Solitons in Polyacetylene

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We present a theoretical study of soliton formation in long-chain polyenes, including the energy of formation, length, mass, and activation energy for motion. The results provide an explanation of the mobile neutral defect observed in undoped $(CH)_x$. Since the soliton formation energy is less than that needed to create band excitation, solitons play a fundamental role in the charge-transfer doping mechanism.

Polyacetylene, $(CH)_x$, is the simplest linear conjugated polymer. The thermodynamically stable *trans* configuration is sketched in Fig. 1(a) illustrating the σ bonding (sp^2 hybrids) and the π bonding (p_z) in the x-y plane. This dimerized pattern (A) of alternating "single" and "double" bonds forms one of two degenerate structures; the other structure (B) is given by interchanging the "single" and "double" bonds. As a consequence of these degenerate ground states one expects excitations to exist in the form of a topological soliton, or moving domain wall, separating A and B domains.

Early calculations[1-3] indicate that a (charge)

(a)

(b)

FIG. 1. (a) *Trans* configuration of $(CH)_x$. $a = 1.2$ Å.
(b) π-band structure of perfectly dimerized $(CH)_x$.

neutral soliton in a long-chain polyene would have a single unpaired spin localized in the wall. In that work,[3] the wall width was assumed to be of order one bond length, leading to a large activation energy for motion and localization of the wall. Electron spin resonance studies[4,5] of $(CH)_x$ have revealed a narrow line ($g = 2.00263$) resulting from a dilute concentration of neutral defects (of order a few hundred ppm in the *trans* isomer). The narrow width ($\Delta H = 1.650e$ at room temperature) and Lorentzian line shape are indicative of motional narrowing and imply that the resonance results from a highly mobile unpaired electron species, even down to $10°K$. Goldberg et al.[5] suggested that this spin resonance line might arise from bond-alternation domain walls quenched into the undoped polymer during the *cis-trans* isomerization.

Recent interest in this semiconducting polymer has been stimulated by the successful demonstration of doping with associated control of electrical properties over a wide range.[6-16] Analysis of the anomalously small Curie-law contribution to the magnetic susceptibility,[16] the details of the infrared absorption,[17] and the magnitude and temperature dependence of the thermopower[18] in lightly doped samples led to the suggestion that doping may proceed through formation of charged domain walls.

To gain a detailed understanding of solitons in $(CH)_x$ we have studied a model in which the π electrons are treated in a tight-binding approximation[19] and the σ electrons are assumed to move adiabatically with the nuclei. We present in this paper initial results on the energy of formation, length, mass, and activation energy of the neutral and ionized domain walls. The results are discussed briefly in the context of experimental observations.

Let u_n be a configuration coordinate for displacement of the nth CH group along the molecular symmetry axis (x), where $u_n = 0$ for the un-

dimerized chain. The Hamiltonian is
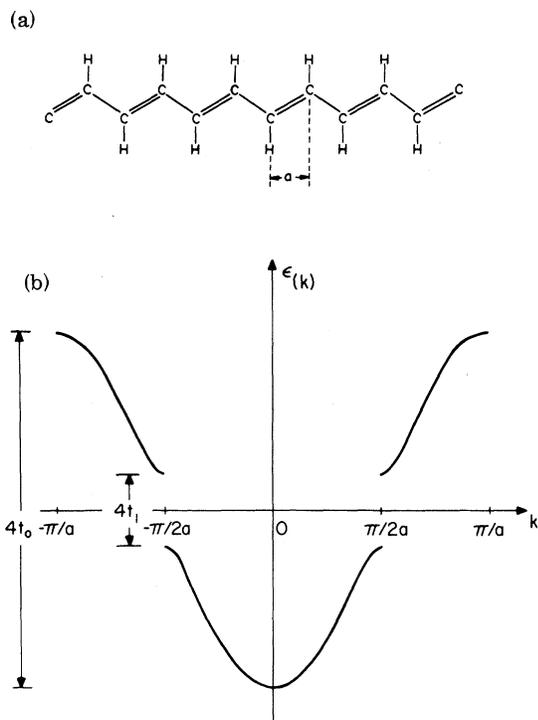
$$H = -\sum_{ns}(t_{n+1,n}c_{n+1,s}{}^\dagger c_{n,s} + \text{H.c.})$$
$$+ \sum_n \tfrac{1}{2}K(u_{n+1} - u_n)^2 + \sum_n \tfrac{1}{2}M\dot{u}_n{}^2 , \qquad (1)$$

