

DYNAMICAL PROCESSES IN CONDENSED MATTER

Edited by

MYRON W. EVANS

University College of North Wales

ADVANCES IN CHEMICAL PHYSICS
VOLUME LXIII

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IN CONDENSED MATTER**

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VOLUME LXIII

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE
STUART A. RICE

PREFACE

Volume LXII of this series was concerned with the axioms developed recently by Professor Grigolini, Professor Pastori, and their co-workers for the solution of the differential equations that govern (for example) the evolution of conditional probability density functions. Numerical algorithms were devised and applied to problems that depend on equations of this type. It was emphasized that one particular class of equations may have applications in several different areas, and that the techniques developed in pursuit of a solution of one type of problem may be of considerable utility in a different discipline. In this way, a large number of seemingly unrelated observations may be explained in terms of a much smaller number of axioms. This is a feature of chemical physics and related disciplines, and it is natural, therefore, to follow Volume LXII, devoted mainly to axioms and applications, with a second volume describing experimental, numerical, and related analytical methods and observations.

It may seem that the only thing common to the articles that follow is that they deal with condensed matter. A symmetry of purpose in what follows may not be found easily without reference to Volume LXII, whose ideas find application, in some way or another, to the subjects reviewed individually in this volume. Each article in this volume is complete in itself, but is also intended to summarize a field of work in which the axioms of Volume LXII have been or could be of use.

The first article, by M. Andretta, R. Serra, and G. Zanarini, industrial specialists of TEMA S.p.A., Bologna, Italy, in association with K. Pendergast, Cross Keys College, is on the nature of soliton diffusion in activated polymers. This class of polymers is already being made the basis for a new high-technology industry following the discovery that their conductivities may range over many orders of magnitude when they are doped with the appropriate ionic or similar material. This clearly written description offers a wide-ranging introductory review.

There follows a useful account by W. T. Coffey of the development and applications of the Kramers equations. Methods akin to those of Volume LXII are applied therein to solve these equations numerically.

The review by L. A. Dissado, R. Nigmatullin, and R. M. Hill develops the relationship between a progressive loss of memory and structure relaxation in various condensed media, for which a universal character of the frequency dependence of properties such as dielectric loss has been estab-

lished over a multidecade range. This review provides some interesting insights into the methods of Volume LXII from a different viewpoint.

The article by G. J. Evans illustrates (with photographs) his recent discovery of the inverse of the important Costa-Ribeiro thermodielectric effect, that is, the ability of electric fields to bring about liquid-to-solid phase changes of technological importance. The theory of such phase changes may well be based in the future on the Kramers equations with external fields, described in Volume LXII. It is already possible in this context to follow analytically another important effect discovered recently and described here by G. J. Evans—that of ultrafine spectral detail in the far-infrared spectrum of liquid water. The analogous work of Bloembergen and Purcell has been reviewed already in the *Advances in Chemical Physics* series.

The review by M. W. Evans and G. J. Evans deals with the formidable array of spectroscopic techniques now available for investigating stochastic processes in condensed matter, and attempts to draw (with the aid of computer simulations) a pattern of conclusions from the results for some liquids, such as dichloromethane, that have been studied intensively using these techniques. This body of results presents an interesting opportunity for testing the self-consistency of the experimental data using the analytical methods of Volume LXII.

The most important development in the study of “pure” molecular dynamics in the last decade has been that of computer simulation. The rapid increase in the power and speed of computers, the introduction of array processing, and the improved comprehensibility of software have made this technique indispensable for the study of, for example, spectral bandshapes in the molecular liquid state. It has been referred to and used extensively in Volume LXII and is again used in the review article by Evans and Evans. It is therefore appropriate that an article be devoted to a description of the many new simulation techniques that have been developed. The article by D. Fincham and D. M. Heyes describes in detail the software of the SERC CCP5 group and others, and includes actual examples of FORTRAN programs for methods such as distributed array processing, constant-pressure simulation, field-effect simulation with the difference method, and the linked-cell method for handling samples of up to 10,000 or even more polyatomic molecules. This article should be of particular interest to non-specialists, who might be encouraged to use the software and documentation available free on request from the SERC's Daresbury Laboratory, near Warrington, U.K.

The nature of vibrational relaxation in molecular liquids is potentially of great interest for the determination and prediction of chemical reactions in solution. The article by M. F. Herman and E. Kluk is therefore timely in its description of vibrational relaxation, and may be cross-referenced to the analytical description, using reduced model theory, in Volume LXII, and to the numerical methods described by Fincham and Heyes in this volume.

Some aspects of the Kramers equation, and of the methods devised by Grigolini for its solution, are mentioned by F. Marchesoni. This article may be cross-referenced to the one by M. W. Evans and G. J. Evans, in which an attempt is made to use a variety of resources for studying selected samples.

Some of the most subtle and beautiful observational results in research on molecular condensed matter have emerged from the study of liquid crystals. J. K. Moscicki reviews some of his recent theoretical and experimental work in this field, carried out at the University College of Wales, Aberystwyth, U.K.; Laboratoire du CNRS Maurice Letoit, France; and Cornell University, U.S.A. The richness and variety of the dynamical behavior of rigid rodlike polymer liquid crystals, revealed through the Kerr effect, and of the equilibrium phase diagrams of these polymers bear ample witness to the interest these results might have for future analysis with a variety of methods.

In his article, W. Schröer describes and extends the results of his Cambridge University Ph.D. thesis on the structural properties of molecular liquids. These are exemplified by the various generalizations he has made of the Kirkwood–Fröhlich theory and of the Clausius–Mosotti function in order to account for the medium-range order imposed by polyatomic molecules in the liquid state. These analytical results are particularly important for interpretation of the numerical indications given by computer simulations. The structure and dynamics of the molecular liquid state are inextricably interwoven, and Schröer's contribution provides an invaluable complement to the dynamical considerations that make up most of Volumes LXII and LXIII.

The final article, by J. K. Vij and F. Hufnagel, focuses on the technology of contemporary microwave and far-infrared spectroscopy, exemplified by Fourier-transform interferometry and klystron and laser spectroscopy. The availability of powerful dedicated computers has yielded a considerable advance in interferometer capability. Completely automated instruments are now available with ranges of $2\text{--}24,000\text{ cm}^{-1}$ at resolutions of 0.01 cm^{-1} . At this limit the experimental behavior is often at its most interesting, and therefore fertile ground for application of the ideas of Volume LXII can be found in these data, particularly at high resolution.

M. W. EVANS

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TRANSPORT PROPERTIES AND SOLITON MODELS OF POLYACETYLENE

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I. INTRODUCTION

Over the last 10 years interest has been increasing in the possible applications of conducting polymers. In principle, it is possible to combine the electrical properties of metals and semiconductors with the mechanical characteristics and workability of polymers. Using such an approach, the problems of weight, mechanical fragility, cost, and so on could be drastically reduced and new applications found.

