Solid state physics : electrons and phonons

Master Nanosciences (M1) UGA

Lecture notes 2020 by Xavier Blase

5.4 Complements to Chapter 5 : the tight-binding approximation (applications)

5.4.1 The Peierls distorsion : see Exercise 16

Polymers are a concret realization of our 1D chain of atoms. It turns out that it is complicated to have conducting polymers because of a phenomenon called Peierls distortion, that is the transformation of a chain of regularly spaced atoms into a chain of dimers. As a matter of fact, the Nobel Prize in Chemistry 2000 was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa "for the discovery and development of conductive polymers." Exercise 16 explains how this Peierls distorsion transforms the metallic chain of atoms at half-filling into an insulator.
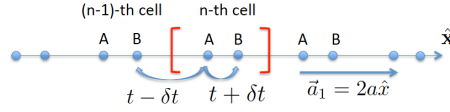
Figure 1: Schematic representation of a Peierls distorsion with spontaneous dimerization, i.e. alternating (short and long) interatomic distances and hoping energies.

This is a variation on the 2-atoms/cell with 1-atomic-orbital/atom exercise treated above but with a hoping energy $(t+\delta t)$ between the atomic orbitals $\phi_A^{at}(r-\tau_A-2na)$ and $\phi_B^{at}(r-\tau_B-2na)$ in the same n-th cell, and $(t-\delta t)$ between the atomic orbital $\phi_A^{at}(r-\tau_A-2na)$ and the atomic orbital $\phi_B^{at}(r-\tau_B-2(n-1)a)$ in the (n-1)-th cell. As such, the onsite energies are not modified but the H_{AB} term now reads:

$$
\begin{aligned}
H_{AB} &= \frac{e^{ik(\tau_B-\tau_A)}}{N_C} \sum_n^{N_C} \left(e^{ik(0)2a}(t+dt) + e^{ik(-1)2a}(t-dt) \right) \\
&= \frac{e^{ik(\tau_B-\tau_A)}}{N_C} N_C e^{-ika} \left(2t\cos(ka) + 2i\delta t\sin(ka) \right) \\
&= e^{ik(\tau_B-\tau_A-a)} \left(2t\cos(ka) + 2i\delta t\sin(ka) \right)
\end{aligned}
$$

The condition to have nonzero (α, β) solutions, that is: $(\varepsilon_k - \varepsilon^0)^2 - |H_{AB}|^2 = 0$

becomes:

$$(\varepsilon_k - \varepsilon^0)^2 = 4t^2\cos^2(ka) + 4\delta t^2\sin^2(ka)$$

that is two $\varepsilon^+(k)$ and $\varepsilon^-(k)$ solutions:

$$\varepsilon_k = \varepsilon^0 \pm 2t\sqrt{\cos^2(ka) + (\delta t/t)^2\sin^2(ka)}$$

The most important feature is that in the standard chain without dimerization there was no gap between the upper and lower bands. Both $\varepsilon^+(k)$ and $\varepsilon^-(k)$ solutions were equal to the onsite energy $\varepsilon 0$ at BZ boundary $\pm\pi/2a$ (see dashed grey line in Fig. 2). After dimerization, since the $\sin(ka)$ function does not cancel at the BZ boundaries $k = \pm\pi/2$, a $4|\delta t|$ gap opens at BZ boundary between the $\varepsilon^+(k)$ and $\varepsilon^-(k)$ bands. At half filling, when only the lowest band is filled by electrons, the highest band being empty, the system becomes more stable upon dimerization since the electrons gain the energy shaded in light grey in Fig. 2. The system distorts spontaneously and becomes an insulator with a gap, killing the conductivity. This is why it is so difficult to have conducting polymers.
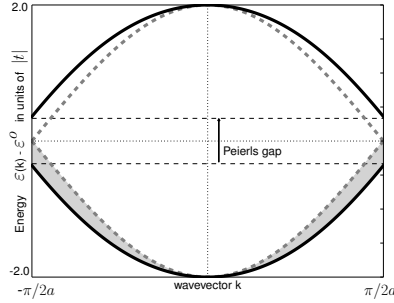
Figure 2: Band structure for the dimerized chain that is compared to the undimerized system (dashed grey line). A gap opens at the BZ boundary with stabilization of the electrons in the lower band (see light grey shaded area). The plot corresponds here to a value $\delta t/t = 0.3$ and we represent $(\varepsilon_k - \varepsilon^0)$ in units of the hoping energy $|t|$ where ε^0 is the onsite energy.

5.4.2   Band structure of the 2D square lattice (the minimal cuprate) : see Exercise 24

The 2D square lattice with interatomic distance "a" is represented in Fig. 3. The primitive lattice vectors are $\mathbf{a}_1 = a\hat{x}$ and $\mathbf{a}_2 = a\hat{y}$. The reciprocal space primitive lattice vectors are $\mathbf{b}_1 = (2\pi/a)\hat{x}$ and $\mathbf{b}_2 = (2\pi/a)\hat{y}$ that verify $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. There is only one atom per unit cell and we further assume in this exercise that there is only one atomic orbital per atom. The only periodic function that

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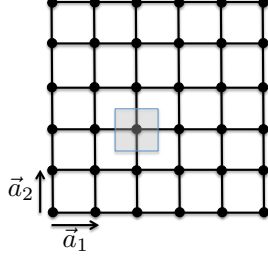
Figure 3: Representation of the 2D square lattice with 1 atom per cell. Each cell (or each atom) is indexed by a lattice vector $\mathbf{R}_{ml} = m\mathbf{a}_1 + l\mathbf{a}_2$. A unit cell is represented in grey shaded. The atom in this cell has four nearest neighbours located $\pm\vec{a}_1$ and $\pm\vec{a}_2$ away.

can be created as a linear combination of atomic orbitals (LCAO) consists in repeating this atomic function periodically in all cells:

$$u(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{ml} \phi^{at}(\mathbf{r} - \mathbf{R}_{ml}) \quad \text{with} \quad \mathbf{R}_{ml} = m\mathbf{a}_1 + l\mathbf{a}_2$$

where we have included the normalization factor $1/\sqrt{N}$ with N the number of cells or atoms. The $\mathbf{R}_{ml}$ are the lattice vectors pointing to all cells, that is to all atoms assuming that each atom is in position $\tau = 0$ in its cell. The only possible Bloch state for a given $\mathbf{k}$-vector[1] is thus of the form (Bloch theorem) :

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r})$$

with $\mathbf{k} = (k_x, k_y)$ in 2D. Using the tight-binding approximation for the phase factor one obtains:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{ml} e^{i\mathbf{k}\cdot\mathbf{R}_{ml}} \phi^{at}(\mathbf{r} - \mathbf{R}_{ml})$$

The energy $\varepsilon(\mathbf{k})$ associated with $\psi_{\mathbf{k}}$ is simply:

$$\varepsilon(\mathbf{k}) = \langle\psi_{\mathbf{k}}|\hat{H}|\psi_{\mathbf{k}}\rangle = \frac{1}{N} \sum_{ml} \sum_{m'l'} e^{i\mathbf{k}\cdot(\mathbf{R}_{m'l'} - \mathbf{R}_{ml})} \langle\phi^{at}(\mathbf{r} - \mathbf{R}_{ml})|\hat{H}|\phi^{at}(\mathbf{r} - \mathbf{R}_{m'l'})\rangle$$

For a given atom indexed by (ml), the sum over (m'l') gives 5 different non-zero contributions:

- (m'l')=(ml) $\Longrightarrow$ the two atomic orbitals are on the same atom and $\langle\phi^{at}(\mathbf{r} - \mathbf{R}_{ml})|\hat{H}|\phi^{at}(\mathbf{r} - \mathbf{R}_{m'l'}) = \varepsilon_0$ the onsite energy

- the atoms in position $\mathbf{R}_{m'l'}$ are first-nearest-neighbours to $\mathbf{R}_{ml}$: this happens for $(\mathbf{R}_{m'l'} - \mathbf{R}_{ml}) = \pm\mathbf{a}_1$ and $\pm\mathbf{a}_2$. For these 4 neighbours, the Hamiltonian matrix elements $\langle\phi^{at}(\mathbf{r} - \mathbf{R}_{ml})|\hat{H}|\phi^{at}(\mathbf{r} - \mathbf{R}_{m'l'}) = t$ the hoping matrix element.

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[1]Note that since for a given $\mathbf{k}$-vector there is only one possible Bloch state, there is no linear combination to be taken here as we did when there were 2 atoms per cell, namely several atomic orbitals per cell.

One obtains thus:

$$\varepsilon(\mathbf{k}) = \frac{1}{N} \sum_{ml} \left(e^{i\mathbf{k}\cdot\mathbf{0}}\varepsilon_0 + e^{i\mathbf{k}\cdot\mathbf{a}_1}t + e^{-i\mathbf{k}\cdot\mathbf{a}_1}t + e^{i\mathbf{k}\cdot\mathbf{a}_2}t + e^{-i\mathbf{k}\cdot\mathbf{a}_2}t \right)$$

$$= \frac{1}{N}N\left(\varepsilon_0 + 2t\cos(k_x a) + 2t\cos(k_y a) \right)$$

$$= \varepsilon_0 + 2t\cos(k_x a) + 2t\cos(k_y a)$$

The corresponding band structure is represented in Fig. 4(Left) within the Brillouin zone: $(k_x, k_y) \in [-\pi/2a, \pi/2a[$. The energy maxima are $\varepsilon_0 \pm 4t$ and the bandwidth is $8|t|$. At half-filling of the band, the Fermi energy is just $\varepsilon_F = \varepsilon_0$. Instead of trying to show the energy for all $\mathbf{k}$-vectors, it is more traditional to show the band structure $\varepsilon(\mathbf{k})$ for $\mathbf{k}$ running along specific directions in the Brillouin zone. This is what is represented in Fig. 4(Right) where $\mathbf{k}$ spans the directions $\mathbf{X\Gamma}$ and $\mathbf{\Gamma M}$. Such a plot gives much less information that Fig. 4(Left) but is much easier to read.

An crucial property is that the ensemble of the $\mathbf{k}$-points such that $\varepsilon(\mathbf{k}) = \varepsilon_0$, namely the Fermi "surface", forms a square at half-filling (see Fig. 4). For exemple the $\mathbf{k}$-points $(0, -\pi/a)$, $(\pi/2a, -\pi/2a)$ and $(\pi/a, 0)$ are all on the Fermi surface and are aligned:

- $\varepsilon(0, -\pi/a) - \varepsilon_0 = t\cos(0) + t\cos(-\pi) = 0$

- $\varepsilon(\pi/2a, -\pi/2a) - \varepsilon_0 = t\cos(\pi/2) + t\cos(-\pi/2) = 0$

- $\varepsilon(\pi/a, 0) - \varepsilon_0 = t\cos(\pi) + t\cos(0) = 0$

As such a large portion of the Fermi surface (one side of the square) can be obtained from another large portion of the Fermi surface (the opposite side of the square) by a translation in reciprocal space of magnitude $\Delta\mathbf{k} = \pm(\pi/a, \pi/a)$ or $\Delta\mathbf{k} = \pm(-\pi/a, \pi/a)$. This property is called **nesting of the Fermi surface**. This means in particular that phonons (vibrational modes) with wavevectors $\Delta\mathbf{k}$ and energy $\hbar\Omega_{vib}$ can scatter ("push") a huge amount of electrons from one side of the BZ to the other side, preserving energy and momentum, and bringing electrons from occupied levels to empty ones as required by Pauli repulsion for fermions. This creates an instability of the Fermi surface by interaction of electrons at the Fermi surface with specific phonons: this instability initiates the superconducting transition.

5.4.3 The graphene band structure: see Exercise 23

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene." Graphene is a 2D materials with 2 carbon atoms (A and B) per unit-cell and an hexagonal structure. We plot below (Fig. 5) in grey a primitive unit cell and the primitive lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. We assume that
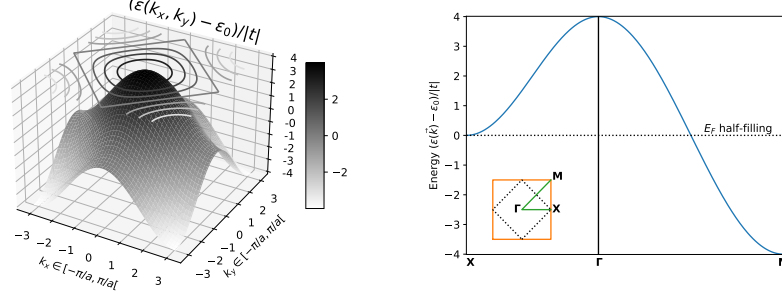
Figure 4: Band structure of the 2D square lattice with one atomic orbital per atom. The energy $\varepsilon(k_x, k_y) - \varepsilon_0$ is represented in units of the hoping energy $|t|$. (Left) Band structure for all **k**-vectors in the BZ. Iso-contours of constant energy are also represented. Notice the square for the $\varepsilon(k_x, k_y) = \varepsilon_0$ isocontour that represents the Fermi surface at half-filling. (Right) Band-structure along specific directions in the BZ as indicated in the Inset by the green lines. Γ is the $(k_x, k_y) = (0, 0)$ zone-center, **X** is $(k_x, k_y) = (\pi/a, 0)$ and **M** is $(k_x, k_y) = (\pi/a, \pi/a)$. The dotted square in the Insert is the ensemble of **k**-vectors such that $\varepsilon(k_x, k_y) = \varepsilon_0$.

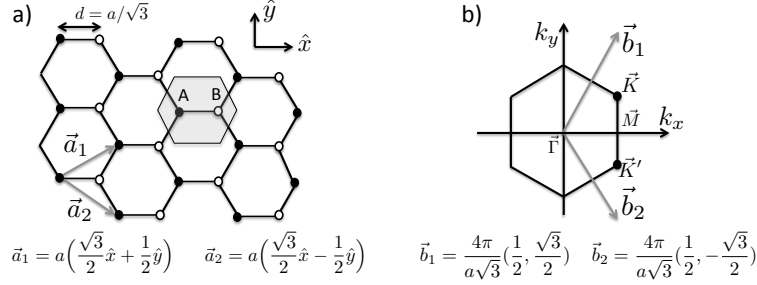there is only one atomic orbital ϕ^{at} per atom, leading to 2 basis Bloch states:

$$\psi_k^A(r) = \frac{1}{\sqrt{N_C}} \sum_{ml} e^{i\mathbf{k}\cdot(\tau_A + \mathbf{R}_{ml})} \phi_A^{at}(r - \tau_A - \mathbf{R}_{ml})$$

$$\psi_k^B(r) = \frac{1}{\sqrt{N_C}} \sum_{ml} e^{i\mathbf{k}\cdot(\tau_B + \mathbf{R}_{ml})} \phi_B^{at}(r - \tau_B - \mathbf{R}_{ml})$$

with $\mathbf{R}_{ml} = m\mathbf{a}_1 + l\mathbf{a}_2$ a lattice vector pointing to a given unit-cell and N_C the total number of unit cells in the crystal. The basis Bloch states ψ_k^A originates from the periodic repetition of the A-type atomic orbitals modulated by the Bloch phase factor, while ψ_k^B originates from the periodic repetition of the B-type atomic orbitals modulated by the Bloch phase factor. As stated above, one can build one basis Bloch state for each atomic orbital in one unit cell.

We must again calculate the Hamiltonian matrix element H_{AB} with here in 2D:

$$H_{AB} = \frac{1}{N_C} \sum_{ml} \sum_{m'l'} e^{-i\mathbf{k}\cdot(\tau_A + \mathbf{R}_{ml})} e^{i\mathbf{k}\cdot(\tau_B + \mathbf{R}_{m'l'})} \langle \phi_A^{at}(r - \tau_A - \mathbf{R}_{ml}) | \hat{H} | \phi_B^{at}(r - \tau_B - \mathbf{R}_{m'l'}) \rangle$$

$$= \frac{e^{i\mathbf{k}\cdot(\tau_B - \tau_A)}}{N_C} \sum_{ml} \sum_{m'l'} e^{i\mathbf{k}\cdot(\mathbf{R}_{m'l'} - \mathbf{R}_{ml})} \langle \phi_A^{at}(r - \tau_A - \mathbf{R}_{ml}) | \hat{H} | \phi_B^{at}(r - \tau_B - \mathbf{R}_{m'l'}) \rangle$$

For the A atom in the cell indexed by the lattice vector $\mathbf{R}_{ml}$ (say the grey shaded unit cell in Fig. 5), there are 3 first-nearest-neighbour B-atoms, one in the same cell with $(\mathbf{R}_{m'l'} - \mathbf{R}_{ml}) = 0$, and 2 others such that $(\mathbf{R}_{m'l'} - \mathbf{R}_{ml}) = -\mathbf{a}_1$ and

$$\vec{a}_1 = a\left(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}\right) \qquad \vec{a}_2 = a\left(\frac{\sqrt{3}}{2}\hat{x} - \frac{1}{2}\hat{y}\right) \qquad \vec{b}_1 = \frac{4\pi}{a\sqrt{3}}\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right) \quad \vec{b}_2 = \frac{4\pi}{a\sqrt{3}}\left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)$$

Figure 5: (a) Graphene hexagonal lattice with 2 carbon atoms labeled A and B per unit cell. The primitive lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are indicated and a unit-cell is represented in shaded. In this Exercise, the interatomic distance is noted d while -a- is here the length of the primitive lattice vectors. Both are related by $d = a/\sqrt{3}$. For the A-atom in the shaded unit cell, there are 3 first-nearest-neighbours B atoms, one in the same cell and 2 in neighbouring cells. These 2 neighbouring cells are obtained by translating the shaded cell by $-\mathbf{a}_1$ and $-\mathbf{a}_2$, respectively. (b) The hexagonal Brillouin zone with the corner $\mathbf{K} = (2\mathbf{b}_1 + \mathbf{b}_2)/3$. One can verify that $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. The primitive lattice vectors make an angle of 60° in real-space and 120° in reciprocal-space.

$(\mathbf{R}_{m'l'} - \mathbf{R}_{ml}) = -\mathbf{a}_2$, leading to:

$$H_{AB} = \frac{e^{i\mathbf{k}\cdot(\tau_B - \tau_A)}}{N_C} \sum_{ml} \left(e^{i\mathbf{k}\cdot(\mathbf{0})}t + e^{i\mathbf{k}\cdot(-\mathbf{a}_1)}t + e^{i\mathbf{k}\cdot(-\mathbf{a}_2)}t \right)$$

$$= \frac{e^{i\mathbf{k}\cdot(\tau_B - \tau_A)}}{N_C} N_C \left(1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2} \right)t$$

$$= tf(\mathbf{k})e^{i\mathbf{k}\cdot(\tau_B - \tau_A)} \quad \text{with} \quad f(\mathbf{k}) = 1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2}$$

The band structure is given again by the condition:

$$(\varepsilon_k - \varepsilon^0)^2 - |H_{AB}|^2 = 0$$

with $H_{AA} = H_{BB} = \varepsilon^0$ the onsite energy associated with the ϕ^{at} atomic orbital (a carbon $2p_z$ atomic orbital in the case of graphene). Simple algebra leads to:

$$|H_{AB}|^2 = |t|\left(3 + 2\cos(\mathbf{k}\cdot\mathbf{a}_1) + 2\cos(\mathbf{k}\cdot\mathbf{a}_2) + 2\cos[\mathbf{k}\cdot(\mathbf{a}_2 - \mathbf{a}_1)]\right)$$

leading to the band structure containing again 2 bands

$$\varepsilon_k = \varepsilon^0 \pm t\sqrt{3 + 2\cos(\mathbf{k}\cdot\mathbf{a}_1) + 2\cos(\mathbf{k}\cdot\mathbf{a}_2) + 2\cos[\mathbf{k}\cdot(\mathbf{a}_2 - \mathbf{a}_1)]}$$

In $\mathbf{k} = \mathbf{0}$ (the Brillouin zone center), one obtains $\varepsilon(\mathbf{k} = \mathbf{0}) = \varepsilon^0 \pm 3t$. In the
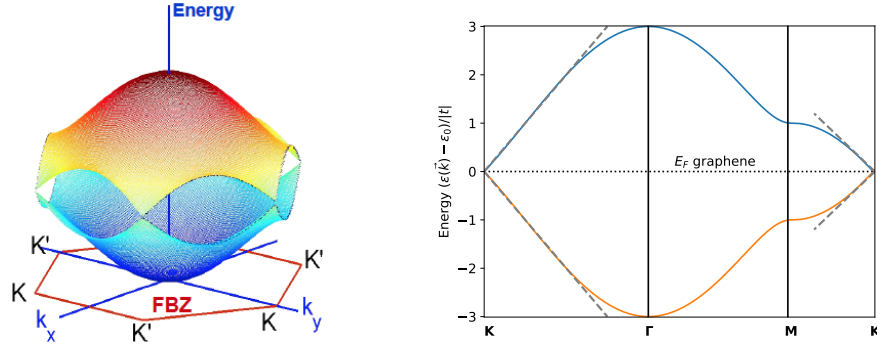
Brillouin-zone "corner" $\mathbf{K} = (2\mathbf{b}_1 + \mathbf{b}_2)/3$ with $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, one obtains:

$$\cos(\mathbf{K} \cdot \mathbf{a}_1) = \cos(4\pi/3) = -0.5$$
$$\cos(\mathbf{K} \cdot \mathbf{a}_2) = \cos(2\pi/3) = -0.5$$
$$\cos[\mathbf{K} \cdot (\mathbf{a}_2 - \mathbf{a}_1)] = \cos(-2\pi/3) = -0.5$$

leading to:

$$|f(\mathbf{K})|^2 = 0 \quad \Longrightarrow \quad \varepsilon_K = \varepsilon^0$$

that is the same energy for the two ε_K^+ and ε_K^- solutions : the lower and upper subbands touch at $\mathbf{K}$. The corresponding band structure is indicated in Fig. 6.

Figure 6: Band structure of graphene : the upper and lower subbands (the ε_k^+ and ε_k^- solutions) touch at the BZ corners $\mathbf{K}$ and $\mathbf{K}'$ with an energy ε^0 that is also the Fermi level energy : in graphene, only the lowest subband is filled. Graphene is called a semi-metal with very few electrons (electrons with a wavevector at the BZ corner) being allowed to "jump" into the empty conduction bands. We represent in (Left) the full band structure and (Right) the band-structure along the $\mathbf{K\Gamma MK}$ directions (see Fig. 5b). In dashed grey, the linear fit of the bands around the $\mathbf{K}$-vector.

Graphene is in the situation of a half-filled band with the Fermi level located at $\varepsilon_F = \varepsilon^0$. Namely, only the lowest "subband" is filled. The "Fermi surface", that is the surface such that $\varepsilon(\mathbf{k}) = \varepsilon_F = \varepsilon^0$ is limited to discrete $\mathbf{k}$-vectors at the BZ corners. Graphene is called a semi-metal since only very few electrons with a wavevector at the BZ corners can jump into the empty bands.

An interesting property is that the dispersion around $\mathbf{k} = \mathbf{K}$ is linear, namely the energy depends linearly with the norm of $\mathbf{q}$ with $\mathbf{k} = \mathbf{K} + \mathbf{q}$ in the vicinity of $\mathbf{K}$. Indeed the Taylor expansion of the exponential function for the norm of q going to zero yields:

$$e^{-i\mathbf{k}\cdot\mathbf{a}_1} = e^{-i\mathbf{K}\cdot\mathbf{a}_1}e^{-i\mathbf{q}\cdot\mathbf{a}_1} = e^{-i4\pi/3}\Big(1 - i\mathbf{q}\cdot\mathbf{a}_1\Big) = \Big(\frac{-1}{2} + i\frac{\sqrt{3}}{2}\Big)\Big(1 - i\mathbf{q}\cdot\mathbf{a}_1\Big)$$

$$e^{-i\mathbf{k}\cdot\mathbf{a}_2} = e^{-i\mathbf{K}\cdot\mathbf{a}_2}e^{-i\mathbf{q}\cdot\mathbf{a}_2} = e^{-i2\pi/3}\Big(1 - i\mathbf{q}\cdot\mathbf{a}_2\Big) = \Big(\frac{-1}{2} - i\frac{\sqrt{3}}{2}\Big)\Big(1 - i\mathbf{q}\cdot\mathbf{a}_2\Big)$$

so that

$$f(\mathbf{K}+\mathbf{q}) = \frac{i}{2}\mathbf{q}\cdot(\mathbf{a}_1+\mathbf{a}_2) + \frac{\sqrt{3}}{2}\mathbf{q}\cdot(\mathbf{a}_1-\mathbf{a}_2) = \frac{i}{2}\mathbf{q}\cdot(\sqrt{3}a\hat{x}) + \frac{\sqrt{3}}{2}\mathbf{q}\cdot(a\hat{y})$$

namely

$$f(\mathbf{K}+\mathbf{q}) = \frac{a\sqrt{3}}{2}(iq_x+q_y)$$

As a result

$$\varepsilon(\mathbf{K}+\mathbf{q}) - \varepsilon^0 = \pm t\sqrt{|f(\mathbf{K}+\mathbf{q})|^2} = \pm t\frac{a\sqrt{3}}{2}|q| = \pm\hbar v_F|q| \quad \text{with} \quad v_F = \frac{a\sqrt{3}|t|}{2\hbar}$$

The linearity of the dispersion around the $\mathbf{K}$-vector (corner of the BZ) is represented in Fig. 6(Right) with the dashed grey lines. In relativistic theory, one has the fundamental relation relating total energy, momentum, and mass of particles : $E^2 = (pc)^2 + (mc^2)^2$. For a massless particle: $E = \pm pc$, namely a linear relation between energy and impulsion. With $\mathrm{p} = \hbar \mathrm{q}$ in the vicinity of $\vec{K}$ and replacing the light velocity c by the Fermi velocity: $v_F \simeq c/300$ in graphene, one obtains a behaviour for graphene electrons at the Fermi energy similar to massless relativistic fermions.