where to first order in the u's,

$$t_{n+1,n} = t_0 - \alpha(u_{n+1} - u_n) . \qquad (2)$$

M is the mass of the CH unit, K is the spring constant for the σ energy when expanded to second order about the equilibrium undimerized systems, and $c_{ns}{}^\dagger$ (c_{ns}) creates (annihilates) a π electron of spin s on the nth CH group. The band structure of the perfect dimerized structure (A or B) is shown in Fig. 1(b), where the π band width[20] $4t_0 \simeq 10$ eV and the dimerization energy gap[6] $E_g \equiv 2\Delta = 4t_1 \simeq 1.4$ eV. In this perfect structure, the displacements are of the form

$$u_{n0} = \pm(-1)^n u_0 , \qquad (3)$$

where (+) corresponds to A and (−) to B. Therefore, the hopping integrals for the perfect chain are

$$t_{n+1,n} = \begin{cases} t_0 - t_1 & \text{``single'' bond} \\ t_0 + t_1 & \text{``double'' bond.} \end{cases} \qquad (4)$$

By using[21] $K = 21$ eV/Å^2 and requiring that the value of u_0 which minimizes the ground-state energy leads to $4t_1 \simeq 1.4$ eV, we find $\alpha/t_0 = 1.65$ Å^{-1} in good agreement with independent estimates of this parameter.[21,22] Also, $u_0 = 0.042$ Å is the amplitude in the x direction of the CH displacement and the bond-length change due to bond alternation is $\sqrt{3}u_0 = 0.073$ Å.

Consider now two domains with B phase to the left and A phase to the right of a soliton which is at rest at the origin $n = 0$, as illustrated in Fig. 2(a). To determine the properties of the soliton (width, energy, mass, spin, etc.) we determine the ground-state energy of the system for an arbitrary displacement pattern which reduces to the A and B phases as one moves to the far right or left. In practice we vary the displacements in a segment containing N CH groups located symmetrically about $n = 0$, and tie onto perfect A and B phases. The ground-state energy is then readily calculated using Green's-function methods for any set of u_n in the segment. It is convenient to define a staggered order parameter

$$\psi_n = (-1)^n u_n , \qquad (5)$$

which reduces to $\pm u_0$ for the A and B phases and is zero by symmetry at the center of the wall.
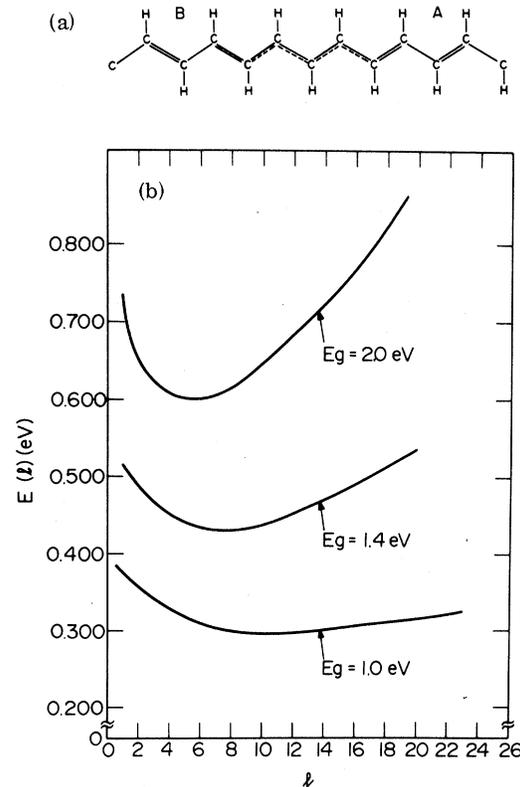
FIG. 2. (a) A soliton separates the A and B phases. (b) Soliton energy as a function of wall width for three values of the energy gap E_g.

As a trial function we take

$$\psi_n = u_0 \tanh(n/l) \qquad (6)$$

and determine the system energy $E(l)$ as shown in Fig. 2(b) for $4t_1 = 1.0$, 1.4, and 2.0 eV. The minimum occurs at $l \simeq 7$ for $4t_1 = 1.4$ eV so that the wall is quite diffuse (for $4t_1 = 2.0$ eV, $l \simeq 5$ and for $4t_1 = 1.0$ eV, $l \simeq 9$). The energy to create the soliton at rest is $E_s \simeq 0.4$ eV for the 1.4-eV gap energy (0.6 eV for $4t_1 = 2.0$ eV; 0.3 eV for $4t_1 = 1.0$ eV). Using the adiabatic approximation for the electronic motion, one can show that the effective mass of the soliton is related to the δu_n for a small change in wall position, δx_s, by

$$M_s = M\sum_n(\delta u_n/\delta x_s)^2 \simeq 4u_0{}^2 M/3la^2 , \qquad (7)$$

where the second equality holds if we use (6) and replace n by $n - x_s/a$ in the derivative. Using the values obtained above for $4t_1 = 1.4$ eV, we estimate $M_s \simeq 6m_e$, where m_e is the electron mass.

