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Electronic transport in random-side-chain polymers

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Abstract. We investigate the electronic transmission properties of polymers which consist of a dimerized backbone chain with randomly distributed side chains of length $2m$. The system is connected to perfect left-hand and right-hand metallic leads, and the transmission spectrum is computed. We find $2m - 2$ high-transmission and 2 low-transmission peaks which reflect resonant extended states in the random system and the gap edges of the dimerized backbone chain, respectively. The temperature dependence of the conductivity is shown to be very sensitive to the position of the Fermi level. The tunnelling current at zero temperature in the presence of a bias voltage gives a region of negative differential conductivity, which is due to a competition between the opening of a transmission window by the applied bias and the suppression of the transmission peaks by the electric field.

1. Introduction

The electronic transport properties of conjugated polymers have attracted a lot of attention during the last decade. The most striking feature of these soft materials is the enhancement of their conductivity upon doping. The room temperature conductivity of heavily doped conjugated polymers reaches very high values—even ones typical of metals [1–3]—despite the fact that these structures are topologically disordered. Moreover, in the theory of disordered systems there is no completely satisfactory theoretical model which can explain these distinguishing electronic transport properties, mostly because the random nature of polymers is usually incompatible with the observed high conductivity. For example, it is also insufficient to represent the complicated polymer structures via simple one-dimensional (1D) disordered systems, since the phenomenon of Anderson localization leads to vanishing conductivity in this case. A more faithful representation of the polymer topology requires dimensionality higher than one. In view of this, single-chain windings [4], random interchain couplings etc [5–8] have been considered. This consideration involved possible mechanisms which lead to the reported almost metallic behaviour, and quasi-extended, rather than localized, eigenstates. This confirms the fact that conjugated polymers are complex quasi-1D disordered systems. Recently, fractal structures with dimension slightly above one have also been considered for modelling transport in conducting polymers with non-metallic conductivity [9].

The aim of this paper is to represent conjugated polymers by another possible random structure, which also deviates from the perfect 1D chain. This involves an ordered host-backbone chain with many side chains attached at random positions. In order to keep

the topology fairly simple, we ignore windings of a single chain and random interchain couplings. Moreover, the randomly attached side chains are taken to consist of a fixed number ($2m$) of atoms. A typical polymer material with side chains has been synthesized by vapour-deposition polymerization in the laboratory, and the electro-optic coefficient was measured [10].

The electronic transmission for the dimerized polymer structure considered (a backbone with randomly attached side chains) is obtained by placing the system between two metallic leads [11]. Our study of the transmission spectrum shows $2m - 2$ high-transmission peaks at certain energies, exactly where internal resonant extended states occur in the absence of the leads. We also obtain smaller peaks at two additional energies which correspond to the gap edges of the pure host-backbone dimerized chain. The smaller peaks correspond to a residual periodicity effect, which persists in the random structure considered. The extended states obtained might be unexpected, since the scaling theory predicts localization of all states in quasi-1D disordered systems [12]; however, delocalization at specific energies is possible due to the fact that extra scattering at the positions where the side chains are attached self-cancels. This mechanism is similar to that known for dimer correlated disordered systems [13, 14], where the waves scattered backward from every dimer scatterer become zero at specific energies, due to quantum interference. The random-side-chain polymer system considered illustrates the presence of resonant extended states and also how such delocalized states can affect the transport properties of the system.

The unusual transmission spectrum for the random polymer structure considered drastically modifies the temperature dependence of the conductivity and can also influence the I - V characteristics. In particular, we obtain non-linear conductivity when the applied voltage is not small and the corresponding I - V characteristics enter a regime of negative differential conductivity. This is attributed to the interplay between two opposite effects of the bias voltage: an increase in the number of states which contribute to the conductivity and the suppression of the transmission peaks, since the applied electric field destroys the resonant extended states in the system.

2. Model and formulae

We study polymers with randomly distributed side chains, sandwiched between two semi-infinite metallic leads [11]. The total Hamiltonian of the system is

$$H = H_b + H_s + H_l + H_c \quad (1)$$

where H_b and H_s are the host-backbone and side-chain Hamiltonians, and H_l and H_c represent the metallic leads and the interfaces between the system and the leads.

