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# Charge-density waves with electron-electron interactions

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Charge-density waves (CDW) in one-dimensional conductors are studied by treating the electron-phonon interaction in the adiabatic limit, while weak-coupling electron-electron interactions are solved by renormalization-group methods. An exponent $\delta$ defines a renormalization of the effective electronic energy and gap. For a half-filled band system with a backward scattering $g_1 > 0$ ($g_1 < 0$), a bond- (site-) centered CDW is enhanced. We also consider effects of disorder, such as in polyacetylene, and estimate $\delta$ by the phonon-gap relation.

The appearance of a charge-density wave (CDW) in the ground state of a one-dimensional (1D) metal was noticed by Peierls[1] in an electron-phonon system. In the last decade or so, many compounds were found which exhibit CDW's,[2,3] and the need for solving a more realistic model became increasingly important.

The Peierls solution involves two assumptions: (a) the adiabatic limit for the phonons, and (b) neglect of direct electron-electron ($e$-$e$) interactions. The first assumption is justified when the phonon frequency $\omega_0$ is low compared with the gap $2\Delta$ in the electron spectrum.[4] This situation is valid in many compounds, particularly in polymers such as polyacetylene. The second assumption, however, may not be justified even for weak interactions. It is thus the aim of this paper to solve the CDW problem in the adiabatic limit but with weak $e$-$e$ interactions.

The problem with on-site and nearest-neighbor interactions was studied by perturbation theory,[5] by finite-chain calculations,[6] by Monte Carlo simulations,[7] and by a variational procedure.[8] Also, the spinless electron case was solved exactly.[9] Here we consider the general situation of $e$-$e$ backward and forward scatterings with couplings $g_1$ and $g_2$, respectively, and umklapp coupling $g_3$, which is present in a half-filled band. We use the renormalization-group (RG) method,[10] which is valid for weak coupling $\Delta \ll \Lambda$, where $\Lambda$ is an electronic cutoff energy ($2\Lambda \simeq$ electronic bandwidth).

For incommensurate systems ($g_3 = 0$), we find that a CDW is enhanced by long-range repulsive interactions. For a half-filled band there is a significant distinction between a bond CDW and a site CDW, i.e., a CDW with its extrema centered on bonds or on sites. For $g_1 > 0$ bond CDW is enhanced, but a site CDW is eliminated by the $e$-$e$ interactions. For $g_1 < 0$ both types of CDW are enhanced, with the site CDW more strongly enhanced. The effect of $e$-$e$ interactions is contained in a single exponent $\delta$, which affects both the gap $2\Delta$ and the renormalized phonon frequency $\omega^R$. By introducing a varying degree of disorder, a functional relation of $\Delta$ and $\omega^R$ is obtained, and this phonon-gap plot can determine $\delta$ and a disorder exponent $p$.

A CDW describes an ion displacement with wave vector $2k_F$ ($k_F$ is the electron's Fermi wave vector) and amplitude $\Delta_d$. The Hamiltonian depends on $\Delta_d$ in the form[11]

$$H_p = \Delta_d \sum_{k,\sigma} a^\dagger_{k_F+k,\sigma} b_{-k_F+k,\sigma} + \text{H.c.} + \Delta_d^2/(2\pi v_F \lambda) \ , \quad (1)$$

where $v_F$ is the Fermi velocity, $\lambda$ is the dimensionless electron-phonon coupling, and $a^\dagger_{k\sigma}$ ($b^\dagger_{k\sigma}$) is the creation operator for a right- (left-) moving electron with wave vector $k$ and spin $\sigma$. The first term in (1) is $H_{e\text{-ph}}$, the electron-phonon coupling, while the second term is the phonon elastic energy. [If the band is not half-filled, $\pm 2k_F$ are independent distortions and the second term in (1) has to be doubled; i.e., $\lambda$ is replaced by $\lambda/2$ (Ref. 11)].

