Low-energy electronic states and heat capacities in graphene strips

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We investigate low-energy electronic states and heat capacity of graphene strips. The density of states of graphene is obtained by diagonalizing a lattice Hamiltonian for graphene strips with zigzag and armchair edges, respectively. The modes localized at strip edges in zigzag geometry reveal a peculiar density of states near the zero-energy line. We find that the overall behavior of the heat capacity $C_v(T)$ in graphene is similar to that of a two-level system, and the low-temperature heat capacity shows unconventional behavior of $C_v \sim T^4$ with $\alpha=2.2$ varying slightly for different choices of various band structure parameters and the width of the strip. Unusual strong enhancement is observed in the heat capacity at low temperatures for zigzag strips, in addition to the $T^4$ behavior of the two-dimensional graphene. This enhancement stems from the states localized along the edges in the strips with zigzag terminations.

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I. INTRODUCTION

Recent experimental realizations of a monolayer graphene have attracted much attention to studies of the electronic properties of the interesting two-dimensional (2D) electron system. The intriguing properties of graphene reveal a behavior of the massless Dirac fermions in low-energy states characterized by a linear dispersion, $e(k) = \pm hv_F |k|$ with $v_F \sim 10^6 \text{ m/s}$, and a strong energy-dependent density of states (DOS) near the Fermi energy at low carrier densities. The linear dispersion has directly been measured by angle-resolved photoemission spectroscopic experiments. However, it has not been clearly understood whether 2D graphene has unusual behavior in the electronic properties due to the opening of gaps on the basis of the time-reversal and mirror symmetries at the two valley points. The interplay between the disorder and extended defects such as edges. The electronic structures of the graphene system depend sensitively on its topology and extended defects such as edges. However, it has not been clearly understood whether 2D graphene has unusual behavior in the electronic properties due to the opening of gaps on the basis of the time-reversal and mirror symmetries at the two valley points. The electronic structures of the graphene system depend sensitively on its topology and extended defects such as edges.

II. LOW-ENERGY STRUCTURE OF GRAPHENE STRIP

The Bravais lattice of the graphene is a 2D hexagonal lattice with a basis of two carbon atoms. We take the primitive translation vectors as $a_1 = a(1,0)$ and $a_2 = a(1,\sqrt{3})/2$, as indicated in Fig. 1. Then, the basis atoms are located at sites $(0,0)$ and $a(1,1/\sqrt{3})/2$ where $a(=0.246 \text{ nm})$ is the graphene lattice constant. Let us call the sublattice formed by the sites obtained from $(0,0)$ $[a(1,1/\sqrt{3})/2]$, through lattice translations $n_a1+n_a2$, by sublattice A (sublattice B). The displacements from an A site to its three nearest neighbor (NN) B sites are given by $d_1 = a/2(1,1/\sqrt{3})$, $d_2 = a(0,-1/\sqrt{3})$, and $d_3 = a/2(-1,1/\sqrt{3})$. The set of displacements to the six next NN (NNN) sites is $\pm a_1, \pm a_2$, and $\pm(a_1-a_2)$. The displacements from a B site to its three NN A sites are obtained from $d_1, d_2$, and $d_3$ by reflection with respect to the $x$ axis.

The first Brillouin zone (BZ) of the graphene lattice is a regular hexagon with two sets of inequivalent vertex points $K$ and $K'$, as shown in Fig. 1(b), where $K = \frac{4\pi}{3a}(1,0)$, $\frac{2\pi}{3a}(-1, \pm \sqrt{3})$ and $K' = \frac{4\pi}{3a}(-1,0)$, $\frac{2\pi}{3a}(1, \pm \sqrt{3})$. Three valley points indicated by $K$ ($K'$) are equivalent since they are connected by linear combinations of the reciprocal lattice vectors $g_1 = \frac{2\pi}{a}(1,-1/\sqrt{3})$ and $g_2 = \frac{2\pi}{a}(0,2/\sqrt{3})$, but the sets of points $K$ and $K'$ are distinct and independent of each other.

