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THE MIXED PEIERLS PHASE AND METALLIC POLYACETYLENE

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The Peierls condensate with density ρ near 1 electron per atom is studied and an effective phase-amplitude Hamiltonian is derived. It is shown that a Hartree–Fock theory removes the $\rho \to 1$ singularity and the phase field exists even at $\rho = 1$. The charge carriers are attracting solitons and the lock-in transition is of first order. If ρ is fixed near 1 the condensate will separate into a commensurate phase ($\rho = 1$) and an incommensurate phase ($\rho \neq 1$). These results can account for the unusual features of doped polyacetylene.

THE PEIERLS INSTABILITY of a quasi-one-dimensional electron system and effects of commensurability with the lattice have been extensively studied in recent years [1–5]. However the simplest commensurate case, corresponding to density ρ of 1 electron per atom, remained as a puzzling special case. It has been argued that in this case a phase mode does not exist [1, 2], and that the free energy cannot be expanded around $\rho = 1$ [5].

The case of ρ near 1 has become particularly interesting in view of recent experiments on doped polyacetylene [6–8], where by doping $\rho = 1 + \delta\rho$ electrons in the conduction band. A dramatic increase in conductivity around $\delta\rho \doteq 0.01$ suggests an insulator to metal transition. Optical absorption indicates [7–9] that doping leads to an additional absorption below ~ 0.5 eV, but surprisingly, absorption at the gap of ~ 1.6 eV persists all the way through the insulator to metal transition.

Furthermore, magnetic susceptibility data indicates that undoped polyacetylene has spin carrying defects, while the excess charge from the doping ions does not carry spin [9]. This is consistent with the theory of Su, Schrieffer and Heeger (SSH) [10] that neutral soliton defects carry spin, while charged solitons do no carry spin.

An alternative theory by Rice [11] suggested that solitons in polyacetylene are amplitude kinks. However, the Landau–Ginzburg functional used by Rice is singular for an amplitude kink [12]. The continuum version of the SSH model, as done by Takayama *et al.* [13] does not suffer from that defect and yields an amplitude soliton.

These theories for solitons in polyacetylene [10, 11, 13] describe the single soliton formation, applicable to very dilute doping of $\delta\rho \lesssim 0.001$, where solitons are isolated from each other. However, the understanding of the metal to insulator transition requires multi-soliton solutions and the understanding of the commensurate to incommensurate (G–I) transition.

In this work we re-examine the Peierls condensate near $\rho = 1$, and show that the elimination of the phase mode for $\rho = 1$ is a deficiency of the Hartree approximation, which was used in previous theories [1, 2, 5]. We then derive an effective phase-amplitude Hamiltonian by using the Hartree–Fock scheme, i.e., including the exchange term. The charged soliton obtained here, does not pass through the singular point where the order parameter vanishes, and therefore a Ginzburg–Landau effective Hamiltonian can be used. In the second part we apply the results to describe the transition near $\rho = 1$. The solitons in the present model can attract each other, condensing into metallic like regions.

The amplitude Δ and phase ϕ of the interacting electron–phonon order parameter $\Delta \exp(i\phi)$ are usually electron-phonon order parameter $\Delta \exp(i\phi)$ are usually identified by the ion displacement pattern $\sim \Delta \cos(2k_F x + \phi)$, where $k_F = \pi\rho/2a$ is the Fermi wavevector and a is the lattice constant. For $\rho = 1$ the ions at $x = na$ are displaced by $(-)^n \cos\phi$. The only ion variable then is the product $\Delta \cos\phi$ and the order parameter appears to be real [2]. However, including interactions between electrons, either by virtual phonon exchange or by Coulomb interaction, can lead to a complex response, i.e. the order parameter, defined by this response, is complex.

To make these ideas more explicit, let us consider a system with $2k_F = \pi/a$. Write the electron wavefunction [12] as

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

and a spinor notation is used $\psi^\dagger(x) = [u_1^*(x), u_2^*(x)]$. The phonon field is written as $\tilde{\chi}(x)\exp(i\pi x/a) = \tilde{\chi}(x)(-)^n$ for $x = na$ and $\tilde{\chi}(x), u_1(x), u_2(x)$ are slowly varying functions. Neglecting second derivatives in $u_{1,2}(x)$ and terms which oscillate fast as $(-)^n$, the Hamiltonian is written as

$$\begin{aligned}\mathcal{H} = \int dx\,\{&-iv_F\psi^\dagger(x)\sigma_3\frac{\partial}{\partial x}\psi(x) + \tfrac{1}{2}\omega_0\tilde{\chi}^2(x)\\ &+ g\psi^\dagger(x)\sigma_1\psi(x)\tilde{\chi}(x)\\ &+ \frac{4\gamma}{N(0)}\psi^\dagger(x)\psi(x)\psi^\dagger(x)\psi(x)\}\end{aligned} \tag{2}$$

where σ_i are the Pauli matrices, $N(0) = 2/\pi v_F$ is the density of states at the Fermi level, g is the electron–phonon coupling, and γ is the strength of the Coulomb coupling. The last term in equation (2) describes a Coulomb interaction with a range longer than a but shorter than the coherence length $\sim v_F/\Delta$.

