Gap to Transition Temperature Ratio in Density Wave Ordering: a Dynamical Mean Field Study

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We use the dynamical mean-field method to determine the origin of the large ratio of the zero temperature gap to the transition temperature observed in most charge density wave materials. The method is useful because it allows an exact treatment of thermal fluctuations. We establish the relation of the dynamical mean-field results to conventional diagrammatics and thereby determine that in the physically relevant regime the origin of the large ratio is a strong inelastic scattering.

Density wave ordering is a transition to a phase in which the electronic charge or spin density has lower symmetry than the underlying lattice. It occurs in a wide range of materials, including quasi-one-dimensional organic conductors [1], dicalogenides such as 2H-TaSe₂ [2], ‘A-15’ materials like V₃Si [3], ‘blue bronzes’ such as KMoO₃ [4], and the ‘Verwey transition’ material Fe₃O₄ [5]. Much recent activity has related to actual or possible stripe density wave order in some members of the high temperature superconductor family [6] and to charge and orbital order in some members of the ‘colossal’ magnetoresistance materials [7].

In most cases the density wave order evolves out of a metallic phase and in this situation it is usually believed [1] to be driven by a fermi surface ‘nesting’ instability. The resulting equations are similar to those of the ‘BCS’ theory of superconductivity and in particular lead to a ratio of \( T = 0 \) density wave gap \( \Delta \) to density wave ordering temperature \( T_c \) which is close to the ‘BCS’ value \( \Delta_{BCS}/k_BT_c = 1.76 \). Almost all density wave materials, however, exhibit much larger \( \Delta/k_BT_c \) ratios. In quasi-one-dimensional materials the large ratio may be understood [1] as a consequence of critical fluctuations in low dimensionality, which decrease the transition temperature more than the \( T = 0 \) gap \( \Delta \). (Indeed, in a strictly one dimensional material, \( T_c = 0 \) while \( \Delta > 0 \).) However, \( \Delta/T_c \) values as large as 10 are also observed in quasi two dimensional systems and in many fully three dimensional materials [2,3,5,6]. These are not explicable either in the BCS approximation or in terms of the Migdal-Eliashberg-McMillan generalization [6] to so-called strong coupling superconductors such as Pb, which exhibit \( \Delta/T_c \) ratios only as large as 2.5.

A generally accepted explanation in the physically relevant regime has not appeared. An extremely large electron-phonon interaction could localize carriers as polarons with a large activation gap; the ordering temperature \( T_c \) would then be controlled by a weak polaron-polaron repulsion and a large gap to \( T_c \) ratio would result. However, this would imply a non-metallic normal state with a resistivity which is large and diverges rapidly as \( T \to 0 \), unlike the systems listed above (except perhaps for Fe₃O₄). McMillan made the intriguing suggestion (which has not been followed up by subsequent workers as far as we know) that the low \( T_c \) (relative to \( \Delta \)) was a phonon entropy effect [10]: thermal fluctuations of the phonons would create areas where the local gap was small compared to the average, and a self consistent process of exciting the electrons into these areas would lead to the destruction of long ranged order.

In this paper we address the issue quantitatively using the dynamical mean-field method [12] in the implementation described in [13]. The technique permits a complete solution at all coupling strengths and temperatures, within a local (momentum independent self-energy) approximation which is now generally accepted as reliable in \( d = 3 \) spatial dimensions [12]. We use it to show that in the weak to intermediate coupling regime relevant to most of the materials listed above, the crucial physics is inelastic scattering of electrons by the phonons involved in the lattice distortions. The phonon entropy effects proposed by McMillan [10] are present, but are found to be less important. This paper builds on the previous work of Ciuchi and DiPasquale who extended the methods of [13] to the density wave ordering case and computed the phase diagram in the intermediate to strong coupling regime [14]. We focus here on weak to intermediate couplings and present new physical interpretations.

We study the Holstein model [11], defined by

\[
H_{\text{hol}} = -\sum_{ij} (t_{i-j} + \mu \delta_{ij}) c_i^\dagger c_j + \frac{1}{2\lambda W} \sum_i r_i^2 + \sum_i r_i \left( c_i^\dagger c_i - n_i \right),
\]

(1)

Here the operator \( c_i^\dagger \) creates an electron on site \( i \) and \( r_i \) is the displacement of the ion on site \( i \) measured from the equilibrium displacement corresponding to a uniform distribution of electrons and rescaled so that the...
electron-phonon coupling is unity. We have written the rescaled phonon stiffness in terms of an electron band-
width parameter $W$ defined below and a dimensionless
coupling $\lambda$. Because it contains all of the physics of rele-
vance to us and simplifies the computation substantially
we have adopted a classical limit (phonon kinetic term
$\sum_{\nu} \frac{p^2}{2m}$ is missing). We comment below on the effects of
the neglected quantum fluctuations. We also assume a
bipartite lattice, which for our purposes is a lattice pos-
sessing a dispersion $\epsilon_k$ (fourier transform of $t_{i-j}$) and
a wavevector $\tilde{Q}$ such that $\epsilon_{\tilde{Q}} - \epsilon_k = -\epsilon_k$ for all $k$ in the
Brillouin zone. An equivalent definition is that the lat-
tice may be divided into two sublattices $A$ and $B$, such
that $t_{i-j}$ only connects $A$ sites to $B$ sites. We further
specialize to $n = 1/2$; this implies $\mu = 0$.

