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TITLE: SOLITONS IN SYNTHETIC AND BIOLOGICAL POLYMERS

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SOLITONS IN SYNTHETIC AND BIOLOGICAL POLYMERS

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1. INTRODUCTION

Nonlinear science has, in recent years, begun to receive truly interdisciplinary attention and to involve a supporting interplay of analysis, computation and experiment. Most of the problems being addressed have a long history but are now benefiting from this new interdisciplinary view. The synergistic impact of computers plays an increasingly important role and there are some new concepts --solitons, topology, "universal" routes to chaos and its characterization, pattern selection and evolution, etc. Significant advances have occurred in our appreciation for the consequences of strongly nonlinear phenomena and our ability to experimentally detect them. In particular the "soliton paradigm"¹ has acquired, in the space of a decade, an astonishing list of applications across the natural sciences. Our focus here is only a small subset of these applications but already vast: namely applications in solid state materials and of those primarily low-dimensional examples (weakly coupled chains or layers). Furthermore, we will not discuss any problems arising in nonlinear diffusion equations, although these are fundamental in their own right for descriptions of reaction-diffusion systems, interface dynamics, nerve-pulse propagation, etc.²

Given the biophysical emphasis of this conference, our main concern is to indicate points of contact with the lessons which have been learned (sometimes painfully) in solid state and statistical physics over the last few years. To date only limited

cross-fertilization has occurred between the nonlinear problems in the synthetic and biological literatures. Yet the parallels can be striking at all levels - mathematical equivalences and computational approaches and, even more importantly, phenomenological implications and suggested experimental probes. Since space is limited we can mostly only list some primary soliton concepts and material applications and give a guide to the relevant existing literature, whilst indicating potential applications in biophysical contexts (§§3-5). By way of illustration we will give a little more discussion of nonlinear effects at phase transitions (§3) and in certain synthetic polymers (§4). The relevant biophysical literature is very well described elsewhere in these proceedings, which we will therefore merely reference as appropriate.

2. SOLITON CONCEPTS AND APPLICATIONS

Good introductions to soliton mathematics include refs. 3-5. Solid state and statistical physics applications continue to expand rapidly but representative examples and surveys can be found in refs. 1,2, 6-8. With regard to potential applications in biophysics we would particularly emphasize the following general points:

- (i) Solitons in one space dimension and with a small number of degrees of freedom at each "site" of a notional lattice, occur in only three forms -- kinks, pulses and envelopes.³⁻⁵

The first two are clear and typified by kink solutions to the sine Gordon (SG) and related equations, or pulse solutions to the Toda lattice or Korteweg-de Vries (KdV) equations. Both are solitons in that they are spatially localized but can propagate without change of shape. Indeed the pulse is just a derivative of the kink. Their physical origins can be very different, however, since their topologies are quite distinct -- the kink interpolates between two unconnected degenerate ground states whereas the pulse does not. Kinks are familiar as dislocations or domain walls, pulses as water wave solitons. Envelope solitons (often called "breathers" or "bions") are sometimes found a more difficult concept and yet in many ways they represent the most important and wide-spread class. Here the envelope prescribes the localized soliton structure which may be moving or not, but there is an additional periodic oscillation of the envelope amplitude or internal carrier wave. In these cases four (not two) canonical variables are needed to specify the soliton's state. Breathers are so important because they can interpolate between linear modes and extremely nonlinear structures such as kinks. Similarly they can always be reached by a suitably high order anharmonic expansion in the linear modes. Thus they lie naturally at the center of controversies in many fields disputing the advantages of

conventional anharmonic perturbation theory versus particle-like soliton gas phenomenologies -- as with the wave-corpuscular nature of light it all depends on the property to be described (and the strength of the nonlinearity). The SG and nonlinear (cubic) Schrödinger (NLS) equations are typical sources of breathers.

(ii) Solitons in nature will rarely if ever be close to the precise objects conceived by mathematicians because of perturbation and/or intrinsic terms which destroy exact integrability of the governing equations of motion (as in the ϕ^4 equation used in §3.) Nevertheless, the basic balances which are present in true soliton equation can act to "label" generic types of soliton systems (and the solitons which follow) and also are often very robust against quite severe perturbations. Thus the generic ingredients of the SG

$$\phi_{xx} - \phi_{tt} = \sin \phi \quad (1)$$

and related equations (ϕ is a field variable; x and t are space and time) are wave-like propagation in the presence of a periodic local potential -- the latter is motivated from a "pinning", "locking", "registering" potential, depending on the physical origin^{1,6,8} (dislocations in a metal, domain walls in a ferromagnet or ferroelectric, fluxons on a Josephson transmission line, discommensurations in a surface epitaxial layer, charged dislocations in a charge-density-wave material, etc.). The KdV equation

$$\phi_t + k\phi\phi_x + \phi_{xxx} = 0 \quad (2)$$

(k constant) characteristically combines weak nonlinearity and weak dispersion. In the case of the NLS equation

$$\psi_{xx} + i\psi_t + k|\psi|^2\psi = 0 \quad (3)$$

we always have in mind slow, long-wavelength self-modulation of an almost monochromatic wave with linear dispersion and weak nonlinearity. In eqn. (3), ψ is a complex (i.e. two-component) field and k is a positive constant for most cases of interest. (The negative sign generates quite different solitons and has fewer physical applications).