We consider a lattice model Hamiltonian written as

$$
H = -t_1 \sum_{(ij)} \sum_{\alpha=\uparrow, \downarrow} [c_{ia}^\dagger c_{ja} + \text{H.c.}] + it_2 \sum_{(ij)} \sum_{\alpha=\uparrow, \downarrow} c_{ia}^\dagger \sigma_{\alpha \beta} c_{ja} c_{j\beta} + iV_R \sum_{(ij)} \sum_{\alpha=\uparrow, \downarrow} c_{ia}^\dagger \cdot (s_{\alpha \beta} \times d_{ij}) c_{j\beta} + \sum_{ia} w_i c_{ia}^\dagger c_{ia}. \tag{1}
$$

Here, $c_{ia}^\dagger$ ($c_{ia}$), $s$, and $d_{ij}$ are, respectively, the creation (destruction) operator of an electron with spin $\alpha$ at lattice site $i$, the Pauli matrix, and the NN lattice vector pointing from site.
While categorized at six corners of the first BZ. The zigzag edge connects the NN site to get to the NNN site and a hexagon. Two sets of inequivalent vertex points are also indicated. In (a), the zigzag (armchair) strip is indicated in terms of the number of zigzag (dimer) lines \( N_d \) (\( N_a \)) along the strip and the lattice constant \( a \) of the 2D hexagonal lattice. The primitive translation lattice vectors \( \vec{a}_1 \) and \( \vec{a}_2 \) are also indicated. In (b), the dark circles are the lattice points in the reciprocal lattice and the first BZ is a (hatched) regular hexagon. Two sets of inequivalent vertex points \( K \) and \( K' \) are indicated at six corners of the first BZ. The \( \vec{g}_1 \) and \( \vec{g}_2 \) are a set of primitive reciprocal translation vectors of the lattice.

\[
\begin{align*}
J & \to i. \text{ In Eq. (1), the first and second terms represent, respectively, the simple NN hopping of matrix element } t_1 \text{ and the spin-dependent NNN hopping of matrix element } t_2. \text{ While } t_1 \text{ describes the intersublattice } (A \to B) \text{ hopping of electrons, } t_2 \text{ describes the intrasublattice } (A \to A \text{ or } B \to B) \text{ hoppings. The second term indicates the intrinsic spin-orbit (SO) interaction in the presence of the mirror symmetry in graphene,}^{11} \text{ where } \nu_{ij} \text{ distinguishes the counterclockwise (ccw) or clockwise (cw) directions of the NNN hopping from site } j \text{ to } i \text{ through } k, \text{ the common NN of sites } j \text{ and } i. \text{ We take } \nu_{ij} = +1 \text{ for the electron turning ccw (cw) at the NN site to get to the NNN site } i. \text{ The third and fourth terms denote, respectively, the NN Rashba spin-orbit (RSO) term of strength } V_R \text{ in the absence of } z \to -z \text{ mirror symmetry and site-dependent inhomogeneity or staggered sublattice potential in the case of broken twofold rotational symmetry in the graphene layer.}

In this work, we consider graphene strips with two different atomic terminations, which are known as zigzag and armchair edges (Fig. 1). The unit cells of the zigzag and armchair strips are depicted in Fig. 1, as solid and dashed rectangles, respectively.\(^ {12} \) We note that there are 2\( N \) carbon atoms in each unit cell of the strip, where \( N \) is the number of zigzag lines \( (N_d) \) for zigzag strips and the number of dimer lines \( (N_a) \) along the strip with armchair edges. Then, the width of the strip is given by \( L_{zz} = \frac{1}{2} (2N - 1) a \frac{a}{3} \) for the one with zigzag edges and \( L_{ac} = \frac{N - 1}{2} a \) for armchair edges. We take the \( x \) axis parallel to the strip and denote the lattice coordinates by \( r_i = (x_i, y_i) = (i, l_i) \). Now let us introduce one-dimensional Fourier transforms

\[
\begin{align*}
c^{A(B)}_{ia} &= \frac{1}{\sqrt{L}} \sum_k c^{A(B)}_{ka}(y_{i}) e^{i k_{x} a} e^{i k_{y} a}, \\
c^{A(B)^{\dagger}}_{ia} &= \frac{1}{\sqrt{L}} \sum_k c^{A(B)^{\dagger}}_{ka}(y_{i}) e^{-i k_{x} a} e^{-i k_{y} a}.
\end{align*}
\]

Here, \( k \) and \( L = Na \) (\( L = \sqrt{3} Na \)) are, respectively, the wave number and the length of the zigzag (armchair) strip, where \( N \) is the number of unit cells in a given strip. Under the transforms given by Eq. (2), Eq. (1) can be written in the momentum space (see the details in the Appendix). By diagonalizing the resulting Hamiltonian, one can obtain the energy structure of a graphene strip with periodic boundary conditions in the \( x \) direction (along the strip).