The coupling of a phase mode to electrons, present in the incommensurate problem, is absent in equation (2). The coupling by the σ_1 matrix means that $a(+2k_F)$ phonon can transfer electrons from type 2 to type 1 (direct process) and also from type 1 to type 2 (Umklapp process). Note that the Coulomb interaction does not involve an Umklapp process. This process is affected by the $4k_F$ component of the interaction which is neglected here compared to the $q \simeq 0$ component. We also assume that the system is charge neutral on the scale of the coherence length, i.e. the dopant ions are not too far from their charge on the polymer chain.

The order parameter is defined by the combined electron–phonon response [12] (not just the ion displacement), i.e. the electron off diagonal self mass correction is $\Delta\cos\phi\sigma_1 - \Delta\sin\phi\sigma_2$.

The procedure of a microscopic derivation of an effective Hamiltonian has been shown in [12]. The new feature here is that the calculation is extended beyond the Hartree (or adiabatic) approximation and this leads to qualitatively new results for the system near $\rho = 1$. More specifically, we use the Hartree–Fock scheme [14] and assume low frequency phonons ($\omega_0 \ll \Delta$) so that the exchange term is dominated by the Coulomb interaction [14]. We obtain the following effective amplitude-phase Hamiltonian

$$\begin{aligned}\mathcal{H}\{\Delta,\phi\} = N(0)\int dx\,&\left\{-\frac{1}{2}\Delta^2\left(\ln\frac{2E_c}{\Delta}+\frac{1}{2}\right)+\frac{1}{2}\alpha\Delta^2\right\}\\ &+\frac{1}{2}\beta\Delta^2(1-\cos 2\phi)+\frac{v_F^2}{8}\left(\phi'^2+\frac{\Delta'^2}{3\Delta^2}\right)\\ &+\frac{1}{8}\left(\dot{\phi}^2+\frac{\dot{\Delta}^2}{3\Delta^2}\right)+\frac{\alpha\beta}{(\alpha+2\beta)\omega_0^2}\\ &\times\left(\frac{\partial}{\partial t}\Delta\cos\phi\right)^2\Bigg\}-\frac{\mu}{\pi}\int\phi'dx\end{aligned} \tag{3}$$

where E_c is the electronic cutoff energy, $\alpha = 1/(2\lambda+\gamma)$, $\beta = \lambda/[\gamma(2\lambda+\gamma)]$ and $\lambda = g^2N(0)/\omega_0$. The slowly varying part of the electron density is [12]

$$\rho = 1 + \frac{a}{\pi}\partial\phi/\partial x. \tag{4}$$

Except for the last term in equation (3), the system is symmetric in the phase gradient, as required for the half filled band [15]. The last term in equation (3) is the electron chemical potential which couples to the electron density [equation (4)]. This term may induce a change in the electron density and breaks the symmetry of the half filled band.

The Hartree approximation corresponds to $\gamma \to 0$ (no exchange term) and then the locking term $\frac{1}{2}\beta\Delta^2(1-\cos 2\phi)$ diverges for $\phi \neq 0$. (The Coulomb interaction is not essential for this; phonon exchange leads to the same effect.) The only finite energy solution in the Hartree approximation is then $\phi = 0$, i.e. the charge density wave is always locked to the lattice and from equation (3) $\rho = 1$! The expansion near $\rho = 1$ is then not possible [5] and there is no phase mode.

Note that for a complex order parameter the form of equation (3) follows essentially from general symmetry arguments [3] and the microscopic derivation serves mainly to identify the various coefficients.

To first order in ϕ the CDW is changed by $\phi\Delta\sin 2k_F x$ which vanishes at the ion positions but *not* otherwise (thus the ions do not couple linearly to phase oscillations). Since $\phi(x, t)$ is defined on a continuum (manifested by the virtual interactions) a non-adiabatic theory yields a phase mode, i.e. the order parameter is complex. Note that the phase mode is not the acoustic mode [1], since it involves CDW motion *relative* to the ions; it is also distinct from the amplitude mode [2] since the latter does couple linearly with the ions.