(iii) The stability against many perturbations (e.g. damping mechanisms, driving fields, impurities, grain boundaries, lattice discreteness, etc.) has naturally lead to the prevalent notion of solitons as "particles", i.e. collective modes, responding to perturbations primarily through a collective co-ordinate describing a center-of-mass motion.^{1,3-8} While this view has much validity and leads to the importance of solitons for dynamics (e.g. as fluxons on Josephson transmission lines), the rigid, dynamic

particle picture should not be used too literally. The equal importance of "solitons" for energetics, structure, statistical properties, etc., does not necessarily require simple dynamics. Thus the deformable nature of solitons (since they are not point particles) should always be considered. Again the effects of a discrete lattice are inherent in solid state and biological applications and act to impede or even freeze ("pin") soliton motion -- indeed this pinning is the origin of a low frequency resonance identified by SCOTT in the model of alpha-helix proteins discussed in these proceedings by LAYNE and LOMDAHL and SCOTT. There are many other examples in solid state -- the Peierls-Nabarro pinning barrier is well-documented in the theory of dislocations, for example. More recently solitons appearing as "discommensurations" in incommensurate solid state phases can (on very long timescales) be randomly ("chaotically") trapped by a lattice pinning potential which overcomes long-range repulsions between discommensurations.

It is particularly important to realize that transport can involve solitons fundamentally without implying simple ballistic or diffusive soliton motion, even though this is the most popularized mechanism -- generalizing the familiar examples of slippage in metals via the motion of dislocations, or fluxon propagation on Josephson transmission lines, or soliton propagation along optical fibers. Hopping motion (of solitons or charges they may carry) can be of equally practical concern (as is likely in the conducting polymers of §4, where solitons appear as various kinds of "polarons", familiar in their own right). In other cases transport only occurs when solitons overlap sufficiently; in such cases an independent soliton picture is quite irrelevant.

(iv) Some of the above remarks will have made it clear that nomenclature is unsettled. The mathematician's soliton equations have very precise meaning related to their integrability. This is directly connected with the remarkable soliton properties of collision stability, S-matrix factorability, Hamiltonian separability etc. One extremely striking consequence is the ability to quantize solitons exactly and construct quantum statistical mechanics. It is now appreciated that this intimately connects soliton systems to those solvable by "Bethe Ansatz" techniques -- indeed it is clear that, via appropriate mappings, quantum soliton systems can be related to almost all exactly solvable problems in many-body and statistical physics and field theory (mostly one-dimensional quantum or two-dimensional classical systems). The importance of exactly solvable models (defining anchor points of precise knowledge about which a fabric of intuition and approximations can be woven) clearly gives true soliton systems a major unifying importance. However the term "soliton" has come to be used much less precisely in most physics literature -- signifying any spatially localized, finite energy, dynamic or static,

intrinsic order-parameter configuration (often termed an inhomogeneous state). Stability is usually guaranteed on topological grounds; non-topological solitons (e.g. the pulses or envelopes above) are stabilized by dynamics or external influences (e.g. impurities, boundaries).

Hopefully nomenclature will evolve to label a polaron a polaron or a vortex a vortex, etc. but the "soliton" label does serve a useful purpose to focus on an important nonlinear paradigm. It is this paradigmatic sense for solitons which is most relevant in both solid state and biophysics.

(v) Applications of paradigmatic (and in a few cases nearly literal) solitons in solid state all center on transport, energetic, or structural properties. The solitons may be excitations (thermal, quantum, critical fluctuations) or ground state structures. In some cases they may be much less populous than linear modes and yet, for appropriate physical properties (e.g. scattering functions, transport) much more important. Earlier references will indicate the immense scope for the soliton paradigm, but the most direct and striking solid state ⁶⁻⁸ examples have probably occurred in low-dimensions. Examples include Josephson transmission lines, certain magnetic chain materials, mercury chain compounds, fast-ion conductors, structurally distortive compounds, etc. There are many other potential applications but the most intensive investigations currently emphasize electronically and magnetically active polymers and charge-transfer salts. ¹⁰ Examples include spin- and charge-density-wave materials (KCP, TCNQ salts, (TMTSF)₂PF₆, NbSe₂, NbSe₃, ...), piezo- and pyro-electric polymers (PVF₂), ² and conducting polymers (§4).

It is natural to look also for applications in biology, prompted both by the frequently low-dimensional (polymer) settings and by basic chemical and structural similarities with low-dimensional solid state systems. For instance, the hydrogen bond plays a pervasive role in biophysics which leads us to expect similarities with structurally phase-transforming materials such as ferroelectrics (there are even some quasi-1-dimensional examples such as CsD₂PO₄, acetanilide, nylon-66, certain polydiacetylenes). Many of the questions posed in DNA are essentially ones of (linear and nonlinear) lattice dynamics (albeit in complicated lattice structures) which have been faced recently in a number of structurally transforming materials (see §3). Ionic and protonic transport mechanics as well as charge-transfer processes are increasingly discussed in biophysics literature but are extremely similar to processes in fast-ion conductors or charge-transfer compounds. Peptide (H···N-C=O) units occurring in ordered (e.g. α -helix proteins or synthetic polypeptides chains) or disordered (e.g. globular proteins) environments have been discussed

extensively in terms of self-trapping of lattice vibrational energy ("excitons") because of nonlinear exciton-phonon coupling. As we shall see this self-trapping produces "solitons" of great similarity to self-localized electrons ("polarons") in synthetic metals (§4), where electron-phonon coupling operates. We list further nonlinear similarities between synthetic-and bio-polymers in §5.

3. NONLINEAR LATTICE DYNAMICS AND STRUCTURAL PHASE TRANSITIONS

Strong nonlinearity is important in all types of phase transitions^{1,6-8} -- from traditional first order (where "droplets" are relevant) and continuous (below) transitions to more recently considered commensurate-incommensurate (below), 2-dimensional melting and martensitic classes. We briefly discuss one class which should have biophysical relevance:

Order-Disorder and Displacive Transitions.

Observing structural transformations in ferro- (and anti-ferro-) distortive (as well as ferroelectric) crystals has a long history, but the role of intrinsic nonlinearity has only recently begun to be confirmed experimentally or theoretically. Key experimental observations may be summarized as precursor effects (mixed or heterophase fluctuations; the occurrence of clusters of the "wrong" phase for $T > T_c$, the critical temperature), central peaks, and soft modes. Emphasizing order-parameter structures (such as short-range clusters) represents a complementary concern to that of "critical exponents" and can be a considerable conceptual tool when visualizing critical or sub-critical dynamics and constructing theoretical frameworks. The temperature regime where nonlinear (cluster) effects are most pronounced is greatest in lower dimensions.