The host backbone is modelled via the dimerized-chain Hamiltonian

$$H_b = \sum_{n=1}^{2N-1} \{ -[t - (-1)^n \Delta] C_n^\dagger C_{n+1} + \text{HC} \} \quad (2)$$

where C_n^\dagger (C_n) is the electronic creation (annihilation) operator at the n th site of the backbone, and $t + \Delta$ or $t - \Delta$ the hopping integral for two nearest-neighbour sites. We assume that the host backbone consists of $2N$ sites having energy dispersion which is described by the two subbands

$$E = \pm 2\sqrt{t^2 \cos^2 ka + \Delta^2 \sin^2 ka}$$

with gap edges at $\pm 2\Delta$. The $2m$ -length side chains are described by a similar Hamiltonian:

$$H_s = \sum_{n_k} \left\{ \sum_{s=1}^{2m-1} [-(t - (-1)^s \Delta) C_s^\dagger(n_k) C_{s+1}(n_k)] - (t - \Delta) C_{2m}^\dagger(n_k) C_{n_k} + \text{HC} \right\} \quad (3)$$

where n_k is the random host-backbone site at which the side chain is attached. The sites n_k appear at random with concentration p .

The non-interacting tight-binding Hamiltonian for the left-hand and right-hand metallic leads is given by

$$H_l = \sum_{n=-\infty}^{-1} (-t_0 C_n^\dagger C_{n+1} + \text{HC}) + \sum_{n=2N+1}^{\infty} (-t_0 C_n^\dagger C_{n+1} + \text{HC}) \quad (4)$$

where t_0 is the hopping integral for two nearest-neighbour sites (set to unity in our calculations), while the left-hand lead ceases at 0 and the right-hand lead starts at $2N + 1$. The energy spectrum of H_l is $E = -2t_0 \cos k$, assuming unit lattice spacing $a = 1$. In addition, the hopping integrals for the two contacts are described by the interface term

$$H_c = -t_1 (C_0^\dagger C_1 + C_{2N}^\dagger C_{2N+1} + \text{HC}). \quad (5)$$

The disorder in the system arises because the side chains are attached at random backbone sites with probability p . We also assume that no more than one side chain is randomly attached (only at the odd backbone sites) in every unit cell. The electronic transmission through the polymer structure considered can easily be computed by the transfer-matrix method. For an incoming electron with energy E and unit site amplitude, the wave function for the left-hand lead can be expressed as

$$a_n = e^{ik_{in}n} + r e^{-ik_{in}n}$$

for $-\infty < n \leq 0$, where r is the reflection amplitude. In the right-hand lead, the outgoing wave function is

$$a_n = t e^{ik_{out}(n-2N-1)}$$

for $2N + 1 \leq n < \infty$, where t is the transmission amplitude. The amplitudes at the sites $2N + 1$ and $2N + 2$ are expressed by

$$\begin{pmatrix} a_{2N+2} \\ a_{2N+1} \end{pmatrix} = \hat{\mathbf{M}}_{out} \hat{\mathbf{T}} \hat{\mathbf{M}}_{in} \begin{pmatrix} a_0 \\ a_{-1} \end{pmatrix} \quad (6)$$

where the matrices $\hat{\mathbf{M}}_{in}$, $\hat{\mathbf{M}}_{out}$ and $\hat{\mathbf{T}}$ are explicitly derived in the appendix. Equation (6) allows the computation of the transmission coefficient, $T(E) = |t|^2$, at a given energy E , for every random configuration. Then the temperature dependence of the conductivity can be obtained from the Landauer formula [15]

$$\sigma(kT, \mu) = \left(\int \left(-\frac{\partial f}{\partial E} \right) T(E) dE \right) / \left(\int \left(-\frac{\partial f}{\partial E} \right) (1 - T(E)) dE \right) \quad (7)$$

where f is the Fermi distribution function:

