Domain Walls in Gapped Graphene

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The electronic properties of a particular class of domain walls in gapped graphene are investigated. We show that they can support midgap states which are localized in the vicinity of the domain wall and propagate along its length. With a finite density of domain walls, these states can alter the electronic properties of gapped graphene significantly. If the midgap band is partially filled, the domain wall can behave like a one-dimensional metal embedded in a semiconductor and could potentially be used as a single-channel quantum wire.

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Graphene is a one-atom thick layer of carbon atoms with a hexagonal lattice structure and where electrons within ~1 eV of the Fermi energy obey a Dirac equation and have a linear dispersion relation $\omega = v_F|\vec{k}|$ with Fermi velocity $v_F \sim c/300$ [1,2]. It has been studied as an analog of relativistic field theory [2] where relativistic quantum mechanics and field theory phenomena special to $2 + 1$ spacetime dimensions [3,4] could be realized in nature. It was identified and studied in the laboratory in 2004 [5], and it turns out to have high conductivity and carrier mobility and other interesting properties which make it a promising material for applications in electronic devices [6–8].

An important current problem is to modify graphene so that it has a gap in its energy spectrum [9]. The idea is that, with a small gap so that electrons obey a Dirac equation with mass, it would retain the good features of graphene and could also be used as a semiconductor in applications where a gap is essential, for example, a field effect transistor. Breaking the symmetry which interchanges the two triangular sublattices of the hexagonal graphene lattice will gap the spectrum [2]. This could be accomplished, for example, by giving electrons residing on A sites a different energy from those on B sites by introducing a staggered on-site energy [2]. It can also arise from deformations of bonds on the graphene lattice [10] analogous to those known from the study of carbon nanotubes [11]. A third possibility is to use multilayer graphene where the layers can be stacked so that their interaction breaks the sublattice symmetry. In all cases, to retain the features of the Dirac equation, the gap should be much less than the nearest neighbor hopping amplitude $t \sim 2.7$ eV.

The diatomic material boron-nitride (BN) has the same lattice structure and valence electrons as graphene and a staggered on-site energy by virtue of having different atoms on the two sublattices. Monolayers have been made in the laboratory [12]. However, the gap is too large ~4.5 eV for Dirac electrons. An approach currently being pursued is to attach a graphene monolayer to a BN substrate. The resulting gap in graphene is estimated to be ~53 meV [13], which is in the interesting range. Another approach is the epitaxial growth of graphene on a silicon-carbide substrate where a larger magnitude gap ~2.6 eV has been observed [14].

In this Letter, we shall consider linelike domain-wall defects in the mass pattern in graphene which is gapped by a sublattice symmetry breaking staggered on-site energy. We find that these defects can have interesting electronic properties. The domain walls are shown in Figs. 1(b) and 1(c) where the zigzag and armchair walls form boundaries between regions where the staggered on-site energy is shifted between the two sublattices. Such domain walls could be realized naturally in BN and would be inherited by graphene on a BN substrate, for example. We show that they can give rise to a band of midgap states. These states are localized in the vicinity of the wall and propagate along its length. If the midgap band is partially filled, the domain wall can behave like a one-dimensional metal embedded in a semiconductor and could potentially be used as a single-channel quantum wire. One might imagine that, once techniques for deposition of graphene monolayers on substrates are better developed, the conditions for the existence of these domain-wall wires could be created and manipulated to the point where they could be used to print electric circuits on graphene sheets.

