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Transport properties of organic conductors: Influence of the statistics of distances between charged centers

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We address transport in one-dimensional organic conductors within the universal context of the generalized Landauer-Büttiker equations. The conductance is viewed as the transmission of charged excitations through the sample, with contributions from both elastic and inelastic processes evaluated within a quantum-mechanical framework. Results on both charge transfer and conjugated polymer compounds are in agreement with the main trends shown by experiments.

When one addresses the electric conductivity of quasi-one-dimensional organic conductors, the important differences in their electronic structure must be taken into account. For the ionic group one has, for example, the quasi-one-dimensional charge transfer compounds such as tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). Its crystalline structure consists of a separated stacking of donor and acceptor molecules, arranged in a herring-backbone-like structure. Charge transfer between these stacks leads to a weak covalent sharing of the extra charge along the one-dimensional chains. Being a one-dimensional metal of bandwidth $4t_0$, a distortion with wave vector $2k_F$ produces a Peierls transition[1] becoming an insulator with a relatively small gap ($\Delta \approx$ 10 meV). The new period in the electronic structure is seen as a charge density wave (CDW), which can be incommensurable with the lattice if the charge transfer has an irrational value. Besides, the low-energy excitation of a CDW is a local distortion of its phase or soliton. Since it has an associated charge and a defined velocity, its displacement was thought to be responsible for the electronic current. The same mechanism of transport can explain the conductivity of the *metallomacrocyclic polymers*,[2] of which the tetracyanoplatinates family is a prototype. In these compounds, the extra electrons are provided by the metal atoms.

On the other hand, there is a family of strongly *covalent polymers*, of which *trans*-polyacetylene (*t*-PA) is the best studied example. The backbone of carbon chains is dimerized, which is also seen as a consequence of the Peierls instability. The resulting electronic structure has a wide gap (≈ 1.5 eV) as corresponds to the energy scale of a covalent π bonding. The polymer chains are bundled in fibers with the eventual impurities arranged in the interstices. Dopants intercalated between the chains provide the extra charge, which is accommodated as solitonic excitations.[3,4] Early magnetic resonance experiments of spin diffusion have been interpreted[4] as evidence of the mobility of neutral solitons at high temperatures and allow us to distinguish the *t*-PA from its *cis* isomer.

A common feature in the description of both extreme situations represented by TTF-TCNQ and *t*-PA is that their basic electronic structure can be obtained from a tight-binding Hamiltonian with a periodic modulation, in the first cases induced by a temperature-dependent Peierls distortion, in the last case expected from the chemical nature of the covalent chain. The excitations represent departures from the ideal dimerized structure of the pure material and in both, the early explanation of their conductance was based on the diffusion of the charged solitonic excitations. However appealing, this picture does not give a universal explanation of transport in all covalent polymers and needs the inclusion of further *ad hoc* parameters. One early[4] objection was that solitons are closely associated and pinned to the positions of the impurities because both are charged entities. Even results of spin diffusion can be interpreted without the need for mobile neutral solitons.[5] More recently, it was addressed[6] that because quasi-one-dimensional conductors have a three-dimensional environment, phase distortions in a CDW (i.e., the solitons) present a much stronger pinning to individual impurities than was earlier

proposed.[7] Another problem is that there are many conducting polymers in which the nature of solitonic distortion is not obvious. This is particularly true for many of the organic conductors that have been extensively studied over the recent years, such as the polyaniline family.[8] Although in some cases possible solitonic excitations have been identified,[9] the experimental results on dielectric constant of both polyanilines[10] and polypyrroles[11] can be fitted with a modified Drude model. Besides, other authors[12] studied the conductivity using a "tunneling approach" in which fragments of polymer are considered embedded in metallic one-dimensional contacts. This might be thought of as incompatible with the Drude scheme. However, the tunneling approach can be justified within the wider framework of the generalized Landauer-Büttiker equations (GLBE).[13,14] Within this theory, the conductivity σ is governed by the transmittance T_{L_Φ} at the Fermi energy through a one-dimensional portion of the material with dephasing length L_Φ. This is the length an electronic excitation would travel before either interacts with phonons $[L_{e\text{-ph}} \sim (k_B T)^{-1}]$, hops between chains $(L_{t_\perp})$, or reaches the chain end (L). When this length is shorter than the localization length λ, a Drude behavior (with localization corrections) is obtained. In the GLBE, the transmission amplitudes must be evaluated between dephasing channels determining incoherent portions of the same chain and constitute the kernel of an integral equation leading to a self-consistent calculation[13] of the chemical potential. We emphasize that within this description, there is no need of metallic leads attached to every polymer portion and that there is a temperature dependence implicit in the dephasing length. An approximate solution of the GLBE at low temperatures provides a conductance of the form[14,13]

