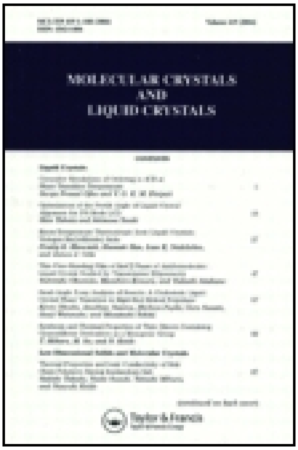

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Solitons, Twistons, Bubbles and Crystallinity in Conducting Polymers

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SOLITONS, TWISTONS, BUBBLES AND CRYSTALLINITY IN CONDUCTING POLYMERS.

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ABSTRACT We discuss the interference of π - electronic and structural defects for the crystal structure in polyacethylene. We consider the local crystallografic modifications caused by solitons and the special type of backbone solitons - the twistons. The role of twistons in formation of hexagonal or tetragonal phases with unhindered rotations at finite dopant concentration is discussed.

INTRODUCTION

The principal problem in physics of topological solitons (the kinks) in polyacethylene (PA) is related to effects of interchain ordering. For an isolated chain the kink can be located at any point, but in a system of interacting chains the divergence of a pair of kinks or the deviation of one kink from the chain's end corresponds to the nucleation of another phase which results in a linear growth of energy. This is the confinement energy, which is defined as: $W_{conf} = |W_{inphase} - W_{antiphase}| = Fl$, where F is the confinement force, l-the distance between kinks, or the distance from a kink to the end of the chain[1,2].

Thus the single kink should be localized at the chain's ends, and for charge solitons the confinement to bipolarons is possible[1,2]. However the experimental data[3] show that the spins are delocalized at least at a distance of 10^2A. Since the interaction between the chains is not very small the plausibility of a soliton mechanism for PA appears questionable.

We shall show that in PA the structural defects can exist, which are topologically equivalent to the kinks[4]. These excitations are the special mechanical deformations of a polymeric backbone - "twistons". Their interaction with kinks results in formation of combined particles (kink-twiston complexes) for which the confinement is absent. The complex can move freely along the chain, but the kink is localized in the region of it's center. The degree of localization is determined by quantum or thermal fluctuations.

Then we discuss the interference of electronic selftrapped states with the crystal ordering in polymers. All kinds of solitons: kinks, polarons, bipolarons can affect the local backbone crystalline packing. In this way the doping can nucleate the changes in the crystal structure. We consider the local crystallografic modifications caused by solitons and their role in formation of loosely packed doped phases.

THE EFFECT OF CRYSTAL STRUCTURE ON SOLITONS

There are two types of interchain interactions: the interatomic and the π-electronic ones. The situation would be quite clear if we always deal with the loosely packed structures like hexagonal[5] or tetragonal[6] phases of doped materials. In these cases the exponentially decreasing π-electronic interchain interaction may be neglected and we are left with the Van der Waals interactions both for the backbones and for the dimerizations. The estimation for the ratio of the potential part of the confinement energy to the Van der Waals energy of backbone interactions is

$$\frac{W_{conf}}{W_{backbone}} \sim \left(\frac{d}{a}\right)^2 \sim 10^{-3}$$

Here a is the interatomic distance in PA chain, d is the amplitude of dimerization. Then the confinement energy per CH-unit is $W_{conf} \sim 10^{-4} eV/CH$, which corresponds to the computer calculations[7]. For a characteristic temperature length ($Fl_T = T$) of two solitons we obtain $l_{300K} \sim 150A$ and for the Coulomb length ($e^2/l_Q = Fl_Q$) $l_Q \sim 300A$. So the solitons are well defined. At room temperatures confinement is not important and the soliton's mobility is allowed at distances $\leq 100A$. These results are valid for the loosely packed phases. We shall show below that these phases are even able to completely eliminate the confinement and to let the kinks to move individually. It is achieved by binding the kink as dimerization defect to the special backbone defect -the twiston[4]. The resulting combined particle has no topological constrains to be mobile.