The simplest model Hamiltonian we might consider has the familiar double-well on-site potential (Ginzburg-Landau expansion) form. In one dimension (1-d) we write this as:

$$H[U] = \sum_{i=1}^N \left[\frac{1}{2}m \left(\frac{\partial U_i}{\partial t} \right)^2 + \frac{1}{2}AU_i^2 + \frac{1}{4}BU_i^4 + C(U_{i+1} - U_i)^2 \right] \quad , \quad (4)$$

where m is particle mass and the order parameter U_i might be, e.g., rotation, displacement (for example of a light mobile lattice relative to an immobile heavy ion or fictitious reference lattice). For simplicity we take $A < 0$, $B > 0$, $C > 0$ and all constant. We then have a crude model of a uniaxial unstable lattice system with harmonic ferrodistorptive coupling and local double-well potentials at each lattice site (Fig. 1a). At high temperatures we can expect that the particles will oscillate above the double-well

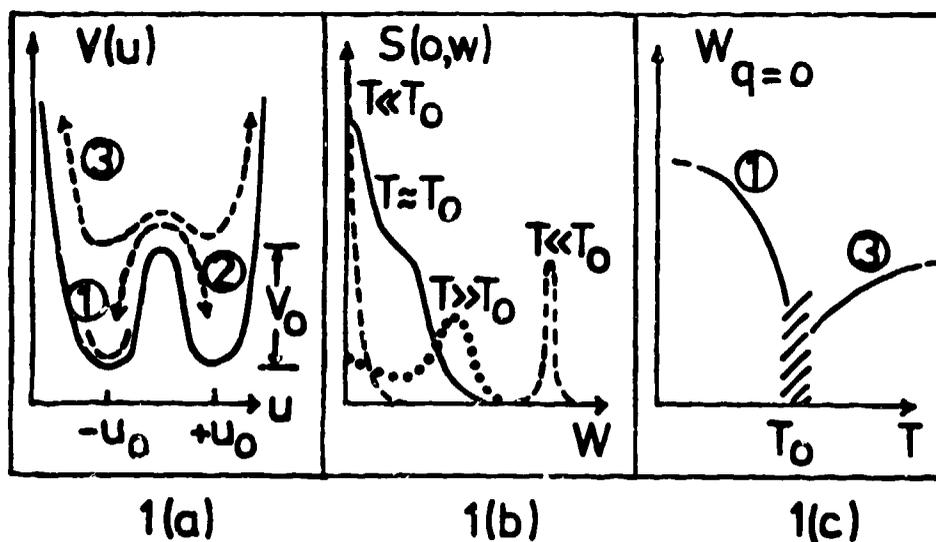


Fig. 1 (Schematic). (a) Local ϕ^4 potential in Hamiltonian (4). Stable modes are 1) low-T "phonons", 2) domain walls, 3) high -T phonons; (b) soft mode-central peak characteristics for ϕ^4 model; (c) softening of $q = 0$ phonon (incomplete in 1 - d). Hatched region may sustain 1) and 3). Type 2) responses appear for $T \lesssim T_0$, yielding a central peak.

structure with approximately uniform probability distribution but at low temperatures they will preferentially occupy one of the degenerate wells. Notice that we do not include a mean-field "Ginzburg-Landau" temperature dependence in A of the form $A = a(T-T^0)$. We have in mind situations where T^0 is a high mean field scale temperature and we operate at $T \ll T^0$. The model will then have a true transition temperature T^* quite independent of T^0 (in fact $T^* = 0$ in 1-d). There is no difficulty including thermodynamic field dependences in the coefficients and this is sometimes essential -- as in mean field descriptions of multiphase equilibria or discommensuration defects. Model (4) is of course highly oversimplified in several respects. It is, however, able to isolate dominantly nonlinear effects and considerable generalizations are possible, particularly within molecular dynamics simulations.

If variations in U are small on the scale of a lattice spacing $\ell \equiv x_{i+1} - x_i$, then a continuum representation is valid: $U_i - U_{i+1} \cong \ell^2 (\partial U / \partial x)^2$. This situation will hold when the intersite coupling is strong, $C > |A|$, and we term it the "displacive" limit. Kink widths will be $\gg 2$ and the kink energy E_K will be an "activation energy" for $k_B T < E_K$. The opposite regime, $C \ll |A|$, can be termed "order-disorder"; kinks will be sharp and particles distributed with a thermal randomization and activation energy $|V|$ (Fig. 1a). As we approach this limit, the discrete lattice can severely modify the excitation dynamics. In the displacive regime we can introduce a continuum Hamiltonian density and the coupled Euler-Lagrange equations of motion for $\{U_i\}$ reduce to a partial differential equation for $U(x)$. From (4) we find

$$m U_{tt} - m C_0^2 U_{xx} - |A|U + BU^3 = 0, \quad (5)$$

where $C_0^2 = 2C\ell^2/m$ is the harmonic sound velocity for this system. We refer to (4) and (5) as the " ϕ^4 " Hamiltonian and nonlinear equation respectively.

Traditionally, a sharp distinction has been drawn between order-disorder and displacive systems. However, it is now appreciated that these are merely extremes of a general class. Indeed sufficiently close to T_c there is a crossover to universal order-disorder behavior in all cases -- as is confirmed^{6,8,11} by analytic approaches and supported by molecular dynamics simulations as well as real experiments.

