CHAPTER 1

INTRODUCTION

1.1.0 Quasi 1D: a brief introduction

One dimension (1D) has always attracted a lot of attention to the physicists, due its simplicity in model calculation compared to three dimension (3D), and in many cases problems can be solved analytically. The reduction of dimensionality may hinder some phenomena to occur or exhibit some interesting behavior. There are numerous phenomena, exhibiting interesting quantum mechanical effects in condensed matter which only or mainly occur due to 1D confinement, in particular, when the confinement approaches the electronic wavelength. Fundamental concepts of physics, like the Fermi liquid theory of interacting charged particles break down in 1D and needs to be replaced by collective excitations [1,2] theory. Thermal fluctuations strongly influence the physical properties in 1D and may destroy the ordered phase implying the absence of otherwise expected phase transition.
Approximation of a real system into a 1D system to check the theoretical predictions is an interesting task in material science. The ideal 1D system would be an infinite chain of atoms in vacuum; close enough to interact with their neighbors, but completely isolated from the environment. In condensed matter, 1D systems can be achieved in various ways. The obvious example is a narrow channel of electron gas, down to nano-meter (nm) length-scale, formed at the interface of semiconductor hetero-structure grown by molecular beam epitaxy (MBE) [3]. Employing electron beam lithography and advanced etching technology, 1D quantum wires are fabricated with an effective width comparable to the wavelength of the electrons. Besides the enormous technological effort, the disadvantage of this approach is that these structures are embedded in bulk materials and are not easily accessible for further experiments. There are other methods of growing quantum wires in which wires are not embedded in bulk. An enormous potential of applications is seen in another sort of filaments solely consisting of carbon atoms: carbon nanotubes. They can be grown easily using arc discharge method or in chemical route. Carbon nanotubes are rolled-up sheets of graphite, with electrical properties very much depending on the winding ratio. Single-wall carbon nanotubes with a small diameter and the right winding ratio are excellent realizations of one-dimensional conductors [4].

By far the most successful approach to one-dimensional physics are highly anisotropic crystals. Here $K_2Pt(CN)_4Br_{0.3}H_2O$, known as Krogmann’s salt [5], represents the most intuitive example which consists of a chain of platinum ions with overlapping $d$ orbitals. The Br counter-ions remove electrons from the planar $Pt(CN)_4$ units and the resulting fractional charge $Pt_{1.7}(CN)_4$ leads to a partially filled electron band, the prerequisite for metallic behavior. The room temperature conductivity along the chain direction is very high $\sigma_\parallel = 10^2$
1.1. Quasi 1D: a brief introduction

...(cm)$^{-1}$. The anisotropy ratio is $\sigma_{\parallel}/\sigma_{\perp} = 10^5$. Transition metal oxides are known for decades to form low-dimensional crystal structures [6]. Varying the composition and structural arrangement provides the possibility to obtain one- and two-dimensional conductors or superconductors. Organic conductors form a class of solids with no metal atoms present (or relevant); instead the $\pi$-electrons distributed over the entire organic molecule form the orbitals which might overlap and lead to band-like conductivity. The additional degree of freedom, tailoring these molecules, supplements the structural arrangement in the crystal and makes it possible to fine-tune competing contributions for the desired properties. This makes organic materials superior for studying low-dimensional physics and ordering phenomena in solids. Nanofibers that are made of conjugated polymers are another example of 1D systems.

1.1.1 Speciality of 1D electronic systems

Electronic transport properties of 1D systems are very interesting as interactions and disorder play a very important role in determining them, also quantum fluctuations become very important here. In absence of columbic interactions properties of many-fermion system can be described by fermi gas model which is a quantum mechanical version of ideal gas model. In presence of impurity all the charge carriers in 1D non-interacting system would be localized (Anderson localization). To explain the properties of interacting fermions in higher dimension (more than 1) Landau gave a successful theory - Fermi liquid theory, where elementary excitations can be considered as a collection of free quasi-particles obeying Fermi statistics [7,8]. In presence of interactions Fermi liquid theory breaks down in 1D systems [1,2]. For 1D electronic system
the ground state is strongly correlated in presence of electron-electron interactions (EEI) and the low energy excitations are bosonic sound-like density waves (plasmons). Depending upon the range of EEI the properties of these system can be described by Luttinger liquid (if the interaction is short-range) or Wigner crystal (for long range interactions) [1, 2, 9, 10].

