Soliton Lattice in Polyacetylene, Spin-Peierls Systems, and Two-Dimensional Sine-Gordon Systems

Baruch Horovitz
Department of Nuclear Physics, The Weizmann Institute of Science, Rehovot, Israel
(Received 25 August 1980)

An exact solution for the soliton lattice in the half-filled-band Peierls condensate is found. In the limit of weak coupling (infinite momentum cutoff Λ) the soliton-soliton interaction decays as a repulsive exponential while for finite Λ it decays as (distance)$^{-1}$ and is attractive! This yields phase separation in doped polyacetylene or a first-order lock-in transition of a spin-Peierls system. A mapping into the low-temperature two-dimensional sine-Gordon system is shown, where a lock-in transition has exponent $\beta = 1$ for finite Λ.

PACS numbers: 72.15.Nj, 71.30.+h

Solitons have become a common feature of almost any nontrivial problem in one-dimensional (1D) physics.[1] I consider here soliton solutions which are common to three systems: a fermion system, a boson system, and a magnetic system.

The *fermion system* is that of solitons in polyacetylene,[2-6] i.e., the adiabatic electron-phonon system in one dimension. There is considerable evidence that at low doping levels ($\lesssim 0.1\%$) the added charge forms solitons.[2] An insulator-to-metal transition was observed at $\sim 1\%$ doping,[7] and the conductivity increase was associated with either metallic particles[8] or with a soliton liquid.[9] The multisoliton solutions, which are derived here, are essential for the understanding of the system with these higher doping levels.

The *boson system* is that of the weak-coupling 1D quantum sine-Gordon system,[10,11] or, equivalently,[12] the low-temperature classical sine-Gordon system in two space dimensions. The critical behavior of the lock-in transition in this system is of considerable theoretical interest.[12-15] Here I show that this problem is equivalent to that of solitons in polyacetylene, and that the critical behavior is very different if the momentum cutoff of the continuum excitations is infinite or finite.

The *magnetic system* is that of a 1D spin-phonon (or spin-Peierls) system[16] where a magnetic field can change a dimerized spin-$\frac{1}{2}$ antiferromagnetic chain into an incommensurate structure with finite magnetization. Experimentally, a first-order transition was observed[17] in TTF-BDT(Cu) [tetrathiafulvalene-*bis*-*cis*-(1,2-perfluoromethylethylene-1,2-dithiolato)-copper] at low temperatures; this is explained here in terms of attracting solitons.

In earlier works[18,19] on the fermion problem, my collaborators and I have included direct electron-electron scattering in a Hartree-Fock scheme, and solved the problem by a derivative expansion of the Green's function. We have found that solitons attract each other if the electron-electron coupling is not too strong, compared with the electron-phonon coupling. However, the derivative expansion is not valid when the electron-electron coupling is too small, and in particular when it vanishes[6]; this is precisely the case which I now solve.

I start from the continuum model for coupled electrons and ion displacement field $\Delta(x)$ in the adiabatic approximation.[5,6] The electron eigenfunctions $u_n(x)\exp(i\pi x/2a) - iv_n(x)\exp(-i\pi x/2a)$ are written as a spinor $\psi_n^{+}(x) = (u_n^{*}(x), v_n^{*}(x))$ of right- and left-moving electrons (a is the underlying lattice constant). The momentum cutoff $\Lambda = \pi/2a$ defines the allowed range $(-\Lambda, \Lambda)$ of wave vectors for $\psi_n(x)$. In the half-filled-band system $\Delta(x)$ acts as a symmetric backscattering potential, i.e., the electron energy eigenvalues ϵ_n are determined by[6]

$$\epsilon_n\psi_n(x) = iv_F\sigma_3\frac{\partial\psi_n(x)}{\partial x} + \Delta(x)\sigma_1\psi_n(x), \tag{1}$$

where σ_i are the Pauli matrices and v_F is the Fermi velocity. The total energy is

$$E_0 = \sum_n{}'\epsilon_n + \int dx\ \Delta^2(x)/2\lambda\pi v_F, \tag{2}$$

where λ is the dimensionless electron-phonon coupling constant, and the prime indicates summation over the occupied states.