$$f = \frac{1}{e^{(E-\mu)/kT} + 1}.$$

The conductivity $\sigma(kT, \mu)$ is the linear response of the system to a small external field. However, if the applied voltage is not small, we also expect non-linear components to

merge into the total current. In this case we compute the I - V characteristics from the semi-classical formula

$$I(V) = eN_0 \int_{-2t_0}^{2t_0 - eV} \rho(E)v(E + eV)|t^2|(f(E) - f(E + eV)) dE \quad (8)$$

which was previously proposed for investigating tunnelling currents in semiconductor superlattices [16]. The electron charge is e , the electronic density in the leads N_0 , the density of states of the leads is expressed as

$$\rho(E) = \frac{1}{\pi\sqrt{4t_0^2 - E^2}}$$

and $v(E)$ is the electron velocity in the leads obtained from the semi-classical relation

$$v(E) = \frac{1}{\hbar} \frac{\partial E}{\partial k} = \frac{1}{\hbar} \sqrt{4t_0^2 - E^2}.$$

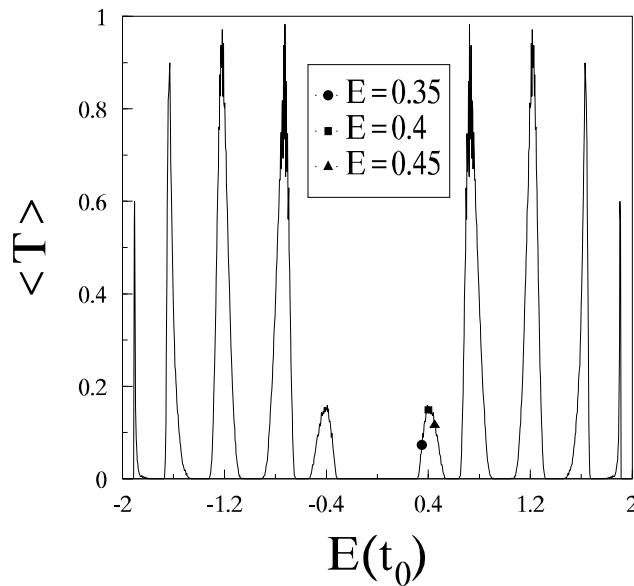


Figure 1. The electronic transmission of a finite side-chain polymer structure with $p = 0.5$. The backbone length is $2N = 200$, the length of each side chain is $2m = 10$ and the rest of the parameters are: $t = 1.0$, $\Delta = 0.2$, $t_1 = 0.8$, with $t_0 = 1$ which sets the energy unit.

3. Results

In figure 1, we plot the transmission spectrum of a side-chain polymer with $2N = 200$ dimerized backbone sites and randomly distributed side chains of length $2m = 10$, with concentration $p = 0.5$, taking averages over 1000 random configurations. In the appendix it is shown that states with energies

$$E_l = \pm \sqrt{2 \cos\left(\frac{l\pi}{m}\right)(t^2 - \Delta^2) + 2(t^2 + \Delta^2)} \quad l = 1, 2, \dots, m - 1$$

are perfectly extended in the absence of the leads. However, the system studied here, with finite random side chains, is inserted into perfect left-hand and right-hand chains so that at every E_l the transmission coefficient becomes large close to, but not exactly at, unity. The reason for the system not reaching transmission exactly equal to unity is the additional scattering of the incident waves at the two contacts, between the side-chain polymer and the leads. This phase mismatch makes the system at E_l nearly, rather than completely, transparent. On the other hand, we find two extra transmission peaks of considerable magnitude close to the gap edges $\pm 2\Delta$ of the backbone chain. These peaks persist for various lengths $2m$ of the side chains if the length $2N$ of the backbone is not extremely long.

In order to explain our results, we consider the $p = 0$ limit, where $H_s = 0$ and the spectrum consists of two subbands and a gap. At the gap edges ($\pm 2\Delta$), the wave functions have smaller amplitudes at the odd sites (where the side chains are randomly attached for $p \neq 0$) than at the even sites. This leads to weaker scattering by the side chains in the random ($p \neq 0$) case, so two peaks emerge in the transmission spectrum. They demonstrate a residual periodicity in the finite random sample. When the backbone length increases, these peaks at the gap edges diminish. For example, for $2N = 2000$ the two peak values become of the order of $\sim 10^{-5}$.

