

### Exercise 5.1 Graphene

We want to calculate the  $\pi$ -energy bands of graphene using the tight-binding method. Those bands are due to electrons in the  $2p_z$  orbitals. Graphene has two inequivalent carbon atoms per unit cell, which we call  $A$  and  $B$ .

The primitive lattice vectors  $\mathbf{a}_i$  join atoms on the same sublattice ( $A$  or  $B$ ), so that the reference points of the unit cells (the  $A$ -atoms in figure 1) form a triangular lattice. Setting the lattice constant  $a$  to unity they are given by

$$\begin{aligned}\mathbf{a}_1 &= \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right) \\ \mathbf{a}_2 &= \left( \frac{\sqrt{3}}{2}, \frac{-1}{2} \right).\end{aligned}\tag{1}$$

The reciprocal lattice vectors  $\mathbf{c}_i$  can be found as usually by demanding that they satisfy

$$\mathbf{c}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}.\tag{2}$$

This leads to

$$\begin{aligned}\mathbf{c}_1 &= \frac{4\pi}{\sqrt{3}} \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right) \\ \mathbf{c}_2 &= \frac{4\pi}{\sqrt{3}} \left( \frac{1}{2}, \frac{-\sqrt{3}}{2} \right)\end{aligned}\tag{3}$$

With the reciprocal lattice vectors the Brillouin zone can be constructed and is seen to be a regular hexagon (figure 1). Note that after identifying points that differ by a reciprocal lattice vector only two of the corners are inequivalent.

Next we find the general form of the tight-binding model for the bands originating in the  $p_z$ -orbitals when only nearest neighbor hopping is taken into account. The  $p_z$ -orbitals are symmetric under the rotations of the plane so that the hopping matrix elements do not depend on the direction. Hence we have only one hopping parameter, which we denote by  $t$ . Furthermore, every  $A$ -atom has neighbors in  $B$  only. The onsite terms have to be the same on both sublattices, so that they can be absorbed into the chemical potential (we work at fixed filling with two electrons per unit cell).

To describe the hopping terms we define the vectors

$$\begin{aligned}\mathbf{b}_1 &= \left( \frac{1}{\sqrt{3}}, 0 \right), \\ \mathbf{b}_2 &= \left( \frac{-1}{2\sqrt{3}}, \frac{1}{2} \right), \text{ and} \\ \mathbf{b}_3 &= \left( \frac{-1}{2\sqrt{3}}, \frac{-1}{2} \right)\end{aligned}\tag{4}$$

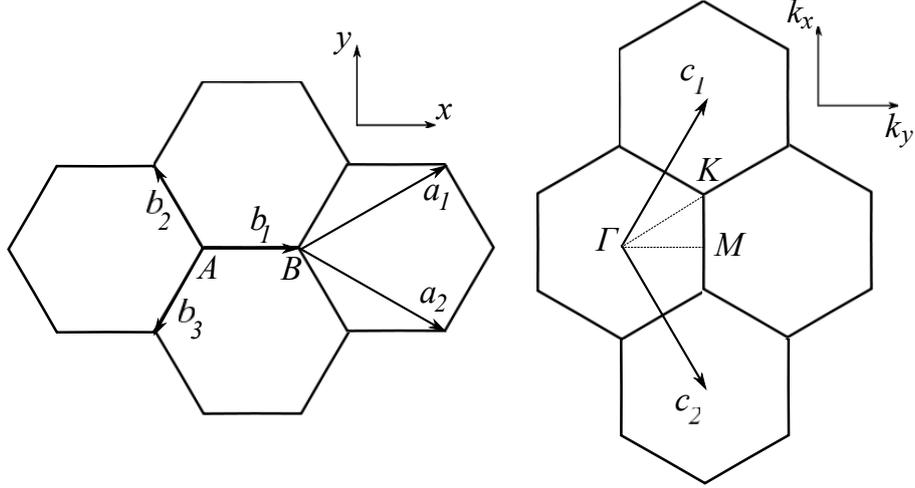


Figure 1: Left: Primitive lattice vectors for the honeycomb lattice. The vectors join points on one triangular sublattice. Right: Hexagonal Brillouin zone constructed from the reciprocal lattice vectors  $\mathbf{c}_1$  and  $\mathbf{c}_2$ .

that point from an  $A$  atom to its three nearest neighbors. Denoting the position of the  $i$ -th atom on sublattice  $A$  by  $\mathbf{R}_{a,i}$ , the Hamiltonian is given by

$$\mathcal{H} = t \sum_i \sum_{j=1}^3 [c^\dagger(\mathbf{R}_{a,i}) c(\mathbf{R}_{a,i} + \mathbf{b}_j) + \text{h.c.}] . \quad (5)$$

Now we use the Fourier transform given on the exercise sheet,

$$\begin{aligned} c(\mathbf{R}_{a,i}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in \text{BZ}} \tilde{a}_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_{a,i}} \\ c(\mathbf{R}_{b,i}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in \text{BZ}} \tilde{b}_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_{b,i}} , \end{aligned} \quad (6)$$

to find

$$\begin{aligned} \mathcal{H} &= \frac{t}{N} \sum_{\mathbf{k}, \mathbf{k}' \in \text{BZ}} \tilde{a}_{\mathbf{k}}^\dagger \tilde{b}_{\mathbf{k}'} \sum_i e^{i\mathbf{R}_{a,i} \cdot (\mathbf{k}' - \mathbf{k})} \sum_{j=1}^3 e^{i\mathbf{k}' \cdot \mathbf{b}_j} + \text{h.c.} \\ &= t \sum_{\mathbf{k} \in \text{BZ}} \begin{pmatrix} \tilde{a}_{\mathbf{k}}^\dagger \\ \tilde{b}_{\mathbf{k}}^\dagger \end{pmatrix} \begin{pmatrix} 0 & \sum_j e^{i\mathbf{k} \cdot \mathbf{b}_j} \\ \sum_j e^{-i\mathbf{k} \cdot \mathbf{b}_j} & 0 \end{pmatrix} \begin{pmatrix} \tilde{a}_{\mathbf{k}} \\ \tilde{b}_{\mathbf{k}} \end{pmatrix} . \end{aligned} \quad (7)$$

The dispersion is found by diagonalizing the  $2 \times 2$ -matrix Hamiltonian which yields

$$\epsilon_{\mathbf{k}} = \pm t \sqrt{3 + 4 \cos\left(\frac{\sqrt{3}}{2} k_x\right) \cos \frac{k_y}{2} + 2 \cos k_y} . \quad (8)$$

The two bands are shown in figure 2. With two electrons per unit cell the lower band is completely filled whereas the upper band is empty, so that  $\mu = 0$ .

Now we can find the position of the Fermi points displayed in figure 2 by solving

$$\sum_{j=1}^3 e^{i\mathbf{k} \cdot \mathbf{b}_j} = 0 . \quad (9)$$

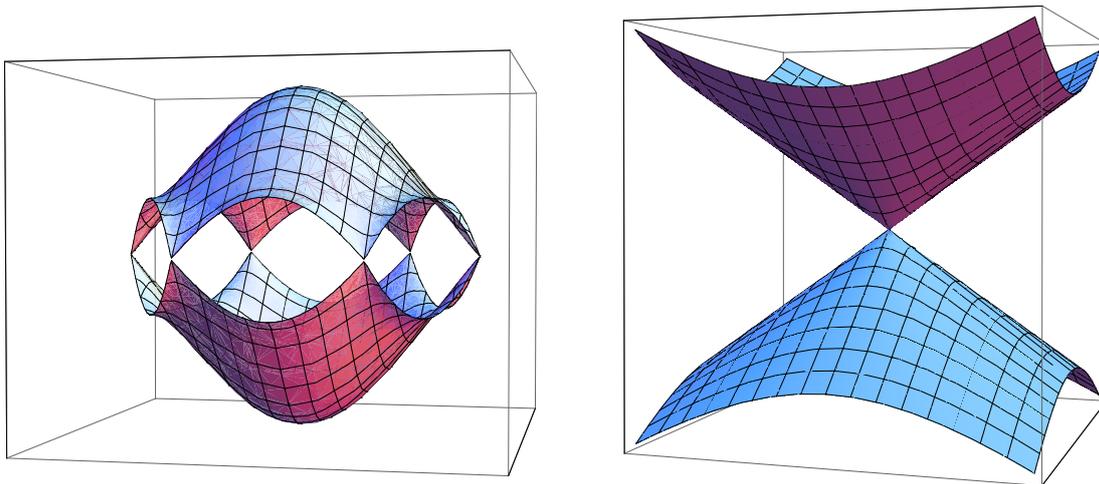


Figure 2: *left*: Dispersion of the two bands of graphene. At half-filling (one electron per  $p_z$ -orbital), the Fermi 'surface' consists of two points at the two inequivalent corners of the Brillouin zone. *right*: Dirac cone in the vicinity of the point  $\mathbf{k} = (2\pi/\sqrt{3}, 2\pi/3)$

Inserting the definition of  $\mathbf{b}_j$  in (4) and writing equations for the real and imaginary parts separately we have

$$\sin\left(\frac{\sqrt{3}}{2}q_x\right) = 0 \text{ and} \quad (10)$$

$$\cos\left(\frac{\sqrt{3}}{2}q_x\right) \sin\left(\frac{q_y}{2}\right) = \frac{-1}{2}, \quad (11)$$

which has as solutions  $\mathbf{q}_1 = \left(\frac{2\pi}{\sqrt{3}}, \frac{2\pi}{3}\right)$  and  $\mathbf{q}_2 = \left(0, \frac{4\pi}{3}\right)$ , i.e. the two inequivalent corners of the Brillouin zone. Note that both bands touch at these points. Next we obtain the low energy Hamiltonian by expanding (7) to linear order around the corners of the Brillouin zone, so that

$$\mathcal{H}_{\text{eff}} \approx -\frac{3\sqrt{3}t}{8\pi} \sum_{\mathbf{k}} \sum_{i=1}^2 \Psi_i^\dagger(\mathbf{k}) (\hat{\sigma}_x \mathbf{q}_i \cdot \mathbf{k} + \hat{\sigma}_y (\hat{\epsilon} \mathbf{q}_i) \cdot \mathbf{k}) \Psi_i(\mathbf{k}), \quad (12)$$

where  $\hat{\epsilon}$  is the antisymmetric tensor and  $\sigma_i$  are the Pauli matrices. The  $\Psi_i$  describe the electrons at the Fermi point  $\mathbf{q}_i$ , and have two components for each  $i$  describing the upper and the lower band. The momenta  $\mathbf{k}$  are relative to the Fermi points (i.e. shifted by  $\mathbf{q}_i$ ). The corresponding low energy dispersion is  $E = \pm v_F |k|$ , which resembles the relativistic energy-momentum relation  $E^2 = m_0 c^4 + p^2 c^2$  for a massless particle and the speed of light replaced by the Fermi velocity. In fact, (12) is equivalent to the Dirac equation in  $(2+1)$ -dimensional spacetime. The Fermi sea below each Fermi point corresponds to the Dirac sea (vacuum for anti-particles), and the two Fermi points correspond to the two different chiralities of spin-1/2 particles in relativistic QFT. This fact allows studying some of the more puzzling aspects of the Dirac equation (such as the Klein paradox, see e.g. M. I. Katsnelson et al., *Chiral tunnelling and the Klein paradox in graphene*, Nature Physics **2**, 620 - 625 (2006)).

## Exercise 5.2 Specific Heat of a Semiconductor and a Metal

- a) We assume that, for  $k_B T \ll E_g$ , only the band edges are important and parametrize the dispersion by effective masses,

$$\varepsilon_v(k) = -\frac{\hbar^2 k^2}{2m_v}, \quad (13)$$

$$\varepsilon_c(k) = E_g + \frac{\hbar^2 k^2}{2m_c}. \quad (14)$$

It is a matter of convention to define the zero in energy to the upper band edge of the valence band. Instead, we could have also measured the energy with respect to the middle of the band gap.

The number of electrons must be equal to the number of holes. This enables us to determine the chemical potential through

$$0 = \int_{\text{BZ}} \frac{d^3 k}{4\pi^2} \{1 - n_F[\varepsilon_v(k)]\} - \int_{\text{BZ}} \frac{d^3 k}{4\pi^2} n_F[\varepsilon_c(k)] \quad (15)$$

$$= \int_{\text{BZ}} \frac{d^3 k}{4\pi^2} \left\{ \frac{1}{e^{-[\varepsilon_v(k)-\mu]/k_B T} + 1} - \frac{1}{e^{[\varepsilon_c(k)-\mu]/k_B T} + 1} \right\} \quad (16)$$

$$\approx \int_{\text{BZ}} \frac{d^3 k}{4\pi^2} \left\{ e^{[\varepsilon_v(k)-\mu]/k_B T} - e^{-[\varepsilon_c(k)-\mu]/k_B T} \right\}, \quad (17)$$

where, in the last step, we have assumed  $\mu \gg k_B T$  and  $E_g - \mu \gg k_B T$ , which gives

$$\frac{1}{e^{\epsilon/k_B T} + 1} \approx 1 + e^{-\epsilon/k_B T}, \quad (18)$$

with  $\epsilon \gg k_B T$ .

From the equation (17) we find

$$0 = \frac{(2k_B T)^{3/2}}{4\pi^3 \hbar^3} \left( \int_{\mathbb{R}^3} d^3 y e^{-y^2} \right) \left\{ m_v^{3/2} e^{-\mu/k_B T} - m_c^{3/2} e^{(\mu-E_g)/k_B T} \right\}, \quad (19)$$

where we have used the fact that the Gaussian integral converges very rapidly so that we can extend the integral over the first Brillouin zone to an integral over  $\mathbb{R}^3$ .

The first two factors in the last equation are strict positive, so the last factor must vanish to fulfill the equation. Hence we find

$$\mu = \frac{E_g}{2} + \frac{3}{4} k_B T \log \left( \frac{m_v}{m_c} \right). \quad (20)$$

For  $T = 0$ , the chemical potential is in the middle of the band gap.

We first calculate the number of excited electrons  $n_e(T)$ , which is equal to the number of holes, where we again can extend the region of integration from the first Brillouin zone to the entire real space in order to perform Gaussian integration.

$$n_h(T) = \int_{\text{BZ}} \frac{d^3 k}{4\pi^3} \{1 - n_F[\varepsilon_v(k)]\} \approx \int_{\text{BZ}} \frac{d^3 k}{4\pi^3} e^{[\varepsilon_v(k)-\mu]/k_B T} \quad (21)$$

$$= e^{-\mu/k_B T} \left( \frac{m_v k_B T}{2^{1/3} \pi \hbar^3} \right)^{3/2} = \left( \frac{k_B T}{2^{1/3} \pi \hbar^3} \right)^{3/2} (m_v m_c)^{3/4} e^{-E_g/2k_B T}. \quad (22)$$

In the last step, we have inserted  $\mu$  from Eq. (20).

Next, we calculate the total energy of electrons and holes

$$\begin{aligned} E_v &= \int_{\text{BZ}} \frac{d^3k}{4\pi^3} [-\varepsilon_v(k)] \{1 - n_F[\varepsilon_v(k)]\} \approx \int_{\text{BZ}} \frac{d^3k}{4\pi^3} \frac{\hbar^2 k^2}{2m_v} e^{[\varepsilon_v(k) - \mu]/k_B T} \\ &= \frac{3}{2} \left( \frac{k_B T}{2^{1/3} \pi \hbar^3} \right)^{3/2} (m_v m_c)^{3/4} e^{-E_g/2k_B T} k_B T = \frac{3}{2} n_h(T) k_B T, \end{aligned} \quad (23)$$

$$\begin{aligned} E_c &= \int_{\text{BZ}} \frac{d^3k}{4\pi^3} \varepsilon_c(k) n_F[\varepsilon_c(k)] \approx \int_{\text{BZ}} \frac{d^3k}{4\pi^3} \left( \frac{\hbar^2 k^2}{2m_v} + E_g \right) e^{[\mu - \varepsilon_c(k)]/k_B T} \\ &= \left( \frac{3}{2} k_B T + E_g \right) \left( \frac{k_B T}{2^{1/3} \pi \hbar^3} \right)^{3/2} (m_v m_c)^{3/4} e^{-E_g/2k_B T} = \left( \frac{3}{2} k_B T + E_g \right) n_e(T). \end{aligned} \quad (24)$$

Note that the energy of holes enters Eq. (23) with the negative value of the energy of the electrons in the valence band,  $-\varepsilon_v(k)$ .

In total, we have

$$E = n(T) \left[ \frac{3}{2} k_B T + \frac{E_g}{2} \right], \quad (25)$$

with the total number of excitations  $n(T) = n_e(T) + n_h(T)$ .

The specific heat is thus given by a ideal gas-like part plus a correction,

$$C = \frac{3}{2} n(T) k_B + \left[ \frac{3}{2} k_B T + \frac{E_g}{2} \right] \frac{\partial n(T)}{\partial T}. \quad (26)$$

We see that the specific heat of a semiconductor is given by a contribution similar to the specific heat of an ideal gas of excitations that are already present in the system due to thermal excitation, plus an additional contribution originating from the excitation of new particle hole pairs  $\sim \frac{\partial n(T)}{\partial T}$ .

Given that

$$\frac{\partial n(T)}{\partial T} = \left( \frac{3}{2} + \frac{E_g}{2k_B T} \right) \frac{n(T)}{T}, \quad (27)$$

we can rewrite the specific heat as

$$C = \left[ \frac{15}{4} k_B + \frac{E_g}{T} \left( \frac{3}{2} + \frac{E_g}{4k_B T} \right) \right] n(T). \quad (28)$$

Thus, the part of the specific heat originating from the excitation of additional particles dominates over the ideal gas-like part for small temperatures!

- b) The density of states for the dispersion relation  $\epsilon_{\mathbf{k}}$  including the spin degeneracy is given by

$$D(\epsilon) = \frac{2}{V} \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}}) = \frac{2}{(2\pi)^3} \int d^3\mathbf{k} \delta\left(\epsilon - \frac{\hbar^2 \mathbf{k}^2}{2m}\right) \quad (29)$$

where we went from a summation to an integral by approximating  $\sum_{\mathbf{k}} \approx V/(2\pi)^3 \int d^3\mathbf{k}$ . We change to spherical coordinates and get that the density of states at the Fermi energy  $E_F$  is

$$D(E_F) = \frac{8\pi}{(2\pi)^3} \int dk k^2 \delta\left(E_F - \frac{\hbar^2 k^2}{2m}\right) = \frac{1}{\pi^2} \int \underbrace{dk}_{=d(k^2)} \frac{2k}{2} \frac{k \delta(2mE_F/\hbar^2 - k^2)}{\hbar^2/2m} \quad (30)$$

where we used that  $\delta(\alpha x) = \delta(x)/|\alpha|$ . Thus, we obtain

$$D(E_F) = \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2mE_F}{\hbar^2}} = \frac{mk_F}{\pi^2 \hbar^2} = \frac{3}{2} \frac{n}{E_F} \quad (31)$$

where we used  $k_F = \sqrt[3]{3\pi^2 n}$ . At  $T = 0$  the particle ensity and the energy density can easily be calculated since only states below the Fermi sea are occupied, i.e.

$$n = \sum_{\epsilon_{\mathbf{k}} < E_F} 1 \quad u = \sum_{\epsilon_{\mathbf{k}} < E_F} \epsilon_{\mathbf{k}} \quad (32)$$

but as we increase the temperature also states above the Fermi energy will be occupied. The occupation number of the states in case of Fermions is described by the Fermi-Dirac distribution function  $f_{FD}(\epsilon)$

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}. \quad (33)$$

The particle density becomes then

$$n(\mu, T) = \sum_{\mathbf{k}} f_{FD}(\epsilon_{\mathbf{k}}) = \int d\epsilon f_{FD}(\epsilon) D(\epsilon) \quad (34)$$

and the energy density is

$$u(\mu, T) = \sum_{\mathbf{k}} f_{FD}(\epsilon_{\mathbf{k}}) \epsilon_{\mathbf{k}} = \int d\epsilon f_{FD}(\epsilon) D(\epsilon) \epsilon \quad (35)$$

which can be verified when you substitute  $D(\epsilon)$  using Eq. (29). In order to calculate the specific heat we need the energy density as a function of  $n$  and  $T$ . Therefore, the goal is to invert Eq. (34) which yields  $\mu(n, T)$  and to plug it in  $u(\mu, T)$ . However, this calculation can not be done analytically. That's why we expand first Eq. (35) and (34) for small  $T$  by using the Bohr-Sommerfeld expansion, i.e. we have

$$n(\mu, T) \approx \int_0^{\mu} d\epsilon D(\epsilon) + \frac{\pi^2}{6} (k_B T)^2 D'(\mu) \quad (36)$$

$$u(\mu, T) \approx \int_0^{\mu} d\epsilon D(\epsilon) \epsilon + \frac{\pi^2}{6} (k_B T)^2 [\mu D'(\mu) + D(\mu)]. \quad (37)$$

Since  $\mu \rightarrow E_F$  for  $T \rightarrow 0$ , we approximate  $\int_0^{\mu} h(\epsilon) d\epsilon \approx \int_0^{E_F} h(\epsilon) d\epsilon + (\mu - E_F) \cdot h(E_F)$  and find then

$$n(\mu, T) \approx \int_0^{E_F} d\epsilon D(\epsilon) + \left[ (\mu - E_F) D(E_F) + \frac{\pi^2}{6} (k_B T)^2 D'(E_F) \right] \quad (38)$$

$$u(\mu, T) \approx \int_0^{E_F} d\epsilon D(\epsilon) \epsilon + E_F \left[ (\mu - E_F) D(E_F) + \frac{\pi^2}{6} (k_B T)^2 D'(E_F) \right] + \frac{\pi^2}{6} (k_B T)^2 D(E_F) \quad (39)$$

where we neglected higher order contributions. If we fix the particle density, then the expression in the brackets has to be constant as well. Thus, we find that

$$\mu = E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(E_F)}{D(E_F)} = E_F \left[ 1 - \frac{1}{3} \left( \frac{\pi k_B T}{2E_F} \right)^2 \right]. \quad (40)$$

Combining Eq. (40) with Eq. (39) we can get rid of  $\mu$  and obtain

$$u(n, T) = u_0 + \frac{\pi^2}{6}(k_B T)^2 D(E_F) \quad (41)$$

with a temperature independent energy offset  $u_0$ . Finally, the specific heat is given by

$$c_v = \left( \frac{\partial u}{\partial T} \right)_n = \frac{\pi^2}{3} k_B^2 T D(E_F) = \frac{\pi^2}{2} \left( \frac{k_B T}{E_F} \right) n k_B \quad (42)$$

where we used Eq. (31).