Polymeric materials have already found vast application as dielectrics. The first attempt to provide polymers with significant electrical conductivity involved mixing metallic powders with the polymer. In 1973¹ metallic conductivity was observed in polymeric crystals of nitrogen and sulfur [(SN)_x]. Although this is the only example of a polymer possessing intrinsically metallic properties, even more important from an applicative standpoint was the practical demonstration that the electrical conductivity of a polymeric material could be changed by impurity-doping analogous to that used in traditional semiconductors. This effect of doping was particularly evident in polyacetylene, (CH)_x, first synthesized by Natta et al.² more than 20 years ago.

Interest in this material has grown only recently, after Shirakawa et al. succeeded in synthesizing it in the form of a film³ and after the discovery by the group at Pennsylvania University that dopants such as AsF₅, alkali metals, and halogens drastically changed its electrical properties.^{4,5} In fact, the electrical conductivity can vary over 12 orders of magnitude as a function of dopant concentration, passing from typical insulator values through the semiconductor range to almost metallic conductivity.

Analogous effects of doping with AsF₅ and alkali metals have been observed in other polymers such as poly(*p*-phenylene) and polypyrrole.¹ Polyacetylene (PAC), however, is the most important conducting polymer, as is shown by the large number of references to (CH)_x in the scientific and patent literature. In this regard we mention only the application of lithium iodide-doped PAC films in lightweight rechargeable batteries and the realization of low-cost (but limited efficiency) solar cells.¹ Potential applications include the use of PAC in thermoelectric generators, piezoelectric converters, high-tension screening, and electrophotography.

The central importance of PAC among electrically active polymers is linked to another aspect, which has motivated the choices made in writing this review: alongside the experimental work, there has been a notable increase

in attempts at a theoretical understanding of the peculiar properties of these polymers. At first, the theoretical work aimed at comparing the properties of polymeric conductors with those of traditional semiconductors, taking advantage of the developments taking place in the field of amorphous semiconductors. These theoretical developments, in turn, were the fruit of a generalized effort to reduce costs in the integrated circuit industry, which has succeeded in finding some applications in which noncrystalline materials can be used.

The attempt to base the theory of electrical conductivity in polymers on that for amorphous semiconductors has, however, had only partial success. As will be shown later, such a theoretical approach cannot constitute a unified framework within which to interpret the increasing amount of experimental data (not only electrical, but also magnetic and optical).

This situation is analogous to that which characterized the field of traditional semiconductors up to the 1940s. Then, Shockley made the decisive step forward for both semiconductor theory and technology by choosing to work with a simple material, crystalline germanium, the most directly accessible theoretically.⁶ The choice of PAC now as the material on which to concentrate experimental and theoretical effort is analogous to the choice of crystalline germanium then.

The development of soliton models, although limited so far to the schematization of a single PAC (or even of a polyene) chain, has led to a unified theoretical framework capable not only of interpreting experimental data, but also of suggesting new experiments. If, however, we examine the ample literature on PAC, the impression we receive is somewhat vague. The urgency of publishing new scientific results, the contrasts between different schools, and the industrial influences in play lead to a confused and fragmentary picture.

The first part of this review applies the main soliton models to the structure of PAC, pointing out the analogies and differences between the different theoretical approaches and briefly comparing the experimental data relating to magnetic and optical properties. The electrical properties are discussed in more detail, forming the second part of the review. The experimental data and theoretical hypotheses are presented in order of increasing dopant concentration, thus allowing the identification of the regions in which the electrical properties show different characteristics and the illustration of the dominant conduction mechanism for each region. Finally, in the appendixes, we discuss the relationship between the continuous and the discrete structural models in more detail.

The literature on the subject is large and ever-growing. This review will therefore be not a complete account of the existing literature, but rather a choice of arguments integrated in a unified picture of the unusual properties of this fascinating material.

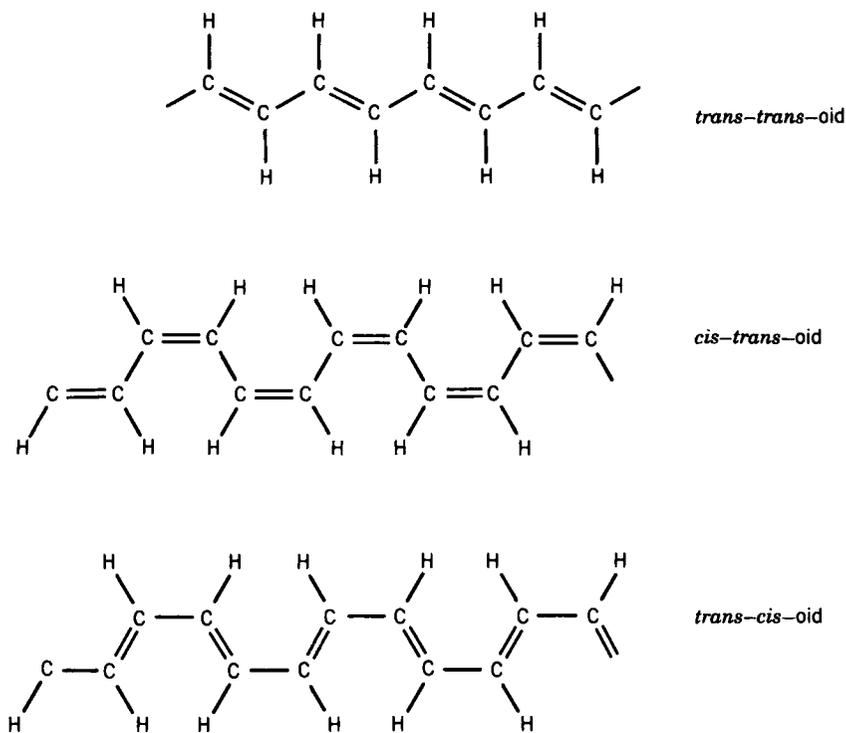


Figure 1. Isomers of polyacetylene.

II. SOLITON MODELS OF POLYACETYLENE

A. General Characteristics of Polyacetylene

There are three isomers of PAC $[(CH)_x]$, the structures of which are shown in Fig. 1. The most thermodynamically stable isomer is the *trans-transoid* (abbreviated as *trans*), which is also the most interesting as regards electrical properties, as well as the most studied.

It is possible to control the *cis/trans* ratio of a PAC film by varying the temperature of polymerization or by thermal isomerization of a predominantly *cis* sample synthesized at low temperature (-78°C).⁷ It is also thought that impurity doping and the addition of oxygen lead to *cis-trans* isomerization.^{8,9}

From here onward, we shall refer only to *trans*-(CH)_x unless otherwise stated.

In order that the reader may better understand the nature of the various electronic bonds in PAC, we will briefly examine the types of orbitals in-

volved. In PAC three of the four valence electrons of each carbon atom give rise to sp^2 hybrid orbitals, which form σ -bonds with both the hydrogen atom and the two neighboring carbon atoms. The wavefunction of the remaining p electron is involved in π -bonding between adjacent carbon atoms.