Midgap states already play an important role in graphene. It was pointed out long ago [2] that an index theorem governs the degeneracy of the $E = 0$ Landau level in graphene in a magnetic field, and this level is half filled in the neutral material. This observation has spectacular experimental confirmation in the half-odd-integer anomalous quantum Hall effect [6,15,16]. In addition, theoretical studies of pointlike vortex defects in a mass condensate due to a Kekule distortion of graphene find midgap electron states which can give the vortices fractional charge [10,17–20], thus giving a two-dimensional realization of a phenomenon previously known to occur in one-dimensional linearly conjugated polymers such as polyacetylene [21–23]. Similar states bound to vortices in a proximity-induced superconducting condensate in graphene could lead to anyonic statistics with potential applications to

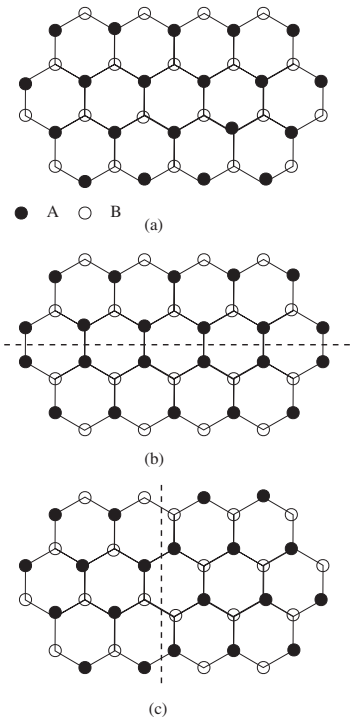

FIG. 1. (a) A hexagonal graphene lattice with triangular sublattices A (black dots) and B (white dots) connected by vectors $\vec{s}_1 = (0, -1)a$, $\vec{s}_2 = (\sqrt{3}/2, 1/2)a$, $\vec{s}_3 = (-\sqrt{3}/2, 1/2)a$ with lattice constant $a = 1.23$ Å. (b) A zigzag domain wall. (c) An armchair domain wall. In (b) and (c), the on-site energies are $-\mu$ on black dots and $+\mu$ on white dots; the sublattices which have higher or lower on-site energies are interchanged at a domain wall, creating a line of mismatched neighbors, denoted by a dashed line.

quantum computing [24]. An essential common feature of these examples is the existence of "zero-mode" midgap states in the spectrum of the Dirac Hamiltonian, which arises from the interaction with fields that have a nontrivial topology. In the case of the vortex, this topology is due to the vorticity. Let us consider a simple example to show that a related phenomenon takes place for a domain wall. Consider the 4×4-matrix graphene Dirac Hamiltonian with the addition of a mass term (which might arise from a staggered on-site energy):

$$H = \hbar v_F \begin{bmatrix} \frac{m v_F}{\hbar} & i\frac{d}{dx} + \frac{d}{dy} & 0 & 0 \\ i\frac{d}{dx} - \frac{d}{dy} & -\frac{m v_F}{\hbar} & 0 & 0 \\ 0 & 0 & \frac{m v_F}{\hbar} & i\frac{d}{dx} - \frac{d}{dy} \\ 0 & 0 & i\frac{d}{dx} + \frac{d}{dy} & -\frac{m v_F}{\hbar} \end{bmatrix}. \quad (1)$$

The two diagonal blocks correspond to the two graphene valleys, which transform into each other under parity and time reversal. A domain wall is described by replacing the mass m in Eq. (1) by a function $m(x)$ which depends on one of the coordinates, x, with a soliton profile:

$$\lim_{x \to -\infty} m(x) = -m < 0, \qquad \lim_{x \to \infty} m(x) = m > 0. \quad (2)$$

The energy spectrum then has the same gapped conduction and valence band branches as would occur if $m(x)$ in Eq. (1) were a constant with the asymptotic value of the mass m: $E = \pm v_F \sqrt{\vec{k}^2 + m^2 v_F^2}$. These describe electrons in the bulk semiconductor away from the wall. As well, there is a gapless midgap branch whose wave functions have support near the wall. Explicitly, the (unnormalized) wave functions and eigenvalues are

$$\psi_L(x, y) = e^{ik_y y/\hbar - (v_F/\hbar^2)\int_0^x dx' m(x')} \begin{bmatrix} i \\ 1 \\ 0 \\ 0 \end{bmatrix}, \qquad E = v_F k_y, \quad (3)$$

$$\psi_R(x, y) = e^{ik_y y/\hbar - (v_F/\hbar^2)\int_0^x dx' m(x')} \begin{bmatrix} 0 \\ 0 \\ 1 \\ i \end{bmatrix}, \qquad E = -v_F k_y. \quad (4)$$

Note that this solution exists and is continuum normalizable for whatever the profile of the position-dependent mass term—it needs only to have the asymptotic behavior of a topological soliton as in Eq. (2) [25]. In particular, it should be applicable to a one lattice spacing thick domain wall such as those drawn in Figs. 1(b) and 1(c).