The function $\Delta(x)$ minimizes the total energy if the self-consistency equation

$$\Delta(x) = -\lambda\pi v_F\sum_n{}'u_n^{*}(x)v_n(x) + \text{H.c.} \tag{3}$$

is satisfied. Equations (1) and (3) have both uniform displacement and single-soliton solutions.[2-6] Also a soliton lattice configuration was found in an approximate numerical study[20] and in a phenomenological model.[4]

Following Takayama, Lin-Liu, and Maki,[5] I de-

fine $f_n = u_n + iv_n$, and $g_n = u_n - iv_n$, and reduce Eqs. (1) to

$$[\epsilon_n^2 + v_F^2 \partial^2/\partial x^2 - \Delta^2(x) + v_F\Delta'(x)]f_n(x) = 0. \quad (4)$$

g_n is determined by f_n through the first-order Eq. (1). Equation (3) now becomes

$$\Delta(x) = -2\lambda\pi v_F[\Delta(x) + \tfrac{1}{2}v_F\partial/\partial x]\sum'|f_n(x)|^2/2\epsilon_n, \quad (5)$$

with $\epsilon_n = 0$ states excluded from the sum.

Note now that Eq. (1), which is a Dirac-type equation, is equivalent to Eq. (4), which is a Klein-Gordon–type equation. Thus, we consider a Bose field $\varphi(x,t)$, whose basis functions are $f_n(x)$, with a Hamiltonian

$$H_B = \int dx\,[\tfrac{1}{2}\Pi^2 + \tfrac{1}{2}v_F^2\varphi'^2 + \tfrac{1}{2}(\Delta^2 - v_F\Delta')\varphi^2] - \int dx\,\Delta^2/4\lambda\pi v_F, \quad (6)$$

where $\Pi = \partial\varphi/\partial t$. When all $\epsilon_n \leq 0$ states in (2) are occupied $E_0 = -2\langle H_B\rangle$; the factor 2 is needed to cancel the $\frac{1}{2}$ of the boson zero-point motion. A variation of Eq. (6) with respect to $\Delta(x)$ yields precisely Eq. (5), confirming the equivalence of the fermion and boson systems.

I have found an exact solution to Eqs. (4) and (5) which is related to soliton solutions of the sine-Gordon system. To motivate this approach, note that Eq. (6) has the form of small oscillations around classical soliton-bearing systems[21] with potential energy $U(\psi)$ when

$$\Delta^2(x) - v_F\Delta'(x) = U''(\psi_s(x)) \quad (7)$$

and $\psi_s(x)$ is a classical soliton. The soliton has a translation mode $f_0(x) \sim \psi_s'(x)$ with eigenvalue $\epsilon = 0$. From Eq. (1) I obtain $\Delta(x) = -v_F\psi_s''(x)/\psi_s'(x)$ and, substituting in Eq. (7), I obtain the classical soliton equation $v_F^2\psi_s''(x) = U'(\psi_s(x))$. Thus Eq. (7) is an important clue in finding the solution.

I next postulate that the potential $U(\psi)$ is the sine-Gordon potential $U(\psi) = \Delta_1^2(1 - \cos\psi)$. This is motivated to some extent by the correspondence between the backscattering electron problem and the sine-Gordon Hamiltonian.[22,23] However, the ultimate proof is by solving Eq. (4) and then verifying Eq. (5).

The general form of $\psi_s(x)$ is a soliton lattice given by[24,25]

$$\sin\tfrac{1}{2}(\psi_s - \pi) = \mathrm{sn}(x/k\xi, k), \quad (8)$$

where sn is a Jacobian elliptic function with parameter k and $\xi = v_F/\Delta_1$. The soliton lattice satisfies $\psi_s(x+l) = \psi_s(x) \pm 2\pi$, where $l = 2\xi kK$ and $K = K(k)$ is a complete elliptic integral. When $l \gg \xi$ (or $k \to 1$), $\psi_s(x)$ is a sequence of well-separated solitons or antisolitons, each of width ξ and at distance l apart.