The Fermi surface of a 1D electron gas is consists of two point one at \( +k_F \) and other at \( -k_F \). The dispersion relation is assumed to be linear and described as

\[
\epsilon_k - \epsilon_F = \hbar v_F (k - k_F) \tag{1.1}
\]

The particular topology of Fermi surface results to a logarithmically divergent response function to an external perturbation. The response of an electron gas to a time independent potential

\[
\phi(\vec{r}) = \int \phi(\vec{q}) e^{i\vec{q}\cdot\vec{r}} d\vec{q} \tag{1.2}
\]

is generally treated within the linear response theory. The induced charge due to this field can be expressed as

\[
\rho^{\text{ind}}(\vec{r}) = \int \rho^{\text{ind}}(\vec{q}) e^{i\vec{q}\cdot\vec{r}} d\vec{q} \tag{1.3}
\]

and is related to \( \phi(\vec{r}) \) through

\[
\rho^{\text{ind}}(\vec{q}) = \chi(\vec{q}) \phi(\vec{q}) \tag{1.4}
\]

where \( \chi(\vec{q}) \) is called Lindhard response function. In \( d \) dimension it has the following form

\[
\chi(\vec{q}) = \int \frac{d\vec{k}}{(2\pi)^d} \frac{f_k - f_{k+q}}{\epsilon_k - \epsilon_{k+q}} \tag{1.5}
\]
where \( f_k = f(\epsilon_k) \) is the Fermi function. For 1D system \( \chi(\vec{q}) \) can be evaluated near \( 2k_F \) (considering linear dispersion (Eq. 1.1)) as

\[
\chi(\vec{q}) = -\frac{e^2}{\pi \hbar v_F} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right|
\]

(1.6)

So it is clear that response function diverges at \( q = 2k_F \). Equation (1.4) implies that an external perturbation leads to a divergent charge redistribution; this suggest, through self-consistency, that at \( T = 0 \) K the electron gas itself is unstable with respect to the formation of a periodically varying electron charge or electron spin density having periodicity

\[
\lambda = \frac{\pi}{k_F}
\]

(1.7)

This divergent response function leads to various instabilities at low temperature and the ground state depends on the electron-electron and electron-phonon interactions.

**a. Charge Density Wave (CDW):**

Charge Density Wave (CDW) generally arises due to electron-phonon interaction. Consider a 1D metal consists of periodic array of atoms having lattice constant \( a \). At \( T = 0 \) K and in the absence of electron-electron or electron-phonon interaction the electrons are field up to Fermi level in the ground state and the system have constant electron density \( \rho_e(x) = \rho_0 \) (see Figure 1.1(a)). In presence of electron-phonon interactions a periodic lattice distortion having period \( \lambda = \pi/k_F \) takes place (known as Peierls transition) and a gap opens up at the Fermi level (see Figure 1.1(b)) [11,12]. For 1D system the states up to \( \pm k_F \) are occupied and the development of a gap leads to lowering of
electronic energy near near the Fermi surface. In one dimension the single particle gap $\Delta$ is proportional to the amplitude of the lattice distortion $u$, and the decrease of electronic energy due to small displacement $u$ is proportional to $u^2 \ln u$. The distortion also cause an increase of elastic energy which is proportional to $u^2$ [13]. Hence for small distortion the total energy of the coupled electron-phonon system is lower than that of undistorted metal.