We have calculated the periodic-lattice–induced activation energy for neutral-soliton motion in
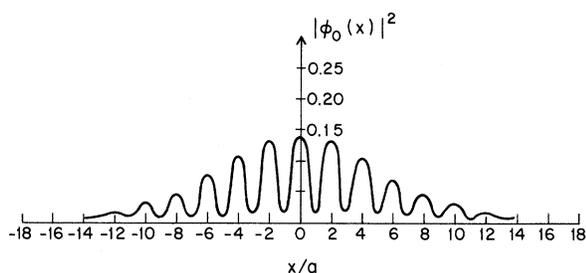
FIG. 3. Probability distribution of the localized electronic state at the center of the gap.

the pure system by rigidly displacing the tanh function in Eq. (6) and find $\Delta E_s \sim 0.002$ eV. Thus, a small activation is predicted, consistent with the electron spin resonance line narrowing observed in undoped specimens down to 10°K.

The electronic structure of the soliton exhibits a localized state φ_0 at the center of the gap, containing one electron for the neutral kink. While this localized state is spin unpaired, the distorted valence band continues to have spin 0. Thus the neutral soliton has spin $\frac{1}{2}$. The static susceptibility therefore will contain a Curie-law contribution and can be used to count the number of soliton defects present. $\varphi_0(x)$ is plotted in Fig. 3 for $4t_1 = 1.4$ eV. For larger l, extra pairs of states enter symmetrically from the conduction and valence bands.

Since the localized state occurs at the gap center, i.e., the chemical potential, the relevance of the solitons to the doping of $(CH)_x$ depends on the energy for creation of a soliton, E_s, as compared with the energy required for making an electron or a hole, $\frac{1}{2}E_g = \Delta$. If $\Delta < E_s$, charge-transfer doping would occur by creating free band excitations; if $\Delta > E_s$, soliton formation would be favored. For $E_g = 1.4$ eV considered above, $E_s \simeq 0.4$ eV $< \Delta = 0.7$ eV. Thus, the soliton-bound hole leads to stabilization over the free hole by $\Delta - E_s \simeq 0.3$ eV with correspondingly larger values if the gap is larger. The same stabilization energy holds for adding an electron, which would occupy $\varphi_0(x)$ of the soliton rather than being placed at the conduction-band edge. Self-consistent–field effects arising from electron-electron interactions would split the ionization and affinity levels of φ_0 about the center of the gap and change these estimates accordingly. We note that the ionized solitons formed upon doping with acceptors (or donors) will be non-magnetic, consistent with the experimental observations[15] for AsF$_5$ and iodine doping.[23,24]

It is important to recognize that the soliton which we are discussing is not a phase soliton or φ particle as discussed by Rice, Bishop, Krumhansl, and Trullinger.[25] Intuitively, one might assume that the interchange of double and single bonds corresponds to a π phase shift of the electronic-charge-density wave. This reasoning leads to the soliton having a charge $\pm e$. Rather, the soliton discussed here is neutral (unless it is explicitly ionized). Instead of satisfying a sine-Gordon–like equation for the phase of a charge-density wave, the soliton discussed here is an amplitude distortion of the field ψ_n which satisfies an equation more akin to the ψ^4 field theory.[26-28]

In the lightly doped system, the charged soliton is bound to the charged impurity by the Coulomb interaction. We assume the impurity to be a point charge, $\mp e$, a distance $d \sim 2$ Å from the chain immersed in a medium of dielectric constant[16] $\epsilon = 10$, and the soliton's charge density to be $\pm e | \varphi_0(x) |^2$. We find the binding energy to be approximately 0.31 and 0.33 eV for $d = 2.4$ Å and $d = 2$ Å, respectively (for $E_g = 1.4$ eV, $l = 7$) as compared to the observed activation energy 0.3 eV for electrical conductivity.[4,10] In the bound state, if the interaction with the impurity is developed to second order in the displacement of the soliton leading to a spring constant K_b, one finds the vibrational energy is approximately $\hbar\omega_s = (k_b / M_s)^{1/2} \simeq 0.07$ and 0.08 eV for $d = 2.4$ and 2.0 Å, respectively. In this analysis we have used the equality of the soliton's kinetic mass M_s defined by Eq. (7) and its inertial mass which enters the analog of Newton's second law. This equality follows from a work-energy theorem for soliton motion.[29] We tentatively associate this mode with the broad infrared absorption observed[16] to peak at ~0.10 eV. The width of the peak may be due to varying distances between the impurity and the chain throughout the system.

