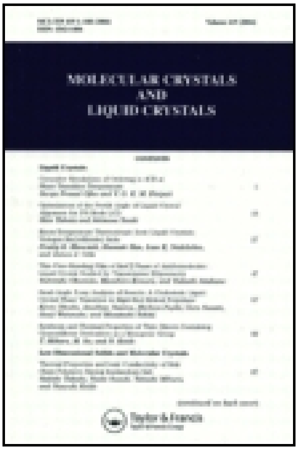

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Nonlinear Adiabatic Dynamics In Polyacetylene and Related Materials

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NONLINEAR ADIABATIC DYNAMICS IN POLYACETYLENE AND RELATED MATERIALS

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Abstract Numerical and analytical studies of the dynamic, mean-field, adiabatic Su-Schrieffer-Heeger model of polyacetylene are shown to reveal the typical importance of strong, coherent anharmonicity, e.g. as "breathers". Examples illustrated include (i) single kink dynamics, (ii) electron-hole (e-h) decay in trans-$(CH)_x$; (iii) e-h decay in cis-$(CH)_x$; (iv) e-h decay in linear polyynes; (v) decay of a photoexcited kink or polaron; (vi) photoexcitation in the presence of bond or site defects.

INTRODUCTION

The simple one-electron tight-binding model of an ideal polyacetylene chain as introduced by Su-Schrieffer-Heeger[1] (SSH) has enjoyed considerable theoretical attention and qualitative experimental support. Nevertheless many features and predictions, as well as modifications, of the model still need clarification. In the absence of adequate techniques to simultaneously handle the important issues of electron-electron coupling, electron-phonon coupling, dynamics, interchain coupling, disorder, etc., we describe here some of our results on mean-field adiabatic dynamics within the SSH model, emphasizing persistent coherent anharmonic phonon ("breather"-like) excitations as well as the more familiar kink or polaron structures. Such coherent anharmonicity is familiar in lattice dynamics, especially in low dimensions, but here the electron-phonon coupling results in self-consistent renormalization of the phonon dynamics and accompanying electronic levels. Despite the absence of explicit electron-electron correlations (which, for instance, excludes traditional exciton formation or change of level occupation), we suggest that coherent anharmonicity is a prevalent behavior particularly for self-focusing of high energy inputs. This is illustrated below with several examples.

We have implemented numerical integration of the SSH model for trans-$(CH)_x$ in the form

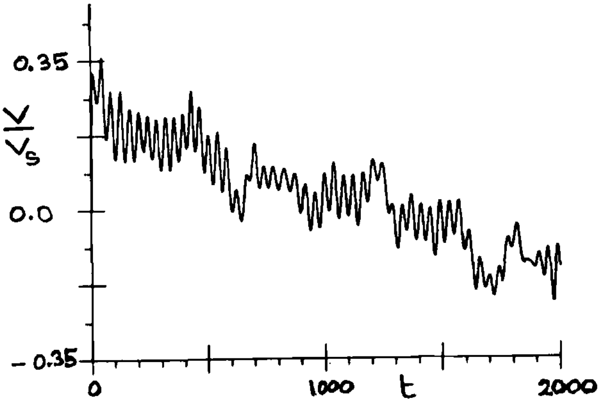
$$H = \sum_n [-t_0 + \alpha(u_n - u_{n-1})][c_n^+ c_{n-1} + h.c.] + \frac{1}{2}M \sum_n \dot{u}_n^2 + \frac{1}{2}k \sum_n (u_n - u_{n-1})^2 \qquad (1)$$

where all the variables have their conventional meanings. (See, e.g., ref. 2). The actual ion displacement at site n is $u_n = (-1)^n \bar{u}_n + n.\delta a$ where δa is the local change in the lattice constant a, and the (slowly varying) $\bar{u}_n$ represents the dimerization relative to the local lattice constant. Thus, to separate optic and acoustic effect, we plot $r_n \equiv \frac{1}{4}(-1)^n[2u_n - u_{n+1} - u_{n-1}] \simeq \bar{u}_n$ and $s_n = \frac{1}{4}[2u_n + u_{n+1} + u_{n-1}] \simeq n.\delta a$ in subsequent figures. For numerical simulations we choose parameter with $\xi \sim 7a$ ("realistic" parameter for $(CH)_x$) and $\xi \sim 2.7a$ (more convenient numerically and useful for investigating discreteness effects). Continuum static solutions to (1) are known analytically[3,4] as a kink (K) and a polaron (P).[4] Of course, in the continuum limit there are no acoustic phonons generated.