What we have found are two bands of midgap states corresponding to one left- and one right-moving one-dimensional massless fermion (for each spin degree of freedom) traveling along the length of the domain wall. An effective Lagrangian describing them would be

$$L = i\sum_s [\psi_{Ls}^\dagger (\partial_t - v_F \partial_x)\psi_{Ls} + \psi_{Rs}^\dagger (\partial_t + v_F \partial_x)\psi_{Rs}], \quad (5)$$

where s labels the two spin states. Effects of impurities and local interactions can be important in one dimension and should be taken into account. Four-fermion operators are perturbatively marginal, and adding those which do not implement umklapp processes yields the Tomonaga-Luttinger model which is a solvable conformal field theory with well-known properties.

To understand the structure of the bands in more detail, we must take a closer look at the tight-binding lattice model of gapped graphene. We shall find features that are not reflected in the continuum analysis, which is only valid in a small region near $E = 0$. The Hamiltonian is

$$H = \sum_{A,i} t b_{A+\vec{s}_i}^\dagger a_A + \sum_{B,i} t a_{B-\vec{s}_i}^\dagger b_B + \sum_A \mu a_A^\dagger a_A - \sum_B \mu b_B^\dagger b_B, \quad (6)$$

where $a_A^\dagger$, a_A, $b_B^\dagger$, b_B are the quantum amplitudes for an electron to occupy sites labeled A and B on the sublattices A and B, respectively. The lattice and sublattices are depicted in Fig. 1(a). The first terms in Eq. (6) describe electron tunneling between nearest neighbor sites. The terms proportional to μ are on-site energies. They break

the sublattice symmetry and generate a gap. The Schrödinger equation is

$$(E-\mu)a_A = t\sum_i b_{A+\vec{s}_i}, \quad (E+\mu)b_B = t\sum_i a_{B-\vec{s}_i}. \tag{7}$$

To study the zigzag domain wall in Fig. 1(b), we solve Eq. (7) with μ replaced by $\mu\ \mathrm{sign}(A_y)$ and $\mu\ \mathrm{sign}(B_y)$. The spectrum has branches corresponding to electrons propagating in the bulk of the gapped graphene away from the wall:

$$E = \pm\sqrt{\mu^2 + t^2\left(2\cos^2\frac{\sqrt{3}a}{2}k_x + \cos\frac{3a}{2}k_y\right)^2 + t^2\sin^2\frac{3a}{2}k_y}. \tag{8}$$

Here (k_x, k_y) are wave vectors. This bulk spectrum has a gap 2μ and is symmetric about $E = 0$. Then, there are two branches with wave functions which fall off exponentially with transverse distance $|A_y|$, $|B_y|$ from the wall and are oscillating functions of the longitudinal A_x, B_x coordinates with wave vector k_x:

$$E = -t - \sqrt{\mu^2 + 4t^2\cos^2\frac{\sqrt{3}a}{2}k_x}, \quad \cos\frac{\sqrt{3}a}{2}k_x \le 0, \tag{9}$$

$$E = t - \sqrt{\mu^2 + 4t^2\cos^2\frac{\sqrt{3}a}{2}k_x}, \quad \cos\frac{\sqrt{3}a}{2}k_x \ge 0. \tag{10}$$