One would therefore suppose, at first sight, that *trans*-PAC has a resonant structure giving rise to C—C bonds of equal length. Experimental data, however, exclude this hypothesis¹⁰ and indicate alternation of short (1.36 Å) with long (1.43 Å) bonds. Moreover, theoretical considerations suggest that the formation of a structure with alternate double bonds ("dimerized structure"[†]), as opposed to a uniform structure, is energetically favored.

The substance of Peierls' argument for this is as follows:¹² the nondimerized structure would correspond to a metallic type of material, since there would be no gap between the π and π^* levels. The introduction of a spatially periodic potential, associated with small changes in the atomic positions with respect to the nondimerized structure, creates a gap at the Fermi level, thus lowering the energy of the ground state. Therefore, there is a reduction in the electronic energy of the chain that is greatest when the distortion has a wavevector equal to twice the Fermi wavevector, K_f , which is defined as a function of the Fermi energy E_f by

$$\frac{\hbar^2 K_f^2}{2m_e} = E_f \quad (1)$$

where m_e is the mass of the electron and \hbar is the reduced Planck constant.

In one-dimensional materials the gain in electronic energy due to Peierls' distortion is always greater than the increase in lattice energy.³ It is thus expected that the ground state is the distorted dimerized one.

The alternating nature of the bonds, which creates a gap at the Fermi level, drastically changes the electrical properties of the material. Thus the nondimerized structure should show a metallic behavior, whereas in this case we clearly have semiconductor characteristics. In fact, the existence of a gap of about 1.4 eV has been observed experimentally in PAC.⁴

PAC, from a model point of view, seems therefore analogous to a traditional disordered semiconductor. The disorder can be attributed both to imperfect crystallization and to structural changes caused by the inclusion of possible impurities.

Anticipating a subject that will be examined more thoroughly in Section III, we note that this hypothetical model is also supported by the existence

[†]The use of the term "dimerized structure" to denote the presence of alternate short and long bonds is now commonplace in the PAC literature.¹¹ This clearly has no correspondence to the term "dimer" as used in organic chemistry.

of a semiconductor-to-metal transition at dopant levels of a few percent, which was initially interpreted as an Anderson transition, typical of disordered materials.¹⁰ It is therefore possible to describe some of the electrical properties of PAC without referring to unusual concepts such as the topological "soliton."

However, more complete understanding of the electrical properties of doped PAC, especially at low dopant levels, is possible within the scope of the soliton model. Moreover, this model also accounts for the magnetic and optical properties of the material, thus providing a unified picture of its electromagnetic behavior.

At this point, therefore, we will take the opportunity of introducing the fundamental concepts of the soliton theories of PAC and comparing them with the principle magnetic and optical experimental data. In the next section we will discuss in more detail the mechanisms proposed to explain PAC's electrical conduction.

The concept at the root of the soliton models of PAC is linked to its magnetic behavior.^{15,16} *Trans*-(CH)_x shows an intense electron spin resonance (ESR) signal, which demonstrates the existence of unpaired spins, at a level of about 1 for every 3000 carbon atoms. It is possible to identify the π -electron system as the origin of the signal. The existence of unpaired spins is also shown by the presence of a Curie-type component in the paramagnetic susceptibility,⁴ which is associated with the presence of magnetic dipoles that can orient themselves freely in an external field, and therefore with the presence of singly occupied levels.^{2‡} The amplitude of the ESR signal suggests that the unpaired spins in PAC have considerable mobility down to a temperature of 9 K. On doping, for example, with AsF₅, there is a drastic reduction in the ESR signal and in the Curie susceptibility, accompanied by a spectacular increase in the electrical conductivity.

Goldberg and coworkers having noted that the presence of free and mobile spins was associated with low conductivity, concluded that the ESR signal had its origin in neutral defects present in the chain.¹⁷ They formulated the hypothesis that these defects were "domain walls" that separated different portions of the polymeric chain, characterized by changes of phase in the alternation of the bonds (see Fig. 2). By analogy with ferromagnetic materials, they supposed that the domain walls of PAC would be delocalized, extending over about 10 lattice constants. The development of this hypothesis by Goldberg et al.¹⁷ has led to the above-mentioned "soliton theory" of PAC.

In reality, several different approaches of this type exist: the soliton hypothesis was independently proposed by M. J. Rice¹⁸ and by Su, Schrieffer, and Heeger¹¹ (SSH) in March 1979. Rice's description is of a more phenom-

[‡]We will return to this subject in Section II.F [Eq. (27)].



Figure 2. A domain wall separating two portions of $trans\text{-(CH)}_x$ by means of a change in phase in the alternation of the bonds.

enological character than that of SSH, who start from a detailed microscopic model of the PAC chain. In August of the same year, Takayama, Lin-Liu, and Maki¹⁹ (TLM) proposed a model of $trans\text{-(CH)}_x$ that may be considered the continuous limit of the SSH model.[‡]

In the following sections, we will review these three models, which give the same qualitative, and often the same quantitative, results, and will discuss the relationships between them.

B. Rice's Model

To understand Rice's hypotheses on PAC, a short discussion of the concept of a charge density wave (CDW) is necessary. We have seen in the previous section that a hypothetical one-dimensional conductor is, in reality, subject to the phenomenon known as Peierls' distortion. Thus the atoms in the lattice will occupy positions different from those of the reference configuration, which, in PAC, corresponds to the nondimerized structure in which all the C—C bonds have the same length. This periodic lattice distortion (PLD) is necessarily accompanied by a periodic distortion in the electron density distribution of the system (i.e., the CDW), as was demonstrated by Fröhlich.²¹

The PLD and the CDW together form the "condensate,"³ the "position" of which may be identified by means of a parameter ϕ . Let us approximate the discrete chain by means of a continuous chain. Both $u(x)$, which specifies the displacement of an atom from its reference position, and $\delta n(x)$, which describes the variation in the macroscopic density of the conduction electrons with respect to the metallic state, would show sinusoidal trends of the type $\sin(qx + \phi)$.

In a translationally invariant system such as that considered by Fröhlich, the condensate energy E_c is independent of ϕ and it can therefore find itself in a state of uniform motion. Fröhlich proposed this mechanism as a possible explanation of the phenomenon of superconductivity, before the formulation of the now generally accepted Bardeen-Cooper-Schrieffer (BCS) theory.²²

[‡]In the same period, S. A. Brazovskii independently formulated a continuous model of PAC to describe soliton excitations.²⁰ We will not discuss this in detail here, as an analysis of this type would not introduce any new fundamental aspects and would only complicate the description.

In recent years, with the experimental realization of almost one-dimensional metals, Lee, Rice, and Anderson²³ have noted that the translational invariance that Fröhlich assumed could be violated by several factors, the main ones being as follows:

1. The presence of lattice defects (particularly charged impurities).
2. Interactions between chains (the presence of CDWs on neighboring chains).
3. The fact that the lattice is discrete and not continuous, so that values of ϕ exist that optimize the energy of interaction between conduction electrons and ions.

