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NON-LINEAR MODES IN THE CONDENSED PEIERLS PHASE

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The equations of motion for the order parameters of a coupled linear chain system in a condensed Peierls phase are derived from a microscopic Hamiltonian. These results now provide the correct non-linear terms which are needed to discuss solitary wave excitation modes. The computation reported here is a mean field result, at $T = 0$, and with interchain electron backscattering. Amplitude solitary waves are energetically disallowed, but phase solitons (ϕ-particles) with small associated amplitude variation are possible.

THE EXISTENCE of solitary waves as an elementary excitation of the order parameter in a Peierls condensate was suggested by Rice *et al.* [1]. These non-linear modes describe localized charge excitations ("ϕ-particles") and may account for the non-linear transport in TTF–TCNQ [2].

The one-dimensional (1D) problem was first treated by Lee, Rice and Anderson [3] (LRA) for small oscillations (i.e. linear) in the order parameter, leading to phase and amplitude phonons. In the absence of a pinning potential the phase may make large excursions, so that non-linear effects need consideration. When we consider excitations of the low temperature condensed Peierls phase, either commensurability or interchain coupling lead to periodic potentials in the phase [3], and non-linear solitary wave solutions [4].

In fact, until now the effective Lagrangian for the non-linear problem has only been inferred from the small oscillation theory of LRA [1], or phenomenologically [5]; a microscopic basis for the non-linear equations was missing. When dealing with intrinsically non-linear excitations a plausible Lagrangian is not sufficient; in particular, phase and amplitude motions of the order parameter are coupled, and it is very important that the correct behavior is known in order to obtain stable solitary (non-linear) solutions.

Thus the main results reported in the letter are: microscopically derived non-linear equations for the amplitude and phase of the order parameter, demonstration that phase solitons can indeed exist when the correct amplitude dependence is considered, and comments on the determination of theoretical parameters from experiment. In the small amplitude regime our results reduce to the linear LRA modes.

The main features of the computation, its assumptions, or restrictions are: we compute the equations of motion for the electron Green's function and the order parameter in real space time to handle non-linearity directly rather than by cumbersome Fourier analysis; we consider $T \to 0$ and that Peierls condensation occurs at some high temperature (compared to Debye frequency), therefore we use the mean field approximation [6]; in this letter we report only results for $T = 0$, but the formalism applies to $T \neq 0$; the Hamiltonian includes on-chain electron–phonon coupling plus interchain coupling which produces on-chain backscattering; we assume that interchain electron transfer is negligible. Long-range Coulomb coupling can be included, but for isolated (solitary) excitations is not qualitatively important, in contrast to the plasma frequency correction to extended phase waves [7, 8]. Also, the long-range Coulomb interactions between the structures obtained can be introduced at the last stage [8].

The electron wave function on the lth chain is written in the form

$$u^l(x) = u_1^l(x)\, e^{ik_F x} + u_2^l(x)\, e^{-ik_F x} \tag{1}$$

where k_F is the Fermi momentum and $u_{1,2}^l(x)$ are assumed to be slowly varying functions, essentially assuming linear dispersion near the Fermi level [3]. Using the spinor field $\psi_l^\dagger(x) = [u_1^l(x)^*, u_2^l(x)^*]$ and neglecting second derivatives in $u(x)$ the Hamiltonian for the bare electrons is

$$H_{el} = -\sum_l \int dx\, \psi_l^\dagger(x) i v_F \sigma_3 \frac{\partial}{\partial x} \psi_l(x) \tag{2}$$

where σ_i are the Pauli matrices, $v_F = k_F/m$ and m is the electron mass. The electron phonon interaction with a coupling constant g is then

$$H_{el-ph} = \frac{-g}{\sqrt{2}} \sum_l \left\{ \int \psi_l^\dagger(x) \sigma_1 \psi_l(x) \phi_l(x)\, dx \right.$$

$$+\int \psi_l^\dagger(x)\sigma_2\psi_l(x)R_l(x)\,dx\Big\} \tag{3}$$

where $\phi_l(x), R_l(x)$ are the phase and amplitude phonon fields [3, 6]. The interchain coupling which corresponds to $\sim 2k_F$ momentum transfer (short-range interaction) between electrons on neighbouring chains has the form

$$H_{\text{int}} = \frac{1}{4}\sum_{l,\gamma}\tilde{g}_\gamma\int dx\,\{\psi_l^\dagger(x)\sigma_1\psi_l(x)\psi_{l+\gamma}^\dagger(x)\sigma_1\psi_{l+\gamma}(x) + (\sigma_1\to\sigma_2)\}. \tag{4}$$

The γ index sums on neighbouring chains with coupling constant $\tilde{g}_\gamma$.