We now analyze and apply the resulting equations of motion in the static limit,

$$\begin{aligned}[\alpha+\beta(1-\cos 2\phi)]\Delta = \Delta\ln(2E_c/\Delta)\\ -(\Delta'^2-\Delta\Delta'')v_F^2/12\Delta^3,\end{aligned} \tag{5}$$

$$4\beta\Delta^2\sin 2\phi = v_F^2\phi''. \tag{6}$$

In the commensurate ground state $\phi = 0$ and $\Delta = \Delta_c = 2E_c\exp(-\alpha)$. (Including time dependence gives phonon frequencies $\omega_\phi \sim \Delta_c\sqrt{8\beta}$ and $\omega_\Delta = \omega_0(2\lambda+\gamma)/\sqrt{2\lambda}$.) In the incommensurate limit

($\pi/a \gg q \gg \sqrt{3\beta}\,\Delta_i/v_F$, $q \equiv 2\mu/v_F$) ϕ is changing rapidly and the cos 2ϕ term in equation (5) contributes just a small second harmonic correction,

$$\phi(x) = \phi_0 + qx - \sin(2qx + 2\phi_0)\beta\Delta_i^2/v_F^2q^2 \quad (7)$$

$$\Delta(x) = \Delta_i + 3\cos(2qx + 2\phi_0)\beta\Delta_i^3/v_F^2q^2 \quad (8)$$

where $\Delta_i = 2E_c \exp(-\alpha - \beta)$, and ϕ_0 arbitrary, reflecting the phase degeneracy of this state. For $\beta \gtrsim 1$, $\Delta_i \ll \Delta_c$ which demonstrates the strong phase–amplitude coupling. In general [1, 2, 13] $\Delta_c \ll 2E_c$ and $\gamma < \lambda$ so that $\beta > \alpha \gtrsim 2$.

For a constant amplitude equation (6) yields the well known sine-Gordon phase solitons [12, 16]. A phase soliton corresponds to a localized change of π in the phase, it contains an energy E_s, a charge $\pm e$ [equation (4)] and spin zero [12]. The charge and spin of this soliton is identical to that of SSH, and the difference is that here we include exchange interaction and a complex order parameter.

The coupled phase–amplitude problem, equations (5) and (6), also has soliton solutions, although the explicit solution is not simple. At the soliton center $\Delta(x)$ has a minimum which can be much smaller than $\Delta(x = \pm\infty) = \Delta_c$. It can be shown that

$$E_s = \tfrac{1}{2}N(0)\int dx\,[\Delta_c^2 - \Delta^2(x)] \quad (9)$$

and a lower bound on E_s can be found. Define $E_1 = \sqrt{8\beta}\,\Delta_i/\pi$ (energy of "phase only" soliton with a constant $\Delta = \Delta_i$) then $E_s/E_i > 4.0$ for $\beta = 3$ and the lower bound increases rapidly for larger β.

We now proceed to discuss the situation for many solitons. This is related to the *C–I* transition, or "lock in" transition, which corresponds to $\rho \to \rho_0$ as function of the chemical potential μ. ρ_0 is a commensurate value of the electron density, $\rho_0 = 2N/M$ where $N, M (N < M)$ are small integers [1], and M is the order of commensurability. For $M \geqslant 3$ this transition was studied and shown to be continuous [2–5].

In equation (3) the net energy for creating a soliton is $E_s - \mu$. Thus for $\mu > E_s$ the system is unstable against accumulation of solitons [3–5, 17]. This is the *C–I* transition described by the soliton density $\rho - 1 = \delta\rho(\mu)$. $\delta\rho$ increases as μ becomes larger compared with the locking potential $\frac{1}{2}B\Delta^2$, i.e. the coefficient of cos 2ϕ in equation (4). However, the phase–amplitude coupling drives an unusual effect: as $\delta\rho$ increases, the amplitude and hence the locking potential, both decrease. Thus unlocking becomes easier and the soliton density can bootstrap itself to higher values without increasing μ. This corresponds to an *attractive* interaction between solitons

Recent numerical studies [18] of the Hamiltonian (3) confirm that solitons indeed have a long range attraction, and form static bound states for $\beta > 1.48$.

In the incommensurate limit ($\mu \gg E_i$) the soliton lattice is described by equations (8) and (9) with a density $\delta\rho = qa/\pi$ (each increment of ϕ by π is one soliton). This limit is a good approximation down to near $\mu \sim E_i$ [3, 4, 14], i.e. for $\delta\rho \gtrsim \delta\rho_1$ where

$$\delta\rho_1 = 2E_i a/\pi v_F \,. \quad (10)$$

Below $\delta\rho_1$ the soliton density would decrease very fast with μ, if $\Delta = \Delta_i$ (dashed line in Fig. 1), but then $\Delta(x)$ increases towards Δ_c and μ must increase to overcome the correct soliton energy.

The dependence $\delta\rho(\mu)$ is shown qualitatively in Fig. 1. This type of behavior happens at least for $\beta \gtrsim 3$, since then we have shown two solutions at $\mu = E_s$: the commensurate state, and the incommensurate solution equations (8) and (9), the latter being valid at $\mu^2/E_i^2 = E_s^2/E_i^2 \gg 1$.

Figure 1 implies that the *C–I* transition is of first order. It is analogous to the density–pressure dependence in a gas–liquid transition. The equilibrium solution (vertical line in Fig. 1), describes two separated phases; a commensurate phase and an incommensurate one with density $\delta\rho^*$. For a given $\delta\rho < \delta\rho^*$ the system will separate into these two phases such that the incommensurate phase occupies a fraction $\delta\rho/\delta\rho^*$ of the chain length. Comparing the energy of equations (7) and (8) to the energy of the commensurate phase gives (for large β) that the equilibrium lines is at

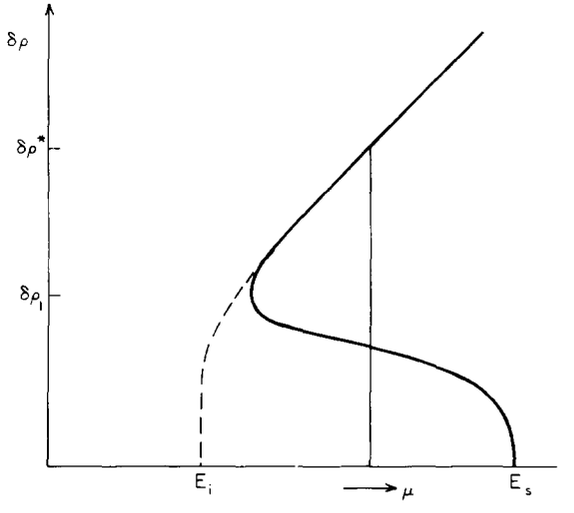

Fig. 1. Qualitative behavior of the excess charge density as a function of the chemical potential. The dashed line corresponds to the (false) case of a constant amplitude $\Delta = \Delta_i$. The vertical line is obtained by a Maxwell construction; it is the equilibrium state for $\delta\rho < \delta\rho^*$ and corresponds to a linear combination of two separated phases.

$\mu \simeq \Delta_c/\sqrt{2}$ and

$$\delta\rho^* \simeq \sqrt{2}\Delta_c a/\pi v_F . \quad (11)$$

This behavior can explain the unusual properties of doped polyacetylene. At very low doping of ~ 0.1% the solitons can be localized by the Coulomb potential of the dopant [8]. As the doping level increases, the attraction between solitons overcomes the dopant pinning and incommensurate regions appear. This process is enhanced if the doping ions can move with the solitons so that the system remains charge neutral on the scale of the coherence length. The incommensurate regions have a higher conductivity than the commensurate regions since (a) the CDW pinning is due just to impurities (no Umklapp scattering), and (b) at finite temperatures the gap Δ_i ($\ll \Delta_c$) is reduced and may even vanish, leading to metallic conductivity.

The i.r. adsorption below ~ 0.5 eV is now explained by the appearance of highly conducting incommensurate regions, while the persisting gap at $2\Delta_c \simeq 1.6$ eV is due to the co-existence of commensurate regions.

The conduction in this system is probably a percolation process between metallic particles embedded in an insulating medium. It was recently noted that a percolation process is consistent with the temperature dependence of the conductivity [19]. As shown here, it is also consistent with the soliton picture for charge carriers.

The conductivity increases strongly around $\delta\rho \simeq 1\%$ which should correspond to the characteristic value $\delta\rho_1$ [equation (10)]. Using a transfer integral of v $v_F/2a \simeq 2$ eV, $E_c \simeq 4$ eV and $\Delta_c \simeq 0.8$ eV we obtain $E_i \simeq 0.2$ eV, $\Delta_i \simeq 0.1$ eV, $\alpha = 2.3$ and $\beta = 4.3$ (or $\lambda = 0.17$, $\gamma = 0.09$). These estimates demonstrate that $\Delta_i \ll \Delta_c$, the phase–amplitude coupling is strong and the qualitative behavior of Fig. 1 is appropriate.

The conductivity should saturate when $\delta\rho \geqslant \delta\rho^*$ since then the whole condensate is incommensurate. Using equation (11) we obtain $\delta\rho^* \simeq 9\%$, in close agreement with the experimental data.

In conclusion, we have shown the existence and significance of a phase field in the electron–phonon order parameter for a condensed half filled band. Excess charge corresponds to phase–amplitude solitons. For low soliton density the interaction between solitons is attractive and leads to phase separation.

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