Since the order parameter ψ_n goes to zero in the center of the wall, one can anticipate a C-C bond-stretch frequency intermediate between that of the single and the double bond. This is consistent with the strong molecular mode observed at 1370 cm^{-1} in the lightly doped polymer.[16] We are currently investigatigating the oscillator strength of the shape oscillation mode of the soliton in which l varies, as well as continuum modes in the presence of the soliton.

In summary, we have presented initial results of a theoretical study of soliton formation in long-chain polyenes, including the energy of formation,

length, mass, spin, and activation energy. The results provide an explanation of the mobile neutral defect observed in undoped $(CH)_x$. Moreover, since the soliton formation energy is less than that needed to create a band excitation, soliton formation plays a fundamental role in the charge-transfer doping mechanism.

[1]L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (W. A. Benjamin, New York, 1966), pp. 516–523.

[2]M. W. Hann, A. D. McLachlen, H. H. Dearman, and H. M. McConnell, J. Chem. Phys. 37, 361, 3008 (1962).

[3]J. A. Pople and J. H. Walmsley, Mol. Phys. 5, 15 (1962).

[4]H. Shirakawa, T. Ito, and S. Ikeda, Makromol. Chem. 179, 1565 (1978).

[5]I. B. Goldberg, H. R. Crowe, P. R. Newman, A. J. Heeger, and A. G. MacDiarmid, J. Chem. Phys. 70, 1132 (1979).

[6]C. R. Fincher, Jr., D. L. Peebles, A. J. Heeger, M. A. Druy, Y. Matsumura, and A. G. MacDiarmid, Solid State Commun. 27, 489 (1978).

[7]H. Skirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, J. Chem. Soc., Chem. Commun. No. 14, 5787 (1978).

[8]C. K Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Skirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, Phys. Rev. Lett. 39, 1098 (1977).

[9]C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, H. Skirakawa, E. J. Louis, A. G. MacDiarmid, and Y. W. Park, J. Am. Chem. Soc. 100, 1013 (1978).

[10]C. K. Chiang, Y. W. Park, A. J. Heeger, H. Skirakawa, E. J. Louis, and A. G. MacDiarmid, J. Chem. Phys. 69, 5098 (1978).

[11]Y. W. Park, M. A. Druy, C. K. Chiang, A. J. Heeger, A. G. MacDiarmid, H. Skirakawa, and S. Ikeda, J. Poly. Sci., Poly. Lett. Ed. 17, 628 (1979).

[12]C. K. Chiang, S. C. Gau, C. R. Fincher, Jr., Y. W. Park, A. G. MacDiarmid, and A. J. Heeger, Appl. Phys. Lett. 33, 181 (1978).

[13]L. R. Anderson, G. Pez, and S. L. Hsu, J. Chem. Soc., Chem. Commun. No. 23, 1066 (1978).

[14]T. C. Clarke, R. H. Geiss, J. F. Kwak, and G. B. Street, J. Chem. Soc., Chem. Commun. No. 12, 489 (1978).

[15]J. F. Kwak, T. C. Clarke, R. L. Greene, and G. B. Street, Bull. Am. Phys. Soc. 23, 56 (1978).

[16]B. R. Weinberger, J. Kaufer, A. J. Heeger, A. Pron, and A. G. MacDiarmid, Phys. Rev. D (to be published).

[17]C. R. Fincher, Jr., M. Ozaki, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B 19, 4140 (1979).

[18]Y. W. Park, A. Denestein, C. K. Chiang, A. J. Heeger, and A. G. MacDiarmid, to be published.

[19]P. M. Grant and J. P. Batra, to be published.

[20]M. Karplus and R. N. Porter, *Atoms and Molecules: An Introduction for Students of Physical Chemistry* (Benjamin, New York, 1970), p. 391.

[21]Y. Oshika, J. Phys. Soc. Jpn. 12, 1238, 1246 (1957).

[22]H. C. Longuet-Higgins and L. Salem, Proc. Roy. Soc. London, Ser. A 251, 172 (1959).

[23]I. B. Goldberg, H. R. Crowe, P. R. Newman, A. J. Heeger, and A. G. MacDiarmid, to be published.

[24]A. J. Epstein, A. J. Heeger, and A. G. MacDiarmid, to be published.

[25]M. J. Rice, A. R. Bishop, J. A. Krumhansl, and S. E. Trullinger, Phys. Rev. Lett. 36, 432 (1976).

[26]J. A. Krumhansl and J. R. Schrieffer, Phys. Rev. B 11, 3535 (1975).

[27]Y. Wada and J. R. Schrieffer, Phys. Rev. B 18, 3897 (1978).

[28]M. J. Rice, Phys. Lett. 71A, 152 (1979).

[29]W. P. Su, J. R. Schrieffer, and A. J. Heeger, to be published.