### A. Low-energy electronic energy structures

Allowing only the NN hopping for 2D graphene, the Hamiltonian reduces to a Dirac Hamiltonian\(^ {13} \) with energy dispersion \( E(\vec{q}) = \pm \hbar v_F |\vec{q}| \) near the six vertices of the first BZ.\(^ {14} \) Here, \( \vec{q} \) is measured from each vertex point. The Fermi level of undoped graphene is located at these six isolated “points” called Dirac points. The appearance of degenerate zero gap states at the vertex points is a direct consequence of the symmetry of the graphene lattice structure. The Fermi velocity of the massless Dirac particle \( v_F \) is related to the NN hopping parameter \( t_1 \) by \( \hbar v_F = \frac{3}{2} t_1 a = 0.58 \text{ eV nm} \) with \( t_1 = 2.7 \text{ eV} \).\(^ {2} \) All the energies are measured in units of the NN hopping strength \( t_1 \) in the rest of the work. In a NN tight-binding approximation, one can easily confirm that the \( \pi \) band structure of a 2D graphene shows zero slope of energy \( \varepsilon = \pm t_1 \) at the midpoints between each pair of Dirac points \( K \) and \( K' \) along the boundary of the first BZ and the band extreme of energy \( \varepsilon = \mp t_1 \) occurs at the center of the first BZ.\(^ {14} \) In a strip with zigzag edges, the linear modes, stemming from the original vertex points \( K \) and \( K' \), appear at \( k = \pm \frac{2 \pi}{3a} \) and, in addition to the extended states across the strip, there occur localized edge states around the zero-energy line near \( 2\pi/3a \leq |k| \leq \pi/3a \).

The low-energy electronic energy bands of zigzag strips are illustrated in Fig. 2. Figure 2(a) shows the energy band

![Diagram showing the Geometrical structure of graphene strips: (a) direct lattice structure and (b) the first BZ of the graphene. In (a), the zigzag (armchair) edges are shown along the horizontal (vertical) direction and the unit cell is denoted by solid (dashed) rectangle for the zigzag (armchair) strip. The width \( L_{zz} \) (\( L_{ac} \)) of the zigzag (armchair) strip is indicated in terms of the number of zigzag (dimer) lines \( N_d \) (\( N_a \)) along the strip and the lattice constant \( a \) of the 2D hexagonal lattice. The primitive translation lattice vectors \( \vec{a}_1 \) and \( \vec{a}_2 \) are also indicated. In (b), the dark circles are the lattice points in the reciprocal lattice and the first BZ is a (hatched) regular hexagon. Two sets of inequivalent vertex points \( K \) and \( K' \) are indicated at six corners of the first BZ. The \( \vec{g}_1 \) and \( \vec{g}_2 \) are a set of primitive reciprocal translation vectors of the lattice.](115410-2)

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structure of the case \( N = 50, t_2 = V_R = w_i = 0 \). The widths of the
conduction and valence bands are \( 3 t_1 \) and edge states form flatbands located at zero-energy line for \( |k| \geq 2 \pi / 3a \) resulting in a strong peak structure in the DOS [see Fig. 5(a) below]. When \( t_2 = 0, V_R = 0, \) and \( w_i = 0 \), the system is particle-hole symmetric, i.e., the Hamiltonian is unchanged under the particle-hole transformation \( c_{i \sigma} \rightarrow (-1) c_{i \sigma} \). The band structure of graphene shows a symmetry of \( \varepsilon(k) = \varepsilon(-k) \). In each half-leaves of Figs. 2(b) and 2(c) [and also of Figs. 3(b) and 3(c)], we displayed only \( \varepsilon(k) \) for values of either \( k < 0 \) or \( k > 0 \) just for convenience. In Fig. 2(b), we show the low-energy electronic band structure of the cases with \( N = 20, t_2 = 0.00, V_R = 0.00, w_i = 0.00 \) (left half-leaf) and \( t_2 = 0.01, V_R = 0.00, w_i = 0.00 \) (right half-leaf). We note that the intrasublattice NNN hopping, i.e., \( t_2 \neq 0 \), opens finite valley gap at \( K \) and \( K' \) and the zero-energy edge band splits into modes with finite ve-