Single Kink Dynamics

Our primary results have been reported elsewhere.[2] Namely, a kink launched with the continuum profile and a Newtonian-boost rapidly

FIGURE 1 Velocity of kink (ξ = 2.7a) vs time with initial velocity ~ 0.33 v_S. Note that there are plateaux in the kink velocity and that the kink changes direction due to discreteness and associated acoustic phonon effects. Time units are 10^{-15} sec here and elsewhere.



(~ 10^{-13}sec) relaxes its shape and speed and reaches an asymptotic propagation state. The energy-speed (v) relationship actually fits quite accurately to a Lorentzian but with a maximum speed v_m, which is neither v_F (the Fermi velocity) nor v_S (the speed of sound ⊟ $\frac{1}{2}\omega_0 a$, with ω_0 the phonon frequency), but a new renormalized scale set by the electron-phonon interaction. As $v \to v_m$, the kink width contracts to only ~ $\frac{2}{3}$ of its static value and uniform translation no longer occurs[2,5] but rather there is an oscillating "tail" structure[2,6] -- one or more anharmonic optical phonon wave-packets. The energy $E_K(v_m)$ ~ $0.1\Delta_0$, as can be deduced in an approximate analytic approach.[2] If kink dynamics are followed for longer time ($\gtrsim$ 1psec) striking new effects are observed[7] which are due to lattice discreteness and acoustic phonon modes. Similar effects have been found in the discrete sine-Gordon equation.[8] Namely, translational energy can be lost by creating acoustic phonons but also there are several quasi steady-state propagation velocities for which phonon loss is small -- only the first of these are recorded in Fig. 1 of refs. 2 and are relevant to the e-h experiments below. An example of longer-time kink propagation is shown in Fig. 1. We have found[7] that a static kink is not a solution to the discrete SSH model: a kink initially at rest accelerates to a speed $\lesssim v_m$ in qualitative agreement with Leblanc et al.[9] We have also studied[7] the effects of a uniform external field (i.e. $\sum_n E_0 n c_n^+ c_n$ added to (1)) and extrinsic damping (in the phenomenological form $-\gamma \dot{u}_n$ added to the lattice eq. of motion). Even with zero γ, a kink accelerates to a terminal speed $> v_m$. This terminal speed decreases with increasing γ, but there seem to be two regimes: for small γ phonon damping dominates; for large γ optical and acoustical phonons are suppressed. Both regimes appear to be non-Newtonian.

Electron-Hole (e-h) Decay in trans -$(CH)_x$-

As has been extensively discussed,[2,10] e-h photoexcitation in trans-$(CH)_x$ leads to the production of a $K\bar{K}$ pair separating with maximum velocity v_m. However photoexcitation adds energy $2\Delta_0$ (the band gap) while each kink has rest energy $\sim 2\Delta_0/\pi$ and kinetic energy $\sim 0.1\Delta_0$ giving a total energy $\sim 1.5\Delta_0$. We found[2] the remaining $\sim 0.5\Delta_0$ to be concentrated in an electrically neutral dynamic anharmonic lattice excitation -- "a breather" (see Fig. 2(a)). We further showed that this breather is persistent for long times (> 5psec) and might be expected to contribute to intra-gap optical absorption. In Fig. 3 we show the numerically calculated[11] difference between the optical absorptions of a 98 atom ring with and without a breather. In comparing with experiment there are a number of caveats: the relative intensity of the subband edge enhancement and above band edge bleaching should not be naively compared as they depend on the density of breathers (here ~ 1%); fine structure due to vibronic effects is not included in this model; neither is bleaching due to other excitations (e.g. kinks). With these limitations in mind the agreement with experiment[12] is good. Using multiple time-scale analysis we have found[2] an approximate analytic breather solution. It is important to note that varying the breather energy over a wide range has little effect[11] on the breather frequency and the associated intra-gap state dynamics and sub-band edge absorption.