The rest of the Hamiltonian contains the electron kinetic energy $H_e$ with the conventional linearized dispersion for the electrons and $H_{e\text{-}e}$ with the $e$-$e$ couplings $g_1$, $g_2$, and $g_3$.[10] (Here $g_i$ are dimensionless; i.e., they are those of Ref. 10 divided by $2\pi v_F$.) These interactions correspond to backward ($g_1$), forward ($g_2$), and umklapp ($g_3$) scatterings. The problem is solved in two steps. First, the $e$-$e$ interactions are eliminated by the RG integration and lead to a renormalized gap $\Delta$ and electron energy $E_i(\Delta_d)$. The second step is to minimize $E_i(\Delta_d)$ together with the last term in (1).

The $2k_F$ vertex coupling $\Delta_d$ corresponds to interacting electrons with energy cutoff $\Lambda$. Perturbation theory in $g_i$ can be used to find the contribution of electron states with energies between $\omega$ and $\Lambda$ ($\omega < \Lambda$) to a vertex function $\Delta(g_i, \omega/\Lambda)$. If this function satisfies a scaling relation[10] then the electron states can be successively integrated down to the largest characteristic energy, which is either $\Delta_d$ or $\Delta$ itself. This procedure sums logarithmically divergent integrals [$\sim \ln(\omega/\Lambda)$], which are present only for $\omega > \max(\Delta_d, \Delta)$. This approach is valid for $g_i \ll 1$ and $\ln(\Delta/\Lambda) \gg 1$ so that the logarithmic terms are indeed dominant.

A straightforward summation of diagrams to second order[12] in $g_i$ yields for the most diverging terms

$$\Delta(g_i, \omega/\Lambda) = \Delta_d \{1 + (2g_1 - g_2 + g_3)\ln(\omega/\Lambda) + [(2g_1 - g_2 + g_3)^2 - \tfrac{1}{2}(g_1 - g_2)^2 + g_1 g_2 - g_3(g_1 + g_2)]\ln^2(\omega/\Lambda)\} \ . \quad (2)$$

 

This is a scaling function if it satisfies a relation of the form

$$\Delta(g_i^R(g_i,\Lambda'/\Lambda),\omega/\Lambda')=Z(g_i,\Lambda'/\Lambda)\Delta(g_i,\omega/\Lambda)\ , \quad (3)$$

where $g_i^R$ are the renormalized couplings with cutoff $\Lambda'$. To first order we need

$$Z(g_i,\Lambda'/\Lambda)=1+(2g_1-g_2+g_3)\ln(\Lambda/\Lambda')+O(g_i^2)\ ,$$

which together with the known $g_i^R$ (Ref. 10) shows that (3) is satisfied also to second order. Equation (3) can now be used to obtain a Lie equation:

$$\frac{\partial}{\partial\omega}\ln\Delta(g_i,\omega/\Lambda)=\frac{\partial}{\partial\omega}\ln\Delta(g_i^R(g_i,\Lambda'/\Lambda),\omega/\Lambda')\Big|_{\Lambda'=\omega}$$
$$=\frac{1}{\omega}[\,2g_1^R(g_i,\omega/\Lambda)-g_2^R(g_i,\omega/\Lambda)$$
$$+g_3^R(g_i,\omega/\Lambda)]\ . \quad (4)$$

The leading behavior is obtained by inserting the fixed point values $g_i^*=g_i^R(g_i,0)$ with the combination $\delta\equiv g_2^*-2g_1^*-g_3^*$. In conventional perturbation theory the integration range is $\Delta_d<\omega<\Lambda$ with $\Delta(g_i,1)=\Delta_d$ and $\Delta(g_i,\Delta_d/\Lambda)=\Delta$. Equation (4) then yields

$$\Delta=\Lambda(\Delta_d/\Lambda)^{1-\delta}\ . \quad (5)$$

Note, however, that for $\delta>0$ the gap is enhanced; $\Delta>\Delta_d$, and therefore the lower integration limit is the renormalized gap $\Delta$. Integrating Eq. (5) between the limits $\Delta(g_i,1)=\Delta_d$ and $\Delta(g_i,\Delta/\Lambda)=\Delta$ yields a self-consistency equation for $\Delta$, $\Delta=\Delta_d(\Delta/\Lambda)^{\delta}$, or

$$\Delta=\Lambda(\Delta_d/\Lambda)^{1/(1+\delta)}\ . \quad (6)$$

The exponents in Eqs. (6) and (7) coincide to first order in $\delta$, but differ in higher orders. As shown below, a CDW is present in the ground state only if $\delta>0$, and then Eq. (6) is appropriate.