The energy of the condensate, E_c , thus depends on the phase, and this gives rise to a bias F_R proportional to $\partial E_c / \partial \phi$. Thus there is a preferential position, ϕ_0 , characterized by $F_R(\phi_0) = 0$. The condensate is thus "pinned."

The distortion of the electron density distribution in PAC has a wavelength equal to $2a$, where a is the lattice constant for the nondimerized reference state (see Fig. 2). Under these conditions the effects of pinning associated with the discontinuity of the lattice are very large, and it is unreasonable to think that the collective translational motion of the CDW, proposed by Fröhlich, could significantly contribute to the electrical conductivity.

Later, Rice et al.²⁴ demonstrated that even a pinned condensate could show dc conductivity due to the presence of nonlinear excitations (solitons), also known as " ϕ particles." These are solutions of the nonlinear equations of motion of the phase of the condensate, and take the form of solitary waves moving with constant velocity. They can be physically interpreted as transition zones separating parts of the chain where the value of the phase is constant.

These mobile solitons contribute to the conductivity with a term proportional to

$$\exp\left(-\frac{E_s}{k_B T}\right)$$

where E_s is the energy of formation of the soliton, T the absolute temperature, and k_B the Boltzmann constant (see also Section III).

Let us now deal with the specific case of PAC.

We will treat the σ -electrons of $(\text{CH})_x$ using the adiabatic approximation and focus our attention on the π -electrons, of which, in the neutral material, there is one for every CH group.

The theory of Peierls leads to the conclusion that the ground state of the chain will be characterized by a periodic distortion with a wavevector equal

to $2K_f$, where K_f , defined by Eq. (1), is related to the number of electrons per site, v , by the relationship²⁵

$$K_f = \frac{\pi}{2a}v$$

In the neutral material, $v = 1$ and thus the CDW, as we have already noted, has a wavelength equal to $2a$ and is commensurate with the lattice.

Let us now consider the changes in the electronic structure associated with the addition or subtraction of electrons from PAC. First, let us study the addition of a single electron, which, as can be seen from the above equation, alters the wavevector of the CDW so that it is no longer commensurate with the lattice. This would cost a large amount of energy. On the other hand, it may be expected that the minimum-energy configuration consists of a large localized distortion (soliton) in a small portion of the chain, which thus maintains the commensurability between the CDW and the lattice for most of its length.

The added electron goes into an electronic level, created by the soliton distortion, at the center of the Peierls gap associated with the structure having $v = 1$.¹⁸

The above case constitutes an example of "frustration,"²⁶ a concept which is central to the understanding of nonlinear systems. The basic idea is that numerous physical systems do not always resolve the competition between opposing tendencies by giving rise to spatially homogeneous compromise solutions. In some cases, they give indeed rise to strong localized distortions that separate essentially unperturbed areas.

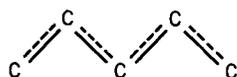
Let us now examine Rice's hypotheses quantitatively. We will, as usual, take the nondimerized structure as our reference, whereas the ground state of a neutral PAC chain actually presents alternating long and short bonds.

Let u_n be the projection along the axis of the chain of the n th CH group with respect to the reference position. Let us also call phase A and phase B the two possible structures of the ground state, which are chemically and energetically identical and distinguishable only by different phases in the alternation of the single and double bonds (see Fig. 3). Phase A and phase B are characterized by the relationships

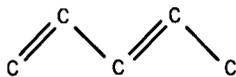
$$\begin{aligned} u_n &= (-1)^n u_0 \quad (\text{phase A}) \\ u_n &= -(-1)^n u_0 \quad (\text{phase B}) \end{aligned} \tag{2}$$

We also define $u(x)$ as the continuous limit of the expression $(-1)^n u_n$.

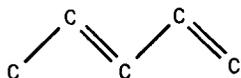
The addition of the electron will cause the formation of a soliton (phase kink) linking two different parts of the chain, one in phase A and the other



Nondimerized structure



Phase A



Phase B

Figure 3

in phase B. Generally, in the case of a static soliton, the function $u(x)$ will take the form

$$u(x) = u_0 f\left(\frac{x - x_0}{L}\right) \quad (3)$$

where u_0 is the amplitude of the distortion in the ground state [see Eq. (2)], $f(y)$ is an odd function of its argument, which rapidly tends toward ± 1 when $|y| > 1$, x_0 is the center of mass of the soliton, and L is a measure of its half-width. The expression for $f(y)$ depends on the specific model chosen for PAC. Rice adopts a Hamiltonian of the type

$$H = \int dx \left[\frac{1}{2} D \left(\frac{\partial u}{\partial t} \right)^2 - \frac{1}{2} C \left(\frac{\partial u}{\partial x} \right)^2 + V(u) \right] \quad (4)$$

with D and C as positive constants. The first term is the kinetic energy of the ionic motion, while the second describes the coupling between closest-neighbor ions in the elastic approximation. The “on site” potential $V(u)$ describes the positive (or negative) attraction toward the reference position and is chosen in a phenomenological manner.

In our case, it is required that the nondimerized configuration ($u = 0$) does not correspond to a position of stable equilibrium, owing to the Peierls distortion. It is also required that two possible stable equilibrium states exist that are energetically degenerate and correspond to phases A and B of Fig. 3. The simplest potential of this type, adopted by Rice, is

$$V(u) = \frac{1}{2} A u^2 + \frac{1}{4} B u^4 \quad (5)$$

with $A < 0$ and $B > 0$ (see Fig. 4).[‡]

[‡]The potential of Eq. (5) (the Landau–Ginzburg potential) is familiar in other fields of physics^{27,28} and has been employed in the description of phase transitions of other kinds associated with the change of sign of the parameter A (see Fig. 4).

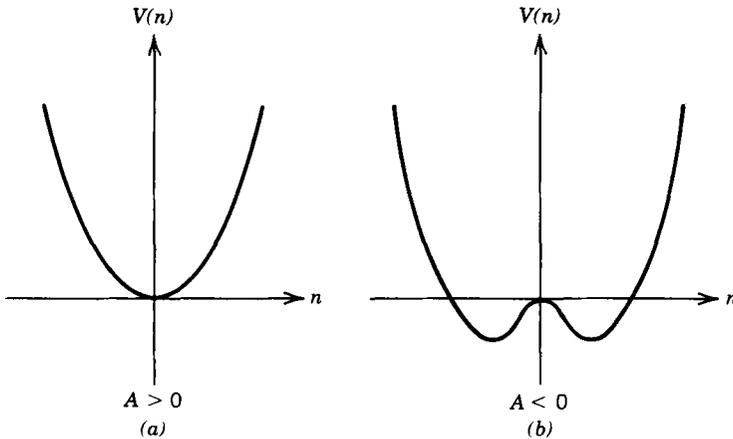


Figure 4

Krumhansl and Schrieffer²⁹ and, independently, Varma³⁰ demonstrated that the equation of motion associated with the Hamiltonian defined by Eqs. (4) and (5) allows a solution of the type

$$u(x, t) = u_0 \tanh\left(\frac{x - vt}{L}\right)$$

which describes a soliton with uniform motion conserving its original shape (L and v constant). The corresponding static solution, of the type defined by Eq. (3), is

$$u(x, t) = u_0 \tanh\left(\frac{x - x_0}{L}\right) \quad (6)$$

This describes a stationary "phase kink," with its center in x_0 , in a chain of infinite length subject to the boundary conditions

$$\lim_{x \rightarrow +\infty} u(x, t) = u_0 \quad \text{and} \quad \lim_{x \rightarrow -\infty} u(x, t) = -u_0 \quad (7)$$

