq 0$ changes the area of the hexagonal lattice while it does not give rise to a shear deformation. Thus, the LO mode $(\mathbf{u}_{LO}(\mathbf{r}))$ satisfies

$$\nabla \cdot \mathbf{u}_{LO}(\mathbf{r}) \neq 0, \quad \nabla \times \mathbf{u}_{LO}(\mathbf{r}) = 0.$$
 (27)

Using Eqs. (22) and (27), we see that the LO mode gives rise to a deformation-induced magnetic field since

$$B_z(\mathbf{r}) \neq 0, \quad \nabla \cdot \mathbf{A}(\mathbf{r}) = 0.$$
 (28)

Since a magnetic field changes the energy band structure of electrons, the LO mode can couple strongly to the electrons even for $\mathbf{q} \neq 0$.

4.4. Deformation-induced gauge field for the RBM

Next, we derive the deformation-induced gauge field $\mathbf{A}^{q}(\mathbf{r})$ for the RBM. When the RBM displacement vector of a carbon atom at \mathbf{r} is $\mathbf{s}(\mathbf{r})=(s_{x}(\mathbf{r}),s_{y}(\mathbf{r}),s_{z}(\mathbf{r}))$, the perturbation to the nearest-neighbor hopping integral is given by

$$\delta \gamma_{0,a}(\mathbf{r}) = \frac{g}{\ell} \mathbf{R}_a \cdot \{ \mathbf{s}(\mathbf{r} + \mathbf{R}_a) - \mathbf{s}(\mathbf{r}) \}.$$
⁽²⁹⁾



Fig. 5. (a) The hexagonal lattice deformed by a phonon displacement vector. Let $\mathbf{u}_{A}(\mathbf{r}) (\mathbf{u}_{B}(\mathbf{r}))$ is a displacement vector of an A (B) site, then the modulation given by optical phonon modes is $\delta \gamma_{0,a} = (g/\ell)\mathbf{u}(\mathbf{r}) \cdot \mathbf{R}_{a}$ where $\mathbf{u}(\mathbf{r}) (=\mathbf{u}_{A}(\mathbf{r}) - \mathbf{u}_{B}(\mathbf{r}))$ denotes a relative displacement vector of a B site relative to the nearest A site. (b) The cross section of a nanotube. The displacement vector for the RBM, $\mathbf{s}(x)$, is decomposed in terms of the normal $s_{z}(x)$ and tangential $s_{x}(x)$ components. The derivative of the normal unit vector $\mathbf{e}_{z}(x)$ with respect to x gives a component along $\mathbf{e}_{x}(x)$, which modifies the net displacement along the x direction.

By expanding $\mathbf{s}(\mathbf{r}+\mathbf{R}_a)$ in a Taylor's series around the displacement $\mathbf{s}(\mathbf{r})$ as $\mathbf{s}(\mathbf{r}+\mathbf{R}_a) = \mathbf{s}(\mathbf{r}) + (\mathbf{R}_a \cdot \nabla)\mathbf{s}(\mathbf{r}) + \cdots$, we approximate Eq. (29) as

$$\delta \gamma_{0,a}(\mathbf{r}) \simeq \frac{g}{\ell} \mathbf{R}_a \cdot \left\{ (\mathbf{R}_a \cdot \nabla) \mathbf{s}(\mathbf{r}) \right\}.$$
(30)

Putting $\mathbf{R}_1 = a_{cc} \mathbf{e}_y$, $\mathbf{R}_2 = -(\sqrt{3}/2)a_{cc} \mathbf{e}_x - (1/2)a_{cc} \mathbf{e}_y$, and $\mathbf{R}_3 = (\sqrt{3}/2)a_{cc} \mathbf{e}_x - (1/2)a_{cc} \mathbf{e}_y$, into the right-hand side of Eq. (30), we obtain the corresponding deformation-induced gauge field of Eq. (19) as

$$\nu_{\rm F} A_{\rm x}^{\rm q}(\mathbf{r}) = \frac{g a_{\rm cc}}{2} \left[-\frac{\partial s_{\rm x}(\mathbf{r})}{\partial x} + \frac{\partial s_{\rm y}(\mathbf{r})}{\partial y} \right],$$
$$\nu_{\rm F} A_{\rm y}^{\rm q}(\mathbf{r}) = \frac{g a_{\rm cc}}{2} \left[\frac{\partial s_{\rm x}(\mathbf{r})}{\partial y} + \frac{\partial s_{\rm y}(\mathbf{r})}{\partial x} \right]. \tag{31}$$

Further, the displacements of carbon atoms give an on-site deformation potential in which the diagonal Hamiltonian matrix elements are modified by the el-ph interaction [44,45]

$$\mathcal{H}_{\rm on} = g_{\rm on} \sigma_0 \left[\frac{\partial s_{\rm X}(\mathbf{r})}{\partial x} + \frac{\partial s_{\rm y}(\mathbf{r})}{\partial y} \right]. \tag{32}$$

Here, $\partial s_x(\mathbf{r})/\partial x + \partial s_y(\mathbf{r})/\partial y$ (= $\nabla \cdot \mathbf{S}(\mathbf{r})$) represents the change of the area of a graphene sheet [46]. According to the density functional calculation by Ref. [28], we adopt the on-site coupling constant $g_{on} = 17$ [eV].