In presence of electron-phonon interaction 1D Hamiltonian can be written as

$$H = \sum_k \epsilon_k a_k^\dagger a_k + \sum_q \hbar \omega_q^0 b_q^\dagger b_q + \sum_{k,q} g(q) a_{k+q}^\dagger a_k \left(b_{-q}^\dagger + b_q\right)$$  \hspace{1cm} (1.8)$$

where $a_k^\dagger (a_k), b_q^\dagger (b_q)$ are the electron and phonon creation (annihilation) op-
erators with momenta $k$ and $q$ respectively. $\epsilon_k$ and $\omega_0^q$ are the electron and phonon dispersion, and $g(q)$ is the electron-phonon coupling constant. Solving the Hamiltonian (Eq. 1.8) using mean field treatment and considering linear dispersion relation (Eq. 1.1) one gets an expression of the gap

$$\Delta = 2D \exp(-1/\lambda')$$

(1.9)

where $D$ is the 1D band width and $\lambda'(=g^2(2k_F)/\omega_0^q)\epsilon_F$ is the dimensional less electron-phonon coupling constant. The spatial dependence of electron density is found to be

$$\rho_e(x) = \rho_0 + \frac{\rho_0 \Delta}{\lambda' v_F k_F} \cos(2k_F x + \phi)$$

$$= \rho_0 + \rho_1 \cos(2k_F x + \phi)$$

(1.10)

where $\rho_0$ is the electron density in absence of electron-phonon interaction and in 1D $\rho_0 = \pi/k_F$. So the ground state exhibits a periodic modulation of charge density due to lattice distortion and the single particle excitations having a gap $\Delta$ at the Fermi level. The charge density wave remains pinned by impurities which are present in the system and under the application of sufficient bias it starts sliding motion [12].

b. Lüttinger Liquid: arises due to short range electron-electron interaction

In presence of short range electron-electron interaction the electronic properties of a 1D system is described by Lüttinger liquid theory [1]. The most striking behavior, which clearly distinguishes the Lüttinger liquid from the Fermi liquid, is the anomalous power-law dependence of various correlation functions
in the low-energy region. For example, the density-density correlation function between two distant positions $x$ and $x'$ exhibits the power-law dependence in the asymptotic region,

$$<\rho_e(x)\rho_e(x')> \sim e^{2ik_F(x-x')(x-x')^{-\alpha}}$$

(1.11)

In contrast to the Fermi liquid, which has the finite density of states at the Fermi level, the tunneling density of states of these systems shows power-law energy dependence $n(\epsilon) \propto \epsilon^\alpha$. The differential conductance shows power-law dependence on either bias or temperature [1,2]

$$\frac{dI}{dV} \propto T^\alpha \text{ for low bias } (V \ll k_BT/e)$$

(1.12)

$$\propto V^\beta \text{ for high bias } (V \gg k_BT/e)$$

(1.13)

Pure (in absence of disorder) Luttinger liquid (LL) state predicts $\alpha = \beta$ and the bias ($V$) and temperature ($T$) dependence of $I$-$V$ curve can be expressed as [14]

$$I = I_0 T^{1+\alpha} \sinh \left( \frac{eV}{2k_BT} \right) \left| \Gamma \left( 1 + \frac{\alpha}{2} + \frac{ieV}{2\pi k_BT} \right) \right|^2$$

(1.14)

where $I_0$ is a constant and $\Gamma(z)$ is the Gamma function. For LL the different temperatures $I$-$V$ characteristics can be scaled to a master curve by plotting $I/T^{1+\alpha}$ versus $eV/(k_BT)$ [14]. The value of the exponent $\alpha$ depends on the number of channels and on the strength parameter $g$ of the LL. Depending on whether the electron tunnels into the bulk or the end of the LL stub, $\alpha$ can be
expressed as [15]

\[
\alpha_{\text{end}} = \frac{(g^{-1} - 1)}{4} \quad (1.15) \\
\alpha_{\text{bulk}} = \frac{(g^{-1} + g - 2)}{8}. \quad (1.16)
\]

Since \( g < 1 \) the exponent \( \alpha \) is larger near the end which is due to the fact that the spread away of an added charge at the end is small compared to the bulk. If \( g \ll 1 \) then \( \alpha_{\text{end}} = 2\alpha_{\text{bulk}} \). In pure LL spin and charge excitations propagate with different velocities which leads to the separation of spin and charge.