The equations of motion for the electron Green's function $G(xt, x't')$ were obtained from the MF diagrams [6]. Exchange terms only renormalize the electron dispersion (coefficients of $1, \sigma_3$ in the Green's function) and therefore can be neglected for evaluating the off diagonal elements (coefficients of σ_1, σ_2). The equation of motion has the form

$$\left[\omega - v_F p\sigma_3 - \Delta_1^l(x,t)\sigma_1 - \Delta_2^l(x,t)\sigma_2 + iv_F\sigma_3\frac{\partial}{\partial x} + i\frac{\partial}{\partial t}\right]G_l(\omega,p,x,t) = 1 \tag{5}$$

where ω and p are Fourier transforms of $t-t'$ and $x-x'$ respectively. The coefficients $\Delta_{1,2}^l(x,t)$ are identified as the two degrees of freedom of the order parameter, and are determined by the self consistency condition

$$\Delta_K^l(x,t) = \frac{ig^2}{\omega_0}\,\text{Tr}\,[\sigma_K G_l(xt,xt)] - \frac{1}{\omega_0^2}\ddot{\Delta}_K^l(x,t) - \frac{\omega_0}{2g^2}\sum_\gamma \tilde{g}_\gamma\Delta_K^{l+\gamma}(x,t) + 0\left(\tilde{g}^2, \tilde{g}\ddot{\Delta}_K^l, \frac{\partial^4}{\partial t^4}\Delta_K^l\right) \tag{6}$$

where $K = 1, 2$, and ω_0 is the bare phonon frequency around $2k_F$. Equations (5) and (6) give our final gap equations which are valid to second order in derivatives and first order in the interchain coupling. Transforming the gap functions to amplitude and phase variables

$$\begin{aligned}\Delta_1^l(x,t) &= \Delta_l(x,t)\cos\varphi_l(x,t)\\ \Delta_2^l(x,t) &= -\Delta_l(x,t)\sin\varphi_l(x,t)\end{aligned} \tag{7}$$

we obtain (all Δ_l, φ_l are function of x, t)

$$\Delta_l = \Delta_l\lambda\ln\frac{2E_c}{\Delta_l} + \frac{1}{\omega_0^2}(\Delta_l\dot{\varphi}_l^2 - \ddot{\Delta}_l) - \frac{\lambda}{12\Delta_l^3}(v_F^2\Delta_l'^2 - v_F^2\Delta_l\Delta_l'' - \dot{\Delta}_l^2 + \Delta_l\ddot{\Delta}_l) - \frac{N(0)}{2\lambda}\sum_\gamma \tilde{g}_\gamma\Delta_{l+\gamma}\cos(\varphi_l - \varphi_{l+\gamma}) \tag{8}$$

$$0 = \frac{1}{\omega_0^2}(2\dot{\Delta}_l\dot{\varphi}_l + \Delta_l\ddot{\varphi}_l) - \frac{\lambda}{4\Delta_l}(v_F^2\varphi_l'' - \ddot{\varphi}_l) - \frac{N(0)}{2\lambda}\sum_\gamma \tilde{g}_\gamma\Delta_{l+\gamma}\sin(\varphi_l - \varphi_{l+\gamma}) \tag{9}$$

where $g^2 = \lambda\omega_0/N(0)$, $N(0)$ is the electron density of states at the Fermi level and E_c is an electronic cut-off energy ($\Delta_l \ll E_c$).

Equations (8) and (9) can be derived from a Lagrangian density of the form

$$\mathfrak{L}(x,t) = \sum_l N(0)\left\{\frac{1}{2}\Delta_l^2\left(\ln\frac{2E_c}{|\Delta_l|} + \frac{1}{2}\right) - \frac{\Delta_l^2}{2\lambda} + \frac{M_\varphi(\Delta_l)}{m}\dot{\varphi}_l^2/8 + \frac{M_\Delta(\Delta_l)}{m}\dot{\Delta}_l^2/24\Delta_l^2 - \frac{v_F^2}{8}(\varphi_l'^2 + \Delta_l'^2/3\Delta_l^2) - \frac{N(0)}{2\lambda^2} \times \sum_\gamma \tilde{g}_\gamma\Delta_l\Delta_{l+\gamma}\cos(\varphi_l - \varphi_{l+\gamma})\right\}. \tag{10}$$

The first term in (10) is the local condensation energy $\sim\int[(\epsilon^2+\Delta^2)^{1/2} - \epsilon]\,d\epsilon$. The electronic kinetic mass is renormalized due to the coupling to the lattice:

$$\begin{aligned}M_\varphi/m &= 1 + 4\Delta^2/\lambda\omega_0^2\\ M_\Delta/m &= 1 + 12\Delta^2/\lambda\omega_0^2.\end{aligned} \tag{11}$$

These masses and the Δ'^2 coefficient depend on $\Delta_l(x,t)$; thus the effective masses and the amplitude coherence length depend on the *local* value of the amplitude $-\Delta_l(x,t)$. This result is new, and of essential importance in the non-linear behavior.