$$\sigma(\varepsilon_F) = 2\left(e^2/h\right) T_{L_\Phi}/L_\Phi, \qquad (1)$$

in agreement with the tunneling approach. At finite temperature, the conductivity becomes an integral over energies of the expression (1),

$$\sigma(T) \sim \int \sigma(\varepsilon)[-df(\varepsilon)/d\varepsilon]\, d\varepsilon, \qquad (2)$$

weighted by the derivative of the Fermi distribution. These equations allow the study of transport properties of both types of systems by calculating the generalized (that is including dephasing and inelastic processes) transmission coefficient through the relevant portions of the chain. Therefore in highly doped samples, solitonic states act as an impurity band and not as moving entities. Then the GLBE leads quite naturally to a temperature activated conductivity similar to what is observed in the covalent polymers.[4] Without even attempting to explain the vast range of phenomena present in one-dimensional conductors, we are going to show that the GLBE is roughly consistent with the observed tendencies in the situations which until now were only described with solitonic transport. Since in this picture transport proceeds through tunneling between regions with high density of states around the Fermi energy $[N_0(\epsilon_F) > 0]$ which represent charged centers, it is reasonable that once the nature of the barrier is fixed, the conductivity is limited by the longest distances between those centers[15] and hence their

statistics determine the conductivity.

Charge transfer compounds

In order to describe the one-dimensional stack of molecules with lattice constant a, we use a tight-binding model for the relevant molecular orbitals[16] describing a band of width $W = 4t_0$. The hopping between molecules $t_0 = 0.1$ eV has a periodic modulation due to the distortion of the lattice. This molecular displacement δu produces a gap $\Delta \propto \delta u$. For temperatures T lower than the critical temperature T_c, the gap Δ is taken to depend on temperature as

$$\Delta = \Delta_0 \sqrt{1 - (T/T_c)^2}. \qquad (3)$$

We consider a charge transfer of e, which, according to the Peierls criteria for a spin degenerate system, leads to exact dimerization. The temperature is considered to create an additional random displacement around the equilibrium position compatible with the harmonic approximation $\frac{1}{2}\alpha \overline{\delta u_n^2} = \left(\frac{1}{2}\right) k_B T$: This justifies a functional dependence on temperature of the form $\delta u_n = \gamma r_n \sqrt{T/T_c}$, where $\gamma \ll 1$ is a fitting constant and r_n is a distribution of random distances in the range $[-a/2, a/2]$. This results in positions of molecules given by

$$x_n = na + (-1)^n (\Delta/2t_0)a + \gamma \sqrt{T/T_c}\, r_n, \qquad (4)$$

where the first term gives the normal spacing, the second the contribution toward dimerization, and the last one the temperature induced distortions. In a linear approximation, the hopping is proportional to the distance between molecular orbitals according to

$$t_{n,n+1} = t_0[(x_{n+1} - x_n)/a], \qquad (5)$$

that is, for $T = 0$, the hopping alternates between the values $t_1 = t_0 + \Delta_0$ and $t_2 = t_0 - \Delta_0$. The Hamiltonian is a tridiagonal matrix with a constant in the diagonal. Therefore, in this model the maximum length limiting the conductance is produced by the random distribution of these distances.

We consider a L_Φ determined by geometrical conditions (interchain hopping $t_\perp \ll t_0$) and then essentially temperature independent. We evaluate a representative transmission coefficient by attaching perfect semi-infinite linear chains on the left and right of the finite length $(L_\Phi/a = 500)$ sample. After all intermediate sites are removed (decimated), matching of the plane waves on the boundaries yields the transmission probability $T_{L_\Phi}(\varepsilon, k_B T)$ as a function of temperature. The results of conductance, according to Eq. (1), for different fragments are shown as a function of temperature in Fig. 1, where T_c is taken as 60 K. The mean value of the average conductivity is in agreement with the measured behavior. We observe that since the length L of the fragments are larger than the localization length, there is a sharp metal insulator transition. For shorter chains $(L_\Phi < \lambda \approx 2a \ln\left[(4t_0^2 + \Delta_0^2)/(4t_0^2 - \Delta_0^2)\right] = 100a)$, the transition would appear less abrupt. Above the critical temperature, the random components, which increase with temperature, are responsible for the subsequent drop off of $T_L(\varepsilon_F, k_B T)$, once the metallic phase is achieved. The noise in the data is eliminated by the energy average
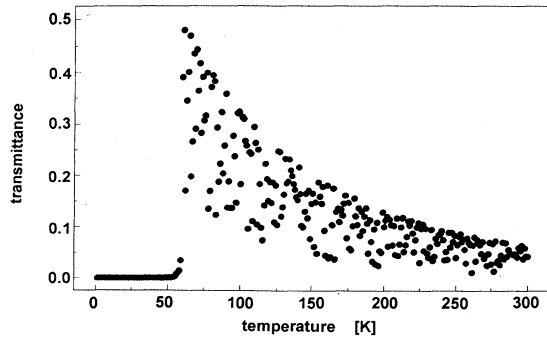
FIG. 1. Conductivity (arb. units) as a function of temperature for TTF-TCNQ using the model described in the text.