Since Eqs. (31) and (32) are proportional to the derivatives of $s_x(\mathbf{r})$ and $s_y(\mathbf{r})$, that is, they are proportional to \mathbf{q} , where \mathbf{q} is the phonon wave vector, then the el–ph matrix element for the inplane longitudinal/transverse acoustic (LA/TA) phonon modes vanishes at the Γ point. Namely, $\mathbf{A}^q(\mathbf{r})=0$ and $\mathcal{H}_{on}=0$ in the limit of $\mathbf{q}=0$. Among the TA phonon modes, there is an out-of-plane TA (oTA) phonon mode. The oTA mode thus shifts carbon atoms on the flat 2D graphene sheet in the *z*-direction [see Figs. 4 and 5(b)]. The oTA mode of graphene corresponds to the RBM of a nanotube even though the RBM is not an acoustic phonon mode [12]. In the following, we will show that the el–ph interaction for the RBM is enhanced due to the curvature of the nanotube as compared with the oTA mode of graphene since the RBM is a bond-stretching mode due to the cylindrical structure of SWNTs.

The displacements of the RBM modify the radius of a nanotube as $r \rightarrow r + s_z(\mathbf{r})$ (see Fig. 5(b)). A change of the radius gives rise to two effects to the electronic state. One effect is a shift of the quantized transverse wave vector around the tube axis. The distance between two wave vectors around the tube axis depends on the inverse of the radius due to the periodic boundary condition, and a change of the radius results in a shift of the wavevector. The other effect is that the RBM can change the area on the surface of the nanotube even at the Γ point. This results in an enhancement of the on-site el-ph interaction. These two effects are relevant to the fact that the normal vector on the



Fig. 6. Dependence of LO and TO phonons on the cutting line. (a) A cutting line near the K-point. The k_1 (k_2) axis is selected as the nanotube circumferential (axis) direction. The amplitude for an electron–hole pair creation depends strongly on the relative position of the cutting line from the K-point. (b) If the cutting line crosses the K-point, then the angle $\theta(\mathbf{k})$ ($\equiv \arctan(k_2/k_1)$) takes $\pi/2$ ($-\pi/2$) values for $k_2 > 0$ ($k_2 < 0$). In this case, the LO mode strongly couples to an electron–hole pair, while the TO mode is decoupled from the electron–hole pair according to Eq. (43).

surface of a nanotube is pointing in a different direction depending on the atom position. To show this, we take a (zigzag) nanotube as shown in Fig. 5(b). Let us denote the displacement vectors of the two carbon atoms at x and x+dx as $\mathbf{s}(x)$ and $\mathbf{s}(x+dx)$, then an effective length for the displacement along the x axis between the nearest two atoms is given by

$$D_x = \mathbf{e}_x(x+dx) \cdot [\mathbf{s}(x+dx) - \mathbf{s}(x)]. \tag{33}$$

By decomposing $\mathbf{s}(x)$ in terms of a normal and a tangential unit vector as $\mathbf{s}(x) = s_z(x)\mathbf{e}_z(x) + s_x(x)\mathbf{e}_x(x)$ (see Fig. 4(b)), we see that Eq. (33) becomes

$$D_x = s_x(x+dx) + s_z(x+dx)\mathbf{e}_x(x+dx) \cdot \mathbf{e}_z(x+dx) - s_x(x)\mathbf{e}_x(x+dx)$$

$$\cdot \mathbf{e}_{x}(x) - s_{z}(x)\mathbf{e}_{x}(x+dx) \cdot \mathbf{e}_{z}(x) = dx \left\{ \frac{\partial s_{x}(x)}{\partial x} + \frac{s_{z}(x)}{r} \right\} + \cdots,$$
(34)

where we have used the following equations:

$$\mathbf{e}_{z}(x+dx) = \mathbf{e}_{z}(x) + \frac{dx}{r} \mathbf{e}_{x}(x) + \cdots,$$
$$\mathbf{e}_{x}(x+dx) = \mathbf{e}_{x}(x) + \frac{dx}{r} \mathbf{e}_{z}(x) + \cdots.$$
(35)

Eq. (34) shows that the net displacement along the *x* axis is modified by the curvature of the nanotube as $\partial_x s_x(\mathbf{r}) \rightarrow \partial_x s_x(\mathbf{r}) + s_z(\mathbf{r})/r$. The correction is negligible for a graphene sheet $(r \rightarrow \infty)$, but appears as an enhancement factor to the el-ph interaction in SWNTs.