FIG. 2. (Color online) Energy structure of a zigzag graphene strip. (a) Energy band structure of the case \( N = 50, t_2 = V_R = w_i = 0 \). (b) Low-energy electronic energy bands of the strip with \( N = 20 \) and \( t_2 = 0.00, V_R = 0.00, w_i = 0.00 \) (left half-leaf) and \( t_2 = 0.01, V_R = 0.00, w_i = 0.00 \) (right half-leaf). Energy is measured in units of the NN hopping strength \( t_1 \).

FIG. 3. (Color online) Energy structure of an armchair graphene strip. (a) Energy band structure of the case \( N = 50, V_R = w_i = 0 \). (b) Low-energy electronic energy bands of the strip with \( N = 20 \) and \( t_2 = 0.00, V_R = 0.00, w_i = 0.00 \) (left half-leaf) and \( t_2 = 0.01, V_R = 0.00, w_i = 0.00 \) (right half-leaf). (c) Low-energy electronic energy bands of the strip with \( N = 20 \), \( t_2 = 0.01, V_R = 0.05, w_i = 0.00 \) (left half-leaf) and \( t_2 = 0.01, V_R = 0.05, w_i = 0.02 \) (right half-leaf). Energy is measured in units of the NN hopping strength \( t_1 \).
locity as is shown on the right half-leaf of Fig. 2. The Rashba SO term introduces the communication between the spin-up and spin-down states and thus removes the twofold spin degeneracy in the extended band, as can be seen by comparing the right half-leaf of Fig. 2 and the left half-leaf of Fig. 2. The staggered sublattice potential removes further degeneracy as is shown in the right half-leaf of Fig. 2, which is the result of the case $N=20$, $t_2=0.01$, $V_R=0.05$, $w_i=0.02$.

We also observe that, although the particle-hole symmetry ($e \leftrightarrow -e$ symmetry) is retained for individual terms of ISO and RSO, the combination of ISO and RSO terms removes the particle-hole symmetry, as is shown in Fig. 2, resulting in the asymmetry of the DOS: $g(e) \neq g(-e)$. See, for example, Fig. 4(a). For small values of $t_2$, a pair of nearly flat bands exists over the region $2\pi/3 \leq |k| \leq \pi$. For reasonable values of $t_2$ and $w_i$, the edge states continue to cross the valley gap passing the zero-energy line at $k = \pm \pi/a$, as indicated in Figs. 2(b) and 2(c). As the strength of ISO coupling decreases, the dispersion of the edge states flattens and enormous DOS is observed at zero energy with vanishing ISO coupling [see also Fig. 5(a)]. For small values of $V_R$ and $w_i$, edge states approach and cross the zero-energy line.

In an armchair strip of metallic phase, the massless Dirac particle-like behavior of linear dispersion appears at $k=0$, and the localized edge-state band disappears, unlike the case of zigzag strips. Figure 3(a) shows the energy band structure of an armchair strip for the case $N=50$, $V_R=w_i=0$. The strip of $N=50$ belongs to metallic strips since it corresponds to $N=3M-1$ with integral value of $M=17$. The widths of the conduction and valence bands are $3t_1$ but edge-state band does not occur in the geometry of armchair terminations. The

![FIG. 4. Density of states of (a) zigzag and (b) armchair strips of width $N=50$ for $t_2=0.01$, $V_R=0.05$, $w_i=0$. Energy is measured in units of the NN hopping strength $t_1$.](image)