Two characteristic temperatures have to be appreciated. The first is the true long-range ordering temperature -- $T_c = 0$ in strict 1-d and small for anisotropic coupled chains. A second temperature, T_0 , is not a true critical temperature but marks an incipient first order "condensation" or "local ordering" -- for $T > T_0$ particles have sufficient energy to oscillate above the on-site double well structure, whereas for $T < T_0$ they prefer to oscillate in an individual displaced well; however for $T > T_0$ $\langle U \rangle = 0$ so "clusters" of particles oscillating in the same well are separated from neighboring clusters in the other well by "domain walls" (our kinks in the 1-d problem). The temperature T_0 can be characterized in various equivalent ways. The self-consistent phonon approximation (SCPA) finds the optimal harmonic description for particle oscillations and at a temperature $\sim T_0$ predicts a first order transition from in-well to above-well oscillations. (i.e. $T_0 \leftrightarrow$ "soft mode temperature"). It is incapable of accounting for the kink solutions which are the reason for an incipient condensation only. Alternatively, one can study the single-particle probability distribution and identify T_0 with the temperature below which a double hump distribution develops. More sensitive

many-particle distributions must be studied¹¹ for isotropic higher-d. We find according to these criterion: $k_B T_0 \sim 2|V|(C/|A|)^{1/2}$. A very reasonable interpretation of T_0 is that it is the temperature at which the kink excitations become thermally unstable. To operate this criterion we need to include a "thermally renormalized" kink energy at high T. This can be accomplished approximately by comparing with static correlation function estimates, which suggest¹²

$$k_B T_0 \sim E_K(T_0) \sim 0.4 E_K(0) \sim 2|V|(C/|A|)^{1/2} \quad (6)$$

The "scaling" dependence on $(A/C)^{1/2}$ follows automatically from the displacive approximation (5).

The SCPA has enjoyed popularity as a soft mode description for displacive systems. It can indeed be successful in a substantial range of (T, ω, q) (temperature, frequency, wave-vector) space but fails in certain regimes. The SCPA replaces $-1/4|A|U_1^2 + 1/4BU_1^4$ (equ. (4)) with $1/4(-|A| + 1/4B\langle U^2 \rangle)U_1^2 = 1/4A^*(T-T_0)U_1^2$. Thus distinct sectors of excitations space (below) are omitted. Calculations of the dynamic structure factor $S(q, \omega)$ in 1-d can be interpreted to show that (i) the SCPA is valid for all T if $q \geq 2^{-1}(|A|/C)^{1/2} \propto d^{-1}$ (the kink width $2d$ increases as C/A increases); (ii) it is valid for $T \geq T_0$; the SCPA dispersion,

$$\omega_q^2 = \omega_{sm}^2 + (2C/M)(1 - \cos qd), \text{ with } \omega_{sm}^2 = (|A|/M)(3\langle U^2 \rangle / \langle U^2 \rangle - 1)$$

is only valid for $\omega_q > \omega_{sm}^*$ where ω_{sm}^* is smaller for more displacive systems (C/A increasing). Remark (iii) is the fact that there is only an incipient soft mode. In fact the strongly anharmonic regions where SCPA fails for 1-d are characterized by the dominance of kink excitations and the appearance of a central peak associated with them.

In the displacive 1-d case in particular, a quite complete phenomenology can be constructed from a knowledge of the general traveling wave solutions to the continuum equation (3), i.e. available lattice dynamic modes. The general solutions appear, see e.g. Ref. 13, in the form of Jacobi elliptic functions. The linearly stable types are illustrated in Fig. (1a). Physically, they represent (i) "low-T" or "in-well" phonons; (ii) "high-T" or "above-well" phonons ("phonon" here includes general anharmonic periodic solutions); (iii) domain-walls or kinks. These excitations give a better description of the transition region $T \sim T_0$ than the enforced harmonic modes of the SCPA. Snapshot distributions are not transparently "separable" for $T \geq T_0$ but response functions are much more so. As AUBRY has emphasized,¹³ the mean energy per unit length ϵ_0 , for the three excitations as a function of ω and q , is an important quantity. See Fig. 1 of Ref. 13.

Note the softening of $\omega(q=0)$ for low- and high-T phonons as $\epsilon \rightarrow |V|$ (Fig. 1a). It remains to relate temperature to ϵ . In a non-integrable anharmonic system equipartition of energy between modes has to be an approximate procedure. However it is known that for $q \gtrsim q_0$ (above) the available motions are essentially harmonic at all T, so that one can conjecture that the energy per particle to be associated with large amplitude anharmonic motions, $E_a(T)$, is

$$E_a(T) \approx k_B T \left[1 - q_{bz}^{-1} \int_{q_0}^{q_{bz}} dq \right] \propto (A/C)^{1/2} k_B T$$

This procedure works remarkably well in explaining the location of strong response characteristics at all T: a mode will be thermally active (with signature in $S(q,\omega)$) if $\epsilon(\omega,q) < E_a(T)$. Also note that $E_a(T) \approx |V|$, which from Fig. 1 of Ref. 13 we expect to be associated with the soft mode-central peak onset, implies $T \approx T_0 \approx E_k(T)$ as suggested in (6). To include broadening of resonances in $S(q,\omega)$ we need in general to improve this independent excitation gas phenomenology by including interactions.

Dynamics correlation functions (and the Fourier transform $S(q,\omega)$) cannot be calculated analytically in the strongly anharmonic region, however the combination of phenomenology (above) and molecular dynamics leads unambiguously¹¹⁻¹³ to the picture shown schematically in Fig. 1. At low T most motions are low amplitude, and response characteristics of an extended periodic mode ("low-T phonon") appear. This softens as $T \rightarrow T_0$ and is replaced at higher T with the "high-T phonon" response. The kink excitations give rise to the very different central peak response. This appears as T is lowered as a broad, low intensity resonance around the incipient soft mode temperature T_0 and becomes sharper and more intense as T is further lowered, diverging at $T = 0$ (the 1-d critical temperature). The central peak appears strongly at $q = 0$ and disappears for $q \gtrsim q_0$. It is solely due to the kink excitations in the simpler models, and should be thought of as a dynamic and incomplete (i.e. having width in ω and q space) Bragg peak. The central peak width is partly determined by the inverse average kink separation and effective kink velocity: for $T \approx T_0$ there are numerous stable, mobile kinks but none at $T = 0$.