The el-ph interaction for the RBM is included by replacing $\partial_x s_x(\mathbf{r})$ with $\partial_x s_x(\mathbf{r}) + s_z(\mathbf{r})/r$ in Eqs. (31) and (32). Furthermore, in Eq. (31), we have an additional deformation-induced gauge field,

$$v_{\rm F} A_{\rm X}^{\rm q}(\mathbf{r}) = -\frac{g a_{\rm cc}}{2} \frac{s_z(\mathbf{r})}{r}$$
(36)

for the RBM mode which gives rise to a shift of the wavevector around the tube axis even at $\mathbf{q}=0$. In Eq. (32), it is shown that the RBM produces an additional on-site deformation potential of $g_{on}\sigma_0(s_z(\mathbf{r})/r)$. Finally, we obtain the el-ph interaction for the Γ point ($\mathbf{q}=0$: $\mathbf{s}(\mathbf{r})$ is a constant) RBM, as

$$\mathcal{H}_{\text{RBM}} = -\frac{ga_{\text{cc}}s_z}{2}\sigma_x + g_{\text{on}}\frac{s_z}{r}\sigma_0 = \frac{2s_z}{d_t} \begin{pmatrix} g_{\text{on}} & -\frac{ga_{\text{cc}}}{2} \\ -\frac{ga_{\text{cc}}}{2} & g_{\text{on}} \end{pmatrix}.$$
 (37)

This representation is for zigzag SWNTs. For a general (n,m) SWNT with a chiral angle θ , the el-ph interaction for the



Fig. 7. The el-ph matrix element for the electron-hole pair creation process relates to the pseudospin of the electronic state.

RBM becomes

$$\mathcal{H}_{\text{RBM}}(\theta) = \frac{2s_z}{d_t} \begin{pmatrix} g_{\text{on}} & -\frac{ga_{\text{cc}}}{2}e^{+i3\theta} \\ -\frac{ga_{\text{cc}}}{2}e^{-i3\theta} & g_{\text{on}} \end{pmatrix}.$$
 (38)

See Ref. [11] for more details.

5. Kohn anomaly effect

Here we consider the el-ph matrix element as a function of the electron wavevector **k** for the LO and TO phonon modes and the RBM with $\mathbf{q}=\mathbf{0}$ (i.e., Γ point). The displacement vector with $\mathbf{q}=\mathbf{0}$ is expressed by a position independent $\mathbf{u}=(u_x,u_y)$, by which an electron-hole pair is excited. The el-ph interaction with $\mathbf{q}=\mathbf{0}$ is relevant to phonon-softening phenomena for all three kinds of modes.

5.1. Matrix element for electron-hole pair creation

Let us first consider the case of a zigzag SWNT. In Fig. 4, we denote y (x) as a coordinate along (around) the axis of a zigzag SWNT, and u_y (u_x) are assigned to the LO (TO) phonon mode.¹² Thus, from Eq. (22), we have

$$v_{\rm F} \mathbf{A}_{\rm LO}^{\rm q} = g(u_y, 0),$$

 $v_{\rm F} \mathbf{A}_{\rm TO}^{\rm q} = g(0, -u_x).$ (39)

The direction of the gauge field $\mathbf{A}^{q}(\mathbf{r})$ is perpendicular to the phonon eigenvector \mathbf{u} and the LO mode shifts the wavevector around the tube axis, which explains how the LO mode may induce a dynamical energy band-gap in metallic nanotubes [24]. Putting Eq. (39) into Eq. (23), we get

$$\mathcal{H}_{\rm LO}^{\rm zig} = v_{\rm F} \mathbf{A}_{\rm LO}^{\rm q} \cdot \boldsymbol{\sigma} = g u_y \sigma_x,$$

$$\mathcal{H}_{\rm TO}^{\rm zig} = v_{\rm F} \mathbf{A}_{\rm TO}^{\rm q} \cdot \boldsymbol{\sigma} = -g u_x \sigma_y.$$
 (40)

The el-ph matrix element $V_{\mathbf{k}}$ for the electron-hole pair generation is given from Eqs. (14), (15) and (40), by ($\lambda = \text{LO},\text{TO}$)

$$\langle \mathbf{eh}(\mathbf{k}) | \mathcal{H}_{\lambda}^{\text{zig}} | \omega_{\lambda} \rangle \equiv \int (\psi_{c,\mathbf{k}}^{\text{K}}(\mathbf{r}))^{\dagger} \mathcal{H}_{\lambda}^{\text{zig}} \psi_{\nu,\mathbf{k}}^{\text{K}}(\mathbf{r}) d^{2}\mathbf{r}.$$
(41)

 $^{^{12}}$ In case of the \varGamma point phonon, the definitions of the LO and TO are not unique. It seems standard that the LO is taken as the mode parallel with respect to the tube axis and the TO mode is the one perpendicular to the tube axis.



Fig. 8. The E_F dependence of the LO (red curve) and TO (black curve) phonon energy in the case of the (10,10) armchair SWNT. The data are taken at room temperature. Only the energy of the LO mode is shifted, with the TO mode frequency being independent of E_F . The decay width (Γ) is plotted as an error-bar. The blue curve is given by the analytic result of Eq. (49). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

By calculating Eq. (41) for the LO mode with $(u_x, u_y) = (0, u)$ and for the TO mode with $(u_x, u_y) = (u, 0)$, we get

 $\langle eh(\mathbf{k}) | \mathcal{H}_{LO}^{zig} | \omega_{LO} \rangle = -igusin\Theta(\mathbf{k}),$

$$\langle \operatorname{eh}(\mathbf{k}) | \mathcal{H}_{\mathrm{TO}}^{\mathrm{Zig}} | \omega_{\mathrm{TO}} \rangle = -igu\cos\Theta(\mathbf{k}),$$
(42)

where $\Theta(\mathbf{k})$ is defined by an angle of $\mathbf{k} = (k_x, k_y)$ measured from the k_x axis.