![FIG. 5. Density of states of graphene zigzag strips of width $N=50$. (a) $t_2$ dependence of the DOS for $V_R=w_i=0$. (b) $V_R$ dependence of the DOS for $t_2=0.01$ and $w_i=0$. (c) $w_i$ dependence of the DOS for $t_2=0.01$ and $V_R=0.05$. Energy is measured in units of the NN hopping strength $t_1$.](image)
linear mode crossing the point \( k=0 \) remains intact for variation of \( t_2 \) in armchair strips. In Figs. 3(b) and 3(c), the variation of the low-energy band structure is shown for different values of \( t_2 \), \( V_R \), and \( w_i \) in an armchair strip consisting of 20 (=N) dimer lines. We note that an armchair strip consisting of 20 dimer lines (\( N=20 \)) also shows metallic behavior. Effects of the intrasublattice hopping of strength \( t_2 \) and staggered sublattice potential would mostly be seen in the low-lying states near the zero-energy line. Finite value of \( t_2 \) shifts all the bands, except the ones with linear dispersion crossing at \( k=0 \), away from the zero-energy line as is shown in Fig. 3(b), but the energy shift is negligible for small values of \( t_2 \) (\( \approx \)0.01\( t_1 \)). As we turn on the Rashba SO coupling, twofold spin degeneracy is removed as can be seen by comparing the right half-leaf of Fig. 3(b) and the left half-leaf of Fig. 3(c). The right half-leaf of Fig. 3(c) shows that the staggered sublattice potential \( w_i \) opens a valley gap at \( k=0 \) in an armchair strip. We also note that, as in the case of zigzag strips, the combination of \( t_2 \) and \( V_R \) breaks the particle-hole symmetry in the armchair strip, as can apparently be seen near the low-energy bands in Fig. 3(c).

B. Density of states of the graphene strips

The linear dispersion of the modes in 2D graphene results in unusual behavior such as vanishing effective mass and zero DOS at the Fermi energy. The DOS per unit area \( g(\epsilon) = \frac{2}{\sqrt{2} \pi} \sum_q \delta(\epsilon - \epsilon(q)) \) simply becomes

\[
g(\epsilon) = \frac{|\epsilon|}{\pi h^2 v_F^2}
\]

near \( K \) and \( K' \). We focus our attention on the states near half filling at low temperatures. In the zigzag strip geometry, localized edge states lead to unusual peak structure near the Fermi energy (zero-energy value) and their contribution to DOS is very sensitive not only to the band structure parameters appearing in Eq. (1) but also to \( N \), the width of the strip.

We illustrate the DOS of zigzag and armchair strips, respectively, in Fig. 4 for the case of width \( N=50 \) and \( t_2 = 0.01 \), \( V_R = 0.05 \), \( w_i = 0 \). The singular behavior of the DOS at \( \epsilon = \pm t_1 \) and \( \epsilon = \pm 3t_1 \) comes from the extended states of vanishing slopes in a 2D graphene sheet.\(^{14-16}\) The most important feature of the edge states is the emergence of a sharp peak at the Fermi level (\( \epsilon=0 \)) in the DOS of the zigzag strip, as shown in Fig. 4(a). The asymmetry of the DOS, i.e., \( g(\epsilon) \neq g(-\epsilon) \), demonstrates that the combination of the spin-dependent NNN hopping and the Rashba SO coupling breaks the particle-hole symmetry. When \( t_2=0 \), \( V_R=0 \), and \( w_i=0 \), the system is particle-hole symmetric. The valley extrema of the conduction and valence bands occur at \( K \) and \( K' \), and additional gapless (flat) edge states connect the two valley minima in a zigzag strip, resulting in a strong peak structure at zero energy in Fig. 4(a). The sharpness of the peak reflects the flatness of the edge-state band characterized by the localization of electrons near the edges of the strip. The electronic DOS of an armchair strip is quite similar to that of a 2D graphene sheet because there are no contributions from the edge states in both cases [see Fig. 4(b)]. In the higher energy regime, the profile of the DOS is essentially due to the extended states of the graphene layer, showing typical van Hove singularities of the bands with finite width. The DOS of a \( \pi \) band in a 2D graphene vanishes linearly as energy reduces to zero and reveals van Hove singularities at \( \epsilon = \pm t_1 \) and \( \epsilon = \pm 3t_1 \), as expected from the energy structures shown in Figs. 2(a) and 3(a).

The spin-dependent NNN hopping term (of \( t_2 \)) opens finite gap appearing at Dirac points \( K \) and \( K' \). As we increase \( t_2 \), the valley gaps at \( K \) and \( K' \) increase and the peaked structure at the Fermi level diminishes, as is shown in Fig. 5(a). The reduction in the DOS at Fermi energy reflects the splitting of the fourfold degenerate flatband, appearing over the region \( 2\pi/3 \leq |a| \leq \pi \), into the twofold bands of finite slope [see, for example, Fig. 2(b)].