In isotropic 2- or 3-d, $|T - T_0|$ is substantially smaller than in 1-d and therefore it has been difficult to observe cluster properties experimentally: an excellent history is given by MULLER.⁸ Success has come recently using EPR measurements which discriminate between the fast phonon ($\sim 10^{-11}$ sec) and slow cluster ($\sim 10^{-7}$ sec) timescales. Real anisotropic materials such as polymers offer special advantages of a substantial T_0 and large $|T - T_0|$.¹⁴ It is important to emphasize that clusters are most important

physically because of their impact on dynamics and timescales (as with "critical slowing down"). Central peaks, clusters, and slow time scales can have other origins,¹¹ for example static or dynamic impurities which may trap intrinsic clusters or induce similar distortions -- clearly these intrinsic and extrinsic mechanisms are not mutually exclusive but part of a single unified picture.

There are now many fine examples of structurally transforming materials including hydrogen-bonded ferroelectrics (e.g. KH_2PO_4).¹¹ Quasi-one-dimensional examples include KCP, TTF-TCNQ, TaS_3 ,² NbSe_3 , CsH_2PO_4 (see refs. 10).

In biological contexts one can anticipate numerous examples of ferroelectric, distortive and melting phase transitions -- some examples have been discussed elsewhere.¹⁵ One of the most topical discussions centers on transitions between structures in DNA, e.g. the A and B phases.¹⁵ It is not our intention to describe the existing literature. This is already reviewed elsewhere in these proceedings. However, we do emphasize that the lessons learned in the conventional solid state contexts will surely be paralleled in biopolymers, especially because of their effective low-dimensionality. We must of course recognize that the "crystals" involved are extremely complex, and information (theoretically or experimentally) on lattice structure, lattice dynamics, mode softening, etc., is still at a relatively primitive stage.¹⁵ Nevertheless, we can expect that a proper appreciation of the complementary roles of intrinsic local, large-amplitude conformational distortions and quasi-harmonic extended modes and extrinsic defects will be achieved much more rapidly if the history of soft modes and central peaks is appreciated in the biophysics community.

Finally, we briefly mention one other general class of phase transitions in solid state contexts where strong nonlinearity has been extremely important, namely commensurate-incommensurate transitions.⁹ These occur in many situations where there are competing interactions and periodicities and the ground state can be intrinsically inhomogeneous. Specifically, the system may homogeneously accommodate one interaction ("be commensurate") for some extended regions of space but bridge these regions with incommensurate defects ("discommensurations"), often described by solitons of the SG variety, eqn. (1). The density of these defects tends to zero as a transition is approached from the incommensurate side by varying temperature, pressure, etc. This situation had achieved little attention in solid state physics until the last few years, but is in fact very common -- the competing interactions might be an underlying lattice spacing, spin- or charge- or mass-density-wave period, etc., and the discommensurations might appear in the mass density, spin density, charge density, helical spin period, etc. Theoretical and experimental tools have sharpened rapidly

and there are now many excellent observations of commensurate-incommensurate transitions and even of the discommensurations themselves. Pinning of the discommensurations by the discreteness of the lattice or by extrinsic defects can even lead to random ("chaotic") ordering of the discommensurations and to many nearly equivalent metastable states. Metastability and hysteresis are typical of this class of phenomena. It is very easy to imagine competitions between interactions in biophysical contexts which should fall into this general class and lead to intrinsic structural inhomogeneities. Indeed primitive arguments along these lines have already been put forward.¹⁶

4. SOLITONS IN POLYACETYLENE AND RELATED MATERIALS

Many organic and organo-metallic polymeric materials represent fine settings for the soliton paradigm with structural, energetic and transport consequences.¹⁰ A particular example, which has received intensive theoretical and experimental attention is polyacetylene, $(CH)_x$, synthesized for example as a film which can be doped to near-metallic conductivity levels.¹⁰

We emphasize that the research effort devoted to $(CH)_x$ is driven primarily by its fascinating technological potential.^x Nevertheless it is also fair to claim that soliton concepts have modified the conceptual basis within which experiments and theories are designed in the strongly interdisciplinary field of "conducting polymers", which includes $(CH)_x$. In this brief report, we wish to develop the theoretical status^x of $(CH)_x$ modeling, because it illustrates many general features of soliton research such as the equivalences which solitons reveal between disparate physical contexts: here we will make use of connections with model field theories which are found¹⁷ to have the same kink- and polaron-soliton states as predicted in $(CH)_x$. Likewise the exact solubility of these field theories (using soliton techniques) leads naturally to explicit statements about the structure and excitations of a wide range of other polymer models. Soluble models are of course useful here, as elsewhere, because they can bring physical clarity to complex features which are essentially preserved (e.g. because of symmetry) when exact solubility is not possible.

Descriptions of $(CH)_x$ from a chemical or physical perspective can be found elsewhere.^{10x} Briefly, the major synthesis effort is now devoted to controlled synthesis-morphology-property relation studies, both of $(CH)_x$ and many other members of the growing family of conducting polymers. It is unlikely that $(CH)_x$ will survive as the example of prime technological interest, but its extreme simplicity for modeling purposes has meant that it has played a primary stimulant role for exciting experiments and theories. Even for $(CH)_x$, new syntheses have emerged ranging from almost totally amorphous^x to near single crystal forms.