At low densities, the potential energy grows faster relative to the kinetic energy and eventually dominates it for sufficiently low densities when \( na_B \ll 1 \) where \( n \) is the average density of electrons and the effective Bohr radius \( a_B = \epsilon \hbar^2 / me^2 \) with \( \epsilon \) the dielectric constant. At these low densities, there is a separation of energy scales between the magnetic exchange energy \( J \sim E_F e^{-c/\sqrt{na_B}} \) and Fermi energy \( E_F = (\pi \hbar n)^2 / 8m \), where \( C \) is a positive constant. With increasing distance between charge carriers the exchange energy become exponentially small. For \( na_B \ll 1 \) it is possible to reach a regime where the temperature \( T \) is much larger than the magnetic exchange energy, but still much less than the Fermi energy: \( J \gg T \gg E_F \). This region is known as spin incoherent or magnetically incoherent Luttinger liquid regime [16, 17]. The characteristics of spin incoherent LL can be understood considering Wigner solidlike behavior of electrons (discussed below). However, in one dimension the quantum fluctuations are strong enough to destroy the long-range order, even for long-range Coulomb interactions [18] and a fluctuating Wigner solid can be successfully used for low density strongly interacting Fermions in one dimension. The transport in an infinite magnetically incoherent electron gas is
very much like that of a spinless LL, except that all the quantum-phase transi-
tions are obtained by replacing $g$ by $2g_c$, where $g$ is the interaction parameter
of the spinless LL and $g_c$ is the interaction parameter of the charge sector of a
LL theory for electrons with spin [16,17].

For a strictly 1D system the power-law behavior may be washed out by
quantum fluctuations. However in quasi-1D systems (systems composed of sev-
eral parallel chains) where the different channels are statistically independent
the power-law behavior may be observed clearly due to the averaging of fluc-
tuations. In quasi-1D systems the exponents depend on the number of the 1D
channels [15]. However in these systems if inter-chain electron hopping play a
significant role then the system looses its one-dimensionality and the exponents
becomes equal to zero. This could be the case for quasi 1D systems at very low
temperature where arbitrarily week interchain hopping can drive the system
towards a 3D system [18,19,21]. In disordered 1D systems impurity acts as an
infinite tunneling barrier [15,22]. However presence of disorder in 1D system
can stabilize the LL state, where LL state is preserved between two consecutive
impurities, thus a disordered quasi-1D system can be considered as collection
of LL stub [23]. For such systems weak interchain hopping does not destroy
the LL state at low enough temperature (compared to the minimum excitation
energy of the LL collective modes), and low bias conductivity shows Variable
Range Hopping behavior while high bias conductivity shows power law behav-
ior. Low bias resistance-temperature ($R - T$) behavior of such system follows
Mott’s 3D VRH law for short-range interaction and Efros-Shklovskii law for
long-range interactions between electrons of different segments [23].
C. Wigner Crystal: arises due to long range electron-electron interaction

In the presence of long-range electron-electron interaction in a very low electron density materials if Coulomb repulsion dominates over the kinetic energy of the electrons then electrons get arranged periodically in space forming an electron crystal [10] known as Wigner crystal (WC). To quantify the condition of WC formation, a parameter, strength of interaction is defined as

$$r_S = \frac{a}{2a_B},$$

where \(a\) is the average distance between electrons and \(a_B\) is the effective Bohr radius. At very low electron density \((n_s)\) the separation between electrons become large \((r \propto 1/n_s)\) so \(r_S \gg 1\) and this is the condition for WC formation. It has been found that (a) \(r_S \simeq 36\) for clean unbound system, (b) \(r_S \simeq 7.5\) for disordered unbound system and (c) \(r_S \simeq 4\) for confined system [24–27]. The decrease of \(r_S\) in disordered system is due to the breaking of continuous translational invariance that stabilize the WC state.

