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Conducting Polymers: Solitons or not?

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Abstract

A review is given on the soliton model and its possible relevance for the interpretation of experiments in conducting polymers. It is argued that solitonic states, although being very attractive due to their simplicity and apparent ability to explain several experiments, are strongly distorted by various perturbations. Furthermore predictions based on the soliton model are often not specific enough to discern them from more conventional reasonings.

1. Introduction

The successful synthesis of polyacetylene films[1] and the subsequent discovery that upon doping their electrical conductivity can be increased by many orders of magnitude[2] has stimulated a great activity both among chemists and physicists in trying to characterize this new type of material, and to determine the basic mechanisms which lead to the unusual electrical, magnetic and optical properties[3]. In the meantime other conducting polymers like polyparaphenylene[4] and polypyrrole[5] have been synthesized and found to behave similarly as polyacetylene in many respects. All these materials have planar structures and alternating single and double bonds along the carbon backbones indicating delocalization of π-orbitals over the polymer chain (fig.1). Conjugation[6] appears thus to be a necessary prerequisite for a conducting polymer.

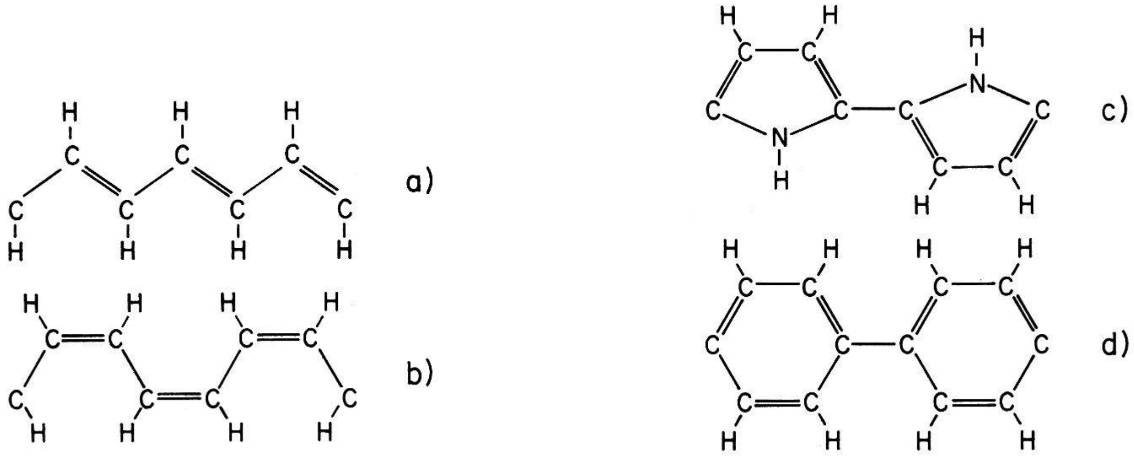

Fig.1 - Structure of conducting polymers: a) trans-polyacetylene b) cis-polyacetylene, c) polypyrrole, d) polyparaphenylene.

We will be concerned mainly with trans-$(CH)_x$ which is the thermodynamically stable isomer form of polyacetylene. Its uniqueness consists in the double degeneracy of the chemical structure with respect to the sequence of bond alternation and the possible formation of mobile bond-alternation defects carrying spin or charge[7,8] (fig.2). The observation of highly mobile spins in trans-polyacetylene led to a revival of this concept[9] and to the formulation of explicit models[10,11] where the bond-alternation defects have the form of domain walls or topological solitons[12] which interpolate between the two ground-state configurations. Since then many experimental findings in polyacetylene have been interpreted in terms of the soliton model while other observations have been used as evidence against solitons or at least as indications that extrinsic effects may be more important than intrinsic nonlinearities[13].