General considerations that we will not go into here allow us to associate this phase kink with an energetic level at the halfway point of the Peierls gap.³¹ There are three possible cases. First, this level may be occupied by a single electron; the soliton is therefore neutral, and may be considered an excited state of the pure material. There are cases in which the ground state (the perfectly dimerized chain) cannot be realized because of topological constraints, for example, when there is an odd number of CH groups be-

tween two carbon atoms that are sp^3 hybridized instead of sp^2 hybridized. The cause of such sp^3 hybridization may be, for example, the presence of cross-linking between the different polymeric chains.

In this case, the configuration in which two portions of the chain having different phases are separated by a kink (see Fig. 2) is the most stable energetically. The ground state of a finite chain of PAC having an odd number of carbon atoms also presents an alternation of phase (with a related soliton), if one takes into account the boundary effects that favor termination with a double bond.³¹⁻³³ This leads us to the conclusion that undoped PAC should have a neutral soliton concentration of the order of about one soliton per chain.

Because the soliton energy level is occupied by a single electron (free spin), it will give rise to an ESR signal and a Curie paramagnetism, whereas a neutral soliton will not contribute to the electrical conductivity. The agreement between these predictions and the experimental results noted in the previous section is evident.

The soliton model is also capable of suggesting a convincing doping mechanism for PAC. If the energy level associated with the soliton is doubly occupied (the case we will consider here to clarify our ideas) or empty, then the soliton will be charged.

A donor impurity will give up its electron to the polymeric chain directly in the conduction band or in the soliton level, depending on which of the two alternatives is energetically favored. By measuring the energy from the Fermi level, Rice estimated that the energy of formation of a charged soliton is

$$E \approx \frac{4\Delta}{3\pi} \quad (8)$$

where 2Δ is the Peierls gap.[‡] The doping mechanism that leads to the formation of charged solitons is thus preferred with respect to direct promotion into the conduction band. A doubly occupied soliton will not give rise to an ESR signal or to Curie magnetism, which is consistent with the observations of Goldberg et al.⁷ cited above.

We will defer discussion of the mechanisms of electric conduction in PAC until the Section III. Here we will limit ourselves to noting that a charged soliton generated by a charged impurity is presumably bound to the latter

[‡] The reasoning, in a nutshell, is as follows: It can be demonstrated that the ratio between the half-width L of the soliton and the lattice constant a is equal to $W/2\Delta$, where W is the amplitude of the π -band (~ 10 eV). Thus $2L \approx 10a$. It can also be shown that the Peierls condensation energy per site, e_c , is equal to $\Delta^2/\pi W$. Thus, Eq. (8) can be deduced from the amplitude of the soliton and the energy per site.

by a Coulomb interaction energy much greater than the thermal energy $k_B T$ at room temperature.¹⁸ Thus charged solitons generated in this way cannot be charge carriers in the material.

Rice and Mele³⁴ extended the original approach to take into account important physical factors that had been ignored. In the initial work, the formation energy of a charged soliton, S^\pm , was the same as that necessary for the creation of a neutral soliton, S^0 , since the Coulomb repulsion between the two electrons (or the two vacancies in a soliton without electrons) occupying the soliton level had been ignored. Rice and Mele took account of this by using an internal potential energy term for the charged soliton of the type

$$V(L) = \left(A + \frac{U_0}{\epsilon} \right) \frac{1}{L} + BL$$

where A , U_0 , and B are positive constants and ϵ is the dielectric constant. The corresponding internal potential energy term for the neutral soliton does not have the term containing U_0 .

Rice and Mele also took into account in an approximate way the stabilizing effect of the Coulomb interaction between the impurity and charged solitons by considering the dopant molecule as a point charge and assuming a uniform charge distribution for the soliton.

The basic results were as follows: A charged soliton far away from impurities has an energy very close to that of ionization in the conduction band. The crudeness of the model does not allow us to determine which of the two alternatives is more convenient. The situation changes drastically, however, if one takes into account the soliton-impurity interaction (at a separation of 2 Å). The energy of formation of the charged soliton is then only slightly higher (by $\sim 10\%$) than that of a neutral soliton. Therefore, even this more detailed analysis confirms the main predictions of the initial model.

Before concluding this discussion of Rice's hypothesis, we note that the use of a phenomenological Hamiltonian, such as that defined by Eqs. (5) and (6), appears at this point to be completely arbitrary. The ability of the model to describe the unusual phenomena in neutral and doped PAC is quite striking, but any attempt at a more complete treatment must, in some way, begin with a microscopic model. As we shall see, the theory of Su, Schrieffer, and Heeger¹¹ fulfills this requirement and also allows us to understand the qualitative success of Rice's simpler approach.

C. The Su, Schrieffer, and Heeger Model

The difference between the bonding and antibonding energies of the σ -electrons of PAC is large (≈ 10 eV) with respect to phonon and soliton en-

ergies (≈ 0.5 eV). This allowed Su, Schrieffer, and Heeger (SSH) to treat the electrons using the adiabatic approximation. The Hamiltonian of the model is the sum of three terms:

$$H = H_K + H_{PI} + H_{EI} \quad (9)$$

The first term is the kinetic energy

$$H_K = \frac{1}{2} \sum_n M \dot{u}_n^2 \quad (10)$$

where M is the mass of the CH group and we sum over all the CH groups of the chain.

There is then a term describing elastic interaction between closest-neighbors of the type

$$H_{PI} = \frac{1}{2} \sum_n K (u_{n+1} - u_n)^2 \quad (11)$$

It is also assumed that the π -electrons can be treated using the strong bonding approximation

$$H_{EI} = - \sum_{n,s} t_{n+1,n} (c_{n+1,s}^\dagger c_{n,s} + c_{n,s} c_{n+1,s}^\dagger) \quad (12)$$

The meaning of the creation and annihilation operators is as follows: $c_{n,s}^\dagger$ ($c_{n,s}$) creates (or destroys) an electron with spin s at the n th CH group; and $t_{n+1,n}$ is the hopping integral, which describes the variation in energy associated with the jumping of an electron between the n th and the $(n+1)$ th carbon atom. It is only by means of this latter term that the coupling between the electronic and phononic degrees of freedom is introduced into the model. It is in fact assumed that it is possible to expand the hopping integral about the value t_0 that it takes in the nondimerized reference state by using the linear expression

$$t_{n+1,n} = t_0 - \alpha (u_{n+1} - u_n) \quad (13)$$

where α is an electron-phonon coupling constant.