It has been predicted theoretically that in 1D WC exhibits the characteristic of a charge density wave (CDW) [18]. The charge-charge correlation function in 1D for long range EEI can be written as

$$\langle \rho_e(x)\rho_e(0) \rangle = A_1 \cos(2k_F x) \exp(-c_2 \sqrt{\ln(x)})/x + A_2 \cos(4k_F x) \exp(-4c_2 \sqrt{\ln(x)}) + \ldots$$

where \(A_1, A_2\) are interaction dependent constants. In the expression other fast decaying Fourier components have been omitted. It is interesting to note that the \(4k_F\) component decays very slowly (much slower than any power law), showing an incipient charge density wave having wave vector \(4k_F\) [18] (in CDW systems, formed due to Peierls transition one observes a \(2k_F\) periodicity). The decay of \(4k_F\) component observed in long range interaction is much slower
compared to short-range interactions where $2k_F$ and $4k_F$ components show power-law decay. As the $4k_F$ oscillation period is same as interparticle spacing the structure is same as 1D WC but true long range order does not exist in such system because of its 1D nature. It should be mentioned that $4k_F$ oscillation arises only due to the long-range nature of the EEI and can exist even for its extremely small value.

It has been reported that WC state may occur in quasi-1D systems [28] or even in nanowires of structurally disordered materials [29]. This electron crystal is pinned by the impurities present in the system. Theoretically it has been shown that if the impurities acts as strong pinning center then quasi-1D WC shows VRH conductivity with various exponents which depends on the impurity concentration [29]. At large impurity concentration conductivity follows Effros-Shklovskii law and at very low impurity concentration Mott’s 3D VRH type behavior is predicted. For weakly pinned Wigner crystals tunneling density of states show a power law behavior with the applied bias [30] and the exponent ranges from $\sim 3$ to $6$ [30–33]. The impurities destroy the long range order, however for weak impurity strength quasi-long range order may exist [34] and a Wigner glass [35–40] may form. Depending upon the pinning strength a pinned WC become non-conducting below a certain threshold field. When an applied field is strong enough to overcome the pinning energy the WC depins and sliding motion starts giving rise to a switching transition similar to CDW systems [41–44].
1.2.0 Polymer nanowire and quasi-1D

1.2.1 Basics

Polymer is composed of several repetitive unit called monomer; the word "poly" means many and "mer" means unit. The term monomer means chemical repeat unit of small molecule that are polymerized to produce a polymer. Like polystyrene which is a polymer which is composed of the repeating unit of $C_8H_8$ and its molecular formula is $(C_8H_8)_n$. Here $n$ is the number of repeating unit within a single chain. In case of polystyrene, $n$ used to be several thousand.

The synthetic polymers can be classified in various groups either based on their structures or on their properties. It is the combination of monomer structure, length and flexibility of macromolecules that generates such versatile properties of polymers. Three broad types of structures are generally used for classification of polymers, namely linear - like polyethylene mentioned before, branched and network combination of monomers. Again one can have three classifications of polymers based on their properties like, (thermo) plastics, rubbers (elastomers) and thermozets. The (thermo) plastics are made of either linear or branched macromolecules and plastics soften or melt above a transition temperature. These polymer materials are easy to mould and are widely used for technological applications. On cooling these plastics generally form a non-crystalline structure below a transition temperature, known as glass transition temperature, $T_g$, from molten state. Some plastic materials may form partially crystalline structure or liquid crystalline phase on cooling. Rubbers or elastomers are generally made of macromolecules that are lightly cross linked to allow reversible stretching and to prevent melting in conventional sense - these
materials do not flow even in molten state. Thermozets are made of heavily
cross-linked macromolecule and are rigid materials that do not soften even at
higher temperature, for example epoxy resin materials like Araldites.