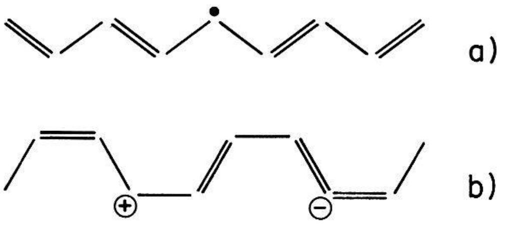

Fig.2 - Bond-alternation defects in polyacetylene: a) neutral defect in trans-$(CH)_x$, b) bound pair of charged defects in cis-$(CH)_x$.

In particular various types of inhomogeneities (connected with the fibrillar morphology, the partial crystallinity, the distribution of chain lengths or the clustering of dopant ions) may be relevant[14].

The paper is organized as follows. After briefly describing the soliton model within the Hückel-type framework (section 2) and its success in explaining several experimental observations (section 3) we discuss its stability with respect to various kinds of interactions and perturbations which are not included in the Hückel approach (section 4) and examine more closely how relevant the solitons are for a quantitative interpretation of experiments (section 5). Finally we try to give a tentative answer to the question of the title (section 6).

2. The Soliton Model

Following Su, Schrieffer and Heeger[11] the Hamiltonian is chosen as

$$H = 1/2 \sum_n [p_n^2/M + K(u_{n+1}-u_n)^2] - \sum_{ns} t_{n,n+1} (c_{ns}^+ c_{n+1s} + c_{n+1s}^+ c_{ns}) \tag{1}$$

where p_n and u_n are, respectively, the momenta and displacements of the CH units of mass M along the chain axis, K is the elastic constant, c_{ns}^+, c_{ns} are creation and annihilation operators for π-electrons at site n and with spin index s and $t_{n,n+1}$ is the hopping integral which is assumed to depend on the displacements as

$$t_{n,n+1} = t - \alpha(u_{n+1} - u_n). \tag{2}$$

The order parameter associated with bond-length alternation is

$$\Delta_n = 2\alpha(-1)^n (u_{n+1} - u_n). \tag{3}$$

Due to the Peierls instability the ground state for the half-filled band is dimerized, $u_n = (-1)^n u$ and, correspondingly there is a gap at the Fermi level

$$2\Delta = 8\alpha u \approx 16t \exp[-(2\lambda+1)/(2\lambda)] \tag{4}$$

where $\lambda = 2\alpha^2/(\pi t K)$. The bond-alternation parameter u has recently been estimated to be of the order of 0.03 Å both from X-ray diffraction[15] and nutation NMR experiments[16]. Together with values for the optical gap $2\Delta = 1.5\text{eV}$, the bandwidth $4t = 10\text{eV}$, and the effective elastic constant $2\lambda K = 20\text{eV}/\text{Å}^2$ (see ref. 3), the model yields a quite consistent parametrization $t = 2.5\text{eV}$, $K=50\text{eV}/\text{Å}^2$ and $\alpha=7\text{eV}/\text{Å}$. The soliton is described by the Ansatz

$$\Delta_n = \Delta \tanh(na/\xi) \qquad (5)$$

where a is the mean C-C distance along the chain axis and the soliton extent ξ is determined by minimalizing the energy. The local suppression of dimerization affects the electronic structure. In addition to a small change in the density of extended states, a localized state appears at mid-gap with wavefunction

$$\Phi_n = \xi^{-1/2} \cos(\pi n/2) \operatorname{sech}(na/\xi). \qquad (6)$$

In the continuum limit[17,18] ($na = x$, $\Delta_n \to \Delta(x)$) the Ansatz (5) turns out to be the exact ground-state configuration for the boundary conditions $\Delta(x) \to \pm \Delta$ for $x \to \pm \infty$. Furthermore the soliton extent is found to be $\xi = 2ta/\Delta \approx 7a$ and the soliton energy is $E_s = 2\Delta/\pi$. The relatively large extent justifies a posteriori the continuum limit and indicates that lattice discreteness will play a minor role, in fact it has been estimated to yield a pinning energy of about 2meV[11]. The soliton mass is obtained by calculating the kinetic energy associated with a moving soliton. One finds[11,18] $M_s=(4u^2/3a\xi)M \approx 3m_e$ indicating a very high mobility. Much of the excitement about these solitonic states arose in connection with their peculiar relationships between charge and spin[19] (or, for the spinless model, the appearance of fractional charge[20]). Indeed, as illustrated in fig.3, depending on the occupancy of the mid-gap state, the soliton carries spin but not charge (S^o) or charge but not spin ($S^{\pm}$).