From the known fixed points[10] the exponent $\delta$ can be determined as summarized in Table I. Note that when $\delta$ is of order 1 the second-order RG used here is not sufficient. More reliable values are known for $-g_1=|g_3|=\frac{5}{6}$ (Ref. 10). In the following, however, we do not need the precise value of $\delta$.

We next derive the gap equation and the electronic energy. The charge-density wave response function is given by[10]

$$\pi v_F N(\Delta)=\int_\Lambda^\Delta\left(\frac{\omega}{\Lambda}\right)^{-2\delta}\frac{d\omega}{\omega}=\frac{1}{2\delta}\left[\left(\frac{\Lambda}{\Delta}\right)^{2\delta}-1\right]\ , \quad (7)$$

where $\delta$ is the same exponent defined above. Note that for $\delta\to 0$ (no $e$-$e$ interactions) this reduces to the Peierls result $\ln(\Lambda/\Delta)$. The phonon propagator with zero frequency is $\sim[1-2\lambda\pi v_F N(\Delta)]^{-1}$, and $\Delta$ is a static solution if the gap equation $1=2\lambda\pi v_F N(\Delta)$ (Ref. 13) is satisfied. An equivalent way of obtaining the gap equation is to minimize the electronic energy $E_i(\Delta_d)$, defined as

$$-2E_i(\Delta_d)/\pi v_F=\langle H_e+H_{e\text{-}e}+H_{e\text{-ph}}\rangle\ ,$$

with the last term in (1), i.e., $\partial E_i(\Delta_d)/\partial\Delta_d=\Delta_d/2\lambda$. Comparison with the other form of the gap equation leads to the electronic energy

$$E_i(\Delta_d)=\int_0^{\Delta_d}\pi v_F N(\Delta_d')\Delta_d'\,d\Delta_d'$$
$$=\frac{1+\delta}{4\delta}\Lambda^2\left(\frac{\Delta_d}{\Lambda}\right)^{2/(1+\delta)}-\frac{1}{4\delta}\Delta_d^2\ . \quad (8)$$

The gap equation is then

$$\Delta=\Lambda\left(\frac{\lambda}{\delta+\lambda}\right)^{1/2\delta}\ , \quad (9)$$

and for the ion displacement

$$\Delta_d=\Lambda\left(\frac{\lambda}{\delta+\lambda}\right)^{(1+\delta)/2\delta}\ . \quad (10)$$

Equations (9) and (10) show that $\Delta$ increases with $\delta$ while $\Delta_d$ reaches a maximum, though at a value beyond our weak-coupling assumption. $N(\Delta)$ diverges at $\Delta\to 0$ for all $\delta>0$, and a CDW is then present in the ground state. For $\delta<0$ the ground state does not show a CDW. Note that a CDW in the present adiabatic limit has long-range order. Allowing a low but finite phonon frequency, the half-filled band still has long-range order,[7] while the incommensurate case has only algebraic order.

We now discuss the results in Table I and compare them with other methods. The most reliable value of $\delta$ is for the incommensurate case with $g_1>0$ (Ref. 13), since $\delta$ is small.