Polymer synthesis and industrial production has came a long way since
the production of first synthetic polymer, cellulose nitrate or celluloid from
cotton in the late 1800. The present day production techniques involved precise
control over monomer chain length, over monomer sequences in copolymers that
use more than one monomer and control over precise molecular weight. It is
also important to note that right from the beginning 'wire' and 'fiber' was an
important product of polymer industries not only for textile industry but also
for other applications like filter materials etc. that requires high surface to
volume ratio.

Nanofibers or nanowires of various polymers can be efficiently used in
varieties of applications like filtration technology, life science and sensor devel-
opment. Apart from all these applications that demands chemical sensitivity
of polymers, two prime physical properties make polymer materials technolog-
ically unique and motivated large amount of research activities for both basic
and applied physics. One is mechanical property, for example Young’s modulus
of two syntectic polymer fibers, made of elastomer and plastic can be 10 MPa
and 350 GPa respectively [45] - that is 35000 times higher. Even more dramatic
is electrical conductivity of polymers - it can vary more than 20 orders of mag-
nitude from a good insulator having conductivity $10^{-18} \, \Omega^{-1} \, \text{cm}^{-1}$ to a good
conductor with conductivity $10^4 \, \Omega^{-1} \, \text{cm}^{-1}$. In this thesis we shall primarily
concentrate on the conductivity of polymers especially when it takes a from of
a nanowire -fascinating new properties are obtained in these research activities.

Polymers are generally electrically insulating materials. It is only after the
discovery by Heeger, MacDiarmid, Shirakawa and co-workers plastic could be made to conduct electricity [46] and this discovery resulted in the Nobel Prize for Chemistry in 2000. Conducting polymers can be both organic (such as Polyacetylene, Polyphenylene, Polyaniline, Polypyrrole, Poly(p-phenylenevinylene), Polythiophene, Poly(3,4-ethylenedioxythiophene) etc.) or inorganic (such as polysulphur nitride ($SN_x$), alkali fulleride compounds ($AC_{60}$)$_n$ (with $A = K$, Rb or Cs) etc.) in nature. Conducting polymer are generally of two types, conjugated polymer and redox polymer. In conjugated polymers alternate double bonds and single bonds (conjugated bonds) occurs along the polymer chain. In a redox polymer a redox-active transition metal based pendant group is covalently bound to the polymer backbone. We will confine our discussion on conjugated polymers.

1.2.2 Conjugate Polymer

![Figure 1.2: Molecular structures of few conjugated polymers.](image)

In conjugated polymers three out of the four valence electrons of carbon form strong $\sigma$ bond (through $sp^2$ hybridization) where electrons are localized
and these helps to form the polymer backbone [47]. The rest unpaired ($\pi$) electron of each carbon atom stays in p-orbital (which is non-localized). The $\pi$ electrons of the successive carbon atoms overlap to form a $\pi$ bond and this leads to the electron delocalization along the polymer backbone. As each carbon atom contributes only one electron a half filled valence band should have been formed by the delocalized $\pi$ orbitals and one should have always observed a metallic behavior. However due to the electron-lattice coupling such long-chain one dimensional (1D) metal is unstable (Peierls instability) and the polymer lower its energy by bond alteration (alternating short bonds and long bonds). This conjugated structure increases the $\pi$ electron density between alternate pair of carbon atoms (due to the formation of double bond the separation between the pair of atoms decreases) and the $\pi$ band is then divided into $\pi$ (bonding) and $\pi^*$ (antibonding) bands. Due to the Pauli exclusion principle each band can accommodate only two electrons per atom (spin up and spin down) leaving a filled $\pi$ band and an empty $\pi^*$ band. An energy gap $E_g$ appears in the middle of the highest occupied state in the $\pi$ band and the lowest unoccupied state in the $\pi^*$ band. Due to the presence of large band gap ($E_g \sim$ eV) and absence of partially filled band, conjugated polymers behave as a high band gap semiconductor [48] with negligible room temperature conductivity.