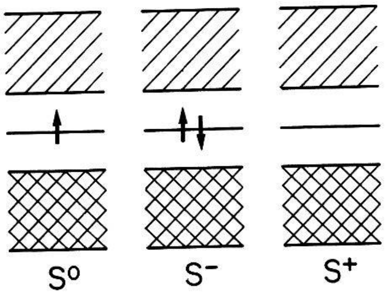

Fig.3 - Electronic structure associated with neutral (S^o) and charged ($S^{\pm}$) solitons.

3. Its Success

Several experimental results have been explained quite convincingly within the soliton model. The strong increase of the magnetic susceptibility upon cis-trans isomerization has been attributed to the formation of neutral solitons[9]. ESR[21,22] and dynamic nuclear polarization experiments[23] show indeed that these spins are quite mobile at room temperature as expected from the soliton model. Furthermore the NMR spin-lattice relaxation rate exhibits the characteristic behaviour of highly one-dimensional diffusion $T_1^{-1} \sim \omega_N^{-1/2}$, where ω_N is the nuclear Larmor frequency, with a high diffusion constant[23].

Trans-polyacetylene has been reported to give rise to photoconduction but not to photoluminescence, whereas the cis form shows photoluminescence but not photoconduction[24]. This result has been related to the fact that the trans form admits free solitons but the cis form does not. Numerical calculations indicate that an electron-hole pair would rapidly relax to a pair of oppositely charged solitons[25]. In the trans form the two solitons separate and contribute to the photoconductivity whereas in the cis form they are confined (due to the energy required to sustain the trans-cisoid structure between the two solitons, see fig. 2b) and recombine radiatively.

The proposal that charged solitons are generated by doping is based on energetic considerations. The polaronic state which is predicted to be formed by adding or removing an electron[25,26,27] has an energy $E_p = 2^{1/2} E_s$, and therefore, if topologically possible, e.g. by adding (or subtracting) two electrons, charged solitons would be preferentially produced. The solitons are predicted to manifest themselves through additional optical absorption, on the one hand due to transitions involving the mid-gap state[28,29], on the other hand due to infrared active vibrational modes of the soliton structure[30]. The observation of additional peaks both in the IR and at mid-gap has been reported by many groups, detailed and rather successful comparisons between the data and the predictions of the soliton model have been made by Etemad et al.[31] for the IR and by Feldblum et al.[32] for the mid-gap absorption.

An important issue is the question how and at which dopant concentration the transition to metallic behaviour occurs. The results of Ikehata et al.[33] using slow doping techniques indicate that the main increase in electrical conductivity occurs below $y=0.01$ where y represents the fraction of dopant atoms per carbon atom. On the other hand the Pauli susceptibility remains small up to $y=0.053$ as compared to its value above $y=0.07$. Therefore an intermediate regime $0.01<y<0.07$ is postulated where transport occurs through spinless charge carriers, i.e. charged solitons.

For very low concentrations where neutral and charged solitons coexist ($y<0.005$ according to ref. 33) Kivelsen has proposed a rather exotic transport mechanism in terms of phonon-assisted hopping between charged and neutral solitons[34]. He makes specific predictions for the conductivity as a function of temperature, frequency and concentration which appear to reproduce quite well the experimental data[35].

4. Theoretical Complications

In the theoretical approach presented in section 2 we have neglected quantum fluctuations of the lattice, electron correlation, interchain coupling and disorder. Let us now discuss to what extent these effects will modify the solitonic states.