Next, we consider the case of an armchair SWNT. In Fig. 4, x(y) is the coordinate along (around) the axis and $u_x(u_y)$ is assigned to the LO (TO) phonon mode. Then, for an armchair SWNT, we get

$$\langle \mathsf{eh}(\mathbf{k})|\mathcal{H}_{\mathsf{LO}}^{\mathsf{arm}}|\omega_{\mathsf{LO}}\rangle = -igusin\theta(\mathbf{k}),$$

$$\langle \mathsf{eh}(\mathbf{k}) | \mathcal{H}_{\mathsf{TO}}^{\mathrm{ann}} | \omega_{\mathsf{TO}} \rangle = -i gu \cos\theta(\mathbf{k}).$$
 (43)

Note that $\theta(\mathbf{k})$ for the armchair nanotube is given by rotating $\Theta(\mathbf{k})$ for the zigzag nanotube by $\pi/2$ ($\theta(\mathbf{k}) = \Theta(\mathbf{k}) + \pi/2$). It is useful to define the $k_1(k_2)$ axis pointing in the direction of a general SWNT circumferential (axis) direction (see Fig. 6), and $\theta(\mathbf{k})$ as the angle for the polar coordinate. Then,

 $\langle eh(\mathbf{k}) | \mathcal{H}_{LO} | \omega_{LO} \rangle = -igusin\theta(\mathbf{k}),$

$$\langle \mathsf{eh}(\mathbf{k}) | \mathcal{H}_{\mathsf{TO}} | \omega_{\mathsf{TO}} \rangle = -igu\cos\theta(\mathbf{k})$$
 (44)

is valid regardless of the tube chirality if the phonon eigenvector of the LO (TO) phonon mode is in the direction along (around) the tube axis. This is because $\hat{\mathbf{p}}$ and $\mathbf{u}(\mathbf{r})$ [and $\mathbf{A}^{q}(\mathbf{r})$] are transformed in the same way when we change the chiral angle [11]. As a result, there would be no chiral angle dependence for the el-ph matrix elements in Eq. (44). Note also that Eq. (44) shows that $\langle \text{eh}(\mathbf{k}) | \mathcal{H}_{\lambda} | \omega_{\lambda} \rangle$ depends only on $\theta(\mathbf{k})$ but not on $|\mathbf{k}|$, which means that the dependence of this matrix element on E^{eh} $(= 2\hbar v_{\text{F}} |\mathbf{k}|)$ is negligible [see Fig. 6(b)].

Where does the $\theta(\mathbf{k})$ dependence in Eq. (44) then come form? The expectation value of σ_x , σ_y , and σ_z with respect to $\psi_{c,\mathbf{k}}^{K}(\mathbf{r})$ defines the pseudospin. Using Eq. (14) with $\Theta(\mathbf{k}) \rightarrow \theta(\mathbf{k})$, we have the expectation values for the Pauli matrices $\langle \sigma_x \rangle = \langle \psi_{c,\mathbf{k}}^{K} | \sigma_x | \psi_{c,\mathbf{k}}^{K} \rangle = \cos\theta(\mathbf{k}), \quad \langle \sigma_x \rangle = \langle \psi_{c,\mathbf{k}}^{K} | \sigma_y | \psi_{c,\mathbf{k}}^{K} \rangle = \sin\theta(\mathbf{k}), \text{ and } \langle \sigma_x \rangle = \langle \psi_{c,\mathbf{k}}^{K} | \sigma_z | \psi_{c,\mathbf{k}}^{K} \rangle = 0$. Then the direction of the pseudospin of $\psi_{c,\mathbf{k}}^{K}(\mathbf{r})$ given by

$$\langle \langle \sigma_x \rangle, \langle \sigma_y \rangle, \langle \sigma_z \rangle \rangle = (\cos\theta(\mathbf{k}), \sin\theta(\mathbf{k}), 0)$$
(45)

is within (k_1,k_2) plane and parallel to **k** (see Fig. 7).¹³ Due to the particle-hole symmetry, $\psi_{v,\mathbf{k}}^{K}(\mathbf{r}) = \sigma_z \psi_{c,\mathbf{k}}^{K}(\mathbf{r})$, the el-ph matrix element for the electron-hole pair creation process can be related to the pseudospin. For example, we see that

$$\langle \mathbf{eh}(\mathbf{k}) | \mathcal{H}_{\mathrm{LO}}^{\mathrm{zig}} | \omega_{\mathrm{LO}} \rangle = g u_{y} \langle \psi_{c,\mathbf{k}}^{\mathrm{K}} | \sigma_{x} | \psi_{v,\mathbf{k}}^{\mathrm{K}} \rangle = g u \langle \psi_{c,\mathbf{k}}^{\mathrm{K}} | \sigma_{x} \sigma_{z} | \psi_{c,\mathbf{k}}^{\mathrm{K}} \rangle$$
$$= -ig u \langle \sigma_{y} \rangle = -ig u \sin \theta(\mathbf{k}). \tag{46}$$

The electron-hole pair creation for the LO mode is relevant to the pseudospin component which is parallel to the tube axis, $\langle \sigma_y \rangle$, while that for the TO mode is relevant to $\langle \sigma_x \rangle$.