The band in Eq. (9) is located inside (and reaches slightly below) the negative energy bulk states Eq. (8). The other branch Eq. (10) covers the interval $[t - \sqrt{\mu^2 + 4t^2}, t - \mu]$. If $t > \mu$, this band crosses zero energy ($E = 0$) at two values of k_x, and thus agrees with the continuum analysis which is valid only when $\mu \ll t$ and which predicts the existence of two zero energy modes—one for each crossing. The spectrum and density of states for $\mu = 0.5t$ are depicted in Fig. 2. Note that, unlike the spectrum of bulk graphene Eq. (8), the zigzag domain-wall spectrum is not symmetric about $E = 0$. This is evident from its structure displayed in Fig. 1(b), where the mismatched sites along the wall are entirely black dots with on-site energy $-\mu$. The zigzag domain wall violates the symmetry which reflects the sign of the energy. There is an antiwall where the mismatched bonds are entirely white dots—with energy $+\mu$. Its domain-wall spectrum would have opposite sign to Eqs. (9) and (10).

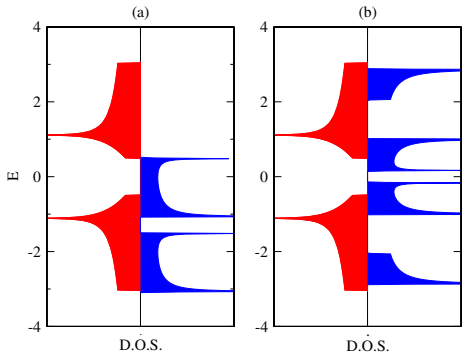

FIG. 2 (color online). Density of states (D.O.S. in arbitrary units, blue or dark gray) versus energy E (in units of t) for (a) a zigzag domain wall and (b) an armchair wall when $\mu = 0.5t$. Also shown is the D.O.S. for bulk bands (red or light gray).

We can get an intuitive understanding of the spectrum in Eqs. (9) and (10) in the limit where μ is large. Initially, neglecting t, there are two energy levels, μ for an electron sitting on a white dot and $-\mu$ for an electron sitting on a black dot in Fig. 1(b). Then, if we turn on small t, the largest effect is for the black dots on each side of the domain wall which have a nearest neighbor at the same zeroth order energy, $-\mu$. Turning on the hopping would split the degeneracy of these sites to $-\mu + t$ and $-\mu - t$. Note that this does not happen for sites in the bulk away from the domain wall, since they are not degenerate with their neighbors—corrections to their spectrum would be at the next higher order in t. The energies $-\mu - t$ and $-\mu + t$ are identical to the Taylor expansions of Eqs. (9) and (10), respectively, to first order in t. The next order in the hopping amplitude, second order perturbation theory, would take into account hopping to an adjacent site with energy $+\mu$ and back, and would be of order t^2/μ, also what one would expect from expanding Eqs. (9) and (10) as well as (8) to second order in t. The order t^2/μ contributions are momentum dependent and the energy levels become bands. Then t is made larger than μ; they spread out into the bands depicted in Fig. 2.

In the neutral ground state, the half of the electron states with lowest energy will be filled. For the zigzag wall there is a profound difference between two cases—when the midgap band Eq. (10) overlaps the negative energy bulk band ($\mu/t < 3/2$) and when it does not ($\mu/t > 3/2$). When it does not, the neutral ground state has the negative energy bulk states Eq. (8) and the lower domain-wall band Eq. (9) completely filled. There is a gap (which could be small) between the top of the filled lower bulk band and the empty upper domain-wall band Eq. (10). When they do overlap [as depicted in Fig. 2(a)], some of the upper domain-wall band Eq. (10) will fill before all of the negative energy bulk states are filled—the domain wall will borrow some electrons from the bulk. It will then have a finite charge density and a partially filled upper band which will behave like a one-dimensional metal, even in neutral graphene.