The Lagrangian (10) can also be derived directly by evaluating the free energy of the system, as was done for the static 1D problem [9]. Thus the free energy functional leads to the correct equations of motion equations (8) and (9) – a result also known for the non-equilibrium state of superconductors [10].

The solutions for $\varphi_l(x,t)$ determine the charge and current distributions, which are the expectation values of the operators 1 and $v_F\sigma_3$. To first order in the derivatives these are found from the same analysis to be

$$\begin{aligned}n_l(x,t) &= n_0[1 + \varphi_l'(x,t)/2k_F]\\ j_l(x,t) &= -n_0\dot{\varphi}_l(x,t)\end{aligned} \tag{12}$$

where $n_0 = 2k_F/\pi$ is the mean electron density. Of course the density has an additional term $-n_0\Delta_l \times \cos(2k_Fx + \varphi_l)/\lambda v_F k_F$ which is the charge density wave (CDW) itself. However, the results (12) are consistent with (2), both describing slow variations on top of $2k_F$ oscillations, and also with the phenomenological theory [5, 7].

We now look for solutions of equations (8) and (9). The ground state is

$$\Delta_l(x,t) = \bar{\Delta}\left[1+\frac{\omega_s^2}{4\Delta^2}\frac{M_\varphi}{m}\right] \tag{13}$$

where $\bar{\Delta} = 2E_c \exp(-1/\lambda)$ and

$$\omega_\gamma^2 = \tilde{g}_\gamma N(0)\frac{2\bar{\Delta}^2}{\lambda^2}\frac{m}{M_\varphi}; \quad \bar{\omega}_\gamma^2 = -\omega_\gamma^2\cos(\bar{\varphi}_l - \bar{\varphi}_{l+\gamma});$$

$$\omega_s^2 = \sum_\gamma \bar{\omega}_\gamma^2. \tag{14}$$

The ground state phases satisfy $\Sigma_\gamma \tilde{g}_\gamma \sin(\bar{\varphi}_l - \bar{\varphi}_{l+\gamma}) = 0$, i.e. for two or four interacting neighbours $\bar{\varphi}_l - \bar{\varphi}_{l+\gamma} = \pi$. For a general case $\omega_s^2 > 0$ but the solution is more complicated [11].

For small oscillations in the amplitude or the phase we obtain the LRA phonons with dispersions

$$\omega_\Delta^2 = \frac{m}{M_\Delta}(12\bar{\Delta}^2 + v_F^2 q^2) - \frac{3M_\varphi}{M_\Delta}\sum_\gamma \bar{\omega}_\gamma^2 \cos q_\gamma$$
$$\omega_\varphi^2 = \frac{m}{M_\varphi} v_F^2 q^2 + 2\sum_\gamma \bar{\omega}_\gamma^2 \sin^2\frac{1}{2}q_\gamma \tag{15}$$

where q, q_γ are momenta along and perpendicular to the chains and M_Δ, M_φ are evaluated at $\bar{\Delta}$.

Next we look for non-linear solutions, particularly those with low excitation energy. The degeneracy of the Lagrangian (10) for $\pm\Delta_l$ suggest a possible amplitude solitary wave interpolating between $\pm\bar{\Delta}$ [12]. However, the explicit dependence in equation (10) of $(\dot{\Delta}_l^2/\Delta_l^2)$, $(\Delta_l'^2/\Delta_l^2)$ on the local value of Δ_l resists the passage of $|\Delta_l|$ through zero; indeed a simple calculation shows the energy to diverge for a pure amplitude kink. By contrast a phenomenological Ginzburg–Landau Lagrangian would have allowed a pure amplitude solitary wave.

The amplitude couples the CDW to various pinning forces such as impurities [8], the lattice (in a commensurate case [3]) or other chains [equation (10)]. Thus a decrease in the amplitude leads to weaker pinning forces and to higher conductivity. Koehler and Lee [13] suggested that for impurity pinning, the condensate can conduct via a phase slippage mode, i.e. the amplitude vanishes at the impurity site so that the phase can jump by 2π and the current will pass. For low temperatures ($T \ll \bar{\Delta}$) the activation energy is much larger than the previous estimate [13] since the amplitude coherence length increases near the phase slippage point, and even diverges there if $T = 0$.

