## PHYSICS 231

## Homework 4, Question 4, Graphene

It has recently become possible to produce samples of graphene one atom thick. A single layer of graphene consists carbon atoms in the form of a honeycomb lattice. There are four valence electrons (two 2s and two 2p electrons). Three of those participate in the chemical bonding and so are in bands well below the Fermi energy. We therefore just consider the bands formed by the one remaining electron. We assume a tight-binding model in which the electron hops between neighboring atoms.

The lattice structure is as shown in Fig. 1. We denote the spacing between neighboring atoms by a.

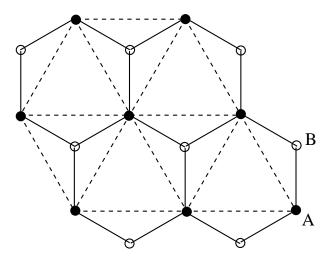


Figure 1: The solid lines indicate the crystal structure of graphene. The basis has two atoms, labeled A and B. The Bravais lattice (consider, e.g, the lattice formed by the A atoms shown by dashed lines) is triangular with a Bravais lattice spacing  $2 \times \sin 60^{\circ} \times a = \sqrt{3}a$ , where a is the spacing between neighboring atoms.

- a. There are two atoms per unit cell so 1 band will be filled.
- b. The Bravais lattice is the same as the lattice formed by all the A atoms, say. As shown in Fig. 1 this is a triangular lattice with lattice spacing  $\sqrt{3}a$ .
- c. From Fig. 1, we see that two basis vectors of the Bravais lattice are

$$\mathbf{a}_1 = \sqrt{3} \, a \, (1, 0), \qquad \mathbf{a}_2 = a \, (\sqrt{3}/2, \, 3/2).$$
 (1)

The Bravais lattices,  $\mathbf{b}_1, \mathbf{b}_2$ , are defined such that

$$\mathbf{b} \cdot \mathbf{a}_{i} = 2\pi \, \delta_{ii} \,. \tag{2}$$

To determine them, either consider the formulae discussed in class for three dimensions, with the third basis vector  $a_3 = \hat{z}$ , a unit vector in the z direction, or just figure it out. The answer is

$$\mathbf{b}_1 = 2\pi \, \frac{\hat{\mathbf{z}} \times \mathbf{a}_2}{|\mathbf{a}_1 \times \mathbf{a}_2|} = \boxed{\frac{2\pi}{3} \, \frac{1}{a} \, (\sqrt{3}, -1),} \tag{3}$$

$$\mathbf{b}_2 = 2\pi \, \frac{\hat{\mathbf{z}} \times \mathbf{a}_1}{|\mathbf{a}_1 \times \mathbf{a}_2|} = \boxed{\frac{4\pi}{3} \, \frac{1}{a} \, (0, 1).}$$
(4)

These basis vectors are of equal length and at  $60^{\circ}$  so the reciprocal lattice is a triangular lattice. The first Brillouin zone is shown in Fig. 2. The distance OA to the center of the edge of the zone is  $(1/2)\mathbf{b}_1 = \boxed{\frac{1}{3}\frac{2\pi}{a}}$ . The distance OC to the corner of the zone is  $OA/\sin 60^{\circ} = \boxed{\frac{2}{3\sqrt{3}}\frac{2\pi}{a}}$ .

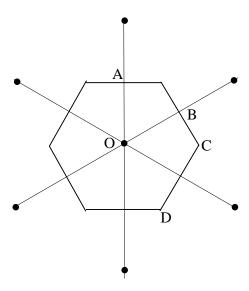


Figure 2: The solid circles indicate points of the reciprocal lattice. The hexagon is the boundary of the (first) Brillouin zone.