The model lacks explicit references to the interactions between electrons, which can be partly taken into account by using "screened" values of the parameters t_0 and α . In any case, this approach would have to be abandoned when the electron-electron repulsion is very strong.

Ignoring the kinetic term, SSH first calculated the energy of the non-dimerized (metallic) state, the band structure of which is shown in Fig. 5.

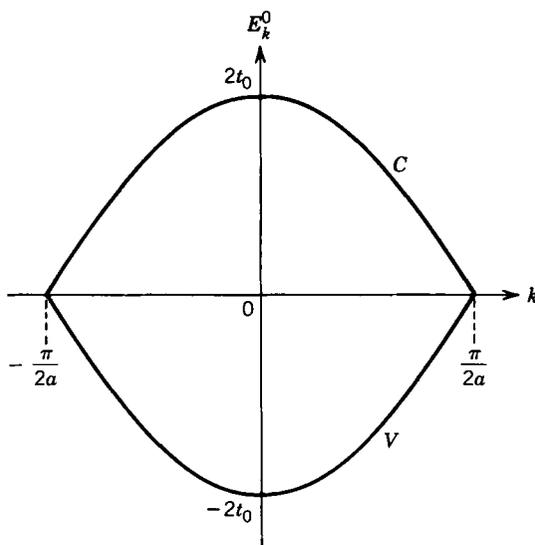


Figure 5. Band structure of the nondimerized state of *trans*-PAC.

They then calculated the energy of the ground state of the chain, which corresponds to the perfectly dimerized structure $u_n = (-1)^n \bar{u}$, with \bar{u} constant. Diagonalizing the Hamiltonian (without the kinetic term) yielded

$$H_d = \sum_{K,s} E_K (n_{K,s}^c - n_{K,s}^v) + 2NK\bar{u}^2$$

where N is the total number of carbon atoms and $n_{K,s}^c, (n_{K,s}^v)$ is the occupancy operator, which has as eigenvalues the numbers of electrons having momentum k and spin s in the conduction (or valence) band. E_K is given by

$$E_K = \sqrt{(2t_0 \cos ka)^2 + (4\alpha\bar{u} \sin ka)^2}$$

The energy of the ground state [$n_{K,s}^v = 1, n_{K,s}^c = 0 \forall (k, s)$] is

$$E_0(\bar{u}) = -2 \sum_K E_K + 2NK\bar{u}^2$$

By substituting an integral for the summation, it is possible to estimate $E_0(\bar{u})$ using the expression

$$E_0(\bar{u}) \approx -\frac{4Nt_0}{\pi} E(1-Z^2) + \frac{NKt_0^2 Z^2}{2\alpha^2}, \quad Z = \frac{2\alpha\bar{u}}{t_0}$$

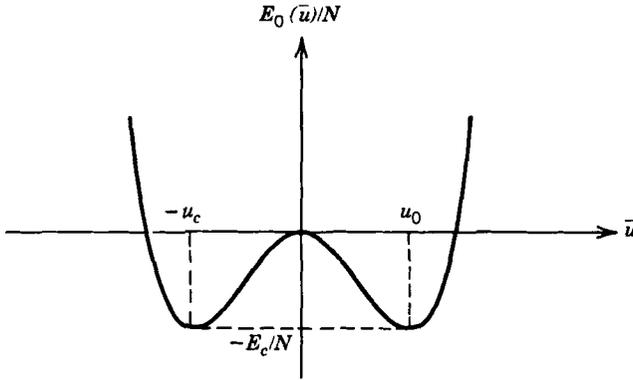


Figure 6. Condensation energy per site as a function of the variable u .

where $E(1 - Z^2)$ is the elliptic integral. In PAC the gap is estimated as $2\Delta \approx 1.4$ eV, the width of the bands as $W = 10$ eV, and the elastic constant as $K = 21$ eV \AA^{-2} . Using these values, the condensation energy per site, $E_0(\bar{u})/N$, shows the behavior illustrated in Fig. 6. The ground state is characterized by a value of $\bar{u} = u_0$ equal to 4×10^{-2} \AA , and the height of the energy barrier is 1.5×10^{-2} eV.

Comparing Fig. 6 with Fig. 4b, which represents the behavior of the “on site” potential of Rice’s model [Eq. (6)], we can understand the “microscopic” reasons why Rice’s description gives qualitatively correct results. In fact, the form adopted for the on-site potential simulates the behavior of the energy as a function of the dimerization parameter \bar{u} , and therefore simulates, at least qualitatively, the interaction between the vibrational and the electronic degrees of freedom of the chain.

Having studied the ground state, SSH then considered an excited configuration, comprising a phase kink, of the type

$$\begin{aligned}
 u_n &= (-1)^n u_0, & n \leq -m \\
 u_n &= -(-1)^n u_0 \tanh\left(\frac{n}{L}\right), & -m < n < m \\
 u_n &= -(-1)^n u_0, & n \geq m
 \end{aligned} \tag{14}$$

The choice of the hyperbolic tangent is not motivated, as in Rice’s model, by the existence of exact solutions of this type. It is to be taken only as a trial function having the desired characteristics. Su, Schrieffer, and Heeger state that the use of other, analogous trial functions does not lead to very different results.

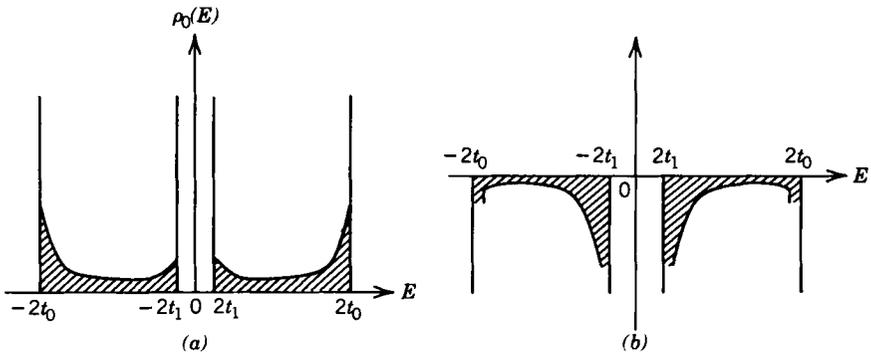


Figure 7. (a) Density of states of phase A or B of PAC. (b) Density of states in the presence of a soliton.

A soliton formation energy, E_s , of about 0.4 eV, corresponding to a gap of 1.4 eV, is obtained, along with a value of L equal to 7. The soliton is thus spread over about 14 atoms, and the pinning effects due to the discrete nature of the lattice are small. The variation in energy associated with the movement of the center of the soliton between two adjacent lattice positions is about 2×10^{-3} eV, which presumably gives the defect a high mobility even at low temperatures (down to about 30 K, as estimated by SSH).