The Rashba term introduces the communication between the spin-up and spin-down states and thus removes the twofold degeneracy in the extended band, as is shown in Fig. 2(c). Figure 5(b) displays the effect of Rashba SO coupling \( (V_R) \) to the DOS in the zigzag strip. Finite value of \( V_R \) alone changes the overall DOS little, but its combination with \( t_2 \) \((\neq 0)\) breaks the symmetry \( g(\epsilon)=g(-\epsilon) \) appreciably. We note that, as we increase the staggered sublattice potential \( (w_i \geq 0.05) \), the band touching of the conduction and valence bands at \( k=\pi/a \) is removed and “edge-state” gap is generated at around \( \epsilon \), as is shown in the top panel of Fig. 5(c) for the case \( w_i=0.1=\frac{1}{7}w_R \) [see also Figs. 2(c) and 3(c)].

Figure 6 shows the strip width \( (N) \) dependence of the DOS for zigzag and armchair strips. As we increase the number of the zigzag or dimer lines in the strip, the shape of DOS becomes similar to that of 2D graphene, as shown in Fig. 6(a) and 6(b), in general. However, in zigzag strips, the edge effect on the electronic structure is expected to diminish rapidly as one increases \( N \). In Fig. 6(a), we illustrate the DOS per electron in order to illustrate the relative importance of the edge states in zigzag strips with different values of strip width. In Fig. 6(b) for an armchair strip with \( N=5 \), a pair of peaks at \( \epsilon = \pm t_1 \) is related to the flatbands occurring at the energies \( \epsilon = \pm t_1 \). It is interesting to note that these flatbands are common for armchair strips with odd values of \( N \).

III. ELECTRONIC HEAT CAPACITY OF GRAPHENE STRIP

The internal energy due to carriers in the sample is given by \( U_{el}=\sum_{\epsilon_{min}}^{\epsilon_{max}} g(\epsilon)f(\epsilon,T) \), where \( f(\epsilon,T) \) is the Fermi-Dirac distribution and \( \epsilon_{min} (\epsilon_{max}) \) is the minimum (maximum) energy available in the band of the graphene strip. The heat capacity is then given by \( C_{el}(T)=\frac{\partial U_{el}}{\partial T} \). The electronic heat capacities of graphene strips (per electron) are displayed in Fig. 7, as a function of \( k_BT \), for the case \( N=50 \), \( t_2=0.01 \), \( V_R=w_i=0 \). Each inset in Fig. 7 shows an overall temperature dependence of \( C_{el}(T) \) in the corresponding strip geometry. It is observed that \( C_{el}(T) \) has maximum value \( \sim 0.67k_B \) at \( k_BT/t_1 \approx 1.0 \). The overall behavior of \( C_{el}(T) \) in graphene is similar to that of a two-level system,\(^{17}\) which reflects the gross shape of the conduction and valence bands with finite width. As the temperature is increased beyond that of
$k_B T / t_1 = 1.0$, $C_{el}(T)$ decreases and vanishes as $T^{-2}$ in the limit of $T \to \infty$. The solid line is the numerical values of $C_{el}(T)$ and dashed lines indicate a power-law behavior of $C_{el}(T) = \gamma T^{-\alpha}$ at low temperatures. Our calculation estimates that $\gamma = 6.8 \pm 0.1 k_B$, and $\alpha = 2.2$, which varies slightly depending on the specific values of the topology and band parameters $t_2$, $V_R$, and $w_i$ of the strip. In a usual 2D electron gas, we have $C_{el} = \gamma T$ at low temperatures. The deviation of $\alpha$ from unity is indicative of the unconventional character of the low-energy excitations in a graphene layer. For massless fermions in 2D, one can easily show that $C_{2D} \propto T^2$ simply using the linear DOS. The low-energy behavior of $C_{el} = \gamma T^\alpha$ clearly shows us the massless fermion feature of the modes in a graphene strip.