produced by Eq. (2) and the ensemble average. However, a better fitting would require a further reduction of the conductivity at high temperatures. This effect would appear if a pseudogap modifying Eq. (3) is allowed as in the case of fluoranthene radical cation salts.[17] This could be generated by fluctuations in the correlation length present above the critical temperature.

Covalent compounds

In this case we performed the calculation using a tight-binding model with hopping parameters, which alternate between the values t_1 and t_2. Since we are mainly considering the case of polyacetylene, close to an impurity the position of the carbons on the lattice is distorted according to a law of the form[3]

$$x_n = na + (-1)^n \delta x \prod_m \tanh[(na - x_m)/\xi], \qquad (6)$$

where the displacement $\delta x = a\Delta_0/t_0$ is proportional to the intrinsic gap, and x_m's are the position of the dopants, which are chosen randomly to satisfy a given mean distance but with an exclusion length of $3a$. As usual $\xi \approx 8a$ is the correlation length of the solitons. The hopping is found again from Eq. (5) but using Eq. (6). The effect of the dopants is then to act as disorder and to decrease the effective dimerization, creating the well known soliton peak at $E = 0$. This manifests in the light absorption curve as a peak at $\hbar\omega = \frac{1}{2}\Delta_0$. For low concentration of impurities ($c < 0.05$), the peaks of the transmittance are rather narrow and hence they are not very effective for transport. This is true even if the Fermi energy lies in a region of high density of states [see Fig. 2(a)]. For high concentration of impurities ($c \geq 0.05$), the peaks in the transmittance are much wider allowing a more effective transport, because at finite temperature one must use Eq. (2), which gives a total conductance which averages those within a window in energy of width $k_B T$ around ε_F. However, this does not give any substantial temperature dependence additional to that introduced by $L_\Phi(T)$.

The results of Figs. 2 and 3 show that the effective gap in polyacetylene increases slightly with impurity concentration. As found previously by Mele and Rice,[18] the soliton bandwidth increases rapidly with concentration. A striking result is that as shown in Fig. 4, for high concentration of impurities the density of states in the soliton band does not show the effect of the random position of the impurities. This also manifests in wide resonances in
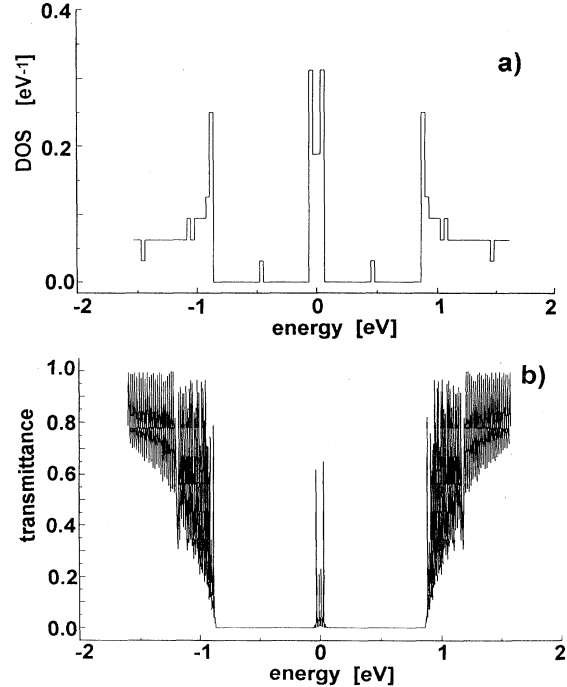

FIG. 2. (a) Density of states as a function of energy for a slightly doped polyacetylene chain. The average distance between centers is 30 units of C-C bonds; (b) transmittance through a portion $L_\Phi = 1000a$ as a function of energy with same parameters.

the transmission coefficients with maxima close to unity, which in turn, by application of Eq. (2), gives an important conductivity. This suggests that we can characterize the soliton (impurity) band through the effective hopping parameter $V_{\rm eff}$ between soliton states at distance d. After a convenient decimation of the atomic orbitals[16] and leaving the soliton states as the relevant ones, we arrive at a simple one-dimensional tight-binding Hamiltonian for this band.