The picture changes drastically when we consider the close packed monoclinic structure of undoped PA. At first glance this phase leaves no chance for mobile soliton picture to survive. In this case the most important contribution to the confinement energy comes from the $\pi - \pi$- electronic exchange . This energy per CH-unit is[8]

$$W_{\pi-\pi} = 2\frac{t_\perp^2}{\pi t_0}$$

where t_0, $t_\perp$ are the intra- and interchain hopping integrals. The estimations for $t_\perp$ range from $0.075eV$[8] to $0.12eV$[9] to give us $W_{\pi-\pi} \simeq 0.003eV/CH$ and $W_{\pi-\pi} \simeq 0.008eV/CH$ correspondingly. Even for lower value of $W_{\pi-\pi}$ we obtain $F \simeq 10^5 eV/cm$, $l_{300K} \simeq 13A$ and $l_Q \simeq 80A$. It means that dimerizations in a system of coupled chains are strongly correlated. All neutral solitons are confined at their intrinsic scale $\sim 10A$. So that they cannot show themselves as mobile particles. Note that charged kinks are still well separated ($l_Q \sim 80A \gg 10A$) and can be identified in the bipolaronic configuration. Such a pair of kinks may effect the local crystal structure towards the loose packing[10].

SCELETAL SOLITON FOR A SYSTEM OF LINEAR MOLECULAR CHAINS

For simplification consider now linear molecular chains (Fig.1). There are: a kink (the topological charge Q=1) on the chain A, undeformed chain B, nonlinear acoustic deformation - the sceletal soliton(Q=1) on chain C. The R.H.S.sign of the dimerization for A and C chains relative to B changes to the opposite. If two solitons of any type are simultaneously present at the same chain, then outside of this pair the dimerization remains unchanged. At the same time confinement between the solitons binds the pair.

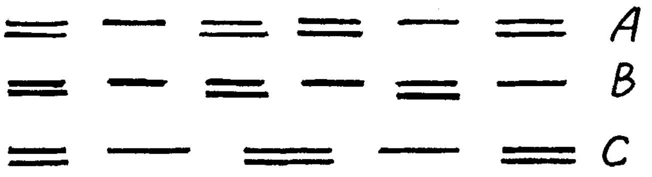

Fig.1. Kink and sceletal soliton on linear molecular chains.

The three following situations are admissible:

1 . Bound state of two kinks - bipolaron, exiton (Q=0).
2 . Bound state of two sceletal solitons (Q=0).
3 . Bound state of a kink and sceletal soliton (Q=0).

The detailed model may be formulated in the following way. The coordinate of n-th atom in dimerized chain x_n^α is given by the number n and two functions which change gradually with respect to n:

$$x_n^\alpha \; = \; na \; + \; \frac{a}{\pi}\varphi^\alpha(na) \; + \; \eta^\alpha(na)(-1)^n d \tag{1}$$

where a is the average interatomic distance; d is the dimerization amplitude ($d \ll a$); $\varphi^\alpha(na)$ - acoustic deformation of the backbone; $\eta^\alpha(na)$ - the form of the kink. The characteristic dimensions of a sceletal soliton ξ_1 and of a kink ξ_0 are large in comparison with the interatomic distance, so we use the continual approximation:

$$\varphi^\alpha(na) \; = \; \varphi^\alpha(x) \quad \eta^\alpha(na) \; = \; \eta^\alpha(x)$$

In the absence of kink

$$\eta^\alpha(x) = \eta^\alpha = \pm 1 \tag{2}$$

the energy of the chain α can be written as

$$W^\alpha \; = \; \int dx\{A(d\varphi^\alpha/dx)^2 \; + \; \sum_\beta U_0(\varphi^\alpha - \varphi^\beta) \; + \; \sum_\beta U_1(\varphi^\alpha - \varphi^\beta)\} \tag{3}$$

The interaction of the backbones U_0 is invariant with respect to translations $\varphi \longrightarrow \varphi + \pi$. U_1 appears with dimerization being taken into account invariant with respect to translations $\varphi \longrightarrow \varphi + 2\pi$ We shall apply the MFA taking into account only the deformations on the chain $\alpha = 0$, $\varphi^0 = \varphi$ and choosing the simplest form of interactions U_0, U_1 compatible with their symmetry :

$$\sum_\beta U_0(\varphi^\alpha - \varphi^\beta) \; = \frac{B}{2}(1 \; - \; \cos 2\varphi); \; \sum_\beta U_1(\varphi^\alpha - \varphi^\beta)\} \; = \; \pm 2C(1 \; - \cos\varphi) \tag{4}$$

Here C is related to the confinement force F and to the confinement parameter γ as $F = \gamma\Delta/\xi_0 \; = \; 4C$, where $\xi_0 \; = \; \hbar v_F/\Delta$ is the kink width, Δ is the dimerization gap. In Eq. (4) signs ($\pm$) stand for the two kinds of dimerization corresponding to the sign in Eq. (2). In the absence of dimerization for sceletal soliton we get

$$\cos\varphi \; = \; \pm th\xi, \;\; \xi = x/\xi_1, \; \xi_1 = \sqrt{A/B} \tag{5}$$