For the RBM, from Eq. (38), the matrix element for an electronhole pair creation is chirality dependent as

$$\langle eh(\mathbf{k}) | \mathcal{H}_{RBM}(\theta) | \omega_{RBM} \rangle = iga_{cc} \frac{s_z}{d_t} \sin(\theta(\mathbf{k}) + 3\theta).$$
 (47)

Thus, the frequency shift of the RBM can have a chiral angle dependence. In particular, armchair SWNTs ($\theta = 30^{\circ}$) exhibit neither a frequency shift nor a broadening, regardless of their diameters because their el-ph matrix element becomes

$$\langle \mathbf{eh}(\mathbf{k}) | \mathcal{H}_{\mathsf{RBM}}^{\mathsf{arm}} | \omega_{\mathsf{RBM}} \rangle = i g a_{\mathsf{cc}} \frac{s_z}{d_t} \cos\theta(\mathbf{k}),$$
 (48)

which is zero for a cutting line for a metallic band: $\theta(\mathbf{k}) = \pm \pi/2$. This $\theta(\mathbf{k})$ dependence of Eq. (48) is the same as that of the TO phonon mode of Eq. (43), so that the absence of a frequency shift of the RBM in armchair SWNTs is similar to the absence of a frequency shift of the TO mode at the Γ point in armchair SWNTs [9].

5.2. Phonon frequency shift

Here we show the calculated results for the phonon frequency as a function of the Fermi energy.

5.2.1. Armchair SWNTs

First, we consider Eq. (44) for a *k*-point ($\mathbf{k} = (k_1, k_2)$) on the cutting line of an armchair SWNT. Since the armchair SWNT is free from the curvature effect, the cutting line for its metallic energy band satisfies $k_1 = 0$ and lies on the k_2 axis. Thus, we have $\theta(\mathbf{k}) = \pi/2$ ($-\pi/2$) for $k_2 > 0$ ($k_2 < 0$). Then, Eq. (44) tells us that only the LO mode can couple to an electron–hole pair and the TO mode does not couple to an electron–hole pair for the metallic energy band of an armchair SWNT. Similarly, Eq. (48) shows that the RBM of an armchair SWNT does not show any phonon softening.

In Fig. 8, we show the phonon energy as a function of $E_{\rm F}$ for a (10,10) armchair SWNT. Here we take 1620 and 1590 cm⁻¹ for $\hbar\omega$ of the LO and TO modes, respectively. The energy bars denote Γ values. The self-energy is calculated for T=300 K and L=10 µm. It is shown that the TO mode does not exhibit any energy change, while the LO mode shows both an energy shift and a broadening. As we have mentioned, the minimum energy is realized at $|E_{\rm F}| = \hbar\omega/2$ (≈ 0.1 eV). There is a local maximum for the spectral peak at $|E_{\rm F}| = 0$. The broadening for the LO mode has a tail at room temperature for $|E_{\rm F}| > \hbar\omega/2$.

In evaluating the LO mode's self-energy according to Eq. (7), we have assumed that the cutoff energy is $E_c=0.5$ eV. The presence of a cutoff energy is reasonable since the matrix element actually depends on the energy of the electron-hole pair (see Ref. [48]). An analytical expression for the E_c dependence of

 $^{^{13}}$ For the pseudospin of the electrons near the K' point, see Ref. [47].

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Fig. 9. (a) The E_F dependence of the LO (red curve) and TO (black curve) phonon energy in the case of the (12,0) zigzag SWNT. The data are taken at room temperature. Not only the frequency of the LO mode but also that of the TO mode is shifted due to the curvature effect. Here we take 1640 and 1590 cm⁻¹ for $\hbar\omega$ of the LO and TO modes, respectively. (b) The E_F dependence of the RBM energy $\hbar\omega$ in the case of the (12,0) zigzag SWNT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the self-energy is easy to obtain by using the effective-mass model, which can be derived from Eq. (7) at T=0 as

$$\operatorname{Re}[\Pi(\omega, E_{\rm F})] \approx -\frac{L}{\pi} \left(\frac{A_{\rm LO}^{\rm q}}{\hbar}\right)^2 \hbar v_{\rm F} \left[\ln \left| \frac{E_c - \frac{\hbar \omega}{2}}{|E_{\rm F}| - \frac{\hbar \omega}{2}} \right| + \ln \left| \frac{E_c + \frac{\hbar \omega}{2}}{|E_{\rm F}| + \frac{\hbar \omega}{2}} \right| \right].$$
(49)

The factor scales as $1/d_t$ because¹⁴

$$\frac{L}{\pi} \left(\frac{A_{\rm LO}^{\rm q}}{\hbar}\right)^2 \hbar v_{\rm F} \approx 4[{\rm meV}] \left(\frac{[{\rm nm}]}{d_t}\right). \tag{50}$$

For comparison, we plot $\hbar \omega + \text{Re}[\Pi(\omega, E_F)]$ vs E_F (Eq. (49)) as the blue curve in Fig. 8.