d. The tight-binding Hamiltonian is

$$\mathcal{H} = -t \sum_{\mathbf{R}, \delta} c_{\mathbf{R} + \delta}^{\dagger} c_{\mathbf{R}}, \tag{5}$$

where **R** is a lattice point, and  $\delta$  is the displacement to a neighboring lattice point. In other words, an electron at site **R** can hop to any of the neighboring sites, i.e. if  $|\mathbf{R}\rangle$  denotes a state with one electron which is at **R** we have

$$\langle \mathbf{R} + \boldsymbol{\delta} | \mathcal{H} | \mathbf{R} \rangle = -t, \tag{6}$$

and, if  $\mathbf{R}$  and  $\mathbf{R}'$  are not neighbors, then

$$\langle \mathbf{R}' | \mathcal{H} | \mathbf{R} \rangle = 0. \tag{7}$$

We look for eigenvalues of the Hamiltonian. Consider a state with amplitude  $\psi_{\mathbf{R}}$  for the electron to be at site labeled by  $\mathbf{R}$ . The eigenvalue equation is then

$$\mathcal{H} \begin{pmatrix} \psi_{\mathbf{R}_1} \\ \psi_{\mathbf{R}_2} \\ \vdots \\ \psi_{\mathbf{R}_N} \end{pmatrix} = \epsilon \begin{pmatrix} \psi_{\mathbf{R}_1} \\ \psi_{\mathbf{R}_2} \\ \vdots \\ \psi_{\mathbf{R}_N} \end{pmatrix} . \tag{8}$$

Considering one row of this equation we have

$$-t\sum_{\delta}\psi_{\mathbf{R}+\delta} = \epsilon\psi_{\mathbf{R}}. \tag{9}$$

We look for amplitudes which vary like  $e^{i\mathbf{k}\cdot\mathbf{r}}$ . There will be different amplitudes  $\psi_A$  and  $\psi_B$  on sublattices A and B, so

$$\psi_{\mathbf{R}} = \begin{cases} \psi_A e^{i\mathbf{k}\cdot\mathbf{r}}, & (\mathbf{R} \in A), \\ \psi_B e^{i\mathbf{k}\cdot\mathbf{r}}, & (\mathbf{R} \in B). \end{cases}$$
 (10)

An atom on sublattice A has neighboring atoms, all on sublattice B, at displacements  $(0,a), (\sqrt{3}a/2, -a/2), (-\sqrt{3}a/2, -a/2)$ . An atom on sublattice B has three neighbors on sublattice A at displacements  $(0,-a), (\sqrt{3}a/2,a/2), (-\sqrt{3}/2,a/2)$ . Hence the eigenvalue  $\epsilon$  and the amplitudes  $\psi_A$  and  $\psi_B$  are determined, for each wavevector  $\mathbf{k}$ , from the two equations

$$-t\left(e^{ik_ya} + 2e^{-ik_ya/2}\cos\frac{\sqrt{3}}{2}k_xa\right)\psi_B = \epsilon\,\psi_A\,,\tag{11a}$$

$$-t\left(e^{-ik_y a} + 2e^{ik_y a/2}\cos\frac{\sqrt{3}}{2}k_x a\right)\psi_A = \epsilon\psi_B.$$
 (11b)

The eigenvalues are given by

$$\epsilon = \pm t \left| e^{ik_y a} + 2e^{-ik_y a/2} \cos \frac{\sqrt{3}}{2} k_x a \right|.$$
 (12)

The absolute value can be expanded out as

$$\epsilon = \pm t \left[ \left( \cos(k_y a) + 2\cos(\frac{1}{2}k_y a) \cos(\frac{\sqrt{3}}{2}k_x a) \right)^2 + \left( \sin(k_y a) - 2\sin(\frac{1}{2}k_y a) \cos(\frac{\sqrt{3}}{2}k_x a) \right)^2 \right]^{1/2},$$
(13)

but Eq. (12) will be more useful for us.