TABLE I. Second-order renormalization-group results for the CDW exponent $\delta$.

| $e$-$e$ couplings | Type of CDW | $\delta$ |
|---|---|---|
| $g_1>0,\ g_3=0$ | incommensurate | $g_2-\frac{1}{2}g_1$ |
| $g_1<0,\ g_3=0$ | incommensurate | $\frac{3}{2}+g_2-\frac{1}{2}g_1$ |
| $g_1>0,\ \lvert g_3\rvert>g_1-2g_2$ | bond | $\frac{3}{2}$ |
| | site | $-\frac{1}{2}$ |
| $g_1<0,\ \lvert g_3\rvert>g_1-2g_2$ | bond | 1 |
| | site | $\frac{5}{2}-\frac{1}{2}[1+(g_1-2g_2)^2-g_3^2]^{1/2}$ |
| $g_1>0,\ \lvert g_3\rvert<g_1-2g_2$ | bond or site | $-\frac{1}{2}[(2g_2-g_1)^2-g_3^2]^{1/2}$ |
| $g_1<0,\ \lvert g_3\rvert<g_1-2g_2$ | bond or site | $\frac{3}{2}-\frac{1}{2}[(g_1-2g_2)^2-g_3^2]^{1/2}$ |

If the long-range coupling dominates $g_2 > g_1/2$, then $\delta > 0$ and the CDW is enhanced. When $\delta$ is of order 1, its value is not exact, but can still be used to compare relative enhancements in different regimes. When $g_1 = g_3 = 0$ a transformation into a boson system followed by a first-order RG (Ref. 14) leads to

$$2\delta = 1 - [(1-2g_2)/(1+2g_2)]^{1/2} \ .$$

A Bethe ansatz solution[9] yields

$$\delta = (2/\pi)\cot^{-1}(g_2/2) - 1 \ ;$$

both results yield, in weak coupling, $\delta = g_2$, as in Table I.

The most studied case in that of the half-filled band with a Coulomb repulsion $2\pi v_F V_m > 0$ between electrons $m$ sites apart. The case with a real $\Delta_d$ implies[11] that the CDW

$$\Delta_d \exp(2ik_F x) + \text{H.c.} = 2\Delta_d \cos(2k_F x)$$

is a site CDW. In this case a decomposition into slowly varying right- and left-moving fields[11] yields $g_1 = g_3 = \sum_m (-1)^m V_m$, while $g_2 = \sum_m V_m$. (These are the $2k_F$ and zero Fourier transforms of $V_m$.) When $\Delta_d$ is imaginary, the CDW is $2|\Delta_d|\sin(2k_F x)$; i.e., it is a bond CDW. Our derivation with a real $\Delta_d$ holds after the transformation $a_{k,s} \rightarrow ia_{k,s}$, since then the form of Eq. (1) is retained with a real $|\Delta_d|$. This transformation has the effect of changing the sign of $g_3$, i.e., $g_1 = -g_3 = \sum_m (-1)^m V_m$. This sign change is significant since $V_m > 0$ and $|g_3| > g_1 - 2g_2$; $g_3$ is then relevant; i.e., it flows to a large value $g_3^R = \text{sgn}(g_3)$. Thus, even if $g_3$ is small, its sign results in a large change in its renormalized value. For $g_1 > 0$ bond order has $\delta = \frac{3}{2}$, while site order has $\delta < 0$; i.e., a site CDW is not a possible phase. If $g_1 < 0$ both types of CDW are possible, with the site CDW more strongly enhanced.

Monte Carlo simulations[7] show that $V_0 (= U)$ enhances the bond CDW while a site CDW is reduced, in qualitative agreement with our results. Finite chain calculations[6] show that $V_1 < U/2$ favors a bond CDW while $V_1 > U/2$ favors a site CDW; a presence of $V_2$ favors bond CDW even if $V_1 > U/2$. This is clearly consistent with our results, since $g_1 = U - 2V_1 + 2V_2$ in this model; $g_1 > 0$ favors bond CDW while $g_1 < 0$ favors a site CDW.