At $n = 1/2$ the ground state of $H_{hol}$ may be shown to be
charge ordered for all $\lambda$ by minimizing $\langle H_{hol} \rangle$ over $r_i$. To compute $\langle H_{hol} \rangle$ we introduce operators $a^\dagger$ and $b^\dagger$ creating
electrons on the $A$ and $B$ sublattices respectively and
make the ansatz that $r_i = \Delta$ on the A sublattice and $r_i =
-\Delta$ on the B sublattice. In momentum space the Hamil-
tonian may be written as the $2 \times 2$ matrix $H_{hol}(\Delta) = \frac{1}{2} N \frac{\Delta^2}{\lambda} + \frac{1}{2} \sum_k \left( a_{\tilde{k}}^\dagger b_k^\dagger \right) \left[ \Delta \tau_z + \epsilon_{\tilde{k}} \tau_x \right] \left( a_{\tilde{k}} \right)$ where $\tau_z$ and $\tau_x$ are the usual Pauli matrices and all $k$-sums are over
the full zone. The resulting energy dispersion is $E_k = \pm \sqrt{\epsilon_k^2 + \Delta^2}$ and the energy of $H_{hol}(\Delta)$ may easily be
found, and minimized over $\Delta$. The equation yielding the minimum value is

$$1 = \lambda W \frac{1}{N} \sum_k \frac{1}{\sqrt{\epsilon_k^2 + \Delta^2}}.$$ 

If $\mu = 0$ the integral, $\langle 3 \rangle$, is logarithmically divergent
as $\epsilon_k \to 0$ and thus a $\Delta > 0$ solution exists. Later
in this paper we use the semicircular density of states
$\rho_0(\epsilon) = \frac{1}{\pi \lambda^2} \sqrt{\lambda^2 - \epsilon^2}$ for which
the solution can be solved analytically, yielding $\Delta = \frac{1}{4W} \sqrt{\lambda^2} e^{-\pi^2} (1 + O(\lambda)).$

We now turn to the treatment of non-zero tempera-
ture, following refs [13][14]. The crucial object in the
analysis is the electron Greens function, which in the $a-b$ basis introduced above is a matrix $G$ given by

$$G_{\tilde{k}, i\omega_n}^{-1} = i\omega_n + \mu - \Sigma_n(i\omega_n) - \epsilon_k \tau_x - \Sigma_{co}(i\omega_n) \tau_x \tag{3}$$

The self-energy $\Sigma$ has a normal (n) component at all
$T$ and an extra $co$ component at $T < T_{co}$. Its $k$-
independence (locality) is the fundamental assumption of the dynamical mean field method. Off diagonal $\sim \tau_x$
components of $\Sigma$ are not local in coordinate space, so do
not appear in the DMFT. The two self energies are fixed by two coupled dynamical mean-field equations [14] for effective fields $(a,b)$:

$$a_n = i\omega_n + \mu - \frac{W^2}{4} G_{BB}(i\omega_n), \tag{4}$$

$$b_n = i\omega_n + \mu - \frac{W^2}{4} G_{AA}(i\omega_n). \tag{5}$$

Here $G_{AA/BB}$ are the two nonzero components of the local Greens function defined by $G_{loc}(i\omega) = 1/N \sum_k G(\tilde{k}, i\omega_n)$. (recall $\sum_k \epsilon_k = 0$. They are related to the effective fields $\{a_n, b_n\}$ by $G_{AA}(i\omega_n) = \frac{2iM}{\omega_n}$ with $Z_A = \int d\omega P(\{a_n\}, r)$ and

$$P(\{a_n\}, r) = e^{-\beta \left[ \frac{1}{2} (r-\mu)^2 + \frac{1}{4} \sum_n \ln(a_n - r) \right]} \tag{6}$$

($G_B$ and $Z_B$ analogous). $P(\{a_n\}, r)$ is the probability
distribution of local distortions on the $A$-sublattice.

For zero temperature we recover the previously dis-
cussed commensurate charge order, because for Eq. [4] at
$T = 0$ $\Sigma_{AA}(\tilde{k}, i\omega_n) = -\Delta$ and $\Sigma_{BB}(\tilde{k}, i\omega_n) = \Delta$. For
$T > 0$ we solve Eq. [4] to [6] using the procedure of Ref.
[13]; we retained $2^{10}$ Matusbara frequencies and extended
the frequency range analytically. We obtained conver-
gen for $T > 0.005$ which is roughly $T_{co}$ for $\lambda = 0.64$

![Fig 1](image)

Fig. 1 Main panel: phase diagram of $H_{hol}$. Solid points: numerically calculated transition temperatures. Open points: 'modified BCS' approximation discussed below [6]. Dashed line: conventional BCS approximation. Shaded region: charge ordered; un-
shaded: no order. Regime I: fermi liquid like normