6 Peierls Transition in Carbon Nanotubes

In this chapter we consider the Peierls instability due to the interaction of electrons with both acoustic and optical phonons. We suggest that such a transition takes place in metallic carbon nanotubes, where the acoustic phonons correspond to a twist deformation of the nanotube lattice and the optical phonons describe a relative shift between the two triangular sublattices of which the hexagonal lattice is composed. Below the transition temperature, a topological excitation can occur which corresponds to the kink-solution of a generalized order parameter. We study its properties and compare them with those of the usual soliton in trans-polyacetylene. Furthermore, we calculate the temperature dependence of the conductivity resulting from the interaction between electrons and acoustic phonons above the transition temperature. We discuss these results in the context of available experimental data for carbon nanotubes.

Section 6.2 is an introduction to physical properties of carbon nanotubes and may be skipped in a first reading of this chapter.

6.1 Introduction

In Chapter 2 we discussed that a half-filled conducting chain is unstable against a doubling of the unit cell, where the bond length between neighboring lattice sites alternates along the chain. The dimerization of the lattice results in an alternation of the electron hopping amplitudes leading to the opening of a Peierls gap in the electron spectrum and turning the system into a semiconductor. In this Peierls instability, the relevant phonons are the optical ones with wave vector \( q = 2k_F \) [1]. These phonons backscatter electrons from the left part of the Fermi surface with electron wave vector \(-k_F\) to the right one with electron wave vector \(+k_F\) and vice versa. It is usually assumed that above the phase transition temperature \( T_c \) these phonons have a finite frequency \( \omega_0 \) and we will, therefore, refer to them as optical phonons. Due to the mixing with the low-energy electron-hole excitations, these phonons soften and at \( T_c \) their frequency vanishes (giant Kohn anomaly) [2].

The problem of structural phase transitions resulting from electron-lattice interactions is of broad interest. In this chapter we show that phonons of small wave vector \( q \) may lead to a similar instability. As a specific example, we will consider the Peierls transition in metallic carbon nanotubes. Carbon nanotubes are well-known for their unique electronic properties and a great deal of work has been done to understand the role of electron-electron interactions, since a metallic carbon nanotube is a typical candidate for an experimental realization of a Luttinger liquid. In this context the bosonization method has been applied [3, 4], as well as a mapping to a two-leg Hubbard model to describe the short-range Coulomb repulsion [5, 6]. A different view is taken in this chapter, where we, in fact, disregard electron correlations and concentrate on the electron-lattice interaction. In metallic carbon nanotubes the Peierls transition arising from the interaction with optical phonons has been studied before [7, 8, 9, 10, 11]. A general conclusion
which has been drawn from these studies is that the opening of a Peierls gap is strongly suppressed for increasing nanotube diameters. This can be interpreted as the consequence of the fact that the elastic energy cost of the Peierls distortion grows proportional to the number of chains around the nanotube circumference. This remains valid when acoustic phonons are taken into account.

In Figure 6-1 an armchair carbon nanotube is shown, which can be considered as composed of a finite number of coupled two-leg ladders around its circumference. Each ladder consists of two coupled zigzag chains that are directed along the axis of the carbon nanotube. The effective low-energy model that describes the nanotube’s electronic properties takes into account electrons which occupy the lowest mode with zero momentum in the circumferential direction of the carbon nanotube and corresponds to a single two-leg ladder tight-binding model. The corresponding electronic spectrum is also shown in Figure 6-1 and is characterized by two Fermi points. At each Fermi point \( (n = 1, 2) \) two electron bands that have a linear dispersion close to the Fermi energy, \( E = 0 \), intersect. While the undistorted armchair carbon nanotube is a half-filled metallic system \([12, 13]\), we will show that electron-lattice interactions with small phonon momenta \( q \) result in the backscattering of electrons at each Fermi point. The resulting coupling between occupied and unoccupied states leads to the opening of an energy gap. The relevant phonons with small wave vector \( q \) are (i) an acoustic phonon mode with small frequency \( \omega_A(q) \propto |q| \), which describes a uniform twist of the nanotube lattice, and (ii) an optical phonon mode with finite frequency \( \omega_0 \), where the lattice distortion corresponds to a relative shift between the two triangular sublattices of which the hexagonal nanotube lattice is composed.

The outline of this chapter is as follows. In Section 6.2 we explain the origin of the unique electronic properties of carbon nanotubes within a single-particle picture, starting from a tight-binding model for a graphene sheet which is rolled up into a seamless cylinder to build a single-wall carbon nanotube. In Section 6.3 we describe the nanotube lattice by the most general continuum model that is compatible with the symmetry of the hexagonal lattice. Furthermore, we calculate the electron-lattice coupling for the long wavelength phonon modes that result in the backscattering of electrons. Then, in Section 6.4, we calculate the renor-
6.2 General introduction to carbon nanotubes

An ideal single-wall carbon nanotube can be thought of as a two-dimensional graphene sheet that has been rolled up into a seamless cylinder. A carbon nanotube can be considered as a onedimensional nanostructure since it has a typical diameter in the order of 1 nm and a large aspect ratio, length/diameter $\approx 10^3 - 10^5$. Carbon nanotubes are well-known for their unique electronic properties due to the quantum confinement of the $\pi$-electrons normal to the nanotube axis. The $\pi$-electrons are confined by the monolayer thickness of the graphene sheet in the radial direction, while around the nanotube circumference their wave functions have to satisfy periodic boundary conditions. The $\pi$-electrons are therefore described by standing waves around the nanotube circumference and can only propagate in the direction along the nanotube axis. In this section we calculate the dispersion relations of the one-dimensional bands, starting from a tight-binding model for a two-dimensional graphene sheet [16]. Such band structure calculations, which show that, depending on their diameter and chirality, carbon nanotubes appear to be either metallic or semiconducting, have received considerable attention in the literature [17, 18]. Furthermore, we show in this section how to derive an effective low-energy model for metallic carbon nanotubes [5, 6]. This model also allows to study the electronic properties of the carbon nanotube for several possible bond alternation patterns [7, 9, 10, 11, 19].

We note that the present section is fairly introductory and addresses the reader who is not familiar with the electronic properties of carbon nanotubes [12, 13, 20, 21].

6.2.1 Classification and electronic structure of carbon nanotubes

A single sheet of graphite is composed of carbon atoms on the sites of a honeycomb lattice. The unit cell contains two carbon atoms that are separated by a distance $a_{CC} = 1.42 \, \text{Å}$. Figure 6-2 shows (a) the unit cell and (b) the Brillouin zone of a two-dimensional graphene sheet and visualizes the notation that will be used throughout this section.
Figure 6-2: (a) The unit cell of a graphene sheet with lattice constant $a = \sqrt{3} a_{CC}$ is shown as the dotted rhombus. The real space unit vectors are given by $\vec{a}_\pm = a(\pm 1/2, \sqrt{3}/2)$ and the displacement vector between the two triangular sublattices, denoted by “•” and “○”, respectively, is given by $\vec{d} = a(0, -1/\sqrt{3})$. (b) The Brillouin zone of a graphene sheet is shown as the shaded hexagon and $\vec{b}_\pm = (2\pi/a)(\pm 1, 1/\sqrt{3})$ are the unit vectors of the reciprocal lattice with lattice constant $b = 4\pi/(\sqrt{3} a)$.

The honeycomb lattice consists of two triangular sublattices with one carbon atom at each site. The sp²-electrons of each carbon atom form covalent bonds with those of their three nearest neighbors, while the nearest neighbor hopping of the remaining electron in the 2p_z-orbital of a carbon atom can be viewed as tunneling between two triangular sublattices (see Figure 6-2). The tight-binding model for the free π-electrons in a graphene sheet reads:

$$H_{gs} = \sum_{\vec{r} \in \mathcal{R}, \sigma} \left\{ -t c_{A\sigma}^\dagger(\vec{r}) c_{B\sigma}(\vec{r} + \vec{a}_+ + \vec{d}) - t' c_{A\sigma}^\dagger(\vec{r}) c_{B\sigma}(\vec{r} + \vec{a}_- + \vec{d}) 
- t'' c_{A\sigma}^\dagger(\vec{r}) c_{B\sigma}(\vec{r} + \vec{d}) + \text{h.c.} \right\},$$

(6.1)

where $c_{i\sigma}$ ($c_{i\sigma}^\dagger$) is the fermion annihilation (creation) operator on the corresponding sublattice $i = A, B$ and $\sigma = \pm 1$ denotes the spin projection. The sum over $\vec{r}$ runs over all triangle lattice vectors $\vec{R} = n_- \vec{a}_- + n_+ \vec{a}_+$, with the real space unit vectors $\vec{a}_\pm = a(\pm 1/2, \sqrt{3}/2)$ and integers $n_\pm$. The displacement vector between the two sublattices is given by $\vec{d} = a(0, -1/\sqrt{3})$. We formally distinguish between electron hopping amplitudes $t$, $t'$, and $t''$ in Eq. (6.1). In the case of an undistorted two-dimensional graphene sheet these hopping amplitudes are equal, however, their values can differ due to curvature effects when the graphene sheet is rolled into a carbon nanotube.

The Hamiltonian Eq. (6.1) can be easily diagonalized in momentum space. We obtain the electron energy spectrum of the graphene sheet,

$$E_{gs}(\vec{k}) = \pm |h(\vec{k})|,$$

(6.2)
Figure 6-3: Contour plot of the energy dispersion $E_{gs}(\vec{k})$. Contours join points on the energy dispersion landscape that have the same value. The shading is such, that it is lighter for values of $E_{gs}(\vec{k})$ that are closer to the Fermi surface ($E = 0$). The bonding and anti-bonding bands touch at the six corner points of the hexagonal Brillouin zone ($t = t' = t''$). Due to the hexagonal symmetry there exist only two inequivalent points $K_\pm$ located at $\vec{K}_\pm = (\pm 4\pi/(3a), 0)$.

where $\vec{k} = (k_x, k_y)$ is the electron momentum and

$$h(\vec{k}) = t \exp(\frac{i}{2}k_x a + \frac{i}{2\sqrt{3}}k_y a) + t' \exp(-\frac{i}{2}k_x a + \frac{i}{2\sqrt{3}}k_y a) + t'' \exp(-\frac{i}{2\sqrt{3}}k_y a).$$

The $\mp$ signs in Eq. (6.2) denote the bonding and anti-bonding bands in the energy spectrum. Since the graphene sheet is a half-filled system (one $\pi$-electron per carbon atom), the bonding band is completely filled and the anti-bonding band is empty. For an undistorted graphene sheet ($t = t' = t''$), the contour plot Figure 6-3 of

$$E_{gs}(\vec{k}) = \pm t \left\{ 1 + 4\cos^2 \left( \frac{k_x a}{2} \right) + 4\cos \left( \frac{k_x a}{2} \right) \cos \left( \frac{\sqrt{3}k_y a}{2} \right) \right\}^{1/2},$$

shows contours that join points in the energy dispersion landscape that have the same energy value. A prominent feature of the band structure is, that the bonding and anti-bonding bands are separated by a finite gap everywhere in the the Brillouin zone, except at two peculiar points $K_\pm$. These points are conventionally called Dirac points because the (gapless) dispersion looks relativistic near $\vec{K}_\pm = (\pm 4\pi/(3a), 0)$, i.e.

$$E_{gs}(\vec{k}, \vec{k}_\pm) = v_F |\vec{k} - \vec{k}_\pm|,$$

with Fermi velocity $v_F = (\sqrt{3}/2)t\alpha$.  


To obtain a carbon nanotube, the graphene sheet is conceptually rolled into a cylindrical shape so that the structure is one-dimensional. While the basic shape of the carbon nanotube is a cylinder, the essential fact about its structure is the orientation of the six-membered carbon ring (hexagon) in the honeycomb lattice relative to the nanotube axis. The variety of possible nanotube geometries is classified by the so-called chiral vector \( \vec{C} \). As indicated in Figure 6-4, \( \vec{C} \) points perpendicular to the nanotube direction and connects two lattice sites that become identical on rolling up the graphene sheet into a seamless cylinder. In terms of the real space unit vectors \( \vec{a}_\pm \), the chiral vector

\[
\vec{C} = c_- \vec{a}_- + c_+ \vec{a}_+ \equiv [c_-, c_+]
\]  

(6.6)
is determined by the set of integers \( c_\pm \), and its absolute value equals the circumference \( C \) of the carbon nanotube,

\[
C = |\vec{C}| = a \sqrt{c_-^2 + c_+^2 + c_- c_+}.
\]  

(6.7)

Related to the chiral vector \( \vec{C} \) is the chiral angle \( \theta \) which denotes the tilt angle of the hexagons with respect to the direction of the nanotube axis. This angle is defined by

\[
\cos \theta = \frac{\vec{C} \cdot \vec{a}_+}{|\vec{C}| |\vec{a}_+|} = \frac{a}{2C} \left( c_- + 2c_+ \right),
\]  

(6.8)

and the hexagonal symmetry of the honeycomb lattice limits the relevant range to \( 0 \leq |\theta| \leq \pi/6 \). A carbon nanotube is uniquely determined by the degree of chirality \( \theta \) and its diameter \( C/\pi \).
A classification of the carbon nanotubes distinguishes between chiral and achiral nanotubes. Only the achiral nanotubes have a reflection symmetry with respect to a plane perpendicular to the nanotube axis. Two types of achiral nanotubes can be distinguished, namely armchair and zigzag nanotubes, where the names refer to the shape of their cross-sectional ring along the direction of $\vec{C}$. As can be seen from Figure 6-5, this shape is cis-type in the case of an armchair nanotube and trans-type for a zigzag nanotube. Chiral nanotubes, on the other hand, have a cross-sectional shape that is a mixture of both cis- and trans-type.

To describe the unit cell of a carbon nanotube we introduce the translation vector $\vec{T}$ which is also shown in Figure 6-4. This vector becomes the unit vector of the one-dimensional carbon nanotube. In terms of the real space unit vectors $\vec{a}_\pm$ and with integers $t_\pm$, the translation vector reads

$$\vec{T} = t_- \vec{a}_- + t_+ \vec{a}_+ \equiv [t_-, t_+] \tag{6.9}$$

and points normal to the chiral vector $\vec{C}$ in the direction of the nanotube axis. Given a chiral vector $\vec{C} = [c_-, c_+]$, it follows from the condition $\vec{C} \cdot \vec{T} = 0$, that

$$t_- = \frac{2c_+ + c_-}{d_{gc}} \quad \text{and} \quad t_+ = \frac{-2c_- + c_+}{d_{gc}}, \tag{6.10}$$

where $d_{gc}$ denotes the greatest common (gc) divisor of $(2c_+ + c_-)$ and $(2c_- + c_+)$, so that $\vec{T}$ points to the first lattice point of the two-dimensional graphene sheet along the direction of $\vec{C}$. The length of the translational vector is given by

$$T = |\vec{T}| = \frac{\sqrt{3}}{d_{gc}} C, \tag{6.11}$$
Figure 6-6: (a) The Brillouin zone of a carbon nanotube represented by the line segment $BB'$. The figure corresponds to the chiral nanotube $\tilde{C} = [2, 4]$ with translation vector $\tilde{T} = [5, -4]$. The allowed wave vectors are represented by the $n = 28$ separate line segments of length $2\pi / \tilde{T}$. (b) The line segments for the allowed nanotube wave vectors are folded into a single hexagon of the reciprocal honeycomb lattice.

where $C$ is the circumferential length Eq. (6.7). The unit cell of the one-dimensional carbon nanotube is the rectangle defined by the vectors $\tilde{C}$ and $\tilde{T}$ (see Figure 6-4). As the unit cell of the graphene sheet is defined by $\tilde{a}_+$ and $\tilde{a}_-$, the number of hexagons per unit cell of the carbon nanotube, $n$, can be calculated from

$$n = \frac{|\tilde{C} \times \tilde{T}|}{|\tilde{a}_- \times \tilde{a}_+|} = \frac{2C^2}{a^2 d_{gc}}. \quad (6.12)$$

Each unit cell of the carbon nanotube contains $2n$ carbon atoms (or $\pi$-electrons). The energy spectrum within the single electron theory contains, thus, $n$ pairs of bands consisting of the bonding ($\pi$) and anti-bonding ($\pi^*$) electron bands.

We can now turn to the construction of the Brillouin zone of a carbon nanotube. The reciprocal lattice vectors $\tilde{k}_\parallel$ along the nanotube axis and $\tilde{k}_\perp$ in the circumferential direction are obtained from the relations

$$\tilde{T} \cdot \tilde{k}_\parallel = 2\pi, \quad \tilde{C} \cdot \tilde{k}_\parallel = 0 \quad \text{and} \quad \tilde{T} \cdot \tilde{k}_\perp = 0, \quad \tilde{C} \cdot \tilde{k}_\perp = 2\pi. \quad (6.13)$$

In terms of the reciprocal lattice vectors of the graphene sheet, $\tilde{b}_\pm = (2\pi / \alpha) (\pm 1, 1 / \sqrt{3})$, and together with Eq. (6.12), we find

$$\tilde{k}_\parallel = \frac{1}{n} \left( c_+ \tilde{b}_- - c_- \tilde{b}_+ \right) \quad \text{and} \quad (6.14)$$

$$\tilde{k}_\perp = \frac{1}{n} \left( t_- \tilde{b}_+ - t_+ \tilde{b}_- \right). \quad (6.15)$$

In Figure 6-6, the allowed wave vectors in reciprocal lattice space are shown for the chiral carbon nanotube $\tilde{C} = [2, 4]$. The first Brillouin zone of this one-dimensional structure contains
the line segment $BB'$ of length $2\pi/T$ along the $\vec{k}_||$-direction. For a carbon nanotube of length $L$, the difference between two allowed wave vectors in the $\vec{k}_||$-direction is given by $\Delta k_|| = 2\pi/L$ and vanishes in the limit $T/L \to 0$, which we consider here. This is, however, not the case for the $\vec{k}_\perp$-direction, where two wave vectors differ by the amount $\Delta k_\perp = 2\pi/C$, which is finite due to the finite circumference $C$ of the carbon nanotube. It follows that the allowed wave vectors are quantized in the $\vec{k}_\perp$-direction associated with the periodic boundary conditions on the chiral vector $\vec{C}$. In Figure 6-6 (a) the allowed wave vectors for the $[2,4]$ nanotube with $n = 28$ hexagons per unit cell are shown by the $n = 28$ separate line segments. The line segments of allowed wave vectors can be folded into a single hexagon of the honeycombs reciprocal lattice space as is shown in Figure 6-6 (b).

The one-dimensional energy dispersion curves of a carbon nanotube, $E_\nu(k)$, are now easily obtained from $E_{gs}(\vec{k})$ of the graphene sheet as given by Eqs. (6.2) and (6.3). The $n$ pairs of bands arise because of $2n$ $\pi$-electrons per unit cell of the carbon nanotube and are labelled by $\nu = 0, 1, ..., n - 1$,

$$E_\nu(k) = E_{gs}(\vec{k}_c) = E_{gs}\left(\frac{\vec{k}_||}{|k||} + \nu \vec{k}_\perp\right),$$

(6.16)

where $k$ takes the values $-\pi/T < k \leq \pi/T$ along the $\vec{k}_||$-direction. Thus, the allowed wave vectors of the one-dimensional carbon nanotube cut along the lines $\vec{k}_c = k \vec{k}_||/|k|| + \nu \vec{k}_\perp$ through the hexagonal Brillouin zone of the graphene sheet (compare Figure 6-3 and Figure 6-6 (b)).

In Figure 6-7 we plot the electronic band structure Eq. (6.16) for the three carbon nanotubes (a) $\vec{C} = 4[1,1]$, (b) $\vec{C} = 7[0,1]$, and (c) $\vec{C} = [2,4]$. Curvature effects are neglected, assuming...
Figure 6-8: The Brillouin zone of the graphene sheet (hexagon) with Dirac points K± together with that of a carbon nanotube (rectangle) containing the line segment BB' of allowed wave vectors. The carbon nanotube is metallic if the length \( l(\mathbf{N}_+, \mathbf{K}_+) \) connecting the two points \( \mathbf{N}_+ \) and \( \mathbf{K}_+ \), or equivalently \( l(\mathbf{N}_-, \mathbf{K}_-) \), is an integer multiple of \( |\mathbf{k}_\perp| \).

all hopping amplitudes to be equal (\( t = t' = t'' \)). Of special interest is the fact, that the calculated electronic band structure of a carbon nanotube can be either gapless (Figure 6-7 (a)) or gapped (Figure 6-7 (b) and (c)), depending on the nanotube’s diameter and chirality. A zero energy gap in a particular energy band \( \nu \) is only obtained if the corresponding cutting line \( \tilde{K}_c \) hits a Dirac point \( \tilde{K}_\pm \), where the bonding and anti-bonding bands of the graphene sheet touch. If, on the other hand, none of the \( n \) cutting lines \( \tilde{K}_c \) contain a Dirac point, then the corresponding carbon nanotube has a finite energy gap between the valence and conduction band. This can be seen in Figure 6-6 (b), where none of the cutting lines for the allowed wave vectors of the \([2,4]\) nanotube hit a Dirac point \( \tilde{K}_\pm \), and, therefore, the corresponding electronic band structure Figure 6-7 (c) equals that of a semiconductor.

Whether a carbon nanotube \([c_-, c_+]\) is metallic or semiconducting can be determined by looking at Figure 6-8, where we show the Brillouin zone of the graphene sheet (hexagon) together with that of a carbon nanotube (rectangle). As argued above, the nanotube \([c_-, c_+]\) is metallic if the length \( l(\mathbf{N}_+, \mathbf{K}_+) \), or equivalently \( l(\mathbf{N}_-, \mathbf{K}_-) \), is an integer multiple of \( |\tilde{K}_\perp| \), as in this case there exists a \( \nu \) for which a cutting line \( \tilde{K}_c \) contains the Dirac points \( \tilde{K}_\pm \). This results in the condition, that the ratio

\[
\frac{l(\mathbf{N}_\pm, \mathbf{K}_\pm)}{|\tilde{K}_\perp|} = \frac{|c_+ - c_-|}{3}
\]

has to be an integer for a metallic carbon nanotube \([c_-, c_+]\). In other words, the condition Eq. (6.17) requires that the \( \tilde{K}_\pm \) point can be folded into the \( \mathbf{N}_\pm \) point. Moreover, two categories of metallic carbon nanotubes can be distinguished and are referred to as, respectively, metal-1 and metal-2. A metal-2 nanotube has two electron bands that intersect at the Fermi energy
Figure 6-9: Metallic and semiconducting carbon nanotubes constructed from a graphene sheet. A metallic carbon nanotube is obtained if the chiral vector $\vec{C}$ connects site “$\bigcirc$” with a site “$\bullet$”. On the other hand, if $\vec{C}$ connects site “$\bigcirc$” with a site “$\bigcirc$”, the corresponding carbon nanotube is semiconducting.

$E = 0$ at two points $k = \pm 2\pi/(3T)$. This is the case for armchair carbon nanotubes (see Figure 6-7 (a)). If, however, in addition to the condition Eq. (6.17), the ratio

$$\frac{\Gamma|N_\pm|}{|k||} = \frac{|c_+|}{d_{gc}}$$

(6.18)

is an integer too, then the two points $N_\pm$ - and equivalently $K_\pm$ - can be folded into the $\Gamma$ point, as $k||$ is a reciprocal lattice vector in this case. A carbon nanotube for which the conditions Eqs. (6.17) and (6.18) are fulfilled is called metal-1, as the intersection of electron bands at the Fermi level occurs in a single point $k = 0$ and is four-fold. Metallic zigzag nanotubes belong to the category metal-1. Independent of their diameter and chirality, all metallic carbon nanotubes have a constant density of states per unit length along the nanotube axis,

$$\rho = \frac{8}{2\pi} \int dk \delta(E - v_F k) = \frac{8}{3\pi a} \,. $$

(6.19)

This is a consequence of the one-dimensional linear dispersion relation close to the Fermi energy and is different from a graphene sheet, for which the density of states vanishes at the Fermi energy.

In general, it follows from the condition Eq. (6.17) for the carbon nanotube to be metallic, that the chiral vector of a metallic carbon nanotube is given by

$$\vec{C}_m \equiv [c_\alpha, c_\alpha + 3c_\zeta] \,,$$

(6.20)

where $c_\alpha$ and $c_\zeta$ are integers that refer to the armchair and zigzag direction. Among the achiral nanotubes, the armchair type ($c_\zeta = 0$) is always metallic, while this is the case for only 1/3 of the zigzag type ($c_\alpha = 0$). Figure 6-9 shows, how metallic (“$\bigcirc$” $\leftrightarrow$ “$\bigcirc$”) and semiconducting (“$\bigcirc$” $\leftrightarrow$ “$\bigcirc$”) carbon nanotubes are obtained according to Eq. (6.17). We finally note that a
detailed analysis of $E_{\nu}(k)$ shows, that even the positions of the finite energy gaps in an arbitrary carbon nanotube are always at $k = \pm 2\pi/(3T)$ or $k = 0$ (see for example Figure 6-7 (b) and (c)). The value of the energy gap in semiconducting nanotubes, $E_g$, has been calculated in $k$-$\overline{p}$-theory near the $K_\pm$ points [22]. It is found to be independent of the nanotube's chiral angle and to scale with the reciprocal nanotube circumference $C$,

$$E_g = \frac{t\pi a}{\sqrt{3}C},$$

which correctly approaches zero in the limit of a two-dimensional graphene sheet ($C \to \infty$).

The electronic properties of carbon nanotubes are a consequence of the quantum confinement of $\pi$-electrons on the cylindrical structure of the nanotube, so that similarly shaped molecules consisting only of carbon atoms show a very different electronic behavior, which depends strongly on their diameter and chirality. For example, while the $[0, 6]$ nanotube is metallic according to Eq. (6.20), the $[0, 7]$ nanotube with only two more carbon atoms in the nanotube unit cell has a band gap in the order of 1 eV (see Figure 6-9 and Figure 6-7 (b)). On the other hand, the $[4, 4]$ nanotube, which has about the same diameter as the $[0, 7]$ nanotube, shows again metallic behavior (see Figure 6-9 and Figure 6-7 (a)). Only recently it has become possible to experimentally examine the electronic properties of isolated single-wall carbon nanotubes as a function of the nanotube's diameter and chiral angle [23, 24, 25, 26]. Using scanning tunneling microscopy (STM) and spectroscopy (STS), atomically resolved images of isolated single-wall carbon nanotubes together with measurements of their current-voltage curves were obtained. These experiments verify the prediction of the existence of metallic and semiconducting nanotubes and the measured energy gaps have been interpreted in terms of the simple tight-binding band structure calculations.

### 6.2.2 Effective low-energy model for metallic carbon nanotubes

Metallic carbon nanotubes are of special interest as they are expected to serve as ideal one-dimensional quantum wires for possible applications in nanometer-sized electronics. However, for a number of reasons the above considerations within the tight-binding model have to be modified in order to obtain a more realistic description of carbon nanotubes. In particular, the Coulomb interaction between $\pi$-electrons and also the interaction between the $\pi$-electrons and the nanotube lattice are not included in the single particle theory. Furthermore, curvature effects in carbon nanotubes with small diameter lead to a difference in the electron hopping amplitudes for the direction along the nanotube axis, $t_\parallel$, and around its circumference, $t_\perp$. We summarize the results of a detailed study of curvature effects [27] in terms of three distinct families of nanotubes:

(i) semiconducting nanotubes with energy gap $E_g \propto 1/C$ (see Eq. (6.21)) and a curvature induced energy gap scaling as $E_g^c \propto 1/C^2$,

(ii) nominally metallic nanotubes that have in fact a curvature induced gap $E_g^c \propto 1/C^2$ and are semiconducting, and

(iii) metallic nanotubes for which a curvature induced gap does not exist by symmetry.

The third family of nanotubes is formed by the carbon nanotubes of armchair type. Curvature effects leave the energy spectrum of armchair carbon nanotubes metallic as the Dirac points in the Brillouin zone are shifted along the cutting lines of the allowed wave vectors. We will,
Figure 6-10: The rectangular Brillouin zone for the $3[1,1]$ armchair nanotube. It is constructed from the hexagonal Brillouin zone of the honeycomb lattice by shifting shaded parts by reciprocal lattice vectors. The allowed transverse momentum $k_\perp$ in the $k_y$-direction takes $c_\alpha = 3$ integer values labelled by $p$ (see Eq. (6.22)). Curvature effects shift the Dirac points along the $k_\perp$-direction, “●” → “○”, leaving the armchair carbon nanotube metallic.

Therefore, focus on the derivation of an effective low-energy model for armchair nanotubes $c_\alpha[1,1]$.

Starting from the tight-binding model of the graphene sheet Eq. (6.1), we first rearrange its hexagonal Brillouin zone into a rectangle. This is achieved by shifting several parts by reciprocal lattice vectors as indicated in Figure 6-10. For the rectangular Brillouin zone the allowed transverse momentum, $k_\perp$, takes $c_\alpha$ integer values:

$$k_\perp = \frac{2\pi}{\sqrt{3}a} \frac{p}{c_\alpha}, \quad p = 0, \pm 1, \pm 2, \ldots, (\pm)\left\lfloor \frac{c_\alpha}{2} \right\rfloor,$$

(6.22)

where “$(\pm)$” means that only one sign is chosen in order to count the total number of modes properly if $c_\alpha$ is an even number. Since only the mode with $k_\perp = 0$ contains the Dirac points in the case of an armchair nanotube, we will use a partial Fourier transformation to construct new fermion operators, that carry a definite transverse momentum. In general, we use the Fourier representation

$$c_{i\sigma}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} c_{i\sigma}(\vec{k}),$$

(6.23)

where $c_{i\sigma}(\vec{r})$ denotes, as in Eq. (6.1), the fermion annihilation operator on the triangular sublattice $i = A, B$ and $\sigma$ is the spin projection. The normalization constant $N_A = N_B = c_\alpha L/a$ denotes the total number of fermion sites of each sublattice for an armchair nanotube of length $L$. The coordinate vector $\vec{r} = (r_\parallel, r_\perp)$ reaches all sites of a sublattice, so that the transverse coordinate $r_\perp$ runs through $c_\alpha$ values at each fixed $r_\parallel$ along the nanotube direction. We parameterize $r_\perp$ according to Figure 6-11:

$$r_\perp = \begin{cases} \sqrt{3}a n_\perp - \delta_{i,B} \frac{1}{\sqrt{3}} a & \text{if } r_\parallel = n_\parallel a \\ \sqrt{3}a n_\perp - \delta_{i,B} \frac{1}{\sqrt{3}} a + \frac{\sqrt{3}}{2} a & \text{if } r_\parallel = (n_\parallel + \frac{1}{2}) a, \end{cases}$$

(6.24)

with the integers $n_\parallel = 1, 2, 3, \ldots$, $L/a$ and $n_\perp = 1, 2, 3, \ldots, c_\alpha$. 

The advantage of the constructed rectangular Brillouin zone (see Figure 6-10) is that it allows us to separate the summation in Eq. (6.23) over all momenta, \( \sum_{k} \), into two independent sums, \( \sum_{k_\perp} \sum_{k_\parallel} \). We define the new fermion operator \( d_{i\sigma}(r_\parallel, p) \) by the partial Fourier transformation
\[
c_{i\sigma}(r_\parallel, n_\perp) \equiv \frac{1}{\sqrt{c_\alpha}} \sum_p e^{i \frac{2\pi}{a} n_\perp p} d_{i\sigma}(r_\parallel, p) ,
\]
(6.25)

where \( p \) has been defined through Eq. (6.22). As the Dirac points lie on the \( k_\perp = 0 \) line of the armchair carbon nanotube, all modes with non-zero transverse momentum are gapped. It can be easily calculated that the value of the energy gap is of order \( t_\parallel/c_\alpha \), being well above \( 10^3 \text{K} \) for a \([10, 10] \) nanotube. In the low-energy model, we neglect all these gapped modes and keep only the zero momentum mode, so that Eq. (6.25) becomes
\[
c_{i\sigma}(r_\parallel, n_\perp) \simeq \frac{1}{\sqrt{c_\alpha}} d_{i\sigma}(r_\parallel, 0) \equiv \frac{1}{\sqrt{c_\alpha}} d_{i\sigma}(r_\parallel) ,
\]
(6.26)

and does not depend on the coordinate \( r_\perp \) anymore. Writing the tight-binding Hamiltonian of the graphene sheet Eq. (6.1) in terms of the new operators, we obtain the two-leg ladder model,
\[
H_{\text{arm}} = \sum_{n_\perp, \sigma} \left\{ -t_\parallel d_{A\sigma}^\dagger(n_\parallel) d_{B\sigma}(n_\parallel - \frac{1}{2}) - t_\parallel d_{A\sigma}^\dagger(n_\parallel) d_{B\sigma}(n_\parallel + \frac{1}{2}) - t_\perp d_{A\sigma}^\dagger(n_\parallel) d_{B\sigma}(n_\parallel) - t_\perp d_{A\sigma}^\dagger(n_\parallel) d_{B\sigma}(n_\parallel + \frac{1}{2}) - t_\parallel d_{B\sigma}^\dagger(n_\parallel) d_{A\sigma}(n_\parallel - \frac{1}{2}) - t_\parallel d_{B\sigma}^\dagger(n_\parallel) d_{A\sigma}(n_\parallel + \frac{1}{2}) + \text{h.c.} \right\} ,
\]
(6.27)
as the effective low-energy model for armchair carbon nanotubes. Note that the corresponding unit cell contains four atoms as a consequence of the two triangular sublattices \( i = A, B \).

In Figure 6-11 we illustrate that the result Eq. (6.27) is not surprising: The two-leg ladder model is nothing else but the \([1, 1] \) armchair nanotube with, thus, exactly the same electronic properties. Moreover, as long as the electrons occupy only the \( k_\perp = 0 \) mode in the circumferential direction of the nanotube, the number of ladders that is added to obtain an arbitrary \( c_\alpha[1, 1] \) nanotube does not change the low-energy electronic properties and the model Eq. (6.27) captures the essential physics also for \( c_\alpha > 1 \). It is straightforward to calculate the energy spectrum of an armchair carbon nanotube within the effective low-energy model Eq. (6.27). In Figure 6-11 we have sketched this one-dimensional energy spectrum in the vicinity of the Fermi energy, \( E = 0 \), which should be compared with that of the armchair nanotube in Figure 6-7 (a). The position of the two Fermi points \((n = 1, 2)\) is given by
\[
k_F = \pm \frac{2}{a} \arccos \left( -\frac{t_\perp}{2t_\parallel} \right) ,
\]
(6.28)

and depends on the ratio \( t_\perp/t_\parallel \) of the electron hopping amplitudes. Close to \( \pm k_F \), the electron energy spectrum consists of two bands that cross with linear energy dispersion
\[
e_n^\pm(k) = \pm v_F k .
\]
(6.29)
Figure 6.11: The electronic low-energy properties of an armchair carbon nanotube are identical to those of the two-leg ladder model. The two triangular sublattices $i = A, B$ are indicated by, respectively, “o” and “•”, and the dashed rectangle indicates the unit cell of the ladder model. The thick arrow points in the direction along the nanotube axis. Close to the Fermi points $n = 1, 2$, the electronic energy dispersion is linear.

Here, $\kappa$ is measured from the Fermi points and the Fermi velocity is given by

$$v_F = a t_\parallel \sin \left( k_F \frac{a}{2} \right).$$

(6.30)

Clearly, for large values of $c_o$ ($\gg 10$), the energy gap of the next higher $k_\perp$-mode is small ($\ll 10^3$ K), so that the applicability of the effective low-energy model becomes strongly limited or even meaningless.

We finally note that a similar mapping procedure can be applied in the case of $c_z [0, 3]$ zigzag carbon nanotubes [6]. This is possible because the corresponding Brillouin zone can also be rearranged into a rectangle, which allows again to separate the sum over momentum $\vec{k}$ into summations over the $k_x$ and $k_y$ components. The Hamiltonian of the resulting effective
low-energy model reads,

\[ H_{\text{zig}} = \sum_{j=1,2} \sum_{n_{\parallel},\sigma} \left\{ -t_+ d_{\alpha\sigma}^+(n_{\parallel}) d_{\beta\sigma}(n_{\parallel} + \frac{1}{2}) \\
- t_- d_{\beta\sigma}^+(n_{\parallel} + \frac{1}{2}) d_{\alpha\sigma}(n_{\parallel} + 1) + \text{h.c.} \right\}, \]  

(6.31)

where the integer \( n_{\parallel} \) labels sites along the zigzag nanotube axis. This model describes two \((j = 1, 2)\) decoupled dimerized chains with electron hopping amplitude

\[ t_\pm = \frac{t_{\parallel} + t_{\perp}}{2} \pm \frac{\Delta}{2} \]  

(6.32)

that contains the gap parameter \( \Delta = |t_{\parallel} - t_{\perp}| \). Instead of gapless points in the one-dimensional energy spectrum, already the lowest \( k_{\perp} \)-mode contains an energy gap \( E_0^c = 2\Delta \) in zigzag nanotubes. Supposing that curvature effects give rise to a relative difference in the hopping amplitudes of only 1\%, one obtains an energy gap \( E_0^c \approx 300K \).

### 6.2.3 Bond alternation patterns in armchair carbon nanotubes

In general, armchair carbon nanotubes are considered to be metallic as their one-dimensional energy bands contain the Dirac points \( K_{\pm} \) even if curvature effects are taken into account. However, a homogeneous deformation of the nanotube lattice may result in the opening of an energy gap turning the armchair carbon nanotube into a semiconductor. In this section, we consider several possible bond alternation patterns in armchair carbon nanotubes within the two-leg ladder model Eq. (6.27) and discuss its expected electronic properties due to the change in the electron hopping amplitudes. Then, in Section 6.3, we derive a continuum model for the nanotube lattice and calculate the relevant lattice eigenmodes as well as their coupling to the electrons in order to study the Peierls transition in armchair carbon nanotubes.

Several bond alternation patterns for armchair carbon nanotubes are depicted in Figure 6-12. The ISO-configuration corresponds to the undistorted armchair nanotube lattice with equivalent bonds. The ALT1-configuration is a lattice deformation that involves only bonds in the circumferential direction. The hopping amplitudes of these bonds, \( t_{\perp} \), differ from the hopping amplitude along the nanotube axis, \( t_{\parallel} < t_{\perp} \). However, this bond alternation pattern does not result in the opening of an energy gap at the Fermi energy, as the two carbon atoms in the unit cell remain equivalent. In fact, very similar to the curvature effects discussed above, this configuration only affects the position of the Dirac points, \( \pm k_F \), and renormalizes the Fermi velocity \( v_F \). In the case of the ALT2- and ALT3-configuration, the electron hopping amplitudes are described by an additional term to the two-leg ladder model Eq. (6.27), which in terms of the operators Eq. (6.26) reads:

\[ H_{\text{dist}}[\Delta, \Theta] = -\frac{\Delta}{2} \sum_{n_{\parallel},\sigma} \left\{ d_{\alpha\sigma}^+(n_{\parallel}) d_{\beta\sigma}(n_{\parallel} - \frac{1}{2}) - d_{\alpha\sigma}^+(n_{\parallel} + \frac{1}{2}) d_{\beta\sigma}(n_{\parallel} - \frac{1}{2}) + \Theta \left[ d_{\beta\sigma}^+(n_{\parallel}) d_{\alpha\sigma}(n_{\parallel} - \frac{1}{2}) - d_{\beta\sigma}^+(n_{\parallel}) d_{\alpha\sigma}(n_{\parallel} + \frac{1}{2}) \right] + \text{h.c.} \right\}. \]  

(6.33)

Here, the relative difference in the hopping amplitudes due to long and short bonds is measured by the gap parameter \( \Delta \propto |u_{n_{\parallel} - u_{n_{\parallel} + 1/2}}| \) which is proportional to the uniform atomic shifts
Figure 6-12: Several bond alternation patterns in the honeycomb lattice of an armchair carbon nanotube that can be described within the two-leg ladder model. Long and short bonds are drawn as thin and thick lines, respectively, and correspond to small and large hopping amplitudes. The thick arrow points in the direction along the nanotube axis.

\[ u_{n_1} \text{ in the direction of the bond. We account for the out-of-phase dimerization in the two legs of the ladder by } \Theta = -1 \text{ for the ALT2-configuration, whereas for the ALT3-configuration with in-phase dimerization } \Theta = +1. \text{ It is straightforward to diagonalize the Hamiltonian } H_{\text{arm}} + H_{\text{dist}} \text{ and we obtain the energy bands } \pm E_{k_1} [\Delta, \Theta] \text{ with} \]

\[ E_{k_1} [\Delta, \Theta] = \left[ 2t_\parallel \cos \left( \frac{k_\parallel a}{2} \right) \pm \frac{1-\Theta}{2} t_\parallel \right]^2 + \Delta^2 \sin \left( \frac{k_\parallel a}{2} \right)^2 \right]^{\frac{1}{2}} \pm \frac{1+\Theta}{2} t_\parallel. \quad (6.34) \]

In the case of the ALT3-configuration (\( \Theta = +1 \)) the energy spectrum Eq. (6.34) does not change close to the two Fermi points \( n = 1, 2 \). As long as \( \Delta \ll t_\parallel \sim t_\perp \), the armchair nanotube remains metallic with \( \varepsilon_{\text{ALT3}, n}^\pm (\kappa) \simeq \pm v_F k \), where \( k \) is measured from \( k_F \). On the other hand, for the ALT2-configuration with out-of-phase dimerization, \( \Theta = -1 \), valence and conduction band states are mixed resulting in the opening of an energy gap at the Fermi energy. Close to the Fermi points, the electronic energy dispersion becomes

\[ \varepsilon_{\text{ALT2}, n}^\pm (\kappa) \simeq \pm \left[ v_F^2 k^2 + \Delta^2 \sin \left( \frac{k_F a}{2} \right)^2 \right]^{\frac{1}{2}}, \quad (6.35) \]

\( \text{where the Fermi wave vector } k_F \text{ and the Fermi velocity } v_F \text{ are given by, respectively, Eqs. (6.28) and (6.30). The ALT2-configuration has a } Z_2 \text{ symmetry for which the potential energy landscape is a double-well potential with degenerate minima corresponding to the two deformations } \Delta = +\Delta_0 \text{ and } \Delta = -\Delta_0. \text{ Similar to the situation in } \text{trans-polyacetylene, the existence of an inhomogeneous kink-solution for } \Delta, \text{ which interpolates between } \pm \Delta_0 \text{ and } \mp \Delta_0, \text{ can be postulated for this type of bond alternation pattern.} \)
Figure 6-13: (a) The Kekulé structure is an in-plane bond alternation with cells labelled A, B and C according to the relative position of long (thin lines) and short (thick lines) bonds in the hexagons. (b) Out-of-plane lattice deformation where “○” and “●” denote, respectively, atomic shifts $+u_z$ and $-u_z$ in the radial direction of the nanotube. The thick arrow points in the direction along the nanotube axis.

Besides the in-plane bond alternation patterns shown in Figure 6-12, there exist also more complicated lattice deformations of which two examples are shown in Figure 6-13. The Kekulé structure depicted in Figure 6-13 (a) is another in-plane bond alternation and has a unit cell which contains six carbon atoms. This lattice configuration leads to the opening of a gap at the Fermi energy in an arbitrary $|c_-, c_+|$ carbon nanotube [19, 11]. Only recently it has been clarified, that the symmetry of the Kekulé structure is not a discrete $Z_3$ symmetry but a continuous $U(1)$ symmetry [28]. This is surprising, as the Kekulé structure tripels the size of the unit cell and one may expect three degenerate minima in the potential energy landscape, that originate from the three possible arrangements of the cells A, B and C (see Figure 6-13). However, this argument is based on the assumption that it is sufficient to consider atomic shifts only along the bond directions. If a generalized Kekulé distortion is considered, however, the energy cost due to a spatial rotation of a displacement vector is found to be so low, that the three degenerate minima in the potential energy landscape become very shallow dips in a mexican hat potential. It follows, that any kind of fluctuations destroys the long-range order in this lattice configuration. This makes the idea of an inhomogeneous kink-solution for the corresponding order parameter meaningless [28].

In Figure 6-13 (b) we show an out-of-plane deformation where carbon atoms are shifted in the radial direction of the nanotube. Assuming that two neighboring atoms are shifted by the same amount but in opposite directions, $+u_z$ and $-u_z$, all carbon-carbon bonds remain equivalent. Thus, all electron hopping amplitudes remain equal and the number of carbon atoms per unit cell is still two in this case. However, the site energies of the two carbon atoms differ due to the difference between the inner ($-u_z$) and outer ($+u_z$) direction of a single-wall carbon nanotube, so that the two atoms of the unit cell are not equivalent anymore. It follows, that the corresponding electronic spectrum has a gap at the Fermi energy which is proportional to the value of the atomic shift $|u_z|$ [10].

We finally consider a twist deformation of the nanotube lattice. This type of lattice deformation corresponds to a shear in the underlying two-dimensional graphene sheet as is shown in Figure 6-14. The uniform twist distortion is described by atomic shifts $u_{\alpha}(n_{\parallel}) = n_{\parallel}u_{\alpha}$ in the circumferential direction perpendicular to the nanotube axis. Very similar to the ALT2-
Figure 6-14: A twist deformation in an armchair carbon nanotube corresponds to a shear of the graphene sheet (dotted lines represent the undistorted honeycomb lattice) and is described by the two-leg ladder model with out-of-phase dimerization in the hopping amplitudes. Thick and thin lines correspond to shrunk and elongated bonds with, respectively, large and small hopping amplitudes. The thick arrow points in the direction along the nanotube axis.

configuration (see Figure 6-12 (c)), the thus obtained long and short bonds describe an out-of-phase alternation in the two-leg ladder model as given by Eq. (6.33) with $\Theta = -1$. The electronic spectrum has a gap at the Fermi energy and equals the expression Eq. (6.35) close to the Fermi points. In Section 6.3 we show that the twist deformation of the nanotube lattice is caused by long wavelength acoustic phonons ($q \to 0$) with frequency $\omega_a \propto q$, while the ALT2-configuration is found to involve an optical phonon with finite frequency $\omega_a$. The coupling between the electrons and both these phonon modes is finite leading to the opening of an energy gap due to the backscattering between left- and right-moving electrons.

6.3 Long wavelength electron-lattice coupling in armchair carbon nanotubes

In this section, we derive the most general continuum model of the armchair nanotube lattice which is compatible with its symmetry. Furthermore, we identify the long wavelength phonon modes that result in the backscattering of electrons.

We consider the lattice of the armchair nanotube $c_\alpha[1,1]$ as an array of $N$ connected rings at a distance $a/2$ along the nanotube axis. Figure 6-15 (a) is an illustration of such a ring containing $2c_\alpha$ carbon atoms, where $c_\alpha$ carbon atoms belong to each of the two triangular sublattices that build up the hexagonal nanotube lattice. We take into account lattice degrees of freedom in the cylindrical nanotube surface and, keeping in mind that the lattice distortion couples to electrons that have zero transverse momentum, we can disregard the dispersion of the atomic displacements in the circumferential direction. Thus, the time-dependent atomic displacement in the $i$'th sublattice,

$$\vec{u}_i(x,t) = (X_i(x,t), Y_i(x,t))^T,$$  \hspace{1cm} (6.36)

is a function of the $x$-coordinate along the nanotube axis only. Within the continuum model a ring of the nanotube lattice is characterized by the atomic displacements $\vec{u}_i$ in the two
sublattices $i = A, B$, and their spatial and time derivatives, respectively, $\ddot{u}_i^r$ and $\dot{u}_i^r$. It is convenient to introduce an eight-dimensional ring-vector

$$\vec{R}(x, t) = (X_A, X_A', Y_A, Y_A', X_B, X_B', Y_B, Y_B')^T,$$

which is to be understood as a mathematical construction that combines all information to describe the distortion in a ring as a function of time and position along the nanotube axis.

The total lattice energy is the sum of the kinetic and the potential lattice energy, $H_{\text{lat}} = T + U$. In terms of the ring-vector $\vec{R}$, the kinetic lattice energy reads

$$T = \frac{1}{2} \int dx \frac{d\vec{R}^T}{dt} \dot{\mathbf{\hat{\rho}}} \frac{d\vec{R}}{dt},$$

where $\dot{\mathbf{\hat{\rho}}} = (\rho_{lm})$ is the mass density matrix and $l, m = 1, \ldots, 8$. The only non-zero elements $\rho_{lm}$ are the diagonal elements that couple the time derivatives $\dot{u}_i$ of the atomic displacements. The potential energy in terms of the ring-vector $\vec{R}$ reads

$$U = \frac{1}{2} \int dx \vec{R}^T \hat{K} \vec{R},$$

where the matrix $\hat{K} = (k_{lm})$ couples all elements of $\vec{R}$ in a ring ($l, m = 1, \ldots, 8$). We note that the matrix elements $\rho_{lm}$ and $k_{lm}$ have to satisfy the conditions that the total lattice energy is invariant under

(i) a constant shift of $\ddot{u}_A$ and $\ddot{u}_B$ that leaves the distance between the two sublattices unchanged and corresponds to a translation of the ring-vector,

$$\vec{R} \rightarrow \vec{R} + \left( C_X, 0, C_Y, 0, C_X, 0, C_Y, 0 \right)^T \text{ with } C_X, C_Y \text{ constant};$$

(ii) a constant shift of $\ddot{u}_A$ and $\ddot{u}_B$ that leaves the distance between the two sublattices unchanged and corresponds to a translation of the ring-vector,

$$\vec{R} \rightarrow \vec{R} + \left( C_X, 0, C_Y, 0, C_X, 0, C_Y, 0 \right)^T \text{ with } C_X, C_Y \text{ constant};$$

(iii) a constant rotation of the ring-vector.

\[ \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \]

\[ \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \]
(ii) a transformation $\vec{R} \rightarrow \hat{\mathbf{U}} \vec{R}$ that is allowed by the symmetry of the hexagonal nanotube lattice.

In Figure 6.15 (b) we visualize the reflection symmetry of the hexagonal nanotube lattice with respect to the $x$-axis and $y$-axis together with the corresponding symmetry transformation matrices $\hat{\mathbf{U}}_x$ and $\hat{\mathbf{U}}_y$. It then follows from the conditions $\hat{\mathbf{U}}_x \hat{\mathbf{U}}_y^\dagger = \hat{\mathbf{I}}$ where $\hat{\mathbf{U}}_x = \hat{\mathbf{U}}_y = \hat{\mathbf{U}}_{xy}$, the only non-zero elements $\rho_{lm}$ are given by $\rho_{11} = \rho_{55} \equiv \rho_x$ and $\rho_{33} = \rho_{77} \equiv \rho_y$. Furthermore, the conditions $\hat{\mathbf{U}}_x \hat{\mathbf{U}}_y^\dagger = \hat{\mathbf{K}}$, where again $\hat{\mathbf{U}}_x = \hat{\mathbf{U}}_y = \hat{\mathbf{U}}_{xy}$, together with condition (i) given above, reduce the number of free coupling parameters $k_{lm}$ from 36 to a set of eight parameters which we denote by $[\alpha_x, \alpha_y, \beta_x, \beta_y, \gamma_x, \gamma_y, \delta_x, \delta_y]$.

It now is convenient to define four new functions, $X_\pm, Y_\pm$, by

$$X_\pm = \frac{1}{\sqrt{2}} (X_A \pm X_B) \quad \text{and} \quad Y_\pm = \frac{1}{\sqrt{2}} (Y_A \pm Y_B) \quad \text{,} \quad (6.41)$$

which enables us to write the total lattice energy of the armchair carbon nanotube in the form:

$$H_{\text{lat}} = \frac{1}{2} \int \text{d}x \left[ \rho_x (|\dot{X}_+|^2 + |\dot{X}_-|^2) + \rho_y (|\dot{Y}_+|^2 + |\dot{Y}_-|^2) +
+ 2\alpha_x |X_-|^2 + 2\alpha_y |Y_-|^2 +
+ (\beta_x + \gamma_x) |X'_+|^2 + (\beta_x - \gamma_x) |X'_-|^2 +
+ (\beta_y + \gamma_y) |Y'_+|^2 + (\beta_y - \gamma_y) |Y'_-|^2 +
+ \delta_x (X'_+ Y'_+ - X'_- Y'_-) + \delta_y (Y'_+ X'_+ + X'_- Y'_-) \right] \quad \text{.} \quad (6.42)$$

This expression represents the most general continuum model of the armchair nanotube lattice which is compatible with its symmetry. We can write Eq. (6.42) in a more compact form, if we define a new ring-vector

$$\vec{\mathbf{R}} = (X_+, Y_+, X_-, Y_-)^T \quad \text{,} \quad (6.43)$$

and use the ansatz $\vec{\mathbf{R}}(x,t) = 1/\sqrt{N} \sum_q \vec{\mathbf{R}}_q \exp[iq x - i\omega t]$. The total lattice energy is then obtained in the simple form

$$H_{\text{lat}} = \frac{1}{2} \sum_q \vec{\mathbf{R}}_q^\dagger \hat{H}_{\text{lat}} \vec{\mathbf{R}}_q \quad \text{,} \quad (6.44)$$

where the matrix $\hat{H}_{\text{lat}}$ reads

$$\hat{H}_{\text{lat}} = \frac{\alpha}{2} \begin{pmatrix}
\omega^2 \rho_x + \frac{q^2}{2} (\beta_x + \gamma_x) & 0 & 0 & iq \delta_y \\
0 & \omega^2 \rho_y + \frac{q^2}{2} (\beta_y + \gamma_y) & -iq \delta_x & 0 \\
0 & iq \delta_x & \omega^2 \rho_x + 2\alpha_x + \frac{q^2}{2} (\beta_x - \gamma_x) & 0 \\
-iq \delta_y & 0 & 0 & \omega^2 \rho_y + 2\alpha_y + \frac{q^2}{2} (\beta_y - \gamma_y)
\end{pmatrix} \quad \text{.} \quad (6.45)$$
Figure 6-16: The (a) negative and (b) positive parity mode of the armchair nanotube lattice. The two triangular sublattices \( i = A, B \) are depicted by, respectively, \( \ast \) and \( \bullet \) in the hexagon of the nanotube lattice. The negative (positive) parity mode describes a bond length alternation along (perpendicular to) the nanotube axis.

It is easy to check that the matrix \( \hat{H}_{\text{lat}} \) is invariant under the parity transformation

\[
\hat{P} = \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\]

with \( \hat{P}^2 = 1 \).

We can thus classify the four eigenmodes of the lattice Hamiltonian Eq. (6.44) by their parity,

\[
\hat{P} \vec{R}_\pm = \pm \vec{R}_\pm, \quad \text{with} \quad \vec{R}_- = (0, Y_+, X_-, 0)^T \quad \text{and} \quad \vec{R}_+ = (X_+, 0, 0, Y_-)^T.
\]

The lattice deformations described by \( \vec{R}_+ \) and \( \vec{R}_- \) are illustrated in Figure 6-16. The negative parity mode describes a bond length alternation along the nanotube axis (\( X_A = -X_B \) and \( Y_A = Y_B \)), which is out of phase in neighboring zigzag chains of the armchair nanotube lattice. The two eigenmodes that belong to the negative parity mode \( \vec{R}_- \) are:

(i) an optical phonon mode with amplitude \( u_o(x,t) \),

\[
\frac{\partial^2}{\partial t^2} u_o(x,t) = -\omega_o^2 u_o(x,t) \quad \text{and frequency} \quad \omega_o \approx \frac{\sqrt{2\alpha_x}}{\rho_x},
\]

(ii) an acoustic phonon mode with amplitude \( u_a(x,t) \),

\[
\frac{\partial^2}{\partial t^2} u_a(x,t) = v_o^2 \frac{\partial^2}{\partial x^2} u_a(x,t),
\]

where the frequency \( \omega_a(q) \approx v_o|q| \) contains the phonon velocity

\[
v_o = \left( \frac{\beta_y + \gamma_y}{\rho_y} - \frac{\delta_x^2}{2\rho_y \alpha_x} \right)^{\frac{1}{2}}.
\]
On the other hand, the positive parity mode describes a shift of the two sublattices against each other in the circumferential direction \((Y_A = -Y_B \text{ and } X_A = X_B)\). This does not affect the length of the bonds along the nanotube axis as can be seen in Figure 6-16 (b). To the positive parity mode \(\vec{R}_+\), belongs an optical phonon mode with frequency \(\tilde{\omega}_O \approx \sqrt{2\alpha_y/\rho_y}\), and an acoustic phonon mode \(\tilde{\omega}_A(q)\) with phonon velocity \(\tilde{v}_0 = ((\beta_x + \gamma_x)/\rho_x - \delta_y^2/(2\rho_x\alpha_y))^{1/2}\). We may conclude from these considerations, that the optical and acoustic phonon modes which belong to the negative parity mode, respectively, Eqs. (6.48) and (6.49), will cause backscattering of electrons for small \(q\). We will now verify this conclusion by an explicit calculation of the electron-lattice interaction.

The effective low-energy model of the armchair carbon nanotube corresponds to a two-leg ladder model and has been derived in Section 6.2.2 for free electrons. At all relevant temperatures, the electrons occupy the lowest mode with zero transverse momentum around the circumference of the carbon nanotube, and can only propagate in the \(x\)-direction along the armchair nanotube axis. Therefore, the nanotube’s electronic properties can be derived from its repeat-unit around the circumference which corresponds to a two-leg ladder as indicated in Figure 6-17. Here, we generalize the Hamiltonian of the two-leg ladder model (see Eq. (6.27)) and take into account that the electron hopping amplitudes depend on the interatomic distances between the electronic orbitals on neighboring atoms. Figure 6-17 visualizes the notation that is used to write the two-leg ladder Hamiltonian in the compact form

\[
H_{\text{arm}} = - \sum_{n_i, \sigma} \sum_{j=1}^{6} T_j \left( d_{A\sigma}^\dagger n_i \| a + a_j \right) d_{B\sigma} n_i \| a + b_j + h.c. \right). \tag{6.51}
\]
The fermionic operator $d_{i\sigma}(n_{||}\alpha)$ ($d_{i\sigma}^{\dagger}(n_{||}\alpha)$) annihilates (creates) an electron in sublattice $i = A, B$ with spin $\sigma$ at position $x = n_{||}\alpha$ along the nanotube axis. The electron hopping amplitudes depend on the atomic displacements Eq. (6.36) and take the form

$$T_j = t_j + \frac{\alpha_j}{\sqrt{c_a}} \tilde{\mathbf{e}}_j \cdot (\tilde{u}_B(n_{||}\alpha + b_j) - \tilde{u}_A(n_{||}\alpha + a_j)) .$$

(6.52)

Here, $t_j$ denotes the hopping amplitude in the absence of electron-lattice interactions, while $\alpha_j/\sqrt{c_a}$ is the electron-lattice coupling and $\tilde{\mathbf{e}}_j$ is a unit vector which is oriented along bond $j$. We note that the electron-lattice coupling in the armchair carbon nanotube with $2c_a$ zigzag chains around its circumference contains a factor $1/\sqrt{c_a}$, which appears as in Eq. (6.26) due to the partial Fourier transformation of the atomic displacements $\tilde{u}_i(\mathbf{x})$ for zero transverse momentum. The explicit expressions of the electron hopping amplitudes $T_j$ are summarized in the table of Figure 6-17 and satisfy the condition that $H_{atm}$ is invariant under the reflection symmetry $X_A \leftrightarrow X_B; \ Y_A \leftrightarrow -Y_B$.

We now derive the continuum model of $H_{atm}$ which describes the system close to the Fermi points. This is done by interpreting $x$ as a continuous variable in the direction of the nanotube axis and by representing the operator $d_{i\sigma}(x + a_j)$ close to each Fermi point as a product of two factors,

$$d_{i\sigma}(x + a_j) \approx \sqrt{\frac{\alpha}{2}} \left( e^{ik_F(x+a_j)}\psi_{i,1,\sigma}(x + a_j) + e^{-ik_F(x+a_j)}\psi_{i,2,\sigma}(x + a_j) \right) .$$

(6.53)

The exponential factor varies fast along the nanotube axis on the scale of the lattice constant $\alpha \sim k_F^{-1}$, while the second factor is the slowly varying function $\psi_{i,1,\sigma}$ at the Fermi point $n = 1, 2$ and is related to the small deviation of the electron momentum from the Fermi wave vector $\pm k_F$. In the absence of the electron-lattice coupling, $\alpha_j \equiv 0$, we obtain from Eq. (6.51) the kinetic energy of the electrons,

$$H_{el} = \frac{v_F}{i} \sum_{n,\sigma} \int dx \psi_{n,\sigma}^{\dagger}(x) \frac{\partial}{\partial x} \psi_{n,\sigma}(x) .$$

(6.54)

The spinor $\psi_{n,\sigma}(x)$ is given by

$$\psi_{n,\sigma}(x) = \begin{pmatrix} \psi_{R,n,\sigma}(x) \\ \psi_{L,n,\sigma}(x) \end{pmatrix} \equiv \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & (-1)^n \\ i & -i(-1)^n \end{pmatrix} \begin{pmatrix} \psi_{A,n,\sigma}(x) \\ \psi_{B,n,\sigma}(x) \end{pmatrix} ,$$

(6.55)

and describes the left- and right-moving electrons at the two Fermi points $n = 1, 2$ with Fermi velocity $v_F = a t_0 \sin(k_F \alpha/2)$ and $k_F = (2a/\alpha) \arccos(-t_\perp/(2t_||))$. Thus, the electron energy spectrum described by $H_{el}$ consists of two Fermi points. At each Fermi point two electron bands with linear dispersion intersect as depicted in Figure 6-1. For finite coupling $\alpha_j$, we obtain from Eq. (6.51) the electron-lattice Hamiltonian,

$$H_{el-lat} = \sum_{n,\sigma} \int dx \psi_{n,\sigma}^{\dagger}(x) \sigma_1 \psi_{n,\sigma}(x) \sum_j (T_j - t_j) \frac{\sin(k_F(a_j - b_j))}{2} ,$$

(6.56)

which describes the backscattering of electrons at each Fermi point $n$. In the derivation of this expression, forward scattering contributions have been omitted, as these processes are of the
type $\Psi_{n,\sigma}^j(x)\Psi_{n,\sigma}(x)$ and do not lead to an instability. The sum over $j$ is carried out using the explicit expressions for the hopping amplitudes $T_j$ according to the table in Figure 6-17 in combination with Eq. (6.52). We find,

$$H_{\text{el-lat}} = \sqrt{\frac{\alpha}{\epsilon}} \sum_{n,\sigma} \left[ \int dx \Psi_{n,\sigma}^\dagger(x) \sigma_1 \Psi_{n,\sigma}(x) \mathcal{N}_\alpha \frac{\partial Y_+}{\partial x} \right],$$  

which shows that, as expected, the backscattering of electrons only depends on $X_-$ and $Y_+$. The latter are linear combinations of the optical and acoustic phonon modes defined in Eqs. (6.48) and (6.49), respectively. To lowest order in the derivatives, the shifts $X_-$ and $Y_+$ and the amplitudes $u_o$ and $u_a$ are related by:

$$\begin{align*}
X_- &= \frac{\delta_x}{2\omega_x} \frac{\partial}{\partial x} u_a + u_o, \\
Y_+ &= -u_a - \frac{\delta_x}{2\omega_x} \frac{\rho_x}{\rho_y} \frac{\partial}{\partial x} u_o, \\
Y_+ &= \frac{\delta_x}{2\omega_x} \frac{\rho_x}{\rho_y} \frac{\partial}{\partial x} X_-. 
\end{align*}$$

(6.58)

We thus see, that the optical as well as the acoustic phonon mode involve atomic shifts in both the direction perpendicular and parallel to the nanotube's axis. However, within a somewhat simplified picture, the optical phonons correspond to a relative shift of the nanotube's two triangular sublattices against each other along its axis. This then leads to a lattice deformation with out-of-phase bond length dimerization in neighboring zigzag chains along the nanotube axis (see Figure 6-12 (c)). Similarly, the acoustic phonons describe a twist of the cylindrical nanotube lattice, which also results in an out-of-phase bond length dimerization (see Figure 6-14).

The electron-lattice interaction Eq. (6.57) can finally be written in the convenient form

$$H_{\text{el-lat}}[\Delta_o + \Delta_a] = \sum_{n,\sigma} \int dx \Psi_{n,\sigma}^\dagger(x) \left( \Delta_o + \Delta_a \right) \sigma_1 \Psi_{n,\sigma}(x).$$

(6.59)

Here we introduced the “order parameter” $\Delta_i$ for optical ($i = o$) and acoustic ($i = a$) phonons, which to the lowest order in the derivatives of the phonon amplitude $u_i$ is given by

$$\begin{align*}
\Delta_o &= \sqrt{\frac{\alpha}{\epsilon}} \frac{\partial}{\partial x} \left( k_F \frac{\pi}{2} \right) u_o \\
\Delta_a &= \sqrt{\frac{\alpha}{\epsilon}} \frac{\partial}{\partial x} \left( k_F \frac{\pi}{2} \frac{2\sqrt{3}b_0 + a\omega_x}{4\sqrt{3}\omega_x} \right) \frac{\partial}{\partial x} u_a.
\end{align*}$$

(6.60)

As is clear from Eq. (6.59), the difference between the optical and acoustic phonons is that $\Delta_o$ is proportional to the amplitude $u_o$, while $\Delta_a$ is proportional to derivative of the amplitude, $\partial u_a/\partial x$.

To study the Peierls transition due to both optical and acoustic phonons, we consider the continuum Hamiltonian

$$H = H_{\text{el}} + H_{\text{el-lat}}[\Delta_o + \Delta_a] + H_{\text{lat}}[\Delta_o] + H_{\text{lat}}[\Delta_a],$$

(6.61)

where $H_{\text{el}}$ and $H_{\text{el-lat}}$ are given by, respectively, Eq. (6.54) and Eq. (6.59). The last two terms in Eq. (6.61) describe the lattice energy of the optical ($i = o$) and acoustic ($i = a$) phonons,

$$H_{\text{lat}}[\Delta_i] = \frac{N_F}{\pi \lambda_i v_F} \int dx \Delta_i^2 + \frac{1}{2\rho_i} \int dx \pi_i^2,$$

(6.62)
where the momentum density is given by \( \tau_i(x, t) = \rho_i \partial u_i(x, t)/\partial t \) and contains the corresponding mass densities \( \rho_\text{e} = \rho_x \) and \( \rho_\text{a} = \rho_y \). We introduced in Eq. (6.62) the factor \( N_F \) which denotes the number of Fermi points, \( n = 1, \ldots, N_F \), at which two electron bands cross with linear energy dispersion. The dimensionless electron-lattice coupling constant for the optical \( (i = o) \) and acoustic \( (i = a) \) phonon mode is defined by

\[
\lambda_i \equiv \frac{2 N_F}{\pi \nu_F} \frac{2 |g_i|^2}{\omega_i}
\]  

and absorbs a factor \( N_F \), so that for \( \Delta_a = 0 \) and \( N_F = 1 \) the Hamiltonian Eq. (6.61) coincides with the Hamiltonian of the Takayama–Lin-Liu–Maki (TLM) model. This is the continuum version of the Su–Schrieffer–Heeger (SSH) model for polyacetylene [14, 29], which we considered in Section 2.2. On the other hand, for \( \Delta_a = 0 \) and \( N_F = 2 \), the Hamiltonian Eq. (6.61) is equivalent to the Hamiltonian describing the electron-twist interactions in the armchair carbon nanotubes [27, 30]. An order parameter \( \Delta_a = \text{const.} \) corresponds to a uniform twist deformation of the armchair carbon nanotube and was, in fact, recently observed by the scanning tunneling microscopy technique [31].

### 6.4 Peierls transition with acoustic and optical phonons

In this chapter, we study the Peierls transition in the electron-lattice system Eq. (6.61), which involves both acoustic and optical phonons. The coupling of the phonons to electrons has two effects which have to be taken into account in a self-consistent treatment of this system: It mixes the bare optical and acoustic phonon modes and it renormalizes their frequencies due to electron-hole excitations. As both types of phonons backscatter left (right) moving electrons into right (left) moving ones, we expect a phase transition similar to the Peierls instability at a certain temperature \( T_c \).

We first apply a Fourier transformation to write the Hamiltonian Eq. (6.61) in momentum space:

\[
\mathcal{H} = \sum_{n, \sigma} \sum_{s = \pm} \sum_p \left[ \varepsilon_n^s(p) \, c_{n, s, \sigma}^\dagger(p) c_{n, s, \sigma}(p) + \frac{s}{\sqrt{\nu_F}} \sum_{i = a, o} \sum_q g_i(q) \left( b_i(q) + b_i^\dagger(-q) \right) c_{n, s, \sigma}^\dagger(p) c_{n, -s, \sigma}(p - q) \right] + \sum_{i = a, o} \sum_q \omega_i(q) \left( b_i^\dagger(q) b_i(q) + \frac{1}{2} \right). 
\]

Here, the fermionic operator \( c_{n, s, \sigma}^\dagger(p) (c_{n, s, \sigma}(p)) \) denotes the creation (annihilation) of an electron with spin projection \( \sigma \) and small momentum \( |p| \ll k_F \) measured from the Fermi point \( n \). The index \( s \) refers to right- \( (s = +) \) and left-moving \( (s = -) \) electrons with linear energy dispersion \( \varepsilon_n^s(p) = s \nu_F p \). The second term in the Hamiltonian is obtained from the quantization of the atomic displacements and describes the backscattering of the electrons \( (s = \pm \leftrightarrow s = \mp) \) due to the interaction with acoustic and optical phonons. The creation (annihilation) of an acoustic, \( i = a \), or optical, \( i = o \), phonon with small momentum \( q \)
is represented by the bosonic operator $\hat{b}^\dagger_i(q)$ $(\hat{b}_i(q))$ and the corresponding electron-lattice coupling constant is given by
\[
\begin{align*}
g_o &= \sqrt{\frac{\alpha_i}{\varepsilon_{\alpha}}} \sin \left( k_F \frac{q}{2} \right) \frac{1}{\sqrt{2\rho_o \omega_o}} \quad \text{for optical phonons,} \\
g_a &= \sqrt{\frac{\alpha_i}{\varepsilon_{\alpha}}} \sin \left( k_F \frac{q}{2} \right) \left[ \frac{2\sqrt{3}\delta_i + a \alpha_s}{4\sqrt{3}\alpha_s} \right] \frac{-q}{\sqrt{2\rho_o \omega_{\alpha}(q)}} \quad \text{for acoustic phonons.} 
\end{align*}
\tag{6.65}
\]

It thus follows that the coupling $g_a(q)$ to the acoustic phonon with frequency $\omega_a = \nu_0 |q|$ is proportional to $\sqrt{q}$, whereas the coupling to the optical phonon, $g_o(q)$, is approximately constant due to the finite frequency $\omega_o$. We note that, though the coupling to acoustic phonons $g_a(q)$ is small for small $q$, the actual strength of the interaction is given by the dimensionless electron-lattice coupling Eq. (6.63) which is finite both for optical and acoustic phonons. The lattice energy of the two modes is given by the third term in Eq. (6.64).

We consider the temperature dependence of the optical and acoustic phonon frequencies at temperatures $T$ above the critical temperature $T_c$. The bare phonon propagation, $\mathcal{D}_0$, is formally written in terms of a $2 \times 2$-matrix,
\[
\mathcal{D}_0 = \begin{pmatrix} D_0^0 & 0 \\ 0 & D_0^a \end{pmatrix}.
\tag{6.66}
\]

This matrix contains the bare acoustic ($i = a$) and optical ($i = o$) phonon propagator
\[
D_i^0(\omega_i, i\omega_m) = -\frac{2\omega_i}{\omega_m^2 + \omega_i^2},
\tag{6.67}
\]
with the bosonic Matsubara frequency $\omega_m = 2m\pi T$ ($m$ is an integer number) and the bare phonon frequency $\omega_i$. Similarly, the free particle Green's function is defined by
\[
G^s_n(p, ip_m) = \frac{1}{ip_m - \varepsilon^s_n(p)},
\tag{6.68}
\]
with the fermionic Matsubara frequency $p_m = (2m + 1)\pi T$ ($m$ is an integer number). The Fermi points are labelled by $n = 1, \ldots, N_F$, denote the crossing of two electron bands with linear energy dispersion close to the Fermi energy. The index $s$ in Eq. (6.68) refers to right- ($s = +$) and left-moving ($s = -$) electrons with $\varepsilon_n^s(p) = s \sqrt{\nu_T} p$. In the matrix formalism, the coupling of the phonons to electrons is given by the interaction matrix
\[
\mathcal{V} = \begin{pmatrix} g_a^* g^s_n & g_a g^s_n \\ g_o^* g^s_n & g_o g^s_n \end{pmatrix} P(q, i\omega_m, T),
\tag{6.69}
\]
which contains the vacuum polarization $P(q, i\omega_m, T)$. The vacuum polarization describes an electron-hole excitation and recombination by absorption and emission of a phonon with momentum $q$ and (Matsubara) frequency $i\omega_m$. In terms of the particle Green's function Eq. (6.68), the vacuum polarization reads
\[
P(q, i\omega_m, T) = \sum_n \frac{2}{L} \sum_p T \sum_{ip_m} \left\{ G^+_{n}(p, ip_m) G^-_{n}(p + q, ip_m + i\omega_m) + \\
+ G^-_{n}(p, ip_m) G^+_{n}(p + q, ip_m + i\omega_m) \right\},
\tag{6.70}
\]
and the Feynman diagram of a matrix element $V_{ij}$ is shown in Figure 6-18. The summation in Eq. (6.70) is over the internal variables at each Fermi point $n$ with $p$ the particle momentum and $i\omega_n$ the particle energy, while the factor 2 accounts for the spin degrees of freedom.

We will calculate the renormalized acoustic and optical phonon frequencies within the random phase approximation. The propagation of phonons that are dressed by the interaction with the electrons is described by the matrix

$$\mathcal{D} = \begin{pmatrix} D_{aa} & D_{ao} \\ D_{oa} & D_{oo} \end{pmatrix},$$

(6.71)

which is related to the bare phonon propagation matrix $\mathcal{D}_0$ by

$$\mathcal{D} = \mathcal{D}_0 + \mathcal{D}_0 \tilde{\mathcal{V}} \mathcal{D}_0.$$  

(6.72)

Thus, $\mathcal{D}$ differs from $\mathcal{D}_0$ by the interaction between the electrons and phonons denoted by $\tilde{\mathcal{V}}$. Within the random phase approximation, this interaction matrix is the solution of the Dyson equation

$$\tilde{\mathcal{V}} = \mathcal{V} + \mathcal{V} \mathcal{D}_0 \tilde{\mathcal{V}},$$

(6.73)

which describes the renormalization of the bare interaction matrix Eq. (6.69) due to the internal coupling of electron-hole excitations by the acoustic and optical phonons. The Feynman diagrams of the processes that are included in the calculation of the dressed phonon propagation matrix are shown in Figure 6-19. The renormalized optical and acoustic phonon frequencies are found from the poles of $\det(\mathcal{D})$, or, equivalently, by solving

$$\det(\mathcal{D}_0^{-1} - \mathcal{V}) = 0.$$  

(6.74)

Thus, as is clear from Eq. (6.69), in order to obtain the renormalized phonon frequencies, we have to calculate the vacuum polarization $P(q, i\omega_m, T)$. This is done in the next section.

### 6.4.1 Analytical calculation of the vacuum polarization

We derive an analytic expression for $P(q, i\omega_m, T)$ starting from its definition Eq. (6.70). First, the frequency summation is evaluated by the standard procedure, where we use Eq. (6.68) to
write the vacuum polarization as

\[ P(q, \omega, T) = \sum_{n} \frac{2}{L} \sum_{p} \left( S^+ + S^- \right), \quad (6.75) \]

where

\[ S^\pm \equiv T \sum_{ip_m} f^\pm(ip_m) = T \sum_{ip_m} \frac{1}{ip_m - \frac{\epsilon^\pm}{p}} \frac{1}{ip_m + \omega_m - \frac{\epsilon^\mp}{p+q}}. \quad (6.76) \]

Instead of directly performing the summation in Eq. (6.76), we consider a contour integration over the product of \( f^\pm(ip_m) \) and the Fermi distribution \( n_F(ip_m) \),

\[ I = \lim_{R \to \infty} \int_{C_R} \frac{dz}{2\pi i} f^\pm(z) n_F(z), \quad (6.77) \]

where we replaced \( ip_m \to z \) and the contour is a large circle with radius \( R \) in the complex \( z \)-plane. The Fermi distribution \( n_F(z) = (e^{\pm/T} + 1)^{-1} \) generates poles at \( z^* = ip_m = (2m+1)\pi T \) with residues \((-T)\), so that

\[ I = -T \sum_{ip_m} f^\pm(ip_m) + \text{Res}_{f^\pm(z)} \left[ f^\pm(z) n_F(z) \right]. \quad (6.78) \]
Here, the second term denotes the contribution from the poles of \( f^\pm(z) \) at \( z_1^* = \varepsilon_n^\pm(p) \) and 
\( z_2^* = \varepsilon_n^\mp(p + q) - i\omega_m \) (see Eq. (6.76)):

\[
\text{Res}_{z^\pm} \left[ f^\pm(z) n_F[z] \right] = \frac{n_F[\varepsilon_n^\pm(p)] - n_F[\varepsilon_n^\pm(p + q)]}{i\omega_m + \varepsilon_n^\pm(p) - \varepsilon_n^\pm(p + q)}.
\] (6.79)

In the limit of a large contour radius, \( R \to \infty \), the integral Eq. (6.77) vanishes, \( I = 0 \), and it follows from Eqs. (6.76) and (6.78), that

\[
S^+ + S^- = \frac{n_F[\varepsilon_n^\pm(p)] - n_F[\varepsilon_n^\pm(p + q)]}{i\omega_m + \varepsilon_n^\pm(p) - \varepsilon_n^\pm(p + q)} + \frac{n_F[\varepsilon_n^\pm(p)] - n_F[\varepsilon_n^\pm(p + q)]}{i\omega_m + \varepsilon_n^\pm(p) - \varepsilon_n^\pm(p + q)}.
\] (6.80)

This allows us to write the vacuum polarization Eq. (6.75) as:

\[
P(q, i\omega_m, T) = \frac{N_F}{2\pi n_F} \int_{-\infty}^{\infty} d\bar{p} \frac{(\bar{p} + \frac{q}{2}) (\tanh \left( \frac{\bar{p} + q}{2} \right) + \tanh \left( \frac{q}{2} \right))}{(i\omega_m + \frac{q}{2})^2}.
\] (6.81)

where the sum over \( p \) has been changed into an integration and we introduced the notation \( \bar{x} \equiv n_F x / T \) for the momenta \( p \) and \( q \). The integral limits contain the energy cut-off \( W \) which is of the order of the electron band width (~ 10 eV).

Proceeding with the \( \bar{p} \)-integration, it turns out to be convenient to split the vacuum polarization into three parts, \( P(q, i\omega_m, T) = I_1 + I_2 + I_3 \), where

\[
I_1 = P(0,0,T),
\]

\[
I_2 = P(q,0,T) - P(0,0,T), \quad \text{and}
\]

\[
I_3 = P(q,i\omega_m,T) - P(q,0,T).
\] (6.82)

It is easy to calculate \( I_1 \), which is found to be logarithmically divergent in the temperature \( T \),

\[
I_1 = -\frac{2N_F}{\pi n_F} \int_0^{\frac{\pi}{2\gamma}} d\bar{p} \frac{\tanh \left( \frac{\bar{p}}{2} \right)}{\bar{p}} = -\frac{2N_F}{\pi n_F} \ln \frac{\gamma W}{\pi T},
\] (6.83)

with \( \gamma = 1.781072... \) denoting the exponential of Euler's constant. Next, we observe that the second part,

\[
I_2 = \frac{N_F \sinh^2 \left( \frac{q}{4} \right)}{\pi n_F} \int_{-\infty}^{\infty} d\bar{p} \frac{\sinh \left( \frac{\bar{p}}{2} \right)}{\bar{p} \cosh \left( \frac{\bar{p}}{2} \right) \cosh \left( \frac{q}{4} \right) \cosh \left( \frac{\bar{p}}{2} + \frac{q}{4} \right)},
\] (6.84)

do not have any singularities on the real \( \bar{p} \)-axis. As the integrand falls off exponentially for \( \bar{p} \to \infty \), we can close the integration contour in the upper half of the complex \( \bar{p} \)-plane and calculate the enclosed residues. The poles are at \( \bar{p}_\pm = i(2l + 1)\pi \pm \frac{q}{2} \) and \( \bar{p}_* = i(2l + 1)\pi \), and we obtain

\[
I_2 = \frac{N_F}{\pi n_F} \sum_{l=0}^{\infty} \left[ \frac{2}{l + \frac{1}{2}} - \frac{1}{l + \frac{1}{2} + \frac{q}{4\pi T}} - \frac{1}{l + \frac{1}{2} - \frac{q}{4\pi T}} \right]
\]

\[
= \frac{N_F}{\pi n_F} \left[ \psi \left( 1 - \frac{i\gamma q}{4\pi T} \right) + \psi \left( 1 + \frac{i\gamma q}{4\pi T} \right) - 2\psi \left( \frac{1}{2} \right) \right].
\] (6.85)
6.4 Peierls transition with acoustic and optical phonons

where \( \Psi(z) \) is the Digamma function, \( \Psi(z) = \frac{d}{dz} \ln \Gamma(z) \). Finally, we consider the dynamical part of the vacuum polarization,

\[
I_3 = \frac{N_F}{2\pi v_F} \left( \frac{\omega_m}{2T} \right)^2 \int_{-\infty}^{+\infty} d\tilde{p} \frac{\sinh[\tilde{p}]}{\tilde{p} \cosh \left( \frac{\tilde{p}}{2} - \frac{q}{4} \right) \cosh \left( \frac{\tilde{p} + q}{2} \right) \left( \frac{\omega_m}{2T} \right)^2 + \tilde{p}^2},
\]

(6.86)

and observe, that we can use the same trick as in the calculation of \( I_2 \), because the integrand again has no singularities on the real \( \tilde{p} \)-axis and falls off exponentially for large values of \( \tilde{p} \). The integral is found to be complex, \( I_3 = \text{Re}[I_3] + i\text{Im}[I_3] \), giving rise to a real and an imaginary part of the vacuum polarization for finite frequencies. Closing the integration contour in the upper half of the complex \( \tilde{p} \)-plane and calculating the residues of the poles at \( \tilde{p} = \pm i\omega_m/(2T) \) for \( \tilde{p} \geq 0 \), we obtain:

\[
\text{Im}[I_3] = -\frac{N_F}{2v_F} \frac{\sinh \left( \frac{i\omega_m}{2T} \right)}{\cosh \left( \frac{i\omega_m - v_F q}{4T} \right) \cosh \left( \frac{i\omega_m + v_F q}{4T} \right)}. \tag{6.87}
\]

The poles of the integrand in \( I_3 \) at \( \tilde{p}_\pm = i(2l + 1)\pi \pm \frac{q}{2} \), on the other hand, gives rise to the real part of \( I_3 \),

\[
\text{Re}[I_3] = \frac{iN_F}{v_F} \left( \frac{\omega_m}{2T} \right)^2 \sum_{l=0}^{\infty} \left[ \frac{1}{\tilde{p}_+^2 \left( \frac{\omega_m}{2T} \right)^2 + (\tilde{p}_+)^2} + \frac{1}{\tilde{p}_-^2 \left( \frac{\omega_m}{2T} \right)^2 + (\tilde{p}_-)^2} \right] \]

\[
= -\frac{N_F}{2\pi v_F} \left[ 2\psi \left( \frac{1}{2} - \frac{i\nu_F q}{4\pi T} \right) + 2\psi \left( \frac{1}{2} + \frac{i\nu_F q}{4\pi T} \right) + \psi \left( \frac{1}{2} + \frac{i\nu_F q + \omega_m}{4\pi T} \right) + \psi \left( \frac{1}{2} - \frac{i\nu_F q + \omega_m}{4\pi T} \right) \right]. \tag{6.88}
\]

Collecting all terms and performing the analytical continuation by a change \( \omega_m \to -i\omega \) of the Matsubara frequencies into frequencies \( \omega \), we obtain the vacuum polarization \( P[q, \omega, T] = \text{Re}[P] + i\text{Im}[P] \). The real part of the vacuum polarization is given by

\[
\text{Re}[P] = -\frac{2N_F}{\pi v_F} \left\{ \ln \frac{\gamma W}{\pi T} - \frac{1}{4} \left[ \psi \left( \frac{1}{2} - \frac{i\nu_F q + \omega}{4\pi T} \right) + \psi \left( \frac{1}{2} + \frac{i\nu_F q - \omega}{4\pi T} \right) + \psi \left( \frac{1}{2} - \frac{i\nu_F q - \omega}{4\pi T} \right) + \psi \left( \frac{1}{2} + \frac{i\nu_F q + \omega}{4\pi T} \right) - 4\psi \left( \frac{1}{2} \right) \right] \right\}, \tag{6.89}
\]

and its imaginary part reads:

\[
\text{Im}[P] = -\frac{N_F}{v_F} \frac{\sinh \left( \frac{i\omega}{2T} \right)}{\cosh \left( \frac{i\omega}{2T} \right) + \cosh \left( \frac{i\nu_F q}{2T} \right)}. \tag{6.90}
\]

We note that the expression for the vacuum polarization in the static limit, \( P[q, 0, T] \), has also been given in Ref. [32]. In the next section, we use this analytical expression for \( P[q, \omega, T] \) to solve Eq. (6.74).
6.4.2 Renormalized phonon frequencies and transition temperature

The renormalized optical and acoustic phonon frequencies denoted by $\tilde{\omega}_o(q)$ and $\tilde{\omega}_a(q)$, respectively, are found from the condition Eq. (6.74), or, equivalently, as the solutions of $(\omega_m \rightarrow -i\omega)$:

$$\omega^4 - \omega^2 (\omega_a^2 f_a + \omega_o^2 f_o) + \omega_a^2 \omega_o^2 (f_a + f_o - 1) = 0. \quad (6.91)$$

The vacuum polarization is hidden in

$$f_i = 1 + \lambda_i \frac{\pi v_F}{2 N_F} P(q, \omega, T), \quad (6.92)$$

and $\lambda_i$ is the dimensionless electron-lattice coupling of the optical ($i = o$) and acoustic ($i = a$) phonon mode as defined by Eq. (6.63). We plot in Figure 6-20 the numerically obtained solutions of Eq. (6.91) for various different temperatures $T \geq T_c$. We take the full $\omega$- and $q$-dependence of $P(q, \omega, T)$ into account in these calculations. Furthermore, we set $\lambda_a = \lambda_o = 0.05$, the Fermi velocity $v_F = 5.3$ eVÅ, the band width $W = 10$ eV, while the frequency of the bare optical phonon mode $\omega_o = 0.18$ eV, and the bare acoustic phonon velocity $v_o = 0.09$ eVÅ. As can be seen in Figure 6-20, the optical phonon frequency is found to be shifted towards lower frequencies but does not change qualitatively as a function of $q$. In contrast, the acoustic phonon velocity is seen to change qualitatively relative to the phonon velocity of the bare acoustic mode and to vanish for small phonon momentum $q$ at the transition temperature $T = T_c$.

Analytical expressions for the renormalized phonon frequencies are obtained in the limit

$$\tilde{\omega}_a(q), \tilde{\omega}_o(q) \ll T \quad \text{and} \quad \tilde{\omega}_a(q) \ll \tilde{\omega}_o(q), \quad (6.93)$$

where the static expression of the vacuum polarization for phonon momenta $v_F q \ll T$ can be used,

$$P(q, 0, T) = -\frac{2N_F}{\pi v_F} \left\{ \ln \frac{\gamma W}{\pi T} - c \left( \frac{v_F q}{T} \right)^2 \right\} + O \left( \left( \frac{v_F q}{T} \right)^4 \right), \quad (6.94)$$

with the constant $c = 7 \zeta(3) / (16\pi^2)$ containing Riemann’s zeta function. In this limit we obtain from Eq. (6.91) the solution

$$\tilde{\omega}_a^2(q) = \omega_a^2(q) \left( \frac{1 - (\lambda_o + \lambda_a) \ln \frac{\gamma W}{\pi T}}{1 - \lambda_o \ln \frac{\gamma W}{\pi T}} + c \lambda_a \left( \frac{v_F q}{T(1 - \lambda_o \ln \frac{\gamma W}{\pi T})} \right)^2 \right) \quad (6.95)$$

for the acoustic phonon mode, and

$$\tilde{\omega}_o^2(q) = \omega_o^2 \left( 1 - \lambda_o \left\{ \ln \frac{\gamma W}{\pi T} - c \left( \frac{v_F q}{T} \right)^2 \right\} \right) \quad (6.96)$$

for the optical phonon mode. We thus see, that the expression for the renormalized optical frequency is independent of $\lambda_a$ and is the same as in the absence of the coupling to acoustic phonons. On the other hand, the renormalized acoustic phonon frequency depends on the sum
never cross and the singularity at $T = T_c$ always occurs in the lower, i.e., acoustic, branch. A similar
acoustic phonon frequency stays finite, i.e., a consequence of the mixing of the optical and acoustic phonons due to their interactions with electrons, which results in the transition between
the acoustic phonon frequencies of the two modes. Because of that, the optical and acoustic branches can
become zero at the transition temperature, whereas the optical phonon frequency stays finite

\begin{equation}
\frac{b}{(b^2 + \Omega^2)^{1/2}} = (b^2 + \Omega^2)^{1/2}
\end{equation}

of the acoustic phonon velocity, or the "softening" in the case means vanishing.

\begin{equation}
\frac{dV}{dx} = \left( \frac{\Omega V + \sqrt{\nu}}{1 - \nu} \right) M \frac{d\alpha}{\nu}
\end{equation}

As a result, the acoustic phonons "soften" first at the critical temperature. Given

\begin{center}
\begin{tabular}{c}
\hline
(a) \hspace{1cm} (b) \hspace{1cm} (c) \hspace{1cm} (d) \hspace{1cm} (e) \hspace{1cm} (f) \\
\hline
\end{tabular}
\end{center}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6-20.png}
\caption{Numerical results for the renormalized phonon frequencies $\omega_0 \Rightarrow \omega_c$ and $\omega_a \Rightarrow \omega_a$ for the transition with acoustic and optical phonons.}
\end{figure}
effect takes place in some ferroelectrics, in which the sound velocity vanishes at the transition temperature because of the mixing of the soft mode, describing the ferroelectric displacement of ions, to acoustic phonons [33].

We also note that, at first sight, Eq. (6.97) resembles the result for the Peierls temperature obtained in Ref. [8]. It should be kept in mind, however, that in that paper the various coupling constants \( \lambda_i \) correspond to contributions from scattering within different electron bands and are not associated with the presence of several phonon modes. The additive effect of the number of electron bands is implicit in our result through the fact that both \( \lambda_o \) and \( \lambda_a \) are proportional to \( N_F \).

It is worthwhile to mention that our considerations can be easily extended to the presence of a number \( N_o \) of optical phonon modes that backscatter electrons with momentum \( q \rightarrow 0 \). The renormalized frequencies are again obtained from the condition Eq. (6.74) where \( \mathcal{D}_0 \) and \( \mathcal{V} \) are \( (N_o + 1) \times (N_o + 1) \)-matrices. The acoustic frequency \( \tilde{\omega}_a \) can be easily calculated in the limit \( \tilde{\omega}_a(q) \ll T \) and \( \tilde{\omega}_{a,j}(q) \ll \tilde{\omega}_{a,j}(q) \) \( (j = 1, \ldots, N_o) \):

\[
\tilde{\omega}_a^2(q) = \omega_a^2(q) \frac{1 - (\lambda_o + \lambda_a) \ln \frac{\gamma \mathcal{V}_{\pi T}}{\pi \mathcal{V}}}{1 - \lambda_o \ln \frac{\gamma \mathcal{V}_{\pi T}}{\pi \mathcal{V}}}.
\] (6.99)

This expression resembles the first term in Eq. (6.95), however, in the present case the optical coupling strength \( \lambda_o \) is the sum of the coupling strengths \( \lambda_{o,j} \) of the optical modes, \( \lambda_o \equiv \sum_{j=1}^{N_o} \lambda_{o,j} \). The corresponding transition temperature Eq. (6.97) reads

\[
T_c = \frac{\gamma}{\pi} W \exp \left( \frac{1}{\lambda_o + \sum_{j=1}^{N_o} \lambda_{o,j}} \right).
\] (6.100)

It should be noted, however, that the value of each coupling strength is to be determined in the presence of the lattice distortion that involves all \( N_o + 1 \) phonon modes. Thus, the electrons interact with a lattice deformation that is composed of the \( N_o + 1 \) eigenmodes. This decomposition gives rise to expansion coefficients that enter each coupling strength and knowledge about the systems full lattice dynamics is necessary to conclude from Eq. (6.100) the value of \( T_c \).

### 6.5 Topological excitations in the Peierls phase

We now discuss properties of the ordered phase below the critical temperature \( T_c \) for the case of a single optical and acoustic phonon mode. Because the lattice distortions, corresponding to the optical and acoustic phonons, are coupled due to electron-lattice interactions, both order parameters, \( \Delta_o(x) \) and \( \Delta_a(x) \), should appear below the transition temperature.

In the mean field treatment of the lattice one has to minimize the total free energy of the model Eq. (6.61) with respect to the two order parameters. The solutions of the resulting self-consistency equations have the following properties:

(i) The sum of the optical and acoustic order parameters corresponds to a generalized order parameter,

\[
\Delta(x) = \Delta_o(x) + \Delta_a(x),
\] (6.101)
which satisfies the same Bogoliubov-de Gennes equations as the order parameter of the TLM model [29] with a single phonon mode, but with the coupling constant

$$\lambda = \lambda_0 + \lambda_\alpha .$$

(6.102)

(ii) The optical (i = 0) and acoustic (i = \alpha) order parameters are proportional to $\Delta(x)$:

$$\Delta_i(x) = \frac{\lambda_i}{\lambda} \Delta(x).$$

(6.103)

It thus follows, that the stationary minimal-energy lattice configuration of the continuum model Eq. (6.61) can be equally deduced from that of the Hamiltonian

$$H = \sum_s \int dx \psi^\dagger_s(x) \left\{ \frac{v_F}{i} \sigma_3 \frac{\partial}{\partial x} + \Delta(x) \sigma_1 \right\} \psi_s(x) + \frac{N_F}{\pi \lambda v_F} \int dx \Delta(x)^2$$

(6.104)

in terms of the generalized order parameter $\Delta(x)$ and the coupling constant $\lambda$. Here, we introduced the index $s = (\sigma, n)$, which is a combination of the electron’s spin degree of freedom $\sigma = \pm 1$ and the number of Fermi points $n = 1, \ldots, N_F$. In other words, an effective internal degeneracy $N_d = 2N_F$ is ascribed to the electrons and each one-electron level can be occupied by up to $N_d$ electrons. The advantage of relating Eq. (6.61) to Eq. (6.104) is, that formally Eq. (6.104) is seen to be equivalent to the Hamiltonian of the TLM model [29], where electrons interact with one optical phonon mode ($\Delta(x) = \Delta_0(x)$) and $N_F = 1$. This model has been discussed in Section 2.2 and its solutions can be used here to study the ordered state in our model.

In particular, the value of the homogeneous solution $\Delta(x) = \Delta_0$ at zero temperature is (see Eqs. (2.55) and (2.60)):

$$\Delta_0 = W \exp \left( -\frac{1}{\lambda} \right) = \frac{\pi}{\gamma} T_c .$$

(6.105)

A homogeneous optical order parameter, $\Delta_0 = \text{const}$., is a “frozen” phonon mode, corresponding to a lattice deformation with out-of-phase bond length dimerization in neighboring zigzag chains along the nanotube axis (see Figure 6-12 (c)). On the other hand, for acoustic phonons, a constant $\Delta_\alpha$ describes a static twist of the cylindrical nanotube lattice (see Figure 6-14) and corresponds to the linearly growing amplitude of ionic displacements: $u_\alpha(x) \propto x$. Such a lattice distortion is not a “frozen” phonon mode, as it corresponds to large deviations of ions from their equilibrium positions in the high-temperature phase.

Furthermore, as has been discussed in Section 2.2.2 within the TLM model, kinks (solitons) in the order parameter, corresponding to a change of sign of the lattice dimerization along the chain, constitute an interesting class of excitations [14]. The analytical expression for the kink is given by [29]:

$$\Delta(x) = \Delta_0 \tanh \left( \frac{x}{\xi_0} \right),$$

(6.106)

where $\xi_0 = v_F/\Delta_0$ is the correlation length. It is easy to verify that the configuration Eq. (6.106)
for the generalized order parameter in our model corresponds to the optical and acoustic lattice distortions given by

\[
\begin{align*}
\bar{u}_o(x) &= \bar{u}_o \tanh \left( \frac{x}{\xi_0} \right), \\
\bar{u}_a(x) &= \bar{u}_a \ln \cosh \left( \frac{x}{\xi_0} \right).
\end{align*}
\] (6.107)

Near the kink both the lattice dimerization, described by \( u_o(x) \), and the derivative of \( u_a(x) \) change sign. This is shown in Figure 6-21 and the combination of a dimerization kink and a change in the sign of the twist angle suggests to call this topological excitation a solitwiston.

In the TLM model (\( u_a = 0 \)), the soliton is the minimal-energy lattice configuration in a chain with antiperiodic boundary conditions on the atomic shifts, \( u_o(x + L) = -u_o(x) \) (\( L \) is the system length). The corresponding discrete model is that of a ring, in which the number of lattice sites, where the dimerization \( \Delta_o \) changes sign around the soliton position. If the number of lattice sites in the ring is even, however, the minimal-energy lattice configuration contains no soliton, corresponding to the continuum model for a chain with periodic boundary conditions (\( u_o(x + L) = u_o(x) \)). The situation is different in the presence of a twist (\( u_a \neq 0 \)). It is easily checked that for a homogeneous ground state lattice configuration with twist angle \( \theta \), \( u_a(x) = \tan(\theta) x \), periodic boundary conditions require that

\[
\frac{\partial u_a(x)}{\partial x} = \tan \theta = n_{w} \frac{C}{L}.
\] (6.108)

Here, we introduced the integer winding number \( n_{w} \), while \( C \) and \( L \) denote, respectively, the circumference and the length of the carbon nanotube. In other words, the optimal value of the twist angle \( \theta \), which follows from Eqs. (6.105) and (6.103), has to be equal to a value of a discrete set that is characterized by \( n_{w} \). The trivial solution, \( n_{w} = 0 \), corresponds to a ground state lattice configuration with \( \Delta = 0 \), while the condition Eq. (6.108) for a homogeneous ground state lattice configuration with \( \Delta = \text{const.} \) is most likely satisfied in carbon nanotubes with ratio \( C/L \to 0 \). To gain energy from the lattice distortion and, at the same time, to satisfy the periodic boundary conditions, \( \int_0^L dx \Delta_o(x) = 0 \), an inhomogeneous ground state lattice configuration could be energetically more favorable. Then, \( u_a(x) \) has to change sign at least two times along the electronic chain and the minimal-energy lattice configuration contains one solitwiston and one antisolitwiston.
6.5 Topological excitations in the Peierls phase

The creation energy $\mu$ of a solitwiston is formally the same as for the usual soliton in the TLM model which has been calculated in Section 2.2.2. Taking into account the internal degeneracy $N_d$ of the electrons in Eq. (6.104), we find

$$\mu = \frac{N_d \Delta_0}{\pi} = \frac{4 \Delta_0}{\pi}.$$  \hspace{1cm} (6.109)

The dynamical properties of the kinks in our model are, however, quite different from those in the TLM model. In the latter, the soliton can propagate with velocity $v$ along the chain, without changing its profile. This results from the independence of the soliton energy of its position and the fact that the kinetic energy density of the moving kink,

$$u_0(x, t) = \tilde{u}_0 \tanh \left( \frac{x - vt}{\xi_0} \right),$$  \hspace{1cm} (6.110)

decays exponentially at distances larger than the correlation length $\xi_0$ away from the kink. Thus, as has been calculated in Section 2.2.2, the mass of the soliton is finite and for trans-polyacetylene was estimated to be $\sim 6 m_e$ (with $m_e$ the electron mass) [14]. On the other hand, the motion of the kink in the model with acoustic phonons ($u_0 = 0$) would result in a constant kinetic energy density at distances larger than $\xi_0$ from the kink. This follows from the substitution of $u_0(x)$ in Eq. (6.107) by $u_0(x - vt)$ and a calculation of the kinetic energy $E_s = (M_s/2)v^2$ for a $c_1[1, 1]$ carbon nanotube. We then find

$$M_s \sim \frac{4 c_a M_C}{\alpha} \frac{a^2}{\xi_0^2} \int_{-L/2}^{L/2} dx \tanh \left( \frac{x}{\xi_0} \right)^2 \propto M_C \frac{L}{\alpha}$$  \hspace{1cm} (6.111)

and, thus, that the mass of a kink is proportional to the product of the mass of a carbon atom, $M_C$, and the system length $L$. It follows that in our model, isolated solitwistrons cannot propagate. This relates to the fact that a translation of the solitwiston configuration Eq. (6.107) changes the coordinates at the boundaries of the system, so that its shift induces a motion of the entire system. Solitwistrons can propagate without affecting the boundaries of the system only together with antisolitwistrons and the mass of such a pair is proportional to its pair size $R (\gg \xi_0)$.

We now turn to a discussion of the solitwiston’s spin-charge relations. Similar to the case of trans-polyacetylene, the single-particle electronic spectrum of the armchair carbon nanotube follows from Eq. (6.104) to consist of a continuum of plane-wave conduction- and valence-band states that are separated by an energy gap $2 \Delta_0$. In addition, the presence of a solitwiston Eq. (6.106) gives rise for a localized midgap state which can be either unoccupied or occupied by up to $N_d = 4$ electrons for $N_F = 2$, instead of $N_d = 2$ electrons as for the soliton in trans-polyacetylene, where $N_F = 1$. The solitwiston’s spin-charge relations, therefore, differ from those of the soliton in trans-polyacetylene and are, instead, the same as those of the topological excitation in polyyne [15].

We briefly mention that polyyne consists of $sp^1$-hybridized carbon atoms that form a chain with alternating bond length: $\ldots - C \equiv C - C \equiv C - \ldots$. Similar to trans-polyacetylene the infinite polyyne chain can be considered as a half-filled Peierls insulator. However, in polyyne the $\pi$-electrons have an effective internal degeneracy $N_d = 4$, since each carbon atom has two degenerate, orthogonal, atomic $\pi$-orbitals which couple to the atomic displacements in an
<table>
<thead>
<tr>
<th>electron occupancy</th>
<th>charge $Q$</th>
<th>spin $S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+2 e</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>+1 e</td>
<td>1/2</td>
</tr>
<tr>
<td>2</td>
<td>0 e</td>
<td>0 or 1</td>
</tr>
<tr>
<td>3</td>
<td>−1 e</td>
<td>1/2</td>
</tr>
<tr>
<td>4</td>
<td>−2 e</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 6-1**: Spin-charge relation of solitwiston states in the Peierls phase of the armchair carbon nanotube. The electron charge is $-e$.

In an identical manner. In contrast, the internal degeneracy $N_d = 4$ in the armchair carbon nanotube with $sp^2$-hybridized carbon atoms follows from the symmetry of the honeycomb lattice that is composed of two triangular sublattices.

Very similar to the procedure in Section 2.2.2, the spin-charge relations of the solitwiston are obtained as summarized in Table 6-1. In the (undoped) armchair carbon nanotube the neutral solitwiston ($Q = 0$) can have spin $S = 0$ or $S = 1$ since two electrons occupy the midgap states at the two Fermi points. If one electron is removed from (added to) the system, the corresponding charged solitwiston is found to have the usual relation between charge $Q = +e$ ($Q = -e$) and spin $S = 1/2$ ($S = 1/2$). Similarly, if two electrons are removed from (added to) the system, the doubly charged solitwiston has spin $S = 0$. The spin-charge relations of the charged solitwiston in armchair carbon nanotubes are thus found to be quite usual, in contrast to the exotic spin-charge relations of solitons in trans-polyacetylene.

We should mention that the model Eq. (6.104) also predicts the existence of a non-topological excitation which corresponds to a bound solitwiston-antisolitwiston pair. The analytical expression of the generalized order parameter is given by

$$
\Delta(x) = \Delta_0 - \Delta_0 k_F \xi_0 \left[ \tanh \left( k_F \left( x + \frac{R_F}{2} \right) \right) - \tanh \left( k_F \left( x - \frac{R_F}{2} \right) \right) \right], \quad (6.112)
$$

for which the corresponding optical, $u_\omega(x)$, and acoustic, $u_\alpha(x)$, lattice distortions,

$$
\begin{align*}
    u_\omega(x, t) &= \tilde{u}_\omega \left[ 1 - k_F \xi_0 \left[ \tanh \left( \frac{x + R_F}{2 \xi_0} \right) - \tanh \left( \frac{x - R_F}{2 \xi_0} \right) \right] \right], \\
    u_\alpha(x, t) &= \tilde{u}_\alpha \left[ \frac{x}{\xi_0} - k_F \xi_0 \left[ \ln \cosh \left( \frac{x + R_F}{2 \xi_0} \right) - \ln \cosh \left( \frac{x - R_F}{2 \xi_0} \right) \right] \right],
\end{align*} \quad (6.113)
$$

are shown in Figure 6-22. In analogy to the polaron in conjugated polymers, we are tempted to call this excitation a **polartwiston** as it describes a local indentation of the acoustic and optical order parameter in the carbon nanotube. We discussed in Section 2.2.2 that the energy spectrum for this type of excitation contains two localized intragap states with energies $\pm \epsilon$ depending on the electron occupancy $n_\pm$ of the intragap states. A self-consistent solution $\Delta(x)$ requires that the pair size $R_F$ satisfies the condition [15]:

$$
\tanh \left( \frac{k_F R_F}{2} \right) = \tan \frac{\phi}{2} \quad \text{with} \quad k_F = \frac{\sin \phi}{\xi_0} \quad \text{and} \quad \epsilon = \Delta_0 \cos \phi, \quad (6.114)
$$
where the electron occupancy of the intragap states is contained in the definition of the angle

\[ \phi = \frac{\pi}{2} \left( 1 + \frac{n_+ - n_-}{N_d} \right). \]  

(6.115)

The creation energy of the polartwiston is found to be [15]:

\[ \mu_p = 2 \mu \sin \phi, \]  

(6.116)

while the maximal change of the generalized order parameter Eq. (6.101), associated with the local indentation around the position of polartwiston, is given by the value [15]:

\[ \delta \Delta = (2 \cos \phi - 1) \Delta_0. \]  

(6.117)

The spin-charge relations of the polartwistons are summarized in Table 6-2. We note that a neutral polartwiston can be created in a system with internal degeneracy \( N_d = 4 \) which does not have a counterpart in the \( N_d = 2 \) system. Its creation energy \( \mu_p = \sqrt{2}\mu \) is less than that of a neutral solitwiston-antisolitwiston pair. However, since two neutral polartwistons are unstable and decay into a solitwiston-antisolitwiston pair, the latter will be the lowest-lying thermal excitations in the armchair carbon nanotube. Finally, it is interesting to note that the

<table>
<thead>
<tr>
<th>electron occupancy ( n_- \ n_+ )</th>
<th>charge ( Q )</th>
<th>spin ( S )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>+3 e</td>
<td>1/2</td>
</tr>
<tr>
<td>2 0</td>
<td>+2 e</td>
<td>0 or 1</td>
</tr>
<tr>
<td>3 0</td>
<td>+1 e</td>
<td>1/2</td>
</tr>
<tr>
<td>3 1</td>
<td>0 e</td>
<td>0 or 1</td>
</tr>
<tr>
<td>4 1</td>
<td>-1 e</td>
<td>1/2</td>
</tr>
<tr>
<td>4 2</td>
<td>-2 e</td>
<td>0 or 1</td>
</tr>
<tr>
<td>4 3</td>
<td>-3 e</td>
<td>1/2</td>
</tr>
</tbody>
</table>

Table 6-2: Spin-charge relation of polartwiston states in the Peierls phase of the armchair carbon nanotube. The electron charge is \(-e\).
creation energy of a polar twiston with charge \( Q = \pm e \) in the \( N_d = 4 \) system is smaller than that of a solitawston, \( \mu_p \approx 0.77\mu \). This is another difference with the \( N_d = 2 \) system and has important consequences for the creation of topological excitations as will be further discussed in the next section.

### 6.6 Numerical simulation: elastic spring model

In this section we present the results of numerical simulations which we perform to study the Peierls state and the appearance of solitawstonis in armchair carbon nanotubes at zero temperature. We use a steepest-descent algorithm to determine the nanotube’s minimal-energy lattice configuration. This has to be done in a self-consistent way since both the electronic energy and the potential lattice energy depend on the atomic displacements.

The electronic energy is calculated within the effective low-energy model for the armchair carbon nanotube and is given by the two-leg ladder Hamiltonian Eq. (6.51). The potential energy of the hexagonal nanotube lattice is obtained within an elastic spring model where two carbon atoms are connected by “springs” that are characterized by a spring constant. We derive this model under the assumption that the potential lattice energy \( U \) depends only on the change in the distance between the carbon atoms. The potential energy consists of three terms,

\[
U = U_{AB} + U_{AA} + U_{BB},
\]  

(6.118)

where \( U_{AB} \) refers to the coupling between carbon atoms of the two different sublattices A and B, while \( U_{AA} \) and \( U_{BB} \) denote the potential lattice energy of sublattice A and B, respectively. Explicitly, we have

\[
U_{ij} = \frac{1}{2} \sum_{l,m} K(R_{lm}) \left( |\mathbf{u}_i(\mathbf{x}_i) - \mathbf{u}_j(\mathbf{x}_m)| \cdot \hat{R}_{lm} \right)^2,
\]

(6.119)

where \( K(R_{lm}) \) denotes the spring constant as a function of the distance \( R_{lm} \) between two carbon atoms that are located at site \( \mathbf{x}_i \) and \( \mathbf{x}_m \) in sublattice \( i \) and \( j \), respectively. In Eq. (6.119), the displacement of a carbon atom from its equilibrium position at \( \mathbf{x}_i \) in the \( i \)’th sublattice is denoted by \( \mathbf{u}_i(\mathbf{x}_i) \). The unit vector \( \hat{R}_{lm} \) points from \( \mathbf{x}_i \) to \( \mathbf{x}_m \) and is defined in terms of the angle \( \theta_{lm} \) by

\[
\hat{R}_{lm} = \frac{\mathbf{x}_m - \mathbf{x}_i}{|\mathbf{x}_m - \mathbf{x}_i|} \equiv \begin{pmatrix} \cos \theta_{lm} \\ \sin \theta_{lm} \end{pmatrix} .
\]

(6.120)

We note that the summation over \( l, m \) in Eq. (6.119) accounts for all carbon atoms in sublattice \( j \) at \( \mathbf{x}_m \) with distance \( R_{lm} \) from site \( \mathbf{x}_i \) in sublattice \( i \). In practice, however, we calculate the potential lattice energy Eq. (6.118) taking only the first three nearest neighbors of a carbon atom into account. This gives rise to three different spring constants, \( K_1, K_2, \) and \( K_3 \), as depicted in Figure 6-23. An additional simplification arises because, as before, only lattice distortions with zero transverse momentum are relevant. It is thus sufficient to consider the two-dimensional atomic displacement vector in the \( i \)’th sublattice to be only a function of
the $x$-coordinate along the nanotube axis,

$$
\tilde{u}_i \left( x = n \frac{a}{2} \right) = \left( \frac{X_i \left( n \frac{a}{2} \right)}{Y_i \left( n \frac{a}{2} \right)} \right).
$$

(6.121)

In other words, as has been explained in Section 6.3, the armchair nanotube lattice can be considered as consisting of $N$ connected rings at a distance $a/2$ along the nanotube axis (see Figure 6-15) and a lattice configuration is completely determined by the set

$$
\{ \tilde{u} \} \equiv \{ \tilde{u}_A[na/2], \tilde{u}_B[na/2] \}
$$

(6.122)

of atomic displacements.

We compute the minimal-energy lattice configuration using a steepest-descent algorithm, where we take into account that both the potential lattice energy Eq. (6.118) and the kinetic energy of the electrons Eq. (6.51) depend on the actual lattice configuration. We start the computation for a randomly chosen lattice configuration and calculate the total ground state energy

$$
E \left[ \{ \tilde{u} \} \right] = \langle 0 | H_{\text{arm}} | 0 \rangle + U,
$$

(6.123)

where $| 0 \rangle$ denotes the electronic ground state associated with the given lattice configuration. Next, we compute the gradient

$$
\nabla E_{n,i} = \frac{\delta E \left[ \{ \tilde{u} \} \right]}{\delta (\tilde{u}_i[na/2])}
$$

(6.124)

in each ring $n$ for both sublattices $i = A, B$ leaving the atomic displacements in all the other rings unchanged. We determine from the sign of $\nabla E_{n,i}$ in which direction the atomic displacement vector $\tilde{u}_i[na/2]$ is to be shifted such that the total ground state energy Eq. (6.123)
is decreased. In this way we obtain a new lattice configuration $[\hat{u}']$. We only accept this new lattice configuration if the total ground state energy

$$E([\hat{u}']) < E([\hat{u}])$$

(6.125)

and the same procedure is repeated until the gradient Eq. (6.124) is equal to zero within the required accuracy of the computation.

We now turn to the discussion of the results for the minimal-energy lattice configurations, which are presented in terms of the shifts

$$Y_+ = \frac{1}{\sqrt{2}} \left( Y_A + Y_B \right) \quad \text{and} \quad X_- = \frac{1}{\sqrt{2}} \left( X_A - X_B \right),$$

(6.126)

in Figure 6-24 and Figure 6-26, respectively, for periodic and free boundary conditions. Clearly, the absolute values of the shifts depend on the parameters used in the calculation, such as the hopping amplitude of electrons $t_||$, the electron-lattice coupling $\alpha_\|$, the three spring constants ($K_1$, $K_2$, and $K_3$), and also on the number $2c_\alpha$ of zigzag chains around the circumference in the armchair carbon nanotube $c_\alpha[1,1]$ under consideration. To obtain a qualitative picture of the Peierls state for a general armchair carbon nanotube, however, the precise values of these parameters are not important and are, instead, chosen to satisfy the following two convenient conditions: (i) For a system of $N = 100$ rings, the correlation length is much smaller than the system size, $\xi_0 = v_F/\Delta_0 \ll \text{Na}/2$. (ii) The coupling between the shifts $Y_+$ and $X_-$ is so small, that the numerical results are directly related to the corresponding acoustic and optical order parameter by

$$\Delta_\alpha \propto \frac{\partial}{\partial x} Y_+ \quad \text{and} \quad \Delta_\alpha \propto X_-.$$  

(6.127)

We first discuss the results for periodic boundary conditions which are summarized in Figure 6-24. For the half-filled system, we obtain a finite shift $X_-$ which corresponds to a lattice dimerization associated with a relative shift of the two triangular sublattices A and B against each other. Furthermore, as is also shown in Figure 6-24 (a), we obtain $Y_+ = 0$ which indicates the absence of a twist deformation in the minimal-energy configuration of the nanotube lattice. We note that this minimal-energy lattice configuration is incompatible with the trivial solution in the continuum model ($n_w = 0$ in Eq. (6.108)), since this would require not only $Y_+ = 0$ but also $X_- = 0$. The minimal-energy lattice configuration in Figure 6-24 (a) is to be interpreted as a consequence of the fact that the numerical simulation is performed for a system of finite size, where (i) the creation of a solitwiston-antisolitwiston pair is energetically unfavorable, and (ii) the optimal value of the twist angle does not happen to correspond to a homogeneous twist deformation with non-zero winding number $n_w$. For the purpose of illustration we sketch in Figure 6-24 (b) a lattice configuration with a homogeneous twist deformation as it would appear if the optimal value of the twist angle would correspond to a non-zero winding number $n_w$.

In Figure 6-24 (c)-(j) we show the effect of doping on the lattice configuration (a) by adding successively one electron to the initially half-filled system ($N_{el} = +1, +2, \ldots , +8$). We discussed in Section 6.5 that by adding one electron the creation of a polarwiston is, in principle, energetically more favorable than the creation of a solitwiston. However, we note here
Figure 6.24: Minimal-energy lattice configuration of the armchair carbon nanotube in the Peierls phase for periodic boundary conditions imposed on the shifts \(X_-\) (dashed line) and \(Y_+\) (solid line). \(N_{el}\) denotes the number of electrons that is added to the half-filled system.
that a necessary prerequisite for the creation of a polartwist at \( x = x_0 \) is the presence of a twist deformation. This can be easily derived from Eq. (6.113) and is a consequence of the fact that the sign of \( u_a(x) \) has to be different to the left and the right of the polartwiston position, \( u_a(x \ll x_0) = -u_a(x \gg x_0) \), which can not be satisfied in the lattice configuration Figure 6-24 (a) with \( Y_+ = 0 \). In other words, a polartwiston appears in the minimal-energy lattice configuration only if the half-filled system would already have contained a twist deformation (as illustrated in Figure 6-24 (b)). In the present case, however, one additional electron in the half-filled system with periodic boundary conditions results in the formation of a solitwiston-antisolitwiston pair (Figure 6-24 (c)). As has been discussed in Section 6.5, a neutral solitwiston is associated with a doubly occupied midgap state that can be occupied by a maximum of four electrons because of the electron's internal degeneracy \( N_d = 4 \). Thus, the solitwiston-antisolitwiston is the minimal-energy lattice configuration for up to four extra electrons in the initially half-filled system (Figure 6-24 (c)-(f)). Then, if the fifth and the sixth electron are added to the system, a polartwiston with charge \( Q = -e \) and \( Q = -2e \), respectively, appears in the carbon nanotube lattice. This non-topological excitation is seen to locally distort the lattice configuration corresponding to an indentation of \( X_+ \) that depends on the number of added electrons. We obtain from Eq. (6.117) that, due to the presence of a polartwiston at \( x = x_0 \) with charge \( Q = -e \) \( (Q = -2e) \), the value of \( |X_+(x_0)| \) is reduced by roughly 15% (60%) from its value at \( x_0 \) for the undistorted lattice. This is in good agreement with the numerical simulation Figure 6-24 (g) (Figure 6-24 (h)).

Furthermore, the polartwiston state can be occupied by one more electron and then carries charge \( Q = -3e \). This is shown in Figure 6-24 (i) for \( N_{el} = +7 \), where the local distortion of the shifts is seen to be quite significant. From Eq. (6.117) the value of \( |X_+(x_0)| \) is expected to be reduced by roughly 123% which is again in quantitative agreement with the numerical calculations, where \( X_+(x_0) \) is seen to change sign compared to its value at \( x_0 \) for the undistorted lattice. Finally, we plot in Figure 6-24 (j) the minimal-energy lattice configuration which is obtained for eight extra electrons in the half-filled system. The periodic boundary conditions require a second solitwiston-antisolitwiston pair to appear which is energetically more favorable than to charge the polartwiston with four electrons.

The appearance of topological excitations in the minimal-energy lattice configuration depends on the imposed boundary conditions. This can be readily understood within the two-leg ladder model and is illustrated in Figure 6-25. If periodic boundary conditions are imposed on the shifts, the number \( N \) of rings in the armchair carbon nanotube has to be even. The out-of-phase dimerization of the minimal-energy lattice configuration is depicted by thick and thin lines in the two-leg ladder. No topological excitations are present if the twist deformation is homogeneous with \( \tan \theta = n_w C/L \) (Figure 6-25 (a)), while otherwise the lattice configuration contains a solitwiston-antisolitwiston pair (Figure 6-25 (b)). The latter configuration is schematically shown by four unpaired electrons which give rise to the two doubly occupied midgap states. If, in the other hand, the boundary conditions on the shifts are free, the number \( N \) of rings in the armchair carbon nanotube can be either even or odd. The corresponding minimal-energy lattice configurations is expected to be quite similar in both cases, since the lattice has the freedom to minimize the energy by a relative shift of the two triangular sublattices \( A \) and \( B \) against each other and by a static twist deformation. This is depicted in Figure 6-25 (c) and (d) by the out-of-phase dimerization in the two-leg ladder. It is important to notice the
difference between periodic and free boundary conditions. For the latter, the half-filled system is seen to contain always two unpaired electrons, independent whether \( N \) is even or odd, which are located at the left and right ends of the system. These electrons give rise to edge states that appear in the middle of the Peierls gap. When doping the system the first two electrons will occupy the midgap electronic level associated with the two edge states and, therefore, the lattice configuration will not change.

That this picture is, in fact, correct can be seen in Figure 6-26 where we plot the results of numerical simulations for free boundary conditions on the shifts \( Y_+ \) and \( X_- \). In Figure 6-26 (a) we show the minimal-energy lattice configuration of the half-filled system. The lattice configuration is, as expected, characterized by a lattice dimerization associated with a relative shift of the two triangular sublattices \( A \) and \( B \) against each other (\( X_- = \text{const.} \)) and by a homogeneous twist deformation (\( Y_+ \propto x \)). We also see that this lattice configuration does not change when the first and second electron are added to the half-filled system (Figure 6-26 (b) and (c)). Inspection of the electron energy spectrum reveals that the two added electrons occupy, in fact, a midgap state associated with the edge states that arise as a consequence of the imposed boundary conditions. Thus, the first two added electrons fill the midgap state and a relaxation of the lattice is only seen when the third electron is added to the system (Figure 6-26 (d)). Although the boundary conditions are, in principle, compatible with the creation of a single solitwiston, it follows from Eq. (6.116) that in the model Eq. (6.104) with internal degeneracy \( N_d = 4 \), the creation of a polartwiston with charge \( Q = -e \) is energetically more favorable: \( \mu_p \approx 0.77 \mu \). Furthermore, the polartwiston is seen to be located at the (right) system boundary, where the presence of the edge state gives rise to a level splitting that minimizes the system’s total energy. In Figure 6-26 (e), we plot the minimal-energy lattice configuration containing four extra electrons (\( N_{e1} = +4 \)). A charged solitwiston with \( Q = -2e \) is now seen to be located in the middle of the armchair nanotube lattice and, beside the two completely occupied edge states, the midgap state associated with the solitwiston is completely occupied by four electrons. In Figure 6-26 (f) we plot the minimal-energy lattice configuration which is obtained when the fifth electron is added to the half-filled system. Similar to the situation in
Figure 6-26: Minimal-energy lattice configuration of the armchair carbon nanotube in the Peierls phase for free boundary conditions imposed on the shifts $X_-$ (dashed line) and $Y_+$ (solid line). $N_{el}$ denotes the number of electrons that is added to the half-filled system.
Figure 6-26 (d), a charged polartwiston with $Q = -e$ is formed and is located at the (left) boundary of the system in order to minimize the system’s total energy due to a splitting of the energy levels. In Figure 6-26 (g) and (h) we plot the minimal-energy lattice configuration for, respectively, six and seven extra electrons in the half-filled system. A comparison with Figure 6-26 (e) and (f) reveals the following general pattern in the minimal-energy lattice configuration as a function of the number $N_{el}$ of added electrons: (i) a charged polartwiston ($Q = -e$) is located at the system’s boundary if the number of added electrons, $N_{el}$, is odd and larger than two; (ii) the number of charged solitwistons ($Q = -2e$) increases by one if the number of added electrons, $N_{el}$, is even and larger than two.

It has been speculated that, in principle, it should be possible to locally probe individual carbon nanotubes using scanning tunneling microscopy and spectroscopy techniques [28]. If electron states associated with solitwistons can be observed in this way, it may be possible to determine the energy and shape of these midgap states.

We now turn to the calculation of the dimensionless electron-lattice couplings $\lambda_\alpha$ and $\lambda_\alpha$ in terms of the spring constants $K_1$, $K_2$, and $K_3$. For this purpose we rewrite Eq. (6.119) using the Fourier representation of the atomic displacement,

$$\vec{u}_i(\vec{x}_i) = (X_i(\vec{x}_i), Y_i(\vec{x}_i)) = \frac{1}{\sqrt{N_i}} \sum_\vec{q} e^{i\vec{q} \cdot \vec{x}_i} (X_i(\vec{q}), Y_i(\vec{q})),$$  \hspace{1cm} (6.128)

where $N_i$ is the number of sites in the $i$'th sublattice and $N_A = N_B$ in armchair carbon nanotubes. Let us choose the origin of the $i$'th sublattice to be located at $\vec{x}_i = 0$ from where we measure the distance to the $m$'th atom in sublattice $j$ by $\vec{R}_m$. If we combine the Fourier components of the atomic displacements in a single vector,

$$\vec{u}(\vec{q}) = (X_i(\vec{q}), Y_i(\vec{q}), X_j(\vec{q}), Y_j(\vec{q})),$$  \hspace{1cm} (6.129)

we obtain Eq. (6.119) in the form

$$U_{ij} = \frac{1}{2} \sum_\vec{q} \vec{u}(\vec{q})^\dagger \hat{R}_{ij} \vec{u}(\vec{q}).$$  \hspace{1cm} (6.130)

Here, the elements of the matrix $\hat{R}_{ij} = (k_{ij})_{ij}$ (with $\alpha, \beta = 1 \ldots 4$) are given by

$$\begin{cases}
  k_{11} = k_{33} = \sum_m K(R_m) \cos^2 \theta_m, \\
  k_{22} = k_{44} = \sum_m K(R_m) \sin^2 \theta_m, \\
  k_{12} = k_{21} = k_{34} = k_{43} = \sum_m K(R_m) \cos \theta_m \sin \theta_m, \\
  k_{13} = k_{31}^* = -\sum_m K(R_m) e^{i\vec{q} \cdot \vec{R}_m} \cos^2 \theta_m, \\
  k_{14} = k_{41}^* = k_{23}^* = k_{32}^* = -\sum_m K(R_m) e^{i\vec{q} \cdot \vec{R}_m} \cos \theta_m \sin \theta_m, \\
  k_{24} = k_{42}^* = -\sum_m K(R_m) e^{i\vec{q} \cdot \vec{R}_m} \sin^2 \theta_m.
\end{cases}$$  \hspace{1cm} (6.131)

We now disregard the transverse momentum component in the matrix elements Eq. (6.131) and write $\vec{q} \cdot \vec{R}_m = q R_m \cos \theta_m$, where $q$ denotes the momentum in the direction along the nanotube axis. Furthermore, it is convenient to use a transformation, $\hat{U}$ with $\hat{U}^\dagger \hat{U} = 1$, such
that the vector with the Fourier components of the atomic displacements Eq. (6.129) becomes
\[ \tilde{u}(\vec{q}) \rightarrow \vec{R}_q = \hat{U} \tilde{u}(\vec{q}) = \frac{1}{\sqrt{2}} \left( X_A + X_B, Y_A + Y_B, X_A - X_B, Y_A - Y_B \right)^T. \] (6.132)

We then obtain the potential lattice energy Eq. (6.118) in the form
\[ U = \frac{1}{2} \sum_q \vec{R}_q^\dagger \hat{R}_q \vec{R}_q, \] (6.133)

where we defined \( \hat{R}_q \equiv \hat{U}(\hat{R}_{AB} + \hat{R}_{AA} + \hat{R}_{BB})\hat{U}^\dagger. \) We note that Eq. (6.133) contains the matrix elements Eq. (6.131) and is, thus, still valid for all values of \( q. \) In the limit of long wavelengths, \( q \rightarrow 0, \) we expand the exponentials in Eq. (6.131) up to second order in \( q \) and obtain the matrix \( \hat{R}_q \) in the form:
\[ \hat{R}_q = \frac{a}{2} \begin{pmatrix} q^2(\beta_x + \gamma_x) & 0 & 0 & iq\delta_y \\ 0 & q^2(\beta_y + \gamma_y) & -iq\delta_x & 0 \\ 0 & iq\delta_x & 2\alpha_x + q^2(\beta_x - \gamma_x) & 0 \\ -iq\delta_y & 0 & 0 & 2\alpha_y + q^2(\beta_y - \gamma_y) \end{pmatrix}. \] (6.134)

The expression Eq. (6.133) is formally identical to the potential lattice energy in Eq. (6.44) and in terms of the three spring constants the eight parameters \( [\alpha_x, \alpha_y, \beta_x, \beta_y, \gamma_x, \gamma_y, \delta_x, \delta_y] \) are given by
\[ \begin{align*}
\alpha_x &= \alpha_y = \frac{3}{a} (K_1 + K_3), \\
\beta_x &= 3\beta_y = \frac{9a}{2} K_2, \\
\gamma_x &= 3\gamma_y = \frac{3a}{2} \left( \frac{1}{4} K_1 + K_3 \right), \\
\delta_x &= -\delta_y = -\sqrt{3} \left( \frac{1}{2} K_1 - K_3 \right).
\end{align*} \] (6.135)

Using these relations we obtain from Eqs. (6.48) and (6.50) the optical phonon frequency
\[ \omega_o = \sqrt{\frac{3(K_1 + K_3)}{M_C}}, \] (6.136)

where \( M_C \) is the mass of the carbon atom, and the acoustic phonon velocity
\[ v_o = a \sqrt{\frac{3(4K_1K_2 + 3K_1K_3 + 4K_2K_3)}{16(K_1 + K_3) M_C}}. \] (6.137)

Furthermore, the corresponding dimensionless electron-lattice coupling \( \lambda_i \) is obtained according to its definition Eq. (6.63) from Eq. (6.65). We obtain for the optical phonon mode
\[ \lambda_o = \frac{12 \alpha^2 \sin(k_F \frac{a}{2})}{\pi t_o \omega_o^2 M_C c_o}, \] (6.138)

with the electron hopping amplitude \( t_o \) along the nanotube axis, and for the acoustic phonon mode
\[ \lambda_a = \lambda_o \frac{27 K_3^2 a^2}{16 M_C^2 \omega_o^2 v_o^2}. \] (6.139)
We first note that the dimensionless electron-lattice coupling for the optical phonon mode, \( \lambda_o \), can be directly calculated using typical values for the electron hopping amplitudes along and perpendicular to the nanotube axis, \( t_\parallel \approx t_\perp \approx 2.5 \text{ eV} \), the electron-lattice coupling, \( \alpha_\parallel \approx 4.1 \text{ eVÅ}^{-1} \), and the experimentally and numerically determined value for the optical phonon frequency, \( \omega_0 \approx 0.18 \text{ eV} \) [34, 35]. We then obtain from Eq. (6.138) that \( \lambda_o \approx 0.24/c_a \). Secondly, we note that within our elastic spring model the dimensionless electron-lattice coupling for the acoustic phonon mode, \( \lambda_a \), is only finite for a non-zero spring constant \( K_3 \). That a twist deformation depends crucially on the elastic coupling between distant atomic neighbors can be readily understood, since the corresponding twist angle \( \theta \) is related to the derivative of the distortion amplitude, \( \tan \theta = (u_a(x+a) - u_a(x))/a \). In order to estimate \( \lambda_a \), we first have to determine the values of the three spring constants within our model. Two conditions are given by Eq. (6.136) and Eq. (6.137), which we require to yield the experimentally and numerically obtained values for, respectively, the optical phonon frequency \( \omega_0 \approx 0.18 \text{ eV} \) [34, 35] and the sound velocity \( v_0 \approx 14 \text{ km/s} \) [12, 35]. The third condition is imposed by fitting the value of the acoustic phonon frequency at \( q = \pi/a \) where the acoustic branch deviates from its linear \( q \)-dependence and the frequency is known to be approximately \( \omega_a(\pi/a) \approx 0.07 \text{ eV} \) [12, 35]. For this purpose we calculate from Eq. (6.133) the acoustic phonon frequency in terms of the three spring constants at \( q = \pi/a \) and find:

\[
\omega_a \left( \frac{\pi}{a} \right) = \left( \frac{2K_1 + 16K_2 + K_3 - \sqrt{4K_1^2 + 2K_1(4K_2 - K_3) + (K_3 - 4K_2)^2}}{2 M C} \right)^{\frac{1}{2}}.
\] (6.140)

We then obtain \( K_1 \approx 25 \text{ eVÅ}^{-2} \), \( K_2 \approx 1.1 \text{ eVÅ}^{-2} \), and \( K_3 \approx 8.1 \text{ eVÅ}^{-2} \), where it turns out that \( K_3 > K_2 \) is required in order to fulfill all three conditions. This result is counterintuitive and probably is a consequence of the fact that our elastic spring model with three spring constants is rather simple and only gives an effective description of the complicated lattice dynamics. In fact, it is known that more involved force-constant models are required to describe the phonon spectrum of the graphene sheet and of carbon nanotubes [35, 36]. In particular, those studies contain at least four force-constants, namely, two spring constants and two parameters that describe the potential lattice energy as a function of the bond-angles. Clearly, in order to describe a twist deformation in the carbon nanotube, a model that accounts for effects due to changes in the bond-angles is certainly more appropriate. Keeping in mind that the main purpose of our model was to study the twist deformation and the existence of topological excitations qualitatively, we may still use the above values and estimate from Eq. (6.139) the dimensionless electron-lattice constant for the acoustic phonon mode to be \( \lambda_a \approx \lambda_o/4 \).

An alternative quantitative estimate of \( \lambda_a \) has been made within a model that only takes the acoustic phonons into account and relies on the in-plane shear modulus of the graphene sheet [30]. This yields the value \( \lambda_a \approx 0.23/c_a \), which is about four times larger than in our model.
6.7 Electrical conductivity of an armchair carbon nanotube

The acoustic phonons that correspond to a twist deformation of the nanotube lattice couple right and left moving electrons. Since the velocity of the twistons is orders of magnitudes smaller than the Fermi velocity of electrons, these modes are always heavily thermally populated and, in contrast to the high-energy optical phonons, twistons are effective at backscattering electrons. The scattering of electrons on the twistons with the temperature-independent bare phonon dispersion has recently been used to explain the linear temperature dependence of the resistivity of an armchair carbon nanotube [30].

In this section, we reconsider the temperature dependence of the electrical conductivity, \( \sigma(T) \), taking into account the renormalization of the acoustic phonon frequency due to the electron-phonon interactions. We consider armchair carbon nanotubes, \( c_a [1, 1] \), and restrict ourselves to \( T > T_c \). The electrical conductivity is calculated from the Kubo formula,

\[
\sigma(T) = -\frac{4e^2v_F}{\pi} \int dk \tau_k \frac{\partial n_F(\varepsilon(k))}{\partial k}, \tag{6.141}
\]

where \( \tau_k \) is the electron transport lifetime, which depends on the electron wave vector \( k \), and \( n_F(\varepsilon(k)) \) is the Fermi distribution with the linear electron energy dispersion \( \varepsilon(k) = v_Fk \).

The factor 4 in Eq. (6.141) accounts for the spin degrees of freedom and the number of Fermi points \( N_F = 2 \). The transport lifetime is calculated from the imaginary part of the electron self-energy describing the backscattering off the twistons [37]. The Dyson equation for the dressed electron Green's function due to one-phonon scattering processes is shown in Figure 6-27. The corresponding expression for the electron self-energy is given by

\[
\Sigma_{el}(k, i\omega_m) = -\frac{1}{L} \sum_q T \sum_{i\tilde{\omega}_m} |g_a|^2 D_a(q, i\tilde{\omega}_m) G(k + q, i\omega_m + i\tilde{\omega}_m), \tag{6.142}
\]

where \( \omega_m \) and \( \tilde{\omega}_m \) are, respectively, fermionic and bosonic Matsubara frequencies, \( q \) is the phonon momentum, and we set \( k_B = 1 \). The Green's function \( G(k + q, i\omega_m + i\tilde{\omega}_m) \) for the electron with energy dispersion \( \varepsilon(-k - q) \) has been introduced in Eq. (6.68). We denote the dressed phonon propagator by \( D_a(q, i\tilde{\omega}_m) \). It describes the acoustic phonons with renormalized frequency \( \tilde{\omega}_a(q) \) and is obtained from a diagonalization of the propagation matrix \( D \) given by Eq. (6.71). The contribution of the optical phonons to the resistivity can be neglected for temperatures \( T \ll \tilde{\omega}_o \). For \( \lambda_a \ll \lambda_0 \) this inequality may not be fulfilled close to \( T_c \), as the renormalized optical phonon frequency at \( T_c \), \( \tilde{\omega}_o = \omega_0 \sqrt{\lambda_a/(\lambda_a + \lambda_0)} \), may then be small. However, since the optical phonon frequency is large, \( \omega_0 \sim 2000 \text{ K} \), and assuming that \( \lambda_a \) and \( \lambda_0 \) are of approximately the same order in carbon nanotubes, there is no dramatic softening of the optical phonon and the conductivity close to \( T_c \) is dominated by the electron backscattering off acoustic phonons.

\[
\tau_k = \frac{1}{2} \frac{-1}{2Im[\Sigma_{el}(k, \varepsilon(k))]}, \tag{6.143}
\]

Expressing first each Green's function as a frequency integral over its respective spectral function and performing then the frequency summation over \( i\tilde{\omega}_m \), the self-energy Eq. (6.142)
6.7 Electrical conductivity of an armchair carbon nanotube

\[ G_\varepsilon \Rightarrow G = G + G = \Sigma \]

\[ = \Sigma_{el} \]

**Figure 6-27:** Dyson equation for the dressed electron Green’s function \( G_\Sigma \) (double line) due to one-phonon scattering processes. The phonon propagator \( D_a \) (double dashed line) contains the renormalized acoustic frequency \( \tilde{\omega}_a \).

\[ \Sigma_{el}(k, i\omega_m) = \frac{1}{\bar{I}} \sum_q |g_a(q)|^2 \int_{-\infty}^{+\infty} \frac{d\tilde{\omega}}{2\pi} \left( -2 \text{Im}[D_a^{ret}(q, \tilde{\omega})] \right) \frac{n_B(\tilde{\omega}) + n_F(\varepsilon_{-k-q})}{i\omega_m + \tilde{\omega} - \varepsilon_{-k-q}} , \]  

(6.144)

where \( n_B(\tilde{\omega}) = (e^{\tilde{\omega}/T} - 1)^{-1} \) is the Bose-Einstein distribution. The retarded phonon propagator \( D_a^{ret}(q, \tilde{\omega}) \) is obtained from the analytical continuation, \( i\tilde{\omega}_m = \tilde{\omega} + i\delta \), and its imaginary part reads \( (\delta \to 0) \):

\[ \text{Im}[D_a^{ret}(q, \tilde{\omega})] \approx -\pi \frac{\omega_a}{\tilde{\omega}_a} \left[ 1 + O\left( \frac{\omega_a}{\omega_0} \right) \right] \left[ \delta(\tilde{\omega} - \tilde{\omega}_a) - \delta(\tilde{\omega} + \tilde{\omega}_a) \right] . \]  

(6.145)

It thus follows that the imaginary part of the retarded self-energy \( (i\omega_m \to \varepsilon[k] + i\delta \) and \( \delta \to 0 \) is given by:

\[ \text{Im}[\Sigma_{el}(k, \varepsilon[k])] = -\frac{\pi \lambda_a}{16} \int_{-\infty}^{+\infty} dq \frac{\omega_a^2}{\tilde{\omega}_a} \left( 2n_B(\tilde{\omega}_a) + 1 \right) \delta(2k + q) . \]  

(6.146)

Here, we used that the velocity of acoustic phonons is much smaller than the Fermi velocity, \( v(q) \ll v_F \), and took elastic scattering processes into account. The acoustic coupling strength \( \lambda_a \) was defined by Eq. (6.63), and as \( 2n_B(\tilde{\omega}_a) + 1 \approx 2T/\tilde{\omega}_a \) for \( T \gg \tilde{\omega}_a \), we finally obtain according to Eq. (6.143) the transport lifetime

\[ \tau_k = \frac{2}{\pi \lambda_a T} \left( \frac{\tilde{\omega}_a(2k)}{\omega_a(2k)} \right)^2 . \]  

(6.147)

In Figure 6-28 we plot the temperature dependence of the electrical resistivity, \( \rho(T) = \sigma(T)^{-1} \), which is calculated numerically for \( T \geq T_c > 0 \) from

\[ \rho(T) = \frac{\lambda_a \pi^2 T^2}{2 e^2 v_F^2} \left[ \int dk \left( \frac{\tilde{\omega}_a(2k)}{\omega_a(2k) \cosh \left( \frac{v_F k}{2T} \right)} \right)^2 \right]^{-1} . \]  

(6.148)
At temperatures $T \gg T_c$, the resistivity Eq. (6.148) decreases linearly with the temperature,

$$\rho(T \gg T_c) = \kappa_0 \lambda_a T,$$

(6.149)

with $\kappa_0 = \pi^2/(8e^2v_T)$. However, close to $T_c$, due to the vanishing of the acoustic phonon velocity at the critical temperature, the resistivity Eq. (6.148) strongly increases up to some finite value,

$$\rho(T_c) \simeq \kappa_0 \frac{\sqrt{2} \lambda_a^2}{\lambda^2} T_c.$$

(6.150)

This behavior is very similar to the one observed for bundles of single-wall carbon nanotubes [30], where the cross-over between the linear decrease and the sharp upturn of the resistivity occurs at $T^* \sim 10 - 100$ K.

We mentioned already before that the Peierls instability is commonly believed to be irrelevant for carbon nanotubes, because the electron-lattice coupling constant is inversely proportional to the number of zigzag chains around the circumference of the armchair carbon nanotube. This makes $T_c$ negligibly small for $c_a \geq 4$ [12]. We note, however, that previously only the interaction with optical phonons, e.g., the deformations resulting in the ALT2 or Kekulé structure (see Figure 6-12 (c) and Figure 6-13 (a)), of the nanotube lattice was considered. When we take into account the scattering of electrons on acoustic phonons (twistons), we obtain a higher value of the coupling constant $\lambda (= \lambda_a + \lambda_a)$, which gives a correspondingly higher value of $T_c$. In particular, we consider an armchair carbon nanotube with $c_a = 4$, which was recently discussed in the context of possible technological applications [38] and has now also been created experimentally [39]. Using $\lambda_a \sim \lambda_a \simeq 0.23/c_a$, the critical temperature given by Eq. (6.97) is $\sim 10$ K, instead of only a few mK for the Peierls transition temperature without acoustic phonons.

The values of the electron-lattice coupling constants for a carbon nanotube could, in principle, be obtained from the form of the resistivity curve, since $\lambda_a$ determines the slope of $\rho(T)$
at high temperatures, whereas $T_c$ depends on $\lambda_\alpha + \lambda_\beta$. However, it should be kept in mind that the electrical resistivity is in addition to the electron-lattice interaction also affected by the electron-electron interaction. For example, electron correlations have been modelled by an on-site Hubbard interaction, $U$, which introduces umklapp scattering in a half-filled system. As umklapp scattering processes originate from the short-range interaction $U$, they involve a momentum transfer of order $2k_F \sim 1/a$, where two left moving electrons are scattered into two right movers and vice versa. In the presence of the Hubbard $U$, a mapping on an effective low-energy two-leg ladder model can be performed, similar to the procedure described in Section 6.2.2, under the assumption that the interaction does not involve electrons in different energy bands of the armchair carbon nanotube [5, 6]. Since the electrons are spread out around the circumference of the carbon nanotube, the probability of two electrons to be near each other is of order $1/c_a$. Therefore, the on-site Hubbard interaction $U/c_a$ is replaced by the effective interaction $U/c_a$ in the effective low-energy model. The contribution to the electrical resistivity, $\rho_U(T)$, is also found to be linear in the temperature [5],

$$\rho_U(T > E_g) \sim k_0 \left( \frac{Ua}{2\pi v_F c_a} \right)^2 T,$$  \hspace{1cm} (6.151)

at temperatures $T$ larger than the charge gap $E_g \sim (4/\pi)\sqrt{U/W/c_a}\exp\left(-c_a\pi W/(2U)\right)$ (the free electron band width is given by $W \sim 4t_\parallel$). Using the value $\lambda_a \simeq 0.23/c_a$ [30] and estimating $U/t_\parallel \sim 4$ for the carbon nanotube, we obtain $\rho_U(T)$ and $\rho(T)$ to be of the same order in the linear-$T$ regime for armchair carbon nanotubes $c_a [1, 1]$ with $2 < c_a < 10$. In other words, it is not possible to attribute the measured slope of the electrical resistivity of small radius armchair carbon nanotubes to either one of the two scattering mechanisms. The charge gap is associated with the energy cost of doubly occupying a site and for $T < E_g$ an activated behaviour of the resistivity,

$$\rho_U(T < E_g) \sim \exp \left( \frac{E_g}{T} \right),$$ \hspace{1cm} (6.152)

is to be expected [5]. We estimate that in armchair carbon nanotubes with $c_a \leq 5$ the charge gap is of the same order than the Peierls gap, $E_g \sim 2\Delta_0$.

Electron correlations have also been considered within a Luttinger model in which only forward scattering vertices are included [3, 4, 40]. Forward scattering processes are not reduced by a $1/c_a$ suppression factor and involve a small momentum exchange due to the long-range part of the Coulomb interaction. The electron-electron interaction strength is measured in terms of a single parameter $g \leq 1$, where $g = 1$ corresponds to the absence of the electron-electron interaction [3, 4, 40]. The bosonization method has been applied to describe the electronic degrees of freedom within a Luttinger model that also includes the interaction between the electrons and the (unrenormalized) twistons for temperatures $T \gg T_c$. It has been found that the linear temperature dependence of the electrical resistivity $\rho(T)$ for $g = 1$ turns into the anomalous power law behaviour [40],

$$\rho_L(T \gg T_c) \propto \frac{T}{T^{1-1/2}},$$ \hspace{1cm} (6.153)

due to forward scattering ($g < 1$).
So far, most of the measurements have been performed on bundles of carbon nanotubes, in which one cannot control the radius and chirality of individual nanotubes. Measurements of the resistivity of a single carbon nanotube still have to be improved and are under current investigation. We finally note, that we implicitly assumed that the nanotube is infinitely long, $L \rightarrow \infty$. The results obtained here are expected to be valid for temperatures (and also for voltages) well above the electron level spacing, $T \gg \pi \nu_F / L$. In the opposite limit, $T \ll \pi \nu_F / L$, the carbon nanotubes are expected to show interesting mesoscopic effects [4, 41].

6.8 Concluding remarks

In this chapter we studied the Peierls transition resulting from electrons interacting with both optical and acoustic phonons. We found that, independent of the electron-lattice coupling constants, the acoustic phonon velocity vanishes at the critical temperature, whereas the optical phonon frequency remains finite. This is different from the conventional Peierls scenario, in which the optical phonon softens at the critical temperature. In the present case, the coupling of the optical and acoustic phonon modes by electron-hole excitations results in a level repulsion between them. This drives the acoustic phonon frequency to zero at a temperature $T_c$ that is higher than the critical temperature of the conventional Peierls transition in the absence of acoustic phonons.

Structural phase transitions resulting from electron-lattice interactions are of broad interest and our theory is not limited to one particular system. As a specific application, we suggested that such a transition may take place in carbon nanotubes of small radius. We have shown that the Peierls state in these systems contains both a static twist of the carbon nanotube along its axis and a lattice dimerization due to the relative shift of the two triangular sublattices in the carbon nanotube.

While we have attempted to reach more than just a qualitative picture of this Peierls transition and its consequences, it should be stressed that our quantitative results have large error bars. This is a result of the fact that quantities of interest, like the transition temperature, depend exponentially on the electron-phonon coupling constants involved, which are hard to estimate with high precision. In addition, the interactions with other carbon nanotubes or with the substrate may suppress the Peierls transition in practice. We made a link to experiments on carbon nanotubes by calculating the temperature dependence of the electrical resistivity due to electron scattering on acoustic phonons with renormalized frequency. At temperatures that are much larger than the critical temperature, the electrical resistivity is found to have a linear temperature dependence which is in agreement with earlier calculations. However, at low temperature, we find a rise of the electrical resistivity due to the opening of the Peierls gap. We compared these results to previous theoretical work that focused on scattering mechanisms due to the interaction among electrons. We have estimated that the contributions of the two scattering mechanisms become equally important in carbon nanotubes of small radius. This fact makes it extremely difficult to deduce reliable information on, for example, the electron-lattice coupling constant of the acoustic phonons from experimental data of transport measurements.

Furthermore, we studied the existence and properties of topological excitations in the ordered phase at zero temperature. In contrast to the usual soliton in trans-polyacetylene, we referred to the topological excitation in our model as solitwiston, because it corresponds to a
combination of a dimerization kink and a change in the sign of the twist angle. The constituents of the effective model that describes the solitwistons are electrons that have an unusual internal degeneracy $N_d = 4$ (twice the spin degeneracy) as a consequence of the two triangular sublattices of which the hexagonal lattice is composed. We therefore found the solitwiston's spin-charge relations to be equal to those of the soliton in polyyne, where the neutral solitwiston has spin $S = 0$ or $S = 1$, while charged solitwistons have the usual spin-charge relations of electrons. Also the creation energy of this topological excitation equals that of the soliton in polyyne. The solitwiston, however, appears to be immobile, because its mass is proportional to the system length, so that it can only propagate as a pair together with an antisolitwiston.

We performed numerical simulations to determine the minimal-energy lattice configuration of an armchair carbon nanotube. This was done for different boundary conditions on the carbon nanotube lattice and as a function of the number of electrons added to the half-filled system. Depending on the degree of doping, we did not only find solitwistons, but we could also identify a non-topological excitation which corresponds to a local indentation of the order parameter and is best described as a polartwiston. As carbon nanotubes can be examined individually, it will be an interesting challenge to use the scanning tunneling microscopy and spectroscopy to probe the energies and shapes of the intragap states associated with solitwistons and polartwistons.
Bibliography