5.2.2. Zigzag SWNTs

Next we consider "metallic" zigzag SWNTs. When the curvature effect is taken into account, the cutting line does not lie on the K-point, but is shifted by k_1 from the k_2 axis. In this case, $\cos\theta(\mathbf{k}) = k_1/(k_1^2 + k_2^2)^{1/2}$ is non-zero for the lower energy intermediate electron-hole pair states. Thus, the TO mode can couple to the low energy electron-hole pair which makes a positive energy contribution to the phonon energy shift. The high energy electron-hole pair still decouples from the TO mode since $\cos\theta(\mathbf{k}) \rightarrow 0$ for $|k_2| \gg |k_1|$.

In Fig. 9(a), we show calculated results for the LO and TO modes as a function of $E_{\rm F}$ for a (12,0) zigzag SWNT. In the case of zigzag SWNTs, not only the LO mode but also the TO mode couples with electron–hole pairs. The spectrum peak position for the TO mode becomes harder (upshifted) for $E_{\rm F}=0$, since ${\rm Re}(h_+(E^{\rm eh}))$ for $E^{\rm eh} < \hbar \omega$ contributes to a positive frequency shift. The hardening of the TO mode is a signature of the curvature-induced mini-energy gap.

In Fig. 9(b), we show the result for the RBM. The matrix element of Eq. (47) with $\theta = 0^{\circ}$ is proportional to $\sin\theta(\mathbf{k})$. Thus, the high energy electron–hole pair can couple to the RBM and thus contribute to the softening of the RBM. Although the magnitude of the shift is smaller than that for the LO mode, the softening for the RBM can be observed experimentally [10].

5.2.3. Chiral SWNTs

Finally, we examine "metallic" chiral SWNTs. The same discussion for the "metallic" zigzag SWNTs can also be applied to "metallic" chiral SWNTs. However, there is a complication specific to chiral SWNTs, namely that the phonon eigenvector depends on the chiral angle. Reich et al. [49] reported that, for a

chiral nanotube, the atoms vibrate along the direction of the carbon-carbon bonds and not along the axis or the circumference. The phonon eigenvector of a chiral nanotube may be written as

$$\begin{pmatrix} u_{\rm TO} \\ u_{\rm LO} \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix},$$
(51)

where $u_1(u_2)$ is in the direction around (along) a chiral tube axis, and ϕ is the angle difference between the axis and the direction of the vibration. This modifies Eq. (43) as

$$\langle \mathsf{eh}(\mathbf{k})|\mathcal{H}_{\mathsf{LO}}|\omega_{\mathsf{LO}}\rangle = -igusin(\theta(\mathbf{k})+\phi),$$

$$\langle \operatorname{eh}(\mathbf{k}) | \mathcal{H}_{\mathrm{TO}} | \omega_{\mathrm{TO}} \rangle = -igu\cos(\theta(\mathbf{k}) + \phi).$$
 (52)

The identification of ϕ in Eq. (52) as a function of chirality would be useful to compare theoretical results and experiments, which will be explored in the future (see Ref. [50] for example).

5.2.4. Graphene

In the case of 2D graphene, Eq. (43) tells us that the Γ point TO and LO modes give the same energy shift because the integral over $\theta(\mathbf{k})$ gives the same self-energy in Eq. (7) for both the TO and LO modes. This explains why no G-band splitting is observed in a single layer of graphene [51]. Even when we consider that the TO and LO modes not exactly at the Γ point, we do not expect any splitting between the LO and TO phonon energies since the TO mode with $\mathbf{q} \neq 0$ is completely decoupled from the electrons [see Eq. (26)]. Thus, for $\mathbf{q} \neq 0$, only the LO mode contributes to the G band intensity. It is interesting to note that the Γ point LO and TO modes may exhibit anomalous behavior near the edge of graphene because the wave function is not given by a plane wave but rather by a standing wave. The pseudospin for the standing wave is different from that for a plane wave. Moreover, the standing wave near the zigzag edge is different from that near the armchair edge, which gives rise to a selection rule in their Raman spectra [47,48]. The standing wave behavior near the edges in graphene ribbons is beyond the scope of the present paper.