These examples illustrate the need for the proper microscopic calculation which we report.

On the other hand we can find solutions with large phase variation, but minimal variation in the amplitude. To lowest order in $\dot{\varphi}$ and $\tilde{g}$

$$\ddot{\varphi}_l - c_0^2\varphi_l'' - \sum_\gamma \omega_\gamma^2 \sin(\varphi_l - \varphi_{l+\gamma}) = 0 \tag{16}$$

$$\Delta_l = \bar{\Delta}\left\{1 - \frac{M_\varphi}{4m\bar{\Delta}^2}\sum_\gamma \omega_\gamma^2 \cos(\varphi_l - \varphi_{l+\gamma}) + \frac{\dot{\varphi}_l^2}{\lambda\omega_0^2}\right\} \tag{17}$$

where $c_0^2 = v_F^2 m/M_\varphi$ and $M_\varphi = M_\varphi(\bar{\Delta})$. Equation (16) has solitary wave solutions where the relative phase $\varphi_l - \varphi_{l+\gamma}$ has a total variation of 2π. We have already shown [4] that this type of equation has localized solutions where φ_l is a solitary wave on the chain $l = 0$, while $\varphi_{l\neq 0}$ remains constant to order $\tilde{g}$. To this order in $\tilde{g}$, $\varphi_{l=0}(x,t)$ satisfies

$$\ddot{\varphi} - c_0^2\ddot{\varphi} + \omega_s^2 \sin\varphi = 0. \tag{18}$$

This is the sine-Gordon equation with well known solitary waves, for which the "φ particle" phase solitons were proposed earlier [1]. The coupled amplitude variation is given by equation (17).

Equation (18) is valid provided the "φ particle" travels with a low velocity v and that its rest energy E_ϕ is small compared to the gap.

$$v/c_0 \ll \sqrt{\lambda}\omega_0/\omega_s$$

$$E_\phi = \frac{4}{\pi}\omega_s\sqrt{M_\varphi/m} \ll 2\bar{\Delta}. \tag{19}$$

In the region of the solitary wave, the amplitude (17) is reduced slightly. This reduction is smaller for a moving wave due to the centrifugal force – the last term in (17).

For the case of a few solitary waves on different chains the long-range Coulomb interaction between the charges (12) should also be included. This interaction can lead to a "φ" and "anti-φ" bound state [14], and if it is too strong it leads to an instability [4] and higher order derivatives of the order parameter must be considered.

It is important to note that the frequency ω_s in equation (18) in general is not the pinning frequency ω_F observed in infra-red (IR) measurements. In fact, in a pure system of identical chains with an incommensurate CDW the interchain coupling does not lead to pinning and $\omega_F = 0$; impurities lead to pinning $\omega_F \neq 0$, but this ω_F is not related to ω_s. Indeed in a charge transfer salt with inverted band on one type of chains (such as TTF–TCNQ) the charges (12) have opposite signs on the two types of chains, Q and F. Hence the IR active mode of (15) is $\varphi_Q - \varphi_F$ with frequency $\omega_F^2 = -2\Sigma'\omega_\gamma^2\cos(\bar{\varphi}_l - \bar{\varphi}_{l+\gamma})$ and the sum involves only Q–F neighbours. The factor 2, the different summations and the particular ground state $\bar{\varphi}_l$ of TTF–TCNQ [11] lead to different ω_F and ω_s. This may account for the difference in the predicted solitary wave energy [1] and the observed non-linear excitation of 12 K [2]. If

$E_\phi = 12\,\mathrm{K}$ and $M_\varphi/m = 100$ [1] then (19) implies $\omega_s \simeq 1\,\mathrm{K}$. Experimentally ω_F is estimated to be 3–10 K [15]. Note also that for these parameters equation (19) is very well satisfied.

The frequencies ω_s and ω_F are directly related only for a strong commensurability potential [1, 3], so that impurity and interchain coupling can be neglected. Rather interestingly, KCP [15] may be a relevant system. The disorder in the Br ions seems to suppress the phase transition at ambient pressure [8]. However at high pressure [17] there is a well defined phase transition, and the Br ions probably become ordered. If so, the CDWs are commensurate with respect to the Br sublattice, and measurements of non-linear transport in KCP under high pressure may show the existence of solitary waves.

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