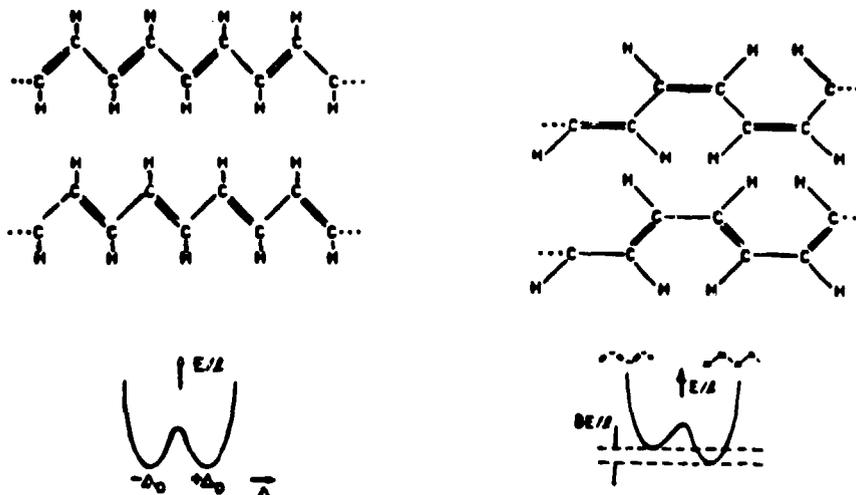


Fig. 2. Schematic bond structures for (a) trans-(CH)_x and (b) cis-(CH)_x. Also included are schematic plots of energy per unit length vs. band gap parameter Δ for uniform Δ . Note the degeneracy in (a) corresponding to the two equivalent ground state conformations. In (b) the lack of degeneracy, $\delta E/2$, has important consequences (§3).

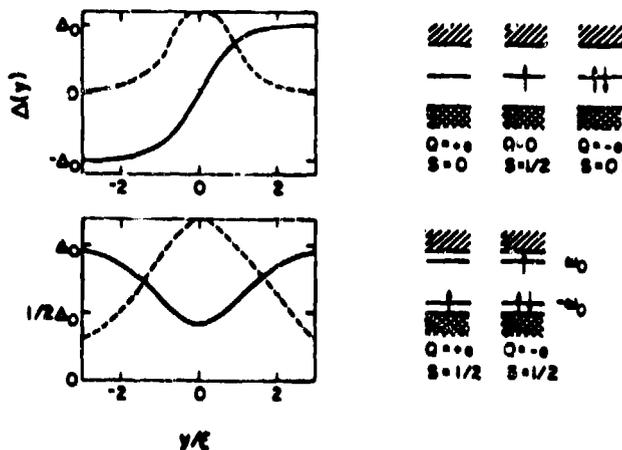


Fig. 3. Intrinsic defect states in trans-(CH)_x and associated electronic levels for (a) a kink, (b) a polaron. Dashed lines indicate localized state probability densities. Q and S denote charge and spin, respectively, and the length scale $\xi_0 = v_F/\Delta_0$. Analytic formulae for the profiles and continuum state phase shifts are given in ref. 17. From the latter we find that a kink removes 1 state from both the conduction and valence bands, whereas the polaron removes 2. This immediately explains the Q-S relations.

For our present purposes, we wish merely to consider^{17,18} an idealized $(\text{CH})_x$ single chain and introduce some primitive chemical language for the two isomers of $(\text{CH})_x$, which we term cis and trans for simplicity. The situation is summarized in Fig. 2. A uniform chain of (CH) monomers would have one unpaired π -electron per monomer (σ orbital bands lie far from the Fermi level and are not important here) and the polymer should be a conductor. The uniform chain is however unstable toward dimerization into the trans-(most stable) or cis-isomeric forms in which all electrons are saturated giving an insulator. Precisely this situation is described in solid state as a Peierls-Fröhlich¹⁸ distortion, which for a half-filled π -band is a dimerization.

A crucial difference between trans- and cis- $(\text{CH})_x$ is the presence of ground state degeneracy in the former, as depicted in Fig. 2a. This will lead to the possibility of "free" kink-soliton states in trans- $(\text{CH})_x$ about which much has been written.^{16,17,18} In contrast only bound kink-antikink (polaron)-solitons¹⁷ are possible if there is no such degeneracy. The idea of conformational defects should be clear as distortions of bond lengths between possible ground state conformations -- either the same ground state or different ones (as for trans- $(\text{CH})_x$). Imagine rupturing a double bond and separating the unpaired spins, leaving free radicals or, upon charging, carbanions or carbonium ions. Indeed the concept of $S-\frac{1}{2}$ conjugation defects in polymers is not at all new. The main addition from the soliton viewpoint is that the conformational defects are typically extended over many C-C lengths. This has important consequences for energetics and dynamics. The conformational defects are of course accompanied by defects in the electronic density as indicated below.

SU, SCHRIEFFER and HEEGER (SSH)¹⁸ introduced a simple tight-binding Hamiltonian for a pure, isolated trans- $(\text{CH})_x$ chain:

$$H = - \sum_{n,s} [t_0 + \alpha(U_n - U_{n+1})] [C_{ns}^+ C_{n+1,s} + \text{h.c.}] \quad (7)$$

$$+ \frac{1}{2} K \sum_n (U_n - U_{n+1})^2 + \frac{1}{2} M \sum_n \dot{U}_n^2 .$$

Here C_{ns}^+ creates an (π) electron of spin s at site n , U_n is the displacement of the (CH) unit at the n th site from its undistorted position, and M is the mass of a (CH) unit. Although very primitive this model has some very interesting properties because of the coupling (α) between the electronic and phonon degrees of freedom. There are of course additional effects neglected in (7) which can be quite important, e.g. interchain coupling or electron correlations. These are now the subjects of intensive studies¹⁰ but we will not consider them here.

For a half-filled π -conduction band, SSH demonstrated in the adiabatic limit that (7) is spontaneously unstable towards one of two degenerate ground states, corresponding to the Peierls-dimerized A and B configurations in Fig. 2a -- distinctions need to be made between even and odd length chains and between sizes $4N$ and $4N+2$ (N integer). In addition, they concluded numerically that excitations or, for electron concentrations close to half-filling, intrinsic defect states in the dimerized pattern appear as kink- or polaron-like conformational distortions, with important spin-charge relations and consequences for doping or photo-generation of carriers. The ground state and excitation structure follow naturally in a continuum theory of (7) which is extremely accurate in the case of $(CH)_x$.