6. Discussion and summary

We have seen that the curvature-induced gap is absent for armchair SWNTs, so that here the LO mode exhibits a strong Kohn anomaly effect. Recently, however, it has been reported that even armchair SWNTs have an energy gap originating from a correlation effect [52]. The correlation-induced gap observed is approximately 80 meV for armchair SWNT with $d_t=2$ nm, and the gap increases with decreasing d_t . Since the presence of a gap suppresses the contribution to the hardening, a local maximum

¹⁴ Here we use a harmonic oscillator model which gives $u = \sqrt{\hbar/2M_cN_u\omega}$ where M_c is the mass of a carbon atom. Using $\hbar\omega = 0.2 \text{ eV}$, we get $\sqrt{N_u}|A_x^q/\hbar| \approx 2 \times 10^{-2} \text{\AA}^{-1}$.

(around $E_F=0$) in the LO frequency vs. E_F plot [see Fig. 8] may disappear, and $E_{\rm F}=0$ would become a global minimum if the correlation gap exceeds 200 meV. Confirming this behavior in a Raman spectroscopy study may provide further evidence for the correlation-induced gap.

Finally, we discuss our results in relation to the experimental results of the Kohn anomaly for the RBMs in metallic SWNTs [10]. The frequency shifts observed are approximately 2 cm^{-1} , which is smaller than the theoretical value for a (12,0) zigzag SWNT, 8 cm^{-1} , shown in Fig. 9(b). This discrepancy may be attributed to the choice of the off-site el-ph matrix element, g, although we have determined this value from a density functional calculation. Indeed, by decreasing the value of g from $g=6.4 \text{ eV}/\text{\AA}$ we find a better agreement with the experimental result, 3 cm^{-1} when g=4 eV/Å. Another possibility is that we have used a harmonic oscillator model for obtaining the magnitude of the displacement vector *u*. The actual value of *u* may be smaller than our estimation, which also gives a better agreement with the experimental result.

In summary, the el-ph interaction with respect to the LO, TO, and RBM features of the Raman spectra for SWNTs is derived in a unified way using the deformation-induced gauge field. Then, we have shown that the matrix element for electron-hole pair creation depends on the position of the cutting line. As a result, the TO mode in "metallic" SWNTs, except for armchair SWNTs, can couple to an electron-hole pair due to the curvature effect which shifts the cutting line away from the K point. In particular, only the low energy electron-hole pairs can couple to the TO mode and give rise to a hardening of the TO mode. The hardening of the TO mode is suppressed for large diameter SWNTs. This is reasonable since the TO mode as well as the LO mode exhibit a softening in the case of graphene samples.

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References

- [1] R. Saito, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, Appl. Phys. Lett. 60 (1992) 2204
- [2] R. Saito, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, Phys. Rev. B 46 (1992) 1804.
- [3] A. Jorio, R. Saito, J.H. Hafner, C.M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, M.S. Dresselhaus, Phys. Rev. Lett. 86 (2001) 1118.
- [4] A. Jorio, M.A. Pimenta, A.G.S. Filho, R. Saito, G. Dresselhaus, M.S. Dresselhaus, New J. Phys. 5 (2003) 139.
- [5] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, Phys. Rep. 409 (2005) 47.
- [6] N. Hamada, S.-i. Sawada, A. Oshiyama, Phys. Rev. Lett. 68 (10) (1992) 1579.

Rev. Lett. 99 (14) (2007) 145506.

J.W. Mintmire, B.I. Dunlap, C.T. White, Phys. Rev. Lett. 68 (5) (1992) 631 [8] H. Farhat, H. Son, G.G. Samsonidze, S. Reich, M.S. Dresselhaus, J. Kong, Phys.