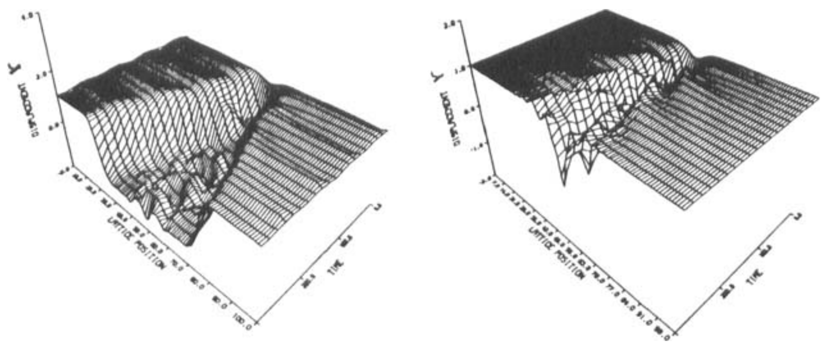


FIGURE 2 r_n vs n for times 0-0.3 psec: (a) trans-$(CH)_x$. Note the oscillating breather between the free kinks; and (b) cis-$(CH)_x$. Here a free $K\bar{K}$ pair is not produced.

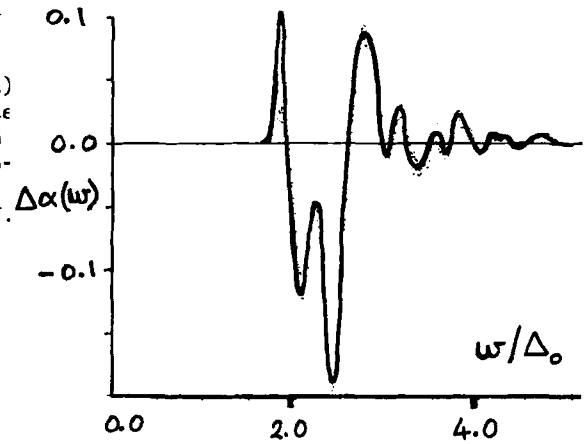


FIGURE 3 Change in optical absorption, $\Delta\alpha(\omega)$, on adding a single (photoexcited) breather to a 98 site ring. Note the good agreement for the location of the peaks with the data of Ref. 12. Band gap $\equiv 2\Delta_0$.

e-h Decay in cis-$(CH)_x$:

The situation here is entirely different as the nondegenerate ground state prohibits kink production.[4,13] A number of suggestions have been made to model this in the discrete Hamiltonian (see Ref. 11): here we add to (1) $-t_C \sum_n (-1)^n [c_n^+ c_{n-1} + h.c.]$. (It is easily shown that this reduces to the Brazovskii[13] term in the continuum limit.) We indeed find[11] (see Fig. 2(b)) that $K\bar{K}$ production is suppressed and an oscillating nonlinear lattice deformation formed. Associated with this is an oscillation of the two singly occupied states at the top of the valence and bottom of the conduction bands. However, this "excitonic breather" is qualitatively different from the trans-$(CH)_x$ breather in that it can only decay by phonon emission following an electronic transition -- which suggests a much weaker temperature sensitivity.

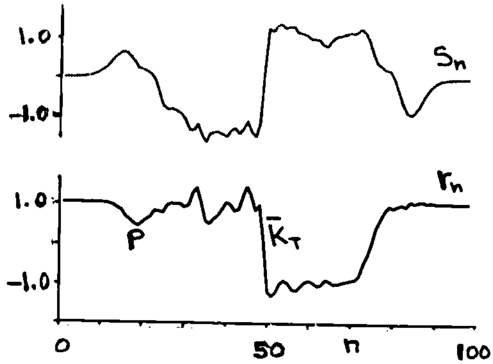
e-h Decay in Linear Polyynes

Linear polyynes $[\leftarrow C{\equiv}C \rightarrow_x]$ have been modeled[14] within the SSH Hamiltonian but with electrons having an effective degeneracy of 4. The model admits kinks of charges ±e, ±2e, ±3e and polarons of charges 0, ±e, ±2e, ±3e: see tables I and II of Ref. 14. In particular it is interesting to note that we find numerically,[11] as was suggested analytically,[14] that the higher effective degeneracy means that photoexcitation of a single e-h pair from the ground state leads to the production of a bound $K\bar{K}$ pair -- a neutral "polarexciton" (c.f. cis-$(CH)_x$) rather than the free $K\bar{K}$ pair and breather found in 2-photon excitation (c.f. trans-$(CH)_x$).