The continuum limit of (7) has been given by several authors and in a mean-field adiabatic approximation results in the following equations for the static 1-particle electron wave-fns.

$$\begin{aligned} \epsilon_n u_{ns}(y) &= -iv_F \frac{\partial}{\partial y} u_{ns}(y) + \Delta(y)v_{ns}(y) \\ \epsilon_n v_{ns}(y) &= +iv_F \frac{\partial}{\partial y} v_{ns}(y) + \Delta(y)u_{ns}(y) \end{aligned} \quad (8)$$

and the self-consistent gap equation

$$\Delta(y) = \frac{-g^2}{\omega_Q^2} \sum'_{ns} [v_{ns}^*(y)u_{ns}(y) + u_{ns}^*(y)v_{ns}(y)] \quad (9)$$

Here y is the continuous variable, $\omega_Q^2/2g^2 = K/4\alpha^2$, $v_F = 2\ell t$ (ℓ is the undistorted lattice constant) $g = 4\alpha(\ell/M)^{1/2}$, u and v are the two components of the electron spinor field linearized around the Fermi surface, and $\Delta(y)$ is proportional to the staggered lattice displacement $\tilde{U} = (-1)^n U$: $\Delta(y) = 4\alpha\tilde{U}(y)$. The prime in (9) indicates summation over occupied states.

The problem posed by (8) and (9) is closely connected with "soliton" problems in many other areas, e.g. superconductivity and nonlinear optics. Alternatively, a simple transformation casts (8) into the form of single particle Dirac equations for massless fermions in a potential $\Delta(y)$, and this problem can be shown to be equivalent to one example of a soluble field theory of interacting massless fermions. Soliton-like properties permit the construction of analytic, closed-form expressions for all static configurations -- the dimerized ground state, a kink (K) or a polaron (kink-antikink, KK , bound state). These are illustrated in Fig. 3. The kink and polaron should be viewed as localized conformational defects with associated localized electronic levels. Note the unusual spin-charge relations for K or \bar{K} , Fig. 3.

There a number of generalizations of the soluble model outlined above. One important family of soluble models was introduced by BRAZOVSKII.¹⁹ The ordered A=B alloy and the SSH model with broken ground state degeneracy (as in cis-(CH)_x) represent two popular members of the family. The 50:50 alloy^x is intriguing because of the possibility of a mechanism for fractionally charged kink-solitons.²⁰ Here Hamiltonian (7) is modified by an alternating atomic orbital on-site energy. Materials such as (poly)carbonitrile are candidates for this model.

The SSH model with groundstate symmetry-breaking (c.f. Fig. 2b) is of extremely general importance: other Peierls-distorted systems with multiple ground states are certainly possible but they are far outnumbered by materials with a unique ground state plus one or more metastable conformations. Some of these have potential as practical conducting polymers (e.g. polypyrroles, poly(para) phenylenes, polydiacetylenes, polythiophenes). The central point is clear and independent of specific modeling. Namely, the energy difference between the unique ground state and any metastable conformations will provide a linear "confinement" potential - imagine trying to create kink and anti-kink and to separate them. This means that kinks cannot be "free" (on the pure chain) and must bind in pairs, i.e. as polarons. The bi-polarons (i.e. two self-trapped charges) will be wider than polarons but not unstable as in trans-(CH)_x. This general idea has now been appreciated in modeling of the more complicated polymers above.²¹ Note that bipolarons can have the same signatures as charged kinks, i.e. charged but spin-0. An explicitly soluble model (using the same soliton techniques as earlier) can be constructed^{17,19} which demonstrates all the confinement features. Introducing $\Delta(y) = \Delta(v) + \Delta_c$, where Δ_c is a constant symmetry-breaking term, results in analytic polaron solutions which have precisely the same functional form as for the trans model (7) but with location of the gap states (c.f. Fig. 3) at $\pm i\omega$ with $\omega/\tilde{\Delta} = \cos\theta$ and $\gamma \tan\theta = (\pi/4)(n^+ - n^- + 2)\theta$, with $\gamma = \Delta_c/\lambda\tilde{\Delta}_0$, n^\pm the occupations of the gap states, and $\lambda^{-1} = \pi v_F \omega_Q^2 / 2g^2$ (a dimensionless coupling constant).¹⁷

The Hamiltonian (7) describes a situation of inter-molecular electron-phonon coupling. In many organic and organo-metallic materials, intra-molecular modes are much more numerous and can be at least as important. In fact inter- and intra-molecular mode couplings may well be in competition and this has lead to suggestions²² of interesting phase diagrams where they are operative together -- both in terms of the allowed ground states and excitations. The simplest model of electrons coupled to intra-molecular phonons is perhaps the "molecular crystal model", familiar²³ in solid state for many years, which in 1-d takes the form²⁴

$$\begin{aligned}
H = & \frac{1}{2}M \sum_n \dot{y}_n^2 + \frac{1}{2}M\omega_0^2 \sum_n y_n^2 \\
& - J \sum_{n,s} (a_{n,s}^+ a_{n+1,s} + a_{n+1,s}^+ a_{n,s}) \\
& - A \sum_{n,s} y_{n,s} a_{n,s}^+ a_{n,s}
\end{aligned} \tag{10}$$

In (10), y_n is a normal coordinate usually referring to some internal vibration of a molecular unit at the n -th site, with an associated mass M and natural frequency ω_0 . $a_{n,s}^+$ ($a_{n,s}$) creates (annihilates) an electron with spin s at the n -th site. The four terms in (10) represent, respectively, the lattice kinetic energy, the vibrational energy of the molecular lattice, the electronic kinetic energy associated with moving an electron between (nearest neighbor) sites, and the coupling of the electron and lattice (phonon) motions.