The eigenvalue equation (4) contains the periodic potential $\Delta^2(x) - v_F\Delta'(x) = \Delta_1^2\cos\psi_s(x)$ with periodicity l. The complete eigenfunctions of this potential are well known, and the spectrum contains a single gap.[24,25] However, since the eigenvalues of the fermion problem are symmetric around $\epsilon_n = 0$ [transform $(f_n, g_n) \to (f_n - g_n)$], the fermion spectrum has two gaps at wave vectors $q = \pm\pi/l$ relative to the half-filled-band position $\pm\pi/2a$. The valence band lies below $\epsilon = -\Delta_1/k$ with wave vectors $-\Lambda < q < -\pi/l$ and the conduction band lies above $\epsilon = +\Delta_1/k$ with $\pi/l < q < \Lambda$. In addition there is a third "midband" at $-\pi/l < q < \pi/l$ with energy levels $-k'\Delta_1/k < \epsilon_q < k'\Delta_1/k$, where $k'^2 = 1 - k^2$.

It is remarkable that there are no additional gaps at multiples of π/l; this is a manifestation of the reflectionless property of the $\cos\psi_s$ potential.[25] The lattice distortions which create these gaps have wave vectors $\pi/a \pm 2\pi/l$; their sum is a lattice reciprocal wave vector so that these two gaps must coexist. Additional gaps displaced by multiples of $2\pi/l$ are indeed not necessary—they will increase the lattice elastic energy and will not lower the electronic energy. The numerical study[20] represented $\Delta(x)$ as a harmonic expansion up to the fifth order. This representation becomes worse as $l/\xi \to \infty$, where spurious gaps were indeed found.

Consider now this soliton lattice where the midband is charged, i.e., it is either full with two spins per state, or empty. In both cases the valence band is full, the conduction band is empty, and the midband is symmetrically occupied and does not contribute to Eq. (5). A tedious but straightforward summation on the valence-band states shows that Eq. (5) is indeed satisfied with the amplitude Δ_1 given by

$$\Delta_1 = \Delta_0[1 - (E/K - \tfrac{1}{2}k'^2)\eta^2/k^2 + O(\eta^4)], \quad (9)$$

where $\Delta_0 = v_F\Lambda\eta(1 + \eta^2/4)$ is the ground-state uniform solution of Eqs. (4) and (5) [$\Delta(x) = \Delta_0$], $\eta = 2 \times \exp(-1/2\lambda)$, and E,K are the complete elliptic integrals. Equation (9) shows that in the weak-coupling limit $\eta \to 0$ (implying $\Lambda \to \infty$ for finite Δ_0) the boson "mass" is unchanged, $\Delta_1 = \Delta_0$.

Consider now the physical consequences of the solution. The ion displacement oscillates between $\pm k\Delta_1/(1 + k')$, passing twice through zero in a single period l. This allows for two charge states[2-6] and the charge density (relative to the half-filled band level) is $\rho = 2/l$. This is indeed the excess charge in the midband.

The gap in the fermion spectrum is $(1-k')\Delta_1/k$. In the incommensurate limit, when $\rho \sim \Lambda$ or $k \sim \eta \ll 1$, this gap becomes $\sim \Delta_0 \eta = 4 v_F \Lambda \exp(-1/\lambda)$ and is much smaller than the commensurate gap Δ_0.

The energy of the soliton lattice, relative to that of the ground state, is

$$E_{SL}/\rho = \frac{2\Delta_0}{\pi k}\left[E - \tfrac{1}{2}k'^2 K + \frac{\eta^2}{k^2}\left(-\frac{E^2}{2K} + \frac{1+k'^2}{6}E - \frac{k'^2}{12}K\right) + O(\eta^4)\right]. \quad (10)$$

The soliton chemical potential $\mu = \partial E_{SL}/\partial\rho$ satisfies $\epsilon_{\pi/l}$ (midband) $< \mu < \epsilon_{\pi/l}$ (conduction) so that the charged soliton lattice is energetically the most favorable charged configuration. Addition of charge to the system proceeds by expanding the midband to accommodate precisely all the additional charge.

In the limit of low soliton density $\rho^{-1} \to \xi \ln(4/k')$ $(k' \to 0)$, I obtain from Eq. (10) my most significant result

$$E_{SL}/\rho = (2\Delta_0/\pi)[1 + 4\exp(-2/\rho\xi_0) - \tfrac{1}{2}\eta^2\rho\xi_0 + \eta^2/6 + O(k'^4 \ln 4/k', k'^2\eta^2, \eta^4)], \quad (11)$$

where $\xi_0 = v_F/\Delta_0$.