In the presence of dimerization the bound state of two sceletal solitons:

$$\cos\varphi_\pm = \mp[1 - \frac{2\mu th^2(\sqrt{1+\mu/2}\xi)}{2+\mu - 2th^2(\sqrt{1+\mu/2}\xi)}], \; \mu = C/B \tag{6}$$

INTERACTION OF KINK AND THE SCELETAL SOLITON

Let us consider the bound state of the kink and the sceletal soliton. Being light the kink should be described as a quantum particle. We are interested in the states which are equilibrium with respect to the classical field φ and stationary with respect to kink's wave function ψ. The variational functional:

$$W = \int_{-\infty}^{\infty} dx\{A(\frac{d\varphi^{\alpha}}{dx})^2 + \frac{B}{2}(1 - \cos 2\varphi) + 2C[1 - \cos\varphi(\int_{-\infty}^{x} \psi^2(y)dy$$

$$- \int_{x}^{\infty} \psi^2(y)dy)] + \frac{h^2}{2m}(\frac{d\psi}{dx})^2 - E\psi^2\} \tag{7}$$

E is the kink eigen energy. By varying functional (7) we arrive at equations

$$\frac{d^2\varphi}{d\xi^2} - \sin\varphi\cos\varphi - \mu\sin\varphi[1 - 2\int_{\xi}^{\infty} \psi^2(\eta)d\eta] = 0 \tag{8}$$

$$\frac{d^2\psi}{d\xi^2} + \psi[\epsilon - \frac{\beta}{2}(\int_{-\infty}^{\xi} (1 + \cos\varphi)d\eta + \int_{\xi}^{\infty} (1 - \cos\varphi)d\eta)] = 0 \tag{9}$$

where $\epsilon = E/E_0$; $\beta = 4C\xi_1/E_0$; $E_0 = h^2/2m\xi_1^2$ For $\beta < 1$ the kink's ground state is localized at the sceletal soliton. The amplitude of the quantum fluctuations is

$$l_0 \sim \xi_1\beta^{-1/4} \sim (\frac{\xi_0}{\xi_1})^{3/4}(\frac{m^*}{\gamma m})^{1/4}$$

The character of the thermal fluctuations depends on the ratio ($\nu = 4C_1\xi_1/T$). For $1 < \nu < \beta$ the kink is found in highly exited states which are classically localized at the sceletal soliton $l_T \sim \xi_1/\nu^{1/4} < \xi_1$. If $\nu < 1$ then the kink moves mostly in the region of pure confinement: $l_T \sim T\xi_0/\gamma\Delta > \xi_1$

TWISTONS ON THE PA-CHAIN

A real PA chain differs from a simplified linear chain model by it's zig-zag structure. Before the dimerization is taken into account there is a two-fold screw axis (glice plane). Admissible defects are those that transfer *chain* $\rightarrow$ *itself*:

1. stretching $\pm 2a$. 2. rotation $\pm 2\pi$. 3. stretching $\pm a$ + rotation $\pm\pi$.

Generalizing (1) we consider now the plane of the deformations which correspond to stretching φ_{tr} and rotation φ_{rot}. There are four equivalent equilibrium positions (Fig.2). The admissible transitions are: $(1 \leftrightarrow 2)$, $(2 \leftrightarrow 3)$, $(3 \leftrightarrow 4)$, $(4 \leftrightarrow 1)$, $(1 \leftrightarrow 3)$, $(2 \leftrightarrow 4)$. The sceletal solitons which correspond to the first four transitions we shall call the twistons. The dimerization lifts up the glice plane symmetry. Then the points come non equivalent and the energy difference is the energy of confinement. Now only two equilibrium points are admissible $(1 \leftrightarrow 3)$ or $(2 \leftrightarrow 4)$. The sceletal soliton between these positions is either a trivial stretching soliton or the complex of two twistons, which are bound by the same confinement force as two kinks. The kink on the chain changes the equilibrium points and restores the previous transitions.

The elastic constants corresponding to the chain rotation and to the stretching are known to be of the same order. Then we can assume that on the plain (φ_{tr}, φ_{rot}) there is a valley along which the transition takes place from one state into another and we arrive the one parametric model of Ch.3. Nevertheless the combined nature of deformation is important with two respects: 1. Cis-trans-isomerization proceeds via consequent rotations of the chain segments. 2. The remnants of cis-segments actually carry out the reflection's operation, so that here is only some translational distortion φ_{tr} required to complete the twiston.