- [9] K. Sasaki, R. Saito, G. Dresselhaus, M.S. Dresselhaus, H. Farhat, J. Kong, Phys. Rev. B 77 (24) (2008) 245441 [10] H. Farhat, K. Sasaki, M. Kalbac, M. Hofmann, R. Saito, M.S. Dresselhaus,
- J. Kong, Phys. Rev. Lett. 102 (12) (2009) 126804. [11] K. Sasaki, R. Saito, G. Dresselhaus, M.S. Dresselhaus, H. Farhat, J. Kong, Phys.
- Rev. B 78 (23) (2008) 235405. [12] R. Saito, G. Dresselhaus, M. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, London, 1998.
- [13] R. Saito, A. Gruneis, G.G. Samsonidze, V.W. Brar, G. Dresselhaus, M.S. Dresselhaus, A. Jorio, L.G. Cancado, C. Fantini, M.A. Pimenta, A.G.S. Filho,
- New J. Phys. 5 (2003) 157. [14] A. Jorio, A.G. Souza Filho, G. Dresselhaus, M.S. Dresselhaus, A.K. Swan, M.S. Ünlü, B.B. Goldberg, M.A. Pimenta, J.H. Hafner, C.M. Lieber, R. Saito, Phys. Rev. B 65 (15) (2002) 155412.
- [15] M.A. Pimenta, A. Marucci, S.A. Empedocles, M.G. Bawendi, E.B. Hanlon, A.M. Rao, P.C. Eklund, R.E. Smalley, G. Dresselhaus, M.S. Dresselhaus, Phys. Rev. B 58 (1998) R16016.
- [16] S. Piscanec, M. Lazzeri, F. Mauri, A.C. Ferrari, J. Robertson, Phys. Rev. Lett. 93 (2004) 185503
- [17] M. Lazzeri, F. Mauri, Phys. Rev. Lett. 97 (26) (2006) 266407.
- 18] K. Ishikawa, T. Ando, J. Phys. Soc. Japan 75 (2006) 084713.
- [19] V.N. Popov, P. Lambin, Phys. Rev. B 73 (8) (2006) 85407.
- [20] N. Caudal, A.M. Saitta, M. Lazzeri, F. Mauri, Phys. Rev. B 75 (11) (2007) 115423.
- [21] A. Das, A.K. Sood, A. Govindaraj, A.M. Saitta, M. Lazzeri, F. Mauri, C.N.R. Rao, Phys. Rev. Lett. 99 (13) (2007) 136803.
- [22] W. Kohn, Phys. Rev. Lett. 2 (9) (1959) 393.
- [23] P.C. Eklund, G. Dresselhaus, M.S. Dresselhaus, J.E. Fischer, Phys. Rev. B 16 (8) (1977) 3330.
- [24] O. Dubay, G. Kresse, H. Kuzmany, Phys. Rev. Lett. 88 (23) (2002) 235506.
- [25] O. Dubay, G. Kresse, Phys. Rev. B 67 (3) (2003) 035401.
- [26] K.T. Nguyen, A. Gaur, M. Shim, Phys. Rev. Lett. 98 (14) (2007) 145504.
- [27] T. Ando, J. Phys. Soc. Japan 77 (2008) 014707.
- [28] D. Porezag, T. Frauenheim, T. Köhler, G. Seifert, R. Kaschner, Phys. Rev. B 51 (19) (1995) 12947.
- [29] T. Ando, J. Phys. Soc. Japan 69 (2000) 1757.
- [30] G.G. Samsonidze, R. Saito, N. Kobayashi, A. Grüneis, J. Jiang, A. Jorio, S.G. Chou, G. Dresselhaus, M.S. Dresselhaus, Appl. Phys. Lett. 85 (2004) 5703.
- [31] V.N. Popov, New J. Phys. 6 (2004) 17.
- [32] C.L. Kane, E.J. Mele, Phys. Rev. Lett. 78 (10) (1997) 1932.
- [33] M. Strano, S. Doorn, E. Haroz, C. Kittrell, R. Hauge, R. Smalley, Nano Lett. 3 (8) (2003) 1091
- [34] S. Bachilo, M. Strano, C. Kittrell, R. Hauge, R. Smalley, R. Weisman, Science 298 (2002) 2361
- [35] M. Ouyang, J.-L. Huang, C.L. Cheung, C.M. Lieber, Science 292 (2001) 702.
- [36] L. Yang, M.P. Anantram, J. Han, J.P. Lu, Phys. Rev. B 60 (1999) 13874.
- [37] L. Yang, J. Han, Phys. Rev. Lett. 85 (2000) 154.
- [38] A. Kleiner, S. Eggert, Phys. Rev. B 63 (7) (2001) 73408.
 [39] T. Miyake, S. Saito, Phys. Rev. B 72 (7) (2005) 73404.
- [40] K. Sasaki, R. Saito, Prog. Theor. Phys. Suppl. 176 (2008) 253.
- [41] K. Sasaki, Y. Kawazoe, R. Saito, Prog. Theor. Phys. 113 (3) (2005) 463.
- [42] K. Sasaki, S. Murakami, R. Saito, J. Phys. Soc. Japan 75 (2006) 074713.
- [43] M. Katsnelson, A. Geim, Philos. Trans. Roy. Soc. A 366 (2008) 195.
- [44] J. Jiang, R. Saito, G.G. Samsonidze, S.G. Chou, A. Jorio, G. Dresselhaus, M.S. Dresselhaus, Phys. Rev. B 72 (2005) 235408.
- [45] R. Saito, H. Kamimura, J. Phys. Soc. Japan 52 (1983) 407.
- [46] H. Suzuura, T. Ando, Phys. Rev. B 65 (23) (2002) 235412.
- [47] K. Sasaki, R. Saito, K. Wakabayashi, T. Enoki, Identifying the orientation of edge of graphene using G band Raman spectra, J. Phys. Soc. Japan (2010), to appear [arXiv:0911.1593].
- [48] K. Sasaki, M. Yamamoto, S. Murakami, R. Saito, M. Dresselhaus, K. Takai, T. Mori, T. Enoki, K. Wakabayashi, Phys. Rev. B 80 (15) (2009) 155450.
- [49] S. Reich, C. Thomsen, P. Ordejón, Phys. Rev. B 64 (19) (2001) 195416.
- [50] J.S. Park, K. Sasaki, R. Saito, W. Izumida, M. Kalbac, H. Farhat, G. Dresselhaus, M.S. Dresselhaus, Phys. Rev. B 80 (2009) 81402.
- [51] J. Yan, Y. Zhang, P. Kim, A. Pinczuk, Phys. Rev. Lett. 98 (16) (2007) 166802. [52] V.V. Deshpande, B. Chandra, R. Caldwell, D.S. Novikov, J. Hone, M. Bockrath, Science 323 (5910) (2009) 106.