To increase the conductivity one need to create sufficient charge carriers in the conduction band; this has been done by doping of conducting polymer [48,49]. In conducting polymer doping can be done by redox reaction which converts the insulating neutral polymer into an ionic complex consisting of a polymeric cation (or anion) and a counterion which comes from the oxidizing agent (or from the reducing agent). This oxidation or reduction process creates p-type or n-type charge carriers respectively in the conjugated polymer. The doping
process in conducting polymer is markedly different from that of conventional inorganic semiconductors (like silicon, germanium etc.). In inorganic semiconductor concentration of dopant atom is very low (\(\sim 1 \times 10^6\) host atoms) and they are substituted directly in the host lattice; but in conducting polymer the dopant ions resides out side the polymer chain and present in several percent with respect to the carbon atoms of the polymer. Doping of polymers can be done using chemical, electrochemical, photoabsorption process and also by charge injection at a metal-semiconducting polymer interface etc [46].

Depending upon the doping level conducting polymer can be insulating or semi-conducting and one can even make a metallic conducting polymer by proper doping [46,50–52]. Several functional groups can be easily attached to conducting polymers using chemical methods to make sensors for chemical and biological applications. Metal decorated conducting polymers can act as hydrogen storage materials and these composite materials find important application in fuel cell technology [53,54]. Conducting polymer has shown its potential for organic electronic memory devices [55–57]. Conducting polymer finds several application in LEDs [58–60], electrochromic devices [61–64], solar cells [65–68], rechargeable batteries [69,70], actuators [71–75] and biological and chemical sensors [76–82].

The electrochemical synthesis of conducting polymers has been very versatile and in this technique counter ions are incorporated into the polymer chains to maintain charge neutrality. The doping level of electrochemically synthesized conducting polymer can be varied by changing the electrochemical potential between polymer and a reference electrode which drives ions into (or out of) the polymer. This change in amount of ion intercalation between polymer chains causes various changes of physical and chemical properties. This
method is used to build electrochemically gated transistors, chemical and biological sensors, actuators, capacitors etc.

1.2.3 Conduction carrier in conducting polymers

Solitons, polarons and bipolarons are the self-localized fundamental excitations of conjugated polymers [50,83,84] and here we shall discuss basics of these process.

Figure 1.3: Creation of charged soliton by removing electrons from the polymer backbone of trans-polyacetylene.

**Solitons:** The ground state of a long-chain quasi-1d polymers like trans-Polyacetylene and Polythiophene having alternate double bond and single bond is doubly degenerate. One can easily understand this with a simple example [50]; consider a polymer chains where atoms are marked by 1, 2, 3....... then
Figure 1.4: Total energy as a function of mean amplitude of distortion. The double minima indicates the presence of twofold-degenerate ground state.

the polymer structure can have two phases $A \rightarrow (1 = 2 - 3 = 4 - 5 = 6 - )$ or $B \rightarrow (1 - 2 = 3 - 4 = 5 - 6 = )$, where $-$ and $=$ represents single and double bonds respectively. It is easy to understand that if all the atoms are identical (as in Polyacetylene) and the system is of infinite extent then the energy of the two phases are same i.e. the ground state is doubly degenerated (see Figure 1.4) [85]. If we remove charges from the polymer chain, a double bond will be replaced by a single bond and an atom will have single bond on both sides (refer Figure 1.3); this broken pattern of alternate double bond and single bond represents a soliton. So soliton can be viewed as domain boundary between two ground state configuration phase '$A$' and '$B$' [50] and the misfit between the '$A$' and '$B$' phases is known as "kink" (see Figure 1.4). With the formation of soliton a localized electronic state is created in the middle of the $\pi-\pi^*$ band gap. Due to presence of structural kink, the mid gap state can accommodate up to 2 electrons. If the state is singly-occupied then it is a neutral soliton and if it is empty (doubly occupied) then one gets a positively (negatively) charged soliton (see Figure 1.5). So unlike other excitation processes, soliton poses un-
Figure 1.5: Band structure of (a) neutral soliton, (b) positively charged soliton
and (c) negatively charged soliton.

usual spin-charge relationship; a neutral soliton is a spin $1/2$ radical whereas a
charged soliton is spin-less [85].