The variation in the density of states $\Delta\rho(E)$ associated with the presence of the domain wall is illustrated in Fig. 7. The presence of a level localized at the center of the gap must be reconciled with the conservation of the total number of electronic states of the π and π^* bands:

$$\int_{-\infty}^{\infty} \Delta\rho(E) dE = 0$$

From this relationship and from the observation that $\Delta\rho(E)$ is an even function, it follows that the valence and the conduction bands each lack one-half of a state with respect to the perfectly dimerized state. Since the valence band is completely filled, the extra electron occupies the halfway level of the gap; the soliton is therefore neutral, with a spin of $\frac{1}{2}$. The addition or removal of an electron gives rise to a charged kink, with zero spin. As we can see, the situation is exactly analogous to that described by Rice.

Also in this case, if we ignore the Coulomb interaction between coupled electrons in the soliton level, the formation energies E_s of a charged and of a neutral kink are the same, being given by

$$E_s \approx \frac{2}{5}\Delta$$

Thus, SSH also sustain the hypothesis that the charge-transfer mechanism after doping consists of the formation of charged solitons, as opposed to direct promotion into the conduction band.

We have so far considered only the static case; a soliton moving uniformly with velocity v may be described by the equation

$$u_n(t) = (-1)^n u_0 \tanh\left(\frac{na - vt}{L}\right) \quad (15)$$

The translational mass M_s of the soliton is defined by the relationship

$$\frac{1}{2}M_s v^2 = \sum_n \frac{1}{2}M \dot{u}_n^2 \quad (16)$$

and turns out to be equal to six electronic masses. This suggests that quantum effects are important, and that the use of models in which the soliton is treated as a classical particle demands great caution.

D. The Takayama, Lin-Liu, and Maki Model

The Takayama, Lin-Liu, and Maki (TLM) model¹⁹ may be considered as the continuous limit of the SSH theory discussed in the previous section. Its importance is that it makes possible an analytical treatment that can give all the static solutions.³⁵

The SSH Hamiltonian in the continuous limit becomes (see Appendix B)

$$H = \frac{K}{8\alpha^2} \int \frac{dx}{a} \Delta^2(x, t) + \frac{M}{32a^2} \int \frac{dx}{a} \left(\frac{\partial \Delta(x, t)}{\partial t} \right)^2 + \int \frac{dx}{a} \psi^\dagger \left[-i v_F \sigma_3 \frac{\partial}{\partial x} + \Delta(x, t) \sigma_1 \right] \psi \quad (17)$$

where $\Delta(x, t)$ is linked to the continuous limit $u(x, t)$ of the quantity $(-1)^n u_n$ (see Section II.B) by the relationship

$$\Delta(x, t) = 4\alpha u(x, t) \quad (18)$$

(M , K , a , and α have the same meanings as in the preceding sections.) $\Delta(x, t)$ is proportional to the local extent of Peierls' distortion: the proportionality constant is chosen so that, in the case of perfect dimerization, it is equal to the half-width, Δ , of the gap. The meanings of the other symbols in Eq. (17) are as follows: v_F is the Fermi velocity, equal to $2t_0 a$, where t_0 is the hopping integral of the nondimerized state [Eq. (13)], whereas ψ is the spinor (two-component wavefunction) that describes the electronic field:

$$\psi(x, t) = \begin{pmatrix} w(x, t) \\ v(x, t) \end{pmatrix} \quad (19)$$

Finally, the σ_i are Pauli matrices.³⁶

Because we are looking for static solutions, for the moment we will ignore the kinetic term. One can demonstrate that the Hamiltonian (17) can be associated with the eigenvalue equation

$$\begin{pmatrix} -i v_F \frac{\partial}{\partial x} & \Delta(x) \\ \Delta(x) & i v_F \frac{\partial}{\partial x} \end{pmatrix} \begin{pmatrix} w_n \\ v_n \end{pmatrix} = \epsilon_n \begin{pmatrix} w_n \\ v_n \end{pmatrix} \quad (20)$$

and with the self-consistent equation

$$\Delta(x) = -\frac{4\alpha a^2}{K} \sum_{n,s} v_n^*(x) w_n(x) \quad (21)$$

In the mean field approximation, the energy of the chain is

$$E_{\text{MF}} = \sum_{n,s} \epsilon_n + \frac{K}{8\alpha^2} \int \Delta^2(x) dx$$

where the summation is extended over all the energetic levels below the Fermi level (at $T = 0$ K).

One can calculate the energy of a soliton of the type

$$\Delta(x) = \tanh\left(\frac{x}{L}\right) \quad (22)$$

The energy is optimized for

$$L = \frac{\hbar v_F}{\Delta} \quad (23)$$

where Δ is the half-width of the gap and is equal to

$$E_s = \frac{2\Delta}{\pi} \quad (24)$$

which is in good agreement with the results of SSH and slightly lower than the value obtained by Rice [Eq. (8)].

For a soliton moving with a constant velocity v , the energy of formation E_s also turns out to be a function of v . Whereas SSH ignored this contribution, TLM were able to calculate it analytically and to demonstrate that it is insignificant in PAC.

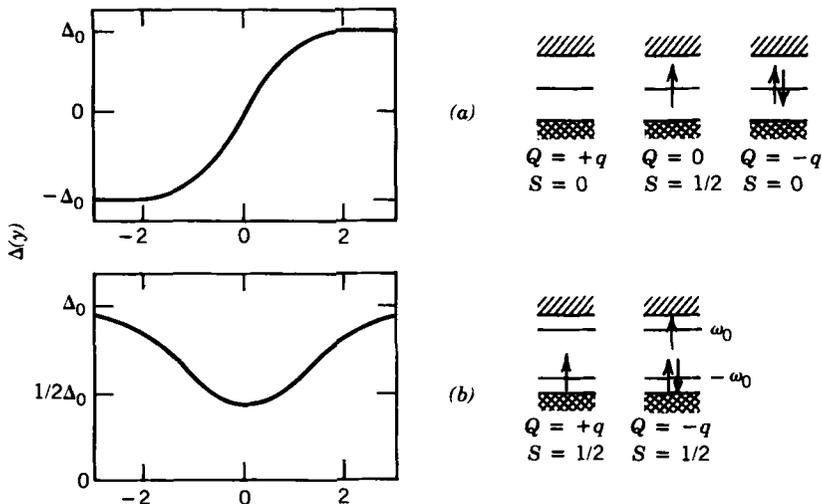


Figure 8. Intrinsic defects of *trans*-PAC with their relative electronic levels: (a) soliton; (b) polaron. [The abscissa represents the spatial coordinate x , and the ordinate the variable $\Delta(y)$.]

It has been shown³⁵ that the TLM equations [Eqs. (20) and (21)] can take solutions of the polaronic type, which can be written

$$\Delta(x) = \Delta - \frac{v_F}{L} \left[\tanh\left(\frac{x+x_0}{L}\right) - \tanh\left(\frac{x-x_0}{L}\right) \right] \quad (25)$$

where L is a parameter defining the shape of the polaron. The soliton [Eq. (22)] links two portions of the chain characterized by different phases of bond alternation, whereas the polaron [Eq. (25)] links two portions having the same phase (Fig. 8).