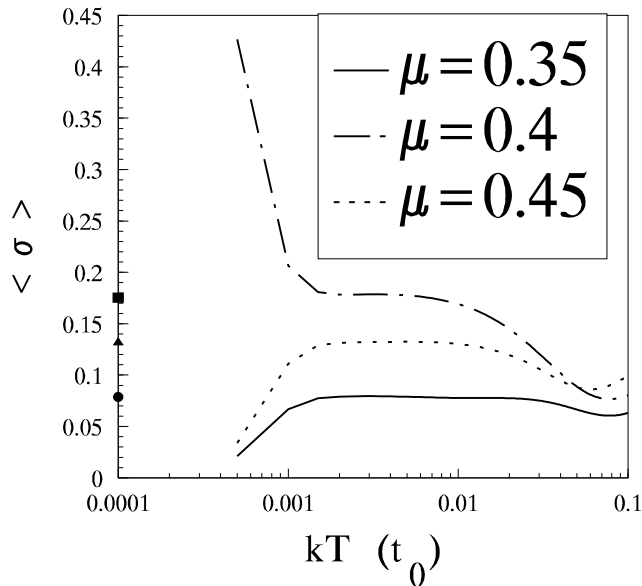


Figure 2. The variation of the dimensionless conductivity versus temperature for three systems with the Fermi levels $\mu = 0.35$, $\mu = 0.4$ and $\mu = 0.45$, corresponding to the points marked by a filled circle, square and triangle, respectively, in figure 1. The rest of the parameters are the same as for figure 1.

In the remainder of this work we show how the complicated transmission spectrum obtained can drastically modify the electronic transport properties of the system. We focus just on cases with Fermi levels around $+2\Delta$, which represents n^+ -type doping. In figure 2 we present the dimensionless conductivity versus temperature for the Fermi levels $\mu = 0.35$, $\mu = 0.40$ and $\mu = 0.45$ at the positions marked by the closed circle, square and triangle on the small peak of figure 1. On the logarithmic x -axis we have the temperature and on

the linear y -axis the conductivity σ . The large zero-temperature conductivity values are marked by the filled circle, rectangle and triangle for the three values of μ studied. For small but non-zero temperatures (e.g., at $kT = 0.0005$), with the Fermi level $\mu = 0.40$, at the peak, the conductivity σ —unlike the case for the other two μ -values—is much larger than its corresponding zero-temperature value. An increase in temperature is seen to give plateaus, which indicate saturation for the contribution from the first peak. At even higher temperature the effect of the first peak vanishes and the curves fall again, approaching close-lying values. Then, for even larger temperatures, the next peak will come into play and the curves will rise again (not shown in the figure).

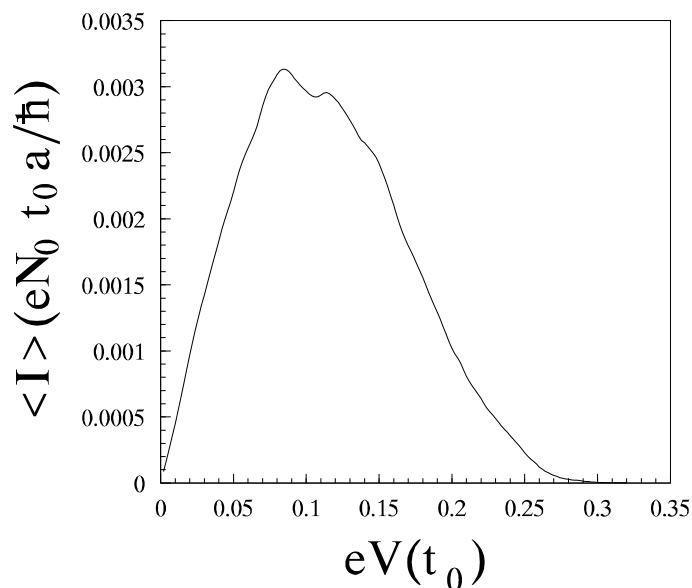


Figure 3. The I – V characteristics of a finite-side-chain polymer at zero temperature obtained with the same parameters as for figure 1.