The armchair domain wall is depicted in Fig. 1(c). It is oriented along the y axis. It has the same gapped bulk branches Eq. (8) as the zigzag wall. We look for wave functions which decay exponentially in distance $|A_x|$, $|B_x|$ from the wall. They are superpositions of two plane waves propagating along the wall with wave vectors k_y and $k_y + 2\pi/3$. (This corresponds to mixing of the graphene valleys.) The spectrum has four bands depicted in Fig. 2(b). It is $E = \pm\sqrt{t^2\sin^2\frac{3a}{2}k_y + \mu^2 K(k_y)}$, where $K(1 - e^{-\sqrt{3}ak_x^{(1)}}) \times (1 - e^{-\sqrt{3}ak_x^{(2)}}) = (1 + e^{-(\sqrt{3}a/2)(k_x^{(1)} + k_x^{(2)})})^2$. $k_x^{(1)}$ and $k_x^{(2)}$

must be determined by solving two equations: $K - 1 = \frac{t^2}{\mu^2}(\cosh\frac{\sqrt{3}a}{2}k_x^{(1)} + \cosh\frac{\sqrt{3}a}{2}k_x^{(2)})^2$ and $\cosh\frac{\sqrt{3}a}{2}k_x^{(2)} = \cosh\frac{\sqrt{3}a}{2}k_x^{(1)} + \cos\frac{3a}{2}k_y$, $|k_y| \le \frac{\pi}{3a}$. We can find explicit solutions in the large and small μ/t limits. When μ/t is large, the spectrum is concentrated at four values:

$$\mu \gg t\text{: } E \approx \begin{cases} \pm(\mu + t + \cdots) \\ \pm(\mu - t + \cdots). \end{cases} \tag{11}$$

Two of these are inside the bulk spectrum and two are in the gap. They agree with what we would expect when μ is large, where there are two energy levels, $-\mu$ and $+\mu$, corresponding to electrons sitting on the black or white dots, respectively, in Fig. 1(c). Then, the leading effect of turning on a small t is that the pairs of adjacent degenerate states that exist at the location of the domain wall are split by tunneling. Now, unlike for the zigzag, there are degenerate pairs with both zeroth order energies $+\mu$ and $-\mu$. The splitting produces four domain-wall energies in Eq. (11). Further corrections are of order t^2/μ, which, when taken into account, spread the four levels into four bands that then get wider as t gets larger.

In the limit $\mu \ll t$, we also find four bands:

$$\mu \ll t\text{: } E \approx \begin{cases} \pm\sqrt{\mu^2 + 4t^2(1 + \cos\frac{3a}{2}k_y)} \\ \pm\sqrt{t^2\sin^2\frac{3a}{2}k_y + \frac{\mu^4}{t^2}\frac{4}{(4-\cos^2\frac{3a}{2}k_y)^2}}. \end{cases} \tag{12}$$

As depicted in Fig. 2, the upper and lower band are entirely within the upper and lower bulk bands. The middle two overlap the bulk energy gap and themselves have a gap which is much smaller than the bulk gap, $\Delta E = 4\mu^2/3t \ll 2\mu$. For a typical small $\mu \sim 25$ meV and $t \sim 2.7$ eV, the gap in the midband states is tiny, less than 1 meV. This existence of a gap in the spectrum of states bound to the domain wall is compatible with the continuum analysis since the gap is vanishingly small in the continuum limit, scaling to zero with the lattice spacing a, so it is not visible to the continuum Dirac Hamiltonian. Intuition for the gap in the armchair spectrum can also be gained by studying Fig. 1(c). Because of the alternating pattern of pairs of black and pairs of white dots as one follows the domain wall, the translation symmetry along the domain wall is by two lattice spacings, rather than one. This reduced translation symmetry will gap the domain-wall spectrum, analogous to gapping created by a Peierls instability. What is surprising here is that the gap is so small.

In summary, we have shown that the simplest domain walls in gapped graphene can have interesting electronic properties. A partially filled domain-wall band will behave like a one-dimensional metal. The continuum analysis suggests that similar behavior can be expected for other types of domain walls, such as those arising from reversing the pattern of a lattice distortion. Analysis of the details of the spectrum in those cases is left to future work. They could also occur in other materials which have a Dirac spectrum, such as the hypothetical flux phases of a square lattice where vortices have recently been discussed [26] and where domain walls, some of which would support zero modes, should exist.

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