The quantum corrections have been studied by Nakahara and Maki[36] using a semiclassical approach, and found to yield a moderate reduction of the soliton energy $\delta E_s \approx -E_s/4$, whereas the change in soliton mass is negligeable. This indicates not only that the soliton remains a stable finite energy excitation but also that the dimerization of the ground state survives the quantum fluctuations, in agreement with Monte Carlo simulations[37,38] and renormalization group arguments[38].

The debate about the role of electron-electron interaction for conjugated polymers has a long history[39] and still now it is not clear whether polyacetylene is an example for weak ($U \ll 4t$),strong ($U \gg 4t$)[40] or intermediate correlation ($U \approx 4t$)[41]. The quite consistent description of experiments in terms of Hückel parameters suggests that polyacetylene belongs to the small U limit. In this case it is found that correlation enhances bond alternation[42] and changes the shape of the soliton[41,43]. The neutral soliton shrinks and, in addition, a localized spin-density wave appears, whereas the charged soliton becomes more extended and is accompanied by a local charge-density wave structure. The energy of the neutral soliton decreases with U whereas it increases in the case of a charged soliton, due to the double occupation of the mid-gap level[44]. Similar results are found if σ-electrons are explicitly taken into account, but in this case the symmetry between positively and negatively charged solitons is lost[45].

The interchain coupling can strongly restrict the motion of solitons since it leads to a coherent (e.g. anti-phase) ordering of the bond-alternation sequences of neighbouring chains. Two solitons on the same chain separated from each other by a distance ℓ produce a misaligned piece of length ℓ within an otherwise well-aligned array of chains. This requires an energy E_c which increases linearly with ℓ. The largest contribution to this confinement energy seems to come from interchain hopping[46] (rather than Coulomb and dispersion forces[47]) giving $E_c = W\ell/a$ where $W = 4t_\perp^2/(\pi t)$. At present it is difficult to obtain reliable values for W mainly due to uncertainties about the size of the transverse hopping integral $t_\perp$. A value of 0,075eV for $t_\perp$ has been extracted from optical absorption experiments[48] whereas recent band structure calculations[49] give $t_\perp = 0.025$eV. With these two values we obtain W = 35K and 4K, respectively.

Polyacetylene is a disordered material, both structurally and because of impurities (dopant ions) which act as pinning centers both for charged and neutral solitons. In addition the impurity potential affects directly the electronic structure by producing bound states in the gap (donor or acceptor states) leading to optical absorption below the interband threshold[50]. Bryant and Glick have studied the competing effects of impurity states and lattice defects and concluded that in the presence of a screened Coulomb potential (representing the dopant ions) the bound polaron has lower energy than the bound soliton[51]. If this result should be confirmed by a self-consistent calculation (allowing for full relaxation of the defects) one would have to conclude that doping proceeds via the formation of polarons rather than charged solitons.

5. How Conclusive are the Experiments?

The picture presented in section 3 reflects the point of view that solitons explain essentially all the experiments performed on undoped and weakly doped polyacetylene. Unfortunately a closer look at the data shows that the actual situation is much more complicated. Let us first discuss the magnetic resonance experiments. Both ESR and NMR measurements give evidence for mobile electronic spins but the diffusion constant D obtained from ESR[21] is three orders of magnitude smaller than the value deduced from proton NMR[23]. Nechtschein and coworkers argue that this discrepancy arises from the coexistence of mobile and static spins[52] which can be considered as free and pinned neutral solitons, respectively[53]. According to their analysis the static spins, while leading to a broadening of the ESR line, would not show up in the NMR signal. On the other hand ESR spin-echo experiments which appear to provide a very direct determination of the diffusion constant again yield a value for D which is at least two orders of magnitude smaller than the NMR result[54]. Maki[55] has studied the soliton diffusion within the SSH model and found a room-temperature value for D comparable to the NMR data. On the other hand his theoretical diffusion constant depends only very weakly on temperature, in disagreement with the behaviour deduced by Nechtschein et al.[53], which is reminescent of Brownian (rather than ballistic) motion. A further complication comes from the recent observation of Scott and Clarke[56] that the relaxation of ^{13}C NMR is markedly different from that of proton NMR. They conclude that, in addition to the diffusion of defects, nuclear spin diffusion takes place.