In the weak-coupling limit $\eta \to 0$, I recover the single soliton energy $E_s = 2\Delta_0/\pi$ as found by Takayama, Lin-Liu, and Maki[5] and an exponentially weak repulsion between solitons. However, when η is small but finite the soliton-soliton interaction is drastically changed. It becomes long range [decays as $(1/\rho)^{-1}$, where $1/\rho$ is the mean distance between solitons] and attractive. This result can be understood by noting that the presence of the midband reduces the phase space of electron states (of order Λ) which contribute to the self-consistency equation by $2\pi/l \sim \rho$. This is why both Δ and E_{SL} are reduced by the terms $\sim \rho/\xi\Lambda^2$.

The attractive interaction leads to phase separation for $\rho < \rho^*$, where the equilibrium soliton density ρ^* minimizes E_{SL}/ρ. In the limit of Eq. (11),

$$4(\rho^*\xi_0)^{-1}\exp(-1/\rho^*\xi_0) = \eta. \quad (12)$$

The application of our results to polyacetylene with[2] $\eta \simeq 0.14$ yields an equilibrium soliton density of $\rho^{*-1} \simeq 5\xi_0 \simeq 35a$ and corresponds to a doping level of 3%. *If* the interactions with the dopant ions are neglected, polyacetylene doped to less than 3% would phase separate into conducting soliton droplets charged to a 3% level, while the rest of the system is insulating. Thus the metal-to-insulator transition at $\sim 1\%$ may be the formation of these droplets or the 3D percolation between them. This is consistent with the observed nonmagnetic conducting phase.[9] Increasing disorder can destroy the dimerization and then the soliton droplets become normal metallic particles.[8]

I turn now to the equivalent boson problem, where $\langle H_B \rangle$ of Eq. (6) gives the lowest-order quantum correction[10,11,21] to the energy of the classical sine-Gordon soliton lattice. This correction is given by Eq. (10), except for a factor of -2, and in addition, the energies $\epsilon_n > 0$ of the midband have to be added, since the cancellation with the $\epsilon_n < 0$ midband states does not occur in the boson problem. For a single soliton, the midband consists of one $\epsilon_n = 0$ state and this addition is zero. Thus the quantum correction of the sine-Gordon soliton $-\Delta_0/\pi$[10] corresponds exactly to the single-soliton energy in the fermion problem $+2\Delta_0/\pi$. For the soliton lattice solution, the addition of the midband states adds another exponentially small repulsive interaction.[15] For $\eta \to 0$ the exponential repulsion leads to logarithmic critical behavior near the lock-in transition, i.e., $\rho \sim (\mu - E_s)^\beta$ with $\beta = 0$. A finite cutoff Λ generates a long-range repulsion (recall the -2!) of the form $\sim \eta^2\rho$, and therefore $\beta = 1$.

Finally, I consider the spin-Peierls problem, which can be mapped into my fermion-phonon system exactly for X-Y spins, and with fermion-fermion interaction for Heisenberg spins.[16] If the latter interaction is averaged in a Hartree-Fock scheme a renormalized fermion-phonon system is obtained[16] (otherwise the approach of Refs. 18 and 19 is relevant). Since these fermions are spinless,[16] each soliton corresponds to the addition of $\pm\frac{1}{2}$ fermion, i.e., $\pm\frac{1}{2}$ spin in the original system. Equations (10) and (11) are now smaller by a factor of 2, $\lambda \to \lambda/2$, and the single-soliton energy becomes Δ_0/π.

An important conclusion from the results of the fermion problem is that the lowest-energy excitation is a localized soliton with spin $\frac{1}{2}$, rather than an extended spin wave with spin 1 as previously believed.[16,17] Also, the lock-in transition in a magnetic field should be first order with a jump to the equilibrium soliton density ρ^* of Eq. (12).

Experiments on the spin-Peierls system TTF-BDT(Cu) show[17] indeed a first-order transition at a magnetic field of $H_c \sim 120$ kG. This yields

$E_s \simeq 8$ °K and, therefore, $\Delta_0 \simeq 25$ °K. The available magnetic susceptibility data above 6 °K has, indeed, an activation energy of ~ 25 °K, while data at lower temperatures should confirm the soliton activation energy. The observed hysteresis at 1.5 °K is ~ 10% and implies strong coupling with $\eta \simeq 0.6$. The hysteresis should vanish when $T \simeq E_s$, and indeed it vanished above 5.5 °K.[17]

Note added.—I wish to thank Dr. S. A. Brazovskii for bringing to my attention, after the submission of this manuscript, his work on the fermion problem.[26] They consider only the fermion problem in the $\Lambda \to \infty$ limit; their result agrees with mine in this limit. I also wish to thank Professor J. R. Schrieffer and Dr. E. Domany for very useful discussions.