Decay of a Photoexcited Kink or Polaron

So far we have considered direct photoexcitation across the full band gap. In the presence of kinks and polarons sub-band edge photoexcitation is possible: (a) A single polaron has rest energy $\sim 2\sqrt{2}\Delta_0/\pi$ and electronic levels $\sim \pm\ \Delta_0/\sqrt{2}$ from midgap. Photoexcitation from the lower to the upper polaron level adds $\sim\sqrt{2}\Delta_0$ so that the excited polaron has energy $\sim 2.3\Delta_0$ above the ground state. Photoexcitation of a polaron leads[11] to $K\bar{K}$ and breather production; (b) Photoexciting from the kink midgap state to the conduction band edge gives the electronic configuration of a kink and a polaron, but only adds energy Δ_0 which is insufficient for both. We indeed find[11] that an oscillating bound state of kink and polaron is produced with no breather excitation.

FIGURE 4 Photoexcitation into the intra-gap impurity level associated with a negatively charged site impurity. ($V_0/\Delta_0 \sim 2.5$). After 0.5 psec a trapped anti-kink ($\bar{K}_T$) and propagating kink have evolved with a dynamic hole polaron (P). r_n, s_n defined in text. (See Ref. 16).



Bond and Site Impurities

In view of the disorder of most conducting polymers, it is clearly important to study the influence of defects in the SSH model. We have investigated both single site and single bond defects.[15] Detailed results will be presented elsewhere,[16] but two conclusions are especially interesting: (i) Photoexcitation in the presence of impurities. A bond defect $[(-1)^n W_0(c_n^+ c_{n-1} + h.c.)$ added to (1)] does not destroy e-h symmetry and photoexcitation results in $K\bar{K}$ and breather production (nucleated at the defect) in qualitative similarity to the pure chain.[2] However a site defect $[V_0 c_n^+ c_n$ added to (1)] does break symmetry and photoexcitations into the intra-gap impurity level or across the gap have a variety of decay channels.[16] But in all cases free and impurity-trapped kinks are produced with additional intra-gap (and ultra-band) time-dependent localized electronic states. A representative example is shown in Fig. 4; (ii) Electron-phonon renormalization. The impurities induce localized electronic states even in the absence of electron-phonon coupling, but this coupling is, as emphasized by Anderson,[17] responsible for finite Franck-Condon renormalizations (unlike for extended states) which may be catastrophic. A striking example here is for bond defects where we find[16] that intragap defect states are less localized with increasing W_0 for sufficiently large W_0, and may even become extended, being compensated by new ultra-gap localized states.

SUMMARY

Using a variety of examples we have shown that the adiabatic dynamics of the SSH electron-phonon model typically exhibits strongly coherent anharmonic excitations, e.g. "breathing" modes. We have emphasized situations, e.g. photoexcitation, in which the energy input is high. Breather generation with spallation neutrons should also be considered, as should thermal production in materials with narrower band gaps. Persistent, localized breathers will also be typical in the presence of "confinement" mechanisms -- whether due to electron-phonon interactions as in cis-$(CH)_x$ (or polythiophenes, polypyrroles, poly(para)phenylenes, etc.) or 1-photon excited polyynes, or due to electron correlations, interchain coupling, strain coupling, damping,[7] etc.

Assessing the relevance of our results for photoinduced photoabsorption experiments[12] awaits further data (for a range of materials) including: psec experiments for "mid-gap" absorption; 2-photon and luminescence studies; isotope dependence, including vibronic fine structure; sensitivity to the exciting laser energy (hot electrons and bottlenecks[16]); we emphasize that indirect kink and breather generation and an Urbach edge are possible from intrinsic (polarons not kinks) and extrinsic (impurities) intra-gap states without quantum fluctuations. We have also seen that bond defects in the SSH Hamiltonian can be susceptible to unusual Franck-Condon renormalizations.[17]

A central remaining theoretical issue is the possibility of complementary roles for strong electron correlations and nonlinear dynamics. Even for short finite polyenes, where a persuasive scenario based on elementary excited correlated states has been advocated,[18] we find[16] that "breathing" dynamics may play and important role.

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