A series of beautiful experiments on the photo-induced changes in the optical absorption spectrum appears to confirm the soliton model at first sight. Below a certain energy (1.6eV in trans, 1.9eV in cis samples) the absorption increases upon illumination[57] whereas above this value it decreases (interband bleaching[58]). Pronounced peaks are found in the additional absorption slightly below the optical gap with a non-exponential decrease in height as a function of time after the application of a short pulse[59]. The bleaching is accompanied by a photo-induced dichroism which also decays rather rapidly[58]. Both the decrease of peak absorption and of the dichroism have been related to the diffusion of the photo-generated carriers giving a diffusion constant in rough agreement with NMR. The IR region has been studied with steady-state methods. The first attempt[60] failed to reveal photo-induced absorption, probably because of limited resolution, but recently, with improved sensitivity, Vardeny et al.[61] have found sharp peaks at 0.157 and 0.170eV, which they attribute to phonons, and an asymmetric broad line at 0.43eV, which they associate with electronic transitions between photo-induced localized states in the gap and the nearest band edge. The photo-induced absorption is very similar to the additional absorption observed upon doping[28,31] which indicates that the two effects share a common origin. It is tempting to associate them with solitons but, on the one hand, the position of the electronic transition at 0.43eV is quite far from mid-gap, on the other hand the soliton model does not explain the additional feature close to the band edge which becomes dominant at low temperatures[57]. Furthermore it has been pointed out by Horovitz[62] that the appearance of IR-active modes is simply a consequence of the loss of translational symmetry due to the additional charge, the configuration of which does not affect the mode frequencies. In a similar way one can argue that the appearance of mid-gap states is not specific for solitons but simply a consequence of the electron-hole symmetry of the Hamiltonian. Indeed the electronic part of the SSH Hamiltonian, eq. (1), changes sign under the canonical transformation $c_{ns} \to (-1)^n c_{ns}$ and thus, given an electronic level at ε_λ there is necessarily also a level at $-\varepsilon_\lambda$. In the case of an odd-numbered chain (with free ends) it follows that there is always a zero-energy state, independent of the values of the hopping integrals and consequently independent of the lattice configuration.

What about the doped material? The dopant-induced IR absorption can hardly be considered as evidence for solitons since it is observed up to the highest doping levels[63,64,65] where the interband transitions (and thus presumably also the dimerization) have disappeared[66,67]. At the same time the optical absorption in the "metallic" phase still has a maximum at the position of the mid-gap peak[32], which represents a puzzle for the soliton model. Other conducting polymers which are not supposed to exhibit solitons show similar mid-gap absorption as polyacetylene[4,5]. The proposal that an intermediate phase exists with high conductivity but no Pauli susceptibility has produced some controversy in the past[54,68]. In any case this cannot be considered a unique property of trans-polyacetylene since it has also been reported for the cis isomer[69,70], polyparaphenylene[71] and polypyrrole[72]. Thus both the peculiar optical and magnetic phenomena in doped polyacetylene seem to be quite commonly observed in conducting polymers and a theory heavily based on the concept of charged solitons appears to be rather artificial.

Let us also mention that the electrical transport in weakly doped trans-polyacetylene can be explained equally well with a theory invoking hopping between random sites[73] as with the Kivelson mechanism[34].

6. Conclusion

The soliton concept represents an attractive framework for an idealized version of a polyacetylene chain. Both the magnetic resonance and the photo-induced optical absorption on pristine polyacetylene give some support to this model, but in important details the experimental data differ from the theoretical predictions. The role of charged solitons in doped polyacetylene is even more uncertain since both the magnetic and optical properties seem to be very similar in other conducting polymers. Therefore the degeneracy of the chemical structure of trans-polyacetylene may have been overstressed in the past, and we conclude that, in many respects, solitons or not - is not the question.

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