To find $V_{\rm eff}$ we performed a calculation with just two solitons and found $V_{\rm eff}(d)$ for $\xi = 8a$. We find (Fig. 4) that $V_{\rm eff}$ is a decreasing function of d. Starting with a weak dependence on d for very short distances, it crosses over to an exponential regime for longer distances. Therefore, for high concentration of impurities (1 soliton every 15 carbons), the relative fluctuation of the hopping is small and the localization length within the band is larger than the chain. Conductivity is then high. This corresponds to a critical concentration of $x = 0.06$, in agreement with the experiment.[4] The transport is dominated again by the distances between solitons (charged centers). For low concentrations, large distances between impurities give values of $V_{\rm eff}$ exponentially small and the band is narrow and so the transmission peaks.

We have shown that an approximate application of the generalized Landauer-Büttiker equations reproduces the main trends in a wide variety of one-dimensional conductors. Using a simple model Hamiltonian for TTF-TCNQ, we reproduced the temperature dependence of the conductivity on undoped material. Since the gap is small, this dependence is very important above the temperature at which the metal insulator transition takes place. In the opposite situation, transport properties in high-
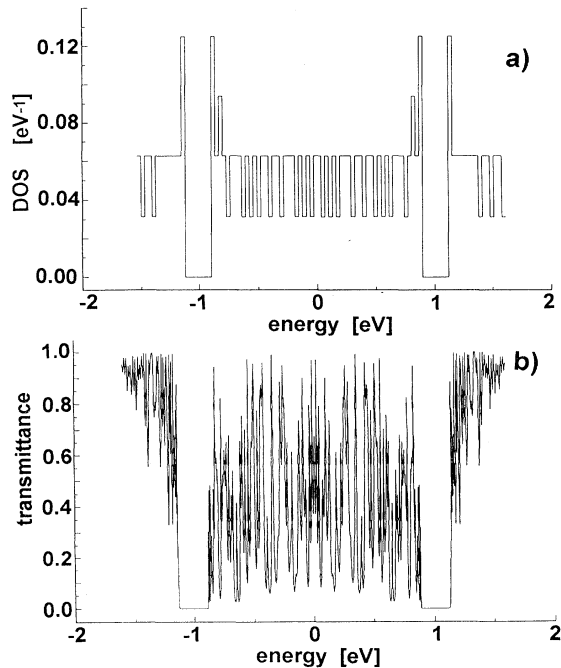
FIG. 3. (a) Density of states as a function of energy for a strongly doped polyacetylene. The average distance between solitonic centers is 10 C-C bonds length units; (b) transmittance as a function of energy with same parameters.

gap *trans*-polyacetylene can be explained with a model of partially filled frozen soliton band (more properly defect band), with a conventional (noncollective) model of low-temperature transport. The present results suggest that even when the commonly accepted free solitonic view can explain certain features of high-temperature transport, a low-temperature description in terms of a theory of quantum transport in which solitonic properties enters only in the spectrum and in the localized nature of the states, is consistent with the measured tendencies. Besides, within this view it appears that there are characteristic lengths in the basic structure of the conductor that limit the transport in agreement to what is observed[19] in several conducting polymers complexes. Furthermore, the same
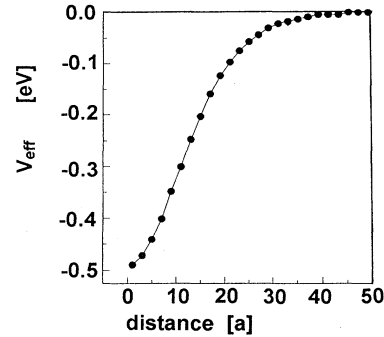

FIG. 4. Effective hopping between solitonic centers as a function of their distance in units of C-C length.

noncollective model works well for quite different compounds. As a common feature, we found the statistics of distances between charged centers to be important. Since these centers are surrounded by gaps in the local density of states, the exponential transmission coefficient between them is limited by the largest separations. Since our picture is also consistent with the picture of electrons hopping in a soliton band,[20] it deserves further study to see how these tunneling ideas can be exploited to produce a microscopic theory of thermally activated hopping.

In summary, we have shown that the main tendencies of transport in one-dimensional conductors, which until now were only attributed to solitonic transport, can also be obtained within the generalized Landauer-Büttiker formulation. These results combined with a more complete evaluation of three-dimensional effects[21] and discussion of other covalent polymers[12] within the tunneling approach (which is included in the GLBE) suggest that further efforts should be done to describe transport within the GLBE framework; particularly interesting would be the study of ac response and the description of the thermally activated regime in three-dimensional models.

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