It will be clear how the terms inter- and intra- arise from a comparison of (7) and (10). We have contrasted these models in detail elsewhere.²⁴ Here we note only that (i) the molecular crystal model was developed²³ explicitly as a generic model for "self-localized (or trapped)" electrons, i.e. polarons, and (ii) despite the explicit differences between (7) and (10), the polarons which they can support are quite similar. In fact, in the weakly-bound polaron limit (i.e. low-amplitude, spatially extended), the two polarons become identical and are described (in a continuum theory by the NLS equation (3)).²⁴ Even more interestingly we note that the same tight-binding model (10) can be, and has been, applied to the self-localization not only of electrons but also magnons and vibrational quanta (sometimes called "excitons"). In this case a_n^+ creates a magnetic or vibrational quanta and the constant A_n refers to the strength of magnon-phonon or exciton-phonon coupling. Note that there is a difference of statistics between electrons (fermions) and magnons or excitons (bosons).

We stress this last point because precisely the same model Hamiltonian has recently been proposed in a biological context without recognizing the very relevant solid state polaron literature -- and therefore the possibility of short-circuiting analysis, the recognition of pitfalls, and the choice of appropriate experiments. We refer to the subject of self-localized excitations ("solitons" of the NLS variety) due to exciton-phonon interactions in polypeptide chains, i.e. $H \cdots N - C = O$ coupled units. The coupling of the longitudinal phonons to peptide vibrations has been suggested both in an inter²⁵ and intra²⁶ form. The biological

contexts may also have lessons for the synthetic ones. For example polypeptide chains occur as 3 coupled strands in α -helix proteins²⁵ (myosins, e-coli, mitochondria, etc.) and the biological discussions have also focussed attention on synthetic polymers with 2-coupled strands (e.g. acetanilide)²⁶ and nearly isolated strands (e.g. in nylon-66 and certain polydiacetylene side groups). The coupling between chains has revealed a variety of chain-sharing localized excitations. The question of interchain coupling is only now receiving corresponding attention in materials such as conducting polymers (above). Again the combined presence of inter- and intra-molecular phonon coupling has so far been discussed for static excitations in the solid state literature,²² whereas the more interesting question of dynamics has been motivated by the biological concerns -- leading, for example, to the suggestion²⁶ of intra-molecular coupling acting as a transient (picosecond scale) self-trapping mechanism nucleating activity in the inter-molecular modes on a longer time scale. This should have wider applications. On the other hand, the effect of disorder (of the lattice locations and/or site energies in (10)) has already been considered in solid state situations with electron- (or magnon- or exciton-) phonon coupling -- e.g. in amorphous semiconductors. From these studies it is already clear that disorder alone can lead to self-localization of the elementary excitations as well as to extended states. (This is the famous theory of "Anderson localization")²⁷ Since the coupling to phonons can also lead to self-trapping^{23,28} (less readily in $d > 1$ than $d = 1$), these effects tend to reinforce each other, and there has been a protracted "chicken-and-egg" discussion about their relative importance.²⁸ This history will necessarily be repeated in the descriptions of coexisting localized and extended stationary states in globular (disordered) proteins, such as the lysozyme discussed by LOMDAHL. The functional roles for self-trapped excitations in biology remain to be clarified but they lend themselves to fascinating speculations.^{15,25}

It should be clear that some of the most intriguing functional consequences (e.g. energy or charge transduction) for localized ("soliton") objects concern their influence on transport. This is true just as much for conducting synthetic polymers as for biopolymers. However, the story is very far from complete in either case. We reemphasize that simple diffusive soliton transport will probably have limited relevance in either case. In general we can expect (thermal or quantum) tunneling to play a major role -- either of the total soliton entity or of the self-trapped^{23,27,28} excitation -- leading to "hopping" transport mechanisms.^{23,27,28} In addition, recent numerical studies²⁹ of semi-classical soliton dynamics have revealed unexpected subtleties, even for so simple a model as the SSH, eqn. (7). For example, the solitons have a maximum velocity which is unrelated to the sound speed. Again,

"breather" solitons (strongly anharmonic phonons), analogous to the dynamic solitons of the NLS equation (3), are readily excited (e.g. by laser stimulation). Soliton dynamics and transport in polymers leave, much to be revealed!

5. SUMMARY

There has been little space in this article to mention the many connections between solid state (e.g. synthetic polymer) and biophysics, with strong nonlinearity playing the unifying role. Striking parallels occur at all important levels: analytical (as in the case of self-trapping mechanisms, §4); numerical techniques; experimental implications, applications, and techniques. (At once, conventional solid state probes are at last being devoted to biopolymers but their complexity is demanding new extremes and techniques -- in a real sense, biopolymers are a new frontier of materials science).

As important as the above connections is the commonality of phenomena. These include: hydrogen-bonding (compare peptide chains or DNA or cellulose with hydrogen-bonded ferroelectrics);¹⁵ structural (and ferro-electric) phase transitions (3§); competing interactions (leading, for example, to commensurate-incommensurate phase transitions and intrinsic structural "chaos", §3); thermal or quantum nucleation (which may be relevant to premelting or intercalation centers in DNA (see SOBELL and ref. 15); self-localization phenomena (§4); transport mechanisms (diffusion or hopping of self-localized states, proton transport (e.g. through biomembranes), ionic diffusion or hopping, charge-transfer, etc., compared with polaron transport in molecular crystals and conducting polymers or transport in fast-ion conductors); piezoelectricity (familiar in synthetic polymers such as poly(vinylidene) fluoride and suggested in materials such as DNA); macromolecular architecture (e.g. in lipid bilayers) and its synthetic parallel in solid state polymerizations such as in single crystal polydiacetylenes.³⁰

There is no space here to give due attention to all these topics. However we can conclude by reiterating two dominant themes: (i) solitons are important in condensed matter, especially in reduced dimensionality, for structure, energetics and transport; and (ii) an interdisciplinary approach to strong nonlinearity has had profound success in many other areas of the natural sciences. It will surely yield similar benefits in biophysics, perhaps with even more significant consequences.

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