Thus, the latter does not enjoy the topological stability properties of the kinks, but is an excited state of the chain that can freely decay to the dimerized ground state. Two energy levels are associated with a polaronic defect. These are placed symmetrically about the gap, with energies $\varepsilon = \pm \omega_0$, where

$$\omega_0 = \sqrt{\Delta^2 - \frac{v_F^2}{L^2}}$$

The relationship for determining the parameter L is

$$\tanh\left(\frac{2u_0}{L}\right) = \frac{v_F}{L\Delta}$$

The neutral polaron has two electrons in the lower level and none in the higher one; for the reasons indicated above it is unstable and relaxes to the ground state. The structure having one or three electrons, however, is stable and requires an energy of formation of about 0.9Δ , whereas that containing four electrons gives rise to a kink-antikink pair that separates.

Another type of static solution of the TLM model is a series of regularly spaced kinks and antikinks (soliton crystal). This solution can be particularly important in the study of the semiconductor-metal transition in *trans*-PAC.

Bredas et al.³⁷ carried out *ab initio* calculations (based on the Hartree-Fock SCF-MNDO method) on "short" (40 carbon atoms) PAC chains showing that in the absence of dopant, there is a difference in bond length of 0.105 \AA between the alternate single and double bonds. They also predicted the existence of solitons having the following properties: The neutral soliton may be fitted satisfactorily using a tanh function with half-width $L = 3$ and an electronic wavefunction covering about 11 carbon atoms. The positively charged soliton extends over about 11 CH groups and has an electronic wavefunction covering about 17 carbon atoms. The negatively charged soliton is much more compact ($L \approx 2$) and is not very well represented by a tanh function. In this case the associated CDW is practically identical to that of the positively charged soliton.

The calculations of Bredas et al. also predict the existence of polarons that, as in the case of solitons, are narrower if negatively charged.

Thus, the *ab initio* calculations qualitatively confirm the results of the more simplified models that use analytical methods. The quantitative discrepancies are due to the fact that Bredas et al. explicitly took into account more specific physical effects, such as the polarization of the π -orbitals.

The results of Bredas and co-workers have been confirmed by Zerbi and Zannoni.³⁸ Their dynamic calculations and the experimental infrared and Raman spectra they obtained show that in doped PAC defects exist that are localized in a symmetrical manner with respect to the dopant molecules. According to Zerbi and Zannoni, these defects extend over about three double bonds, whereas the associated electronic wavefunctions are much more diffuse.

E. Some Observations on Doping Mechanisms

Polarons, which were introduced at the end of the previous section, are also nonlinear excitations of the soliton type, but do not invert the phase and may be considered as bonded kink-antikink pairs.

The study of polarons is of particular importance in the analysis of doping mechanisms in PAC.³⁹ If we imagine that an impurity (e.g., a donor) introduced into the material gives up its electron to an already existing soli-

ton level (a topological kink stabilized by cross-links or edge or other effects), the situation is straightforward. It is possible, however, for dopant levels to be much higher than the concentration of native solitons. Previous considerations, together with the apparent absence of contributions to the electrical conductivity by the extended-state bands, suggest that the impurities themselves can generate further solitonic excitations (kinks or polarons) that play the role of electron acceptors in the charge-transfer process. The introduction of a kink in a chain that is initially all phase A or all phase B leads to a phase change in a large portion of the chain; associated with this change is an activation energy proportional to the length of the same portion of the chain. It is thus plausible that the introduction of the impurity generates a localized effect that does not significantly alter the topology of the chain at large distances from the impurity. This suggests the hypothesis that the doping takes place by the formation of charged polarons rather than solitons.[‡]

We have seen that polarons of the type described by Eq. (25) constitute exact solutions of the TLM equations. Analogous studies have been carried out using the SSH model⁴²⁻⁴⁴ to consider polarons of the type

$$u_n = (-1)^n u_0 \tanh\left(\frac{n - n_0/2}{m}\right) \tanh\left(\frac{n + n_0/2}{m}\right) \quad (26)$$

The results obtained are substantially in agreement with those of the continuous model: a polaron (a state linked to a kink-antikink pair) can exist with a net charge of $+q$, but the addition of a further electron or vacancy destabilizes the system, which relaxes to a configuration having two separate charged kinks in a period that can be estimated, with the help of computer simulation, to be on the order of 10^{-15} .

In conclusion, it is reasonable to suppose that in cases of donor impurity doping, the charge transfer takes place by the formation of polarons with charges of $-q$. The addition of another impurity near the charged polaron thus gives rise to a doubly occupied polaron, which is unstable and generates, in turn, a pair of charged kinks. Different kinks in the same chain then form a soliton crystal, which is associated with a band at the center of the Peierls gap. In the initial doping phase there will also be transfer of electrons from the impurity to the native soliton levels of the material.

[‡] This hypothesis is also supported by numerical calculations by several different authors that demonstrate that in the presence of impurities, the polaron state has a lower energy than the soliton state.^{40,41}

F. Brief Comparison with Experimental Results

The interpretation of the experimental data on PAC is complicated by the disorder present in the material, which is due to both imperfect crystallization and the effect of the introduction of high concentration of impurities. It is particularly difficult to study the different properties as a function of y , the dopant concentration, because the active impurities that play a part in the charge transfer process constitute only a fraction (which is not constant) of the total quantity of dopant introduced into the material.⁴⁴ We therefore do not intend to give a complete review of the experimental results and their relationships with the theoretical models, except for those pertaining to the electrical conductivity, which will be dealt with in detail in the following section.

In this section we will only describe briefly the magnetic and optical properties of PAC within the context of the soliton model. In our opinion, as mentioned above, the importance of this model derives not so much from its explanation of a single experimental fact in such a manner as to exclude alternative explanations as from its ability to explain different phenomena and observations within a single framework and to formulate verifiable predictions and thus stimulate further experiments.

Undoped PAC has a low electrical conductivity, on the order of 10^{-5} ohm⁻¹cm⁻¹, and contains a free spin concentration, as estimated from ESR measurements, of about 1 per 3000 carbon atoms.¹⁴ The width of the resonance indicates that these spins are mobile down to temperatures of only a few degrees Kelvin. It has also been possible to determine experimentally the ratio between the spin diffusion coefficient along the chain, D_{\parallel} , and that in the orthogonal direction, D_{\perp} .^{45,46} Its value is on the order of 10^5 – 10^6 , in agreement, at least qualitatively, with the soliton model. Maki⁴⁷ has also shown that the diffusion coefficient D_{\parallel} calculated with the TLM Hamiltonian is in quantitative agreement with the experimental values.

If the doping takes place with the formation of charged solitons, this would be expected to be accompanied by a decrease in the number of free spins, N_c . This phenomenon was observed by Ikehata et al.⁴⁸ and is illustrated in Fig. 9.

The values of the variables N_c and χ_P (Pauli susceptibility) were obtained by magnetic susceptibility (χ) measurements at different temperatures by using the relationship

$$\chi(T) = \chi_P + \frac{N_c \mu_B^2}{k_B T} \quad (27)$$