[1]For reviews, see *Solitons and Condensed Matter Physics*, edited by A. R. Bishop and T. Schneider (Springer-Verlag, New York, 1978).

[2]W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979), and Phys. Rev. B 22, 2099 (1980).

[3]S. A. Brazovskii, Pis'ma Zh. Eksp. Teor. Fiz. 28, 656 (1978) [JETP Lett. 28, 606 (1978)].

[4]M. J. Rice, Phys. Lett. 71A, 152 (1979); M. J. Rice and J. Tinonen, Phys. Lett. 73A, 368 (1979).

[5]H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B 21, 2388 (1980).

[6]B. Horovitz, Phys. Rev. B 22, 1101 (1980).

[7]C. K. Chiang *et al.*, Phys. Rev. Lett. 39, 1089 (1977).

[8]Y. Tomkiewicz, T. D. Schultz, H. B. Brom, T. C. Clarke, and G. B. Street, Phys. Rev. Lett. 43, 1532 (1979).

[9]S. Ikehata *et al.*, Phys. Rev. Lett. 45, 1123 (1980).

[10]R. F. Dashen, B. Hasslacher, and A. Neveu, Phys. Rev. D 11, 3424 (1975).

[11]K. Maki and H. Takayama, Phys. Rev. B 20, 3223 (1979).

[12]H. Takayama, J. Phys. Soc. Jpn. 48, 1037 (1980).

[13]V. L. Pokrovsky and A. L. Talapov, Phys. Rev. Lett. 42, 65 (1979).

[14]J. Villain, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum, New York, 1979).

[15]B. Horovitz, to be published.

[16]E. Pytte, Phys. Rev. B 10, 4637 (1974).

[17]D. Bloch, J. Voiron, J. C. Bonner, J. W. Bray, I. S. Jacobs, and L. V. Interrante, Phys. Rev. Lett. 44, 294 (1980).

[18]B. Horovitz, Solid State Commun. 34, 61 (1980).

[19]M. Grabowski, K. R. Subbaswamy, and B. Horovitz, Solid State Commun. 34, 911 (1980).

[20]A. Kotani, J. Phys. Soc. Jpn. 42, 416 (1977).

[21]R. Jackiw, Rev. Mod. Phys. 49, 681 (1977).

[22]V. J. Emery, A. Luther, and I. Peschel, Phys. Rev. B 13, 1272 (1976).

[23]R. Heidenreich, B. Schroer, R. Seiler, and D. Uhlenbrock, Phys. Lett. 54A, 119 (1975).

[24]A. L. Fetter and M. J. Stephen, Phys. Rev. 168, 475 (1968).

[25]B. Sutherland, Phys. Rev. A 8, 2514 (1973).

[26]S. A. Brazovskii, S. A. Gordyunin, and N. N. Kirova, Pis'ma Zh. Eksp. Teor. Fiz. 31, 486 (1980) [JETP Lett. (to be published)].

Structural Phase Transitions in Nickel at the Curie Temperature

J. C. Hamilton[a] and Terrence Jach
National Bureau of Standards, Washington, D. C. 20234

(Received 13 January 1981)

It is observed that a reversible step period rearrangement on clean nickel single-crystal surfaces occurs in the immediate vicinity of the Curie temperature. Reversible carbon segregation is observed on the same crystal surfaces below the Curie point. The segregated carbon is carbidic, not graphitic, and indicates a change in the nickel surface electronic structure occurring at the ferromagnetic transition. Measured carbon coverages indicate a change greater than 0.2 eV per carbon atom in the heat of segregation at the Curie point.

PACS numbers: 75.30.Kz, 61.14.Hg, 68.40.+e

Several recent experiments have focused attention on changes in the chemical properties of magnetic surfaces at the Curie temperature.[1-5] These experiments indicate a direct connection between the magnetic state of the surface and the binding energy of adatoms on the surface. In this Letter we report strong evidence of a new and significant phenomenon, a reversible *structural* surface phase transition directly coupled to the ferromagnetic transition of nickel.