An important consequence of our theory is the frequency $\omega_R$ of oscillations in $\Delta_d$, which is measurable by Raman scattering. An effective Lagrangian is obtained from Eq. (9) with the kinetic term $(\partial\Delta_d/\partial t)^2/(2\pi\lambda v_F \omega_0^2)$, where $\omega_0$ is a bare phonon frequency. Expansion around the minimum then yields for $2\tilde{\lambda} = (\omega_R/\omega_0)^2$ [or $2\tilde{\lambda} = \prod_{n=1}^{N} (\omega_n^R/\omega_n^0)^2$ with $N$ normal modes[15]]

$$\tilde{\lambda} = (\lambda + \delta)/(1+\delta) \ . \tag{11}$$

Finally, we comment on Raman scattering data of polyacetylene $(CH)_x$ and show how disorder effects can yield information on the coupling constants. Disorder changes both $\tilde{\lambda}$ and $\Delta$ from their ordered values $\tilde{\lambda}_0$, $\Delta_0$. The resonance condition for Raman scattering allows us to determine $\tilde{\lambda}_0/\tilde{\lambda}$ as a function of $\Delta/\Delta_0$.[16] Data on *trans*-$(CH)_x$ or -$(CD)_x$ show the relation $\tilde{\lambda}_0/\tilde{\lambda} = 1 - 0.37\ln(\Delta/\Delta_0)$ for $0 < \ln(\Delta/\Delta_0) < 0.7$, while for *trans-cis* mixtures $\tilde{\lambda}_0/\tilde{\lambda} = 1 - 1.0\ln(\Delta/\Delta_0)$ in the available range $0 < \ln(\Delta/\Delta_0) < 0.2$.

The effect of disorder is described[16] by adding to Eq. (9) a term $\sim \Delta^p$ or $b\Delta_d^{p/(1+\delta)}$. The power $p$ signifies the type of disorder and $b$ is its strength. Eliminating $b$ from the modified $\omega_R$ and $\Delta$ equations yields the phonon-gap relation

$$\tilde{\lambda}_0/\tilde{\lambda} = 1 - (2-p)\ln(\Delta/\Delta_0) + (2-p)(2-p+\delta)\ln^2(\Delta/\Delta_0) + O(\ln^3(\Delta/\Delta_0)) \ . \tag{12}$$

This relation is consistent with data on mixtures and yields $p = 1$; $\delta$, however, cannot be determined due to the limited range of the data. Data on *trans*-$(CH)_x$ do not fit Eq. (12) with $\delta > 0$. Instead, "intrinsic" disorder is assumed;[16] i.e., $\lambda$ is replaced by $\lambda(1+b)$. The phonon-gap relation becomes

$$\tilde{\lambda}_0/\tilde{\lambda} = 1 - 2\lambda\ln(\Delta/\Delta_0) - 2\lambda\delta\ln^2(\Delta/\Delta_0) + O(\ln^3(\Delta/\Delta_0)) \ . \tag{13}$$

The accuracy with which the linear term fits the data implies $0 < |\delta| < 0.3$. Both types of disorder may correspond to $b$ being a scaling variable. The effect is then described by a crossover function, which for weak disorder replaces $E_i(\Delta_d)$ by

$$E_i(\Delta_d)[1 + b\Delta_d^{(p-2)/(1+\delta)}] \ .$$

Intrinsic disorder has, then, $p = 2$, while "extrinsic" disorder has its leading term with $p = 1$.

The expected fixed point in Table I is $\delta = \frac{3}{2}$. The data then implies that $g_i$ are small and that the RG integration range $[\ln(\Lambda/\Delta) \simeq 2$ in $(CH)_x]$ is not sufficiently large to fully renormalize $g_i$. If $g_i \ln(\Lambda/\Delta) << 1$, then just perturbation theory [Eq. (2)] yields $\delta = g_2 - 2g_1 - g_3$. Note that the on-site interaction $U$ cancels in this expression. Thus an intermediate $U$ can affect soliton excitations,[17] while the effect on the ground state (through $\delta$) is weak.

In conclusion, we have shown that the Peierls model can be solved also with weak $e$-$e$ interactions. Of particular importance are phonon-gap plots which allow us to test the $\omega_R - \Delta$ functional relation and yield information on the microscopic coupling constants.

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