The Landauer formula used applies only to the linear response of the system under an applied electric field. We also consider interesting non-linear effects for relatively large applied voltages. In this case, we calculate the I – V curves, and the results are shown in figure 3, for zero temperature and a system with $\mu = 0.40$; they were obtained by averaging over 100 random configurations. A regime of negative differential conductivity appears. This can be viewed as a result of the competition between the two opposite effects due to the voltage: the increase in the number of states which contribute to the tunnelling current and the suppression of the transmission peaks, since the external voltage violates the conditions for the existence of resonant extended states.

4. Discussion

We have considered the influence of randomly distributed side chains on the electronic transport properties of polymers. For an infinitely long backbone, with side chains of length $2m$, we obtain exactly $2m - 2$ resonant extended states. In the case of finite-side-chain polymers connected to two semi-infinite metal systems, the transmission peaks for the resonant extended states are slightly reduced, because of a phase mismatch induced by

the interface. On the other hand, for the polymer geometry considered, two smaller peaks appear at around $\pm 2\Delta$, which are a sign of a residual periodicity from the backbone. The $2m - 2$ peaks reach their maximum value of unity, only in the absence of the leads, while the two smaller peaks vanish for an infinite system.

The transmission spectrum obtained is shown to affect the conductivity of doped polymers dramatically, when the Fermi level falls around the peaks. The zero-temperature conductivity is large, and its temperature dependence shows a plateau in some temperature range, due to the saturation of the contribution from states in the first peak. We also obtain the $I-V$ characteristics of the system by studying the non-linear behaviour of the tunnelling current for a large external voltage. In this case we find a regime of negative differential conductivity which arises from the competition between the increase in the number of states which are involved in the tunnelling due to the applied voltage and the suppression of the transmission peaks due to the violation of the condition for the presence of extended states by the external field.

In summary, we have shown resonant transmission states, or transmission peaks, for a random-side-chain polymer system with leads. The polymer is represented by side chains randomly attached to a dimerized host chain. Apart from the interesting characteristics of the transmission spectrum that are obtained, we also find some experimentally measurable quantities, such as the temperature-dependent conductivity, which can be used to explore the expected almost metallic nature of conjugated polymers. Our results support the view that conducting polymers can be viewed as low-dimensional disordered substances, having very distinctive conducting properties.

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Appendix. Calculation of the resonant extended states

The one-electron wave-function coefficients for the two nearest-neighbour unit cells of the dimerized-backbone Hamiltonian H_b are related via

$$\begin{pmatrix} a_{2n+3} \\ a_{2n+2} \end{pmatrix} = \begin{pmatrix} \frac{E^2}{(t+\Delta)(t-\Delta)} - \frac{t+\Delta}{t-\Delta} & \frac{E}{t+\Delta} \\ \frac{-E}{t+\Delta} & \frac{-(t-\Delta)}{t+\Delta} \end{pmatrix} \begin{pmatrix} a_{2n+1} \\ a_{2n} \end{pmatrix} = \hat{\mathbf{M}}_{cell} \begin{pmatrix} a_{2n+1} \\ a_{2n} \end{pmatrix}. \quad (\text{A1})$$

If $n = 0$ or $n = N - 1$ the $t - \Delta$ should be replaced by t_1 to include the contacts. If a side chain is attached at the n_k th site of the backbone, the coefficients of the wave function at this site are related to a_{n_k-1} , a_{n_k+1} and $a_{2m}(n_k)$ by the equation

$$Ea_{n_k} = -(t - \Delta)(a_{n_k-1} + a_{2m}(n_k)) - (t + \Delta)a_{n_k+1}.$$

A virtual site with index 0 and amplitude $a_0(n_k) = 0$ is assumed at the free end of the side chain. This condition gives the relationship between the coefficients at the backbone sites which are adjacent to the attached side chain:

$$\begin{pmatrix} a_{n_k+2} \\ a_{n_k+1} \end{pmatrix} = \hat{\mathbf{M}}_{cell} \begin{pmatrix} 1 & 0 \\ q & 1 \end{pmatrix} \begin{pmatrix} a_{n_k} \\ a_{n_k-1} \end{pmatrix} = \hat{\mathbf{M}}_{side} \begin{pmatrix} a_{n_k} \\ a_{n_k-1} \end{pmatrix} \quad (\text{A2})$$

where

$$q = \frac{\left\{ \left[\hat{\mathbf{M}}_{cell} \right]^m \right\}_{(2,1)}}{\left\{ \left[\hat{\mathbf{M}}_{cell} \right]^m \right\}_{(1,1)}}.$$

Finally, the matrix $\hat{\mathbf{T}}$ in equation (6) is a product of N matrices:

$$\hat{\mathbf{T}} = \underbrace{\cdots \hat{\mathbf{M}}_{cell} \cdots \hat{\mathbf{M}}_{side} \cdots}_N \quad (\text{A3})$$

which are either $\hat{\mathbf{M}}_{cell}$ or $\hat{\mathbf{M}}_{side}$, depending on the random configuration. At the two ends of the backbone, $t - \Delta$ should be replaced by t_1 in $\hat{\mathbf{M}}_{cell}$ or $\hat{\mathbf{M}}_{side}$.

The value of q is the same for every side chain and, because $q = 0$ at some energies, this leads to $\hat{\mathbf{M}}_{side} = \hat{\mathbf{M}}_{cell}$. At these energies the corresponding states are extended and, with the help of Chebyshev polynomials, putting $q = 0$ gives

$$\text{Tr}(\hat{\mathbf{M}}_{cell}) = 2 \cos \frac{l\pi}{m}$$

for $l = 1, 2, \dots, m - 1$, or

$$\left[\hat{\mathbf{M}}_{cell} \right]_{21} = 0.$$

The condition obtained gives resonant extended states for the random structure considered at $E = 0$ or

$$E^2 = 2 \cos \left(\frac{l\pi}{m} \right) (t^2 - \Delta^2) + 2(t^2 + \Delta^2)$$

when E lies in the band. Thus, the $E = 0$ state is located in the gap and is not a resonant state. The rest of the energies E obtained lie within the band and correspond to resonant extended states. For side chains of m unit cells, we find exactly $2m - 2$ such resonant states.

In the presence of an applied voltage, the potential at the backbone site i becomes V_i , due to the additional electric field. We assume that the side chains are perpendicular to the backbone, so the potential at every site of the side chains is the same as that at the backbone site to which it is connected; hence

$$\hat{\mathbf{M}}_{cell} = \begin{pmatrix} \frac{(E + eV_{2n+1})(E + eV_{2n+2})}{(t + \Delta)(t - \Delta)} - \frac{t + \Delta}{t - \Delta} & \frac{E + eV_{2n+2}}{t + \Delta} \\ -\frac{E + eV_{2n+1}}{t + \Delta} & -\frac{t - \Delta}{t + \Delta} \end{pmatrix} \quad (\text{A4})$$

and

$$\hat{\mathbf{M}}_{side} = \hat{\mathbf{M}}_{cell} \begin{pmatrix} 1 & 0 \\ q & 1 \end{pmatrix}.$$

The relation of q to $\hat{\mathbf{M}}_{cell}$ is the same when there is a voltage applied as when no voltage is applied. Special care should be taken at the 0th and $(2N + 1)$ th, sites where

$$\hat{\mathbf{M}}_{in} = \begin{pmatrix} -\frac{E}{t_1} & -\frac{t_0}{t_1} \\ 1 & 0 \end{pmatrix}$$

and

$$\hat{\mathbf{M}}_{out} = \begin{pmatrix} -\frac{E + eV}{t_0} & -\frac{t_1}{t_0} \\ 1 & 0 \end{pmatrix}.$$

In the presence of a voltage, q is no longer independent of the position, so the resonant extended states are no longer allowed due to the violation of the resonance condition.

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