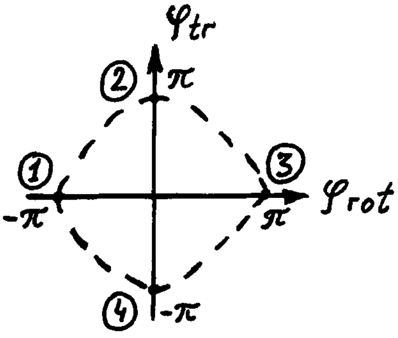

Fig.2. Equilibrium positions on $(\varphi_{rot}, \varphi_{tr})$ plane. Dashed lines show the transitions, corresponding to twistons.

Since twistons are topological objects, they can be eliminated only at the chain ends. Complete healing of twistons is prohibited because of interchain crosslinking.

For twistons in loosely packed phase of PA we estimate the following parameters: the energy $W \sim 0.05eV$, the length $\xi_1 \sim 200A$, the mass $M \sim 10^2 m_e$, amplitudes of quantum and thermal fluctuations are $l_0 \sim 20A$, $l_{300K} \sim 50A$. In a result of kink-twiston confinement the backbone defects are marked by such quantum numbers as spin or charge. This effect can provide a new tool to study the chain slipping in polymers.

In conventional low symmetry dense packed phase we estimate the energy $W \sim 0.05eV$, the length $\xi_1 \sim 200A$, the mass $M \sim 10^2 m_e$, amplitudes of quantum and thermal fluctuations are $l_0 \sim 20A$, $l_{300K} \sim 50A$. Then the twiston-kink complexes can hardly exist until the twistons are preexisting due to the isomerization. from the beginning. In the next chapters we discuss the possibility of twiston's formation and the role of solitons as a trigger in crystallografic transformation[10].

THE EFFECT OF SOLITONS ON THE CRYSTAL STRUCTURE

The interchain coupling of polymeric backbones also comes from two contributions. The first one is the Van der Waals interatomic interaction, which is common for all polymers. The second one is due to π-electronic interchain exchange so it is specific only for the π-conjugated polymers. Except for the total 3d band structures calculations[9] the last effect is usually ignored for traditional polymer consideration.

The Van der Waals interaction energy for two chains can be written as

$$W_{total} = \sum_{n,m} V(\vec{R}_n - \vec{R}_m) = \int V(\vec{R}_{\perp,1} - \vec{R}_{\perp,2}, x_1 - x_2)\frac{dx_1 dx_2}{a^2} + \delta V$$

$$W_{total} = V_{cyl} + \delta V$$

Here $\vec{R}_n$, $\vec{R}_m$ are the atomic positions, V_{cyl} is the main part of interaction energy, Which corresponds the cylindrical approximation. V_{cyl} can be easily calculated dependent only on the density and insensitive to the chain's structure.

The part δV defines the crystal symmetry. From available data for the energy differences in various crystal structures we can estimate $\delta V \simeq 30\% W_{total}$ For the monoclinic structure of PA we find from the data[7]

$$W_{total} \simeq -0.08eV/CH; \quad V_{cyl} \simeq -0.065eV/CH; \quad \delta V \simeq -0.014eV/CH$$

Let us consider the π -electronic exchange. For two chains $i = 1, 2$ we are able to obtain the following expression for the exchange energy

$$W_{\pi-\pi} = \frac{t_{\perp}^2}{\pi t_0}(\Delta_1\Delta_2 - 1)$$

$\Delta_{1,2} = \pm 1$ for different kinds of dimerizations. The most important properties of this interaction are the following:

i for the antiphase ordering the π-electrons give the same contribution to the backbone interaction as to the confinement energy.
ii for the inphase ordering both of these contributions are zero.
iii for close packed structures the π-electronic contribution dominates in the dimerization ordering. At the same time it contributes to about 20% of the backbone interactions being able to effect the type of the crystal ordering, favoring shorter intermolecular distances.

Then we clearly observe that the evident effect of the kinks is to trigger π-interaction on and off. The energy is turned on for the homogeneous structure with antiphase ordering of dimerizations while between the two kinks the $\pi - \pi$ interaction is turned off. The disappearance of the π-contribution between the two kinks on some chain is equivalent to a pressure $\sim 10 Kbar$ exerted onto surrounding chains. If this is not enough for the local crystallografic transformation, then the local dilution of the order of 5% of the Van der Waals radius takes place. It essentially reduces the backbone interaction and the confinement. The bubble is formed around the chain bearing the pair of kinks. Inside the bubble confinement is low, the interaction is essentially less structured. The central chain rotation is facilitated and the way for formation of twistons is open. At finite concentration of twistons the hexagonal phase with unhindered rotations is expected in a correspondence to observations[5,11].

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