Along the x direction, which is to the corner of the Brillouin zone, Eq. (12) is clearly

$$\epsilon = \pm t \left[ 1 + 2\cos\left(\frac{\sqrt{3}}{2}k_x a\right) \right]. \tag{14}$$

The result is plotted in the left part of Fig. 3. We see that the bands meet at the corner of the zone (the largest value of  $k_x$ ), point C in Fig. 2. Along the y direction, which is to the center of the edge of the Brillouin zone, Eq. (12) can be simplified to

$$\epsilon = \pm t \left[ 5 + 4\cos\left(\frac{3}{2}k_y a\right) \right] . \tag{15}$$

This is plotted in the right part of Fig. 3. At the zone edge the energies are  $\pm 1$ . This corresponds to point A in Fig. 2.

The maximum and minimum energies are  $\pm 3$ , and occur at  $\mathbf{k} = 0$ .

e. There are two bands one with positive energy and one with negative energy. They touch at the corners of the Brillouin zone. Because there are two electrons per unit cell the lower band is completely filled and the upper one completely empty. Hence the Fermi energy is at  $\epsilon_F = 0$ .

We want to compute the dispersion relation in the vicinity of the zone corners where the energy tends to zero. We write

$$\mathbf{k} = \mathbf{K} + \mathbf{q} \tag{16}$$

where **K** is the wavevector at the zone corner,  $\mathbf{K} = (4\pi/(3\sqrt{3}a), 0)$  for example, and we will assume that **q** is small.

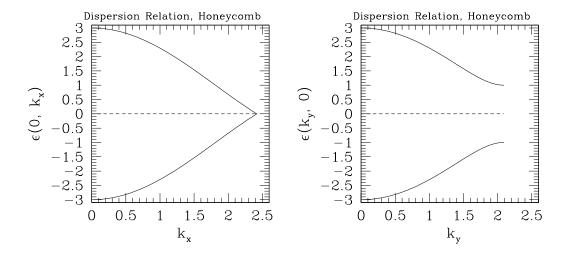


Figure 3: The dispersion relation in graphene along two directions in the Brillouin zone. The left figure is in the direction to the corner of the zone, and the right figure is in the direction to the center of the edge of the zone.

We write the Hamiltonian for a fixed- $\mathbf{k}$ , Eq. (11), as

$$\mathcal{H}(\mathbf{k}) = t \begin{pmatrix} 0 & F(k_x, k_y) \\ F^*(k_x, k_y) & 0 \end{pmatrix}$$
 (17)

where

$$F(k_x, k_y) = e^{ik_y a} + 2e^{-ik_y a/2} \cos \frac{\sqrt{3}}{2} k_x a.$$
 (18)

To lowest order in q we have, after a little algebra,

$$F(k_x, k_y) = \frac{3}{2} a (q_x + iq_y) , \qquad (19)$$

so

$$\mathcal{H}(\mathbf{k}) = \hbar v \, \boldsymbol{\sigma} \cdot \mathbf{q},\tag{20}$$

where the speed v is given by

$$v = \frac{3}{2} \frac{at}{\hbar}, \tag{21}$$

and  $\sigma_x$  and  $\sigma_y$  are Pauli spin matrices. Hence the eigenvalues of the  $\mathcal{H}(\mathbf{k})$  are

$$\epsilon = \pm \hbar v q \,. \tag{22}$$

Hence we have "massless" excitations with a linear dispersion. The speed v is, of course, much less than the speed of light. The cone-like energy surface is shown in Fig. 5.

f. There are pockets of low energy excitations near the corner of the Brillouin zone, see Fig. 6

Hence there are are two pockets of low energy excitations, one for each of the two inequivalent points on the Brillouin zone boundary. Let us compute the density of states in this region (i.e. energy close to zero). We consider unit area, and, for now, just one pocket and one spin state. As

## Dispersion relation of graphene $_{k}^{\mu}$

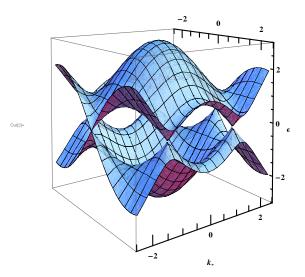


Figure 4: The dispersion relation in graphene. There are two bands, one with positive energy, and the other with negative energy, which touch at the zone corners.