**Polarons & Bipolarons:** During doping if we remove one electron from the
polymer chain then there used to appear a positive charge on the chain. It
means there appears a positively charge hole on the top of the valence band.
According to the band theory, this positive charge can delocalize over the whole
chain. Due to the energy minimization, instead of making this carrier com-
pletely delocalize, there will be local distortion near the positive charge on the
chain and the positive charge become localized. Thus energy minimization will
allow localized charge rather than band modification. This localized charge is
called polaron this process causes the presence of localized electronic states in
the gap due to a local upward shift of the valence band and downward shift
of the conduction band (Figure 1.6). Considering the case of oxidation, i.e.,
the removal of an electron from the chain, we lower the ionization energy by an amount $\Delta \varepsilon$. If $\Delta \varepsilon$ is larger than the energy necessary to distort the lattice locally around the charge, this charge localization process is favorable relative to the band process. We then obtain the formation of what condensed-matter physicists call a polaron. If a second electron is removed from the polymer chain then it is energetically favorable to take out the electron from the polaron (which has already formed during the removal of first electron) rather than to crate another polaron in the polymer chain. This bound state of two polarons which consist of a pair of like charges having opposite spin (so that net spin is zero) combined with strong lattice distortion is called as bi-polaron (see Figure 1.6). Formation of bi-polaron demand that the energy gained by lattice distortion is larger than the Columbic repulsion between the two like charges [86].
As the bi-polarons are spin less its movement contributes to charge transport without any spin transport. Though solitons, polaron and bi-polarons are the fundamental excitations of conjugated polymers their contribution to transport mechanism are largely different; movement of (i) neutral soliton along a polymer chain does not contribute to charge transport, (ii) bi-polaron contributes to charge transport, (iii) polaron contributes to charge and spin transport, only while.

1.3.0 Outline of the thesis

In this thesis we have studied the CDW state of polypyrrole nanotubes and the effect of external incorporated gold nanoparticles on this CDW state. The details of the study is organized in different chapters as follows.

- In Chapter 2 we have presented the synthesis procedure of gold-polypyrrole composite and polypyrrole nanotubes. The synthesized samples are characterized using several characteristic techniques like Scanning electron microscopy, Transmission microscopy, Energy dispersive x-ray spectroscopy, Secondary ion-mass spectroscopy. As well as we have provided details of instrumentation for low temperature measurements and characterization techniques.

- In Chapter 3 we have presented results of studies to understand the effect of incorporated impurities in this quasi-one-dimensional system. Using Hard X-ray Photoemission Spectroscopy (HAXPES) and Magneto-transport measurements we have found out the disorder and doping in these nanotubes. The results of these studies helped us to understand the effect of the gold incorporation on the charge density wave (CDW)
state that controls the low temperature electronic transport properties of these composite nanotubes.

- In Chapter 4 We have presented the study of gold incorporation process within the wall of polypyrrole nanotubes for various nanotubes diameter and for different concentrations of oxidizing agent which helped us to tune the CDW state of this composite nanotubes. As well as we have presented dielectric constant measurements of the CDW state for different wt% of incorporated gold and diameter of nanotubes.

- In Chapter 5 We have studied the CDW state in pure polypyrrole nanotubes using Fukuyama, Lee, Rice hamiltonian. This study has enabled us to find out the dynamics of the CDW state.

- In Chapter 6 we have shown that conducting polymer nanowires giant resistance switching transition, attain metallic state above a threshold bias from a usual insulating state which shows negative temperature coefficient and parabolic magnetoresistance. A possible explanation of the results can be drawn following the models for one dimensional electron systems where insulator-to-metal transition is expected as the ‘range’ of electron-electron interaction increases.

- Chapter 7 summarizes this thesis and closes with an outlook.