Low-temperature behaviors of $C_{el}(T)$ in graphene strips of $N=50$ are illustrated in Figs. 8 and 9 for various values of $t_2$, $V_R$, and $w_i$. In the region of $k_B T \leq 0.01 t_1$, we observe an additional structure in $C_{el}(T)$ of a zigzag strip, as is shown in Fig. 8, unlike the cases of strips with armchair edges shown in Fig. 9. The additional structure in $C_{el}(T)$ appearing in zigzag strips results from the edge-state band with finite slope near the Fermi energy as is shown, for example, in the right half-leaf of Fig. 2(b). In Figs. 8(a) and 9(a), we display the variation of $C_{el}(T)$ for different values of $t_2$. The inset of Fig. 8(a) shows the temperature dependence of $\Delta C_{edge}$, and the peak value of $\Delta C_{edge}(T)$ for $t_2 = 0.005 t_1$ is positioned at $k_B T / t_1 \approx 1.0 \times 10^{-2} t_1$, which corresponds approximately to $T \approx 324$ K with $t_1 = 2.7$ eV. In the region of $k_B T \leq t_2$ (for $t_2 > 0$), the edge-state contribution $\Delta C_{edge}(T)$ to the heat capacity is significantly larger than that due to the extended modes in the strip. We note that $C_{el}(T)$ in graphene strips is insensitive to the variation of $V_R$, as illustrated in Figs. 8(b) and 9(b).

In Figs. 8(c) and 9(c), we show $C_{el}(T)$ for different values of $w_i$ in strips with zigzag and armchair edges, respectively. For finite value of staggered sublattice potential $w_A \neq w_R$, the fourfold degenerate edge-state band (pinned at the Fermi energy) splits into a pair of twofold bands [see Figs. 2(c) and 3(c)]. If we break the sublattice symmetry substantially, for example, by employing $|w_i| = 0.05 t_1$, the edge states stop crossing the zero-energy line leaving energy gap at $k_B t_1 = a \pi / 4$, the boundary point of the first BZ. However, this insulating phase is hardly expected to occur in the graphene, in the absence of strong NN Rashba spin-orbit term, with the NNN
hopping parameter $t_2 \approx 0.2 t_1$ proposed recently.\textsuperscript{18} As $w_i$ is reduced, the edge-state bands approach the zero-energy line and eventually cross the valley gap for small values of staggered sublattice potential giving rise to metallic phase in the strip, as shown in Fig. 2(c).

With vanishing values of $t_2$ in a zigzag strip, sublattice disorder introduces a gap of size $w_A - w_B$ between the two-fold degenerate flatbands (edge state near $\pm w_i$ and, hence, producing a pair of edge-state peak structure in the DOS, as implied in the top panel of Fig. 5 for the case $w_i=0.1$ but with $t_2=0.01$ and $V_R=0.05$). We note that, for
finite staggered sublattice potential \((w_A \neq w_B)\) with vanishing \(t_2\) in zigzag strips, the specific heat (per electron) \(C_{el}(T)\) tends to 0 as \(\sim C_0 e^{-\Delta/k_B T^2}\) in the temperature range of \(k_B T \leq |w_i|\), as illustrated in Fig. 10. This exponential behavior is shown by a solid line in the inset with \(C_0 = 0.05, \Delta = 0.051\) for the case \(t_2 = 0, V_R = 0, w_A = -w_B = 0.05\). This exponential behavior is known typically in a system with finite excitation gap, similar to the phonon heat capacity of an insulating solid within the Einstein model at low temperature.

As the width of graphene strip increases, the relative importance of the edge states is expected to be reduced and, hence, \(C_{el}(T)\) would reveal the behavior of 2D graphene, i.e., \(C_{el} \propto T^\alpha\). Figure 11 illustrates \(C_{el}(T)\) of both zigzag and armchair strips for various values of the strip width when \(t_2 = 0.01, V_R = w_i = 0\). We note that, at low temperatures, \(\Delta C_{edge}\), the localized edge-state contribution in zigzag strips is predominant. Strong width dependence of the edge-state contribution to the specific heat is clearly illustrated in Fig. 11(a). On the other hand, the specific heat is not sensitive to the width of the armchair strip. The narrow armchair strip shows linear dependence on temperature at low temperatures as illustrated for the case \(N=5\) in Fig. 11(b). The DOS of one-dimensional massless Dirac fermion states is independent of momentum in the absence of edge states, as in the armchair strips, and, hence, the specific heat is simply proportional to temperature at low temperatures.

**IV. SUMMARY AND CONCLUSION**

We exploit the low-energy electronic structures of graphene strips in the viewpoint of the topological symmetries of the strips and present the temperature behavior of the electronic heat capacities. We have shown that the overall behavior of \(C_{el}(T)\) in a given graphene geometry is similar to that of a two-level system due to the finite width of the conduction and valence bands. The low-temperature heat capacity shows unusual behavior of \(C_{el} \propto T^\alpha\) with \(\alpha = 2.2\) at extremely low temperatures. The magnitude of \(\alpha\) varies slightly depending on the band parameters (such as NNN hopping strength, Rashba SO coupling, staggered sublattice potential), and the topology and the width of the strip. We also find that the edge states give extra strong enhancement in the heat capacity in the zigzag strips at low temperatures in addition to the \(T^\alpha\) behavior of a 2D graphene layer. The effect of Coulomb interaction on the specific heat in graphene strips is also an interesting problem but is not included in the present discussion. Very recently, we became aware of refined estimates of the SO parameters. More accurate values of SO coupling parameters would modify our observation quantitatively, but the general features of the graphene heat capacity found in this work should be able to be tested in nondestructive thermal measurements.
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APPENDIX: HAMILTONIAN IN MOMENTUM SPACE

Under the transforms given by Eq. (2), Eq. (1) can be written in momentum space. The NN hopping term is written as

\[ H_1 = -t_1 \sum_k \sum_{i=1}^N c_{k\alpha}^{(A)}(i_2)c_{k\alpha}^{(B)}(i_2)2 \cos k a l/2 \]

\[ + c_{k\alpha}^{(A)}(i_2)c_{k\alpha}^{(B)}(i_2 - 1) + \text{H.c.} \] (A1)

Here, by imposing periodic boundary conditions in the x direction along the strip, we have used the identity \( \sum_{i} e^{-i(k_x - k_x' \sin k)} = N_s \delta_{k_x, k_x'} \). Similarly, the NNN hopping term is written, remembering that \( \nu_{ij} = \pm 1 \) for A sites need to be replaced by \( \nu_{ij} = \pm 1 \) for B sites, by

\[ H_2 = -2t_2 \sum_k \sum_{i=1}^N \left[ \begin{array}{c} c_{k\alpha}^{(A)}(i_2 - 1)c_{k\alpha}^{(A)}(i_2) + c_{k\alpha}^{(A)}(i_2 + 1)c_{k\alpha}^{(A)}(i_2) \end{array} \right] \]

\[ \times \sin k a l/2 - c_{k\alpha}^{(A)}(i_2)c_{k\alpha}^{(A)}(i_2) \sin k a + \{A \leftrightarrow B\}. \] (A2)

The Rashba SO term is written by

\[ H_R = iV_R \sum_k \sum_{i=1}^N \left[ \begin{array}{c} c_{k\alpha}^{(A)}(i_2 + 1)c_{k\alpha}^{(B)}(i_2) + \{ \uparrow \leftrightarrow \downarrow \} \\ - \left[ c_{k\alpha}^{(B)}(i_2 - 1)c_{k\alpha}^{(A)}(i_2) + \{ \uparrow \leftrightarrow \downarrow \} \right] + \left[ c_{k\alpha}^{(B)}(i_2)c_{k\alpha}^{(A)}(i_2) \right] \right] \cos k a l/2 + \sqrt{3} \sin k a l/2 \]

\[ - c_{k\alpha}^{(A)}(i_2)c_{k\alpha}^{(B)}(i_2) + \{B \leftrightarrow A\} \text{ and } \uparrow \leftrightarrow \downarrow \right] \cos k a l/2 \]

\[ - \sqrt{3} \sin k a l/2. \] (A3)

The staggered sublattice potential term becomes simply

\[ H_{SL} = \sum_{k_{\alpha} \alpha = \uparrow, \downarrow} \sum_{i=1}^N \left[ w_A n_{k\alpha}^{(A)}(i_2) + w_B n_{k\alpha}^{(B)}(i_2) \right], \] (A4)

where \( n_{k\alpha}^{(X)}(i_2) = c_{k\alpha}^{(X)}(i_2)c_{k\alpha}^{(X)}(i_2) \). By diagonalizing Eqs. (A1)–(A4), one can obtain energy band structure of a graphene strip.


4 C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 146802 (2005); 95, 226801 (2005).


10 K.-S. Park and K. S. Yi, J. Korean Phys. Soc. 50, 1873 (2007), and the references therein.


20 See, for example, G. Burns, Solid State Physics (Academic Press, New York, 1985), Chap. 11.