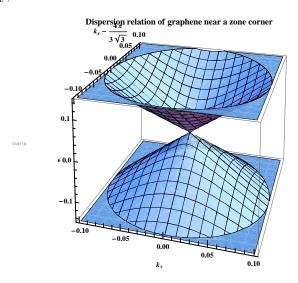


Figure 5: The dispersion relation in graphene near a corner of the Brillouin zone showing the linear dispersion.

above, we define  $\mathbf{k} = \mathbf{K} + \mathbf{q}$ , and assume  $\mathbf{q}$  is small. Counting states in a (two-dimensional) box, as we have done several time before in this course, the number of states with energy in between  $\epsilon$  and  $\epsilon + d\epsilon$  can be written as

$$\rho(\epsilon) d\epsilon = \frac{1}{(2\pi)^2} 2\pi q dq.$$
 (23)

Assuming that  $\epsilon$  is positive, we have  $\epsilon = \hbar vq$ , where v is the speed of the low energy (massless) particles, so Eq. (23) gives  $\rho(\epsilon) = \hbar^2 \epsilon/2\pi v^2$ . If  $\epsilon$  is negative then  $\epsilon = -\hbar vq$  and combining both possibilities gives the final result for the density of states per unit area (per pocket and per spin

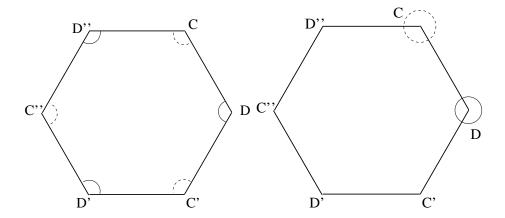


Figure 6: The points C, C', and C'' at the corners of the zone are equivalent because they are connected by a reciprocal lattice vector. Similarly for points D, D', and D''. However, C is not equivalent to D, so there are two distinct corners of the Brillouin zone. Consequently, in the repeated zone (right hand figure) one sees that there are two separate pockets of low energy excitations.

direction) to be  $\rho(\epsilon) = \frac{\hbar^2}{2\pi v^2} |\epsilon| \,. \eqno(24)$ 

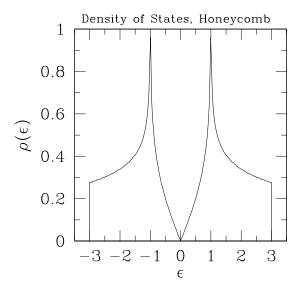


Figure 7: The density of states of graphene computed numerically. Note the linear variation near  $\epsilon=0$ . This comes from the linear dispersion near the corners of the Brillouin zone, as discussed in the text. There are also Van Hove singularities. The discontinuity at the end points  $\epsilon=\pm 3$  comes from a maximum or minimum of the dispersion relation in two dimensions. (These are at  $\mathbf{k}=0$ ). The logarithmic divergence at  $\epsilon=\pm 1$  comes from a saddle point in the dispersion relation at the middle of the edges of the boundary of the Brillouin zone, point A in Fig. 2.

The density of states of graphene, computed numerically, is shown in Fig. 7. The linear density of states near zero energy is clearly seen, as is the discontinuity at the top of the upper band and bottom of the lower band (an example of a Van Hove singularity in two dimensions at a maximum or minimum of the dispersion relation). One can also see a logarithmic divergence in the density of states, which is a Van Hove singularity coming from saddle points in the dispersion relation at points A and B in the figure of the Brillouin zone, Fig. 2.

Hence graphene is on the border between a metal, which has a finite density of states at the Fermi energy, and an insulator which has a band gap. It is perhaps best thought of as a semi-metal (which is a metal with a small density of states at the Fermi energy). Alternatively, one could perhaps view it from the other direction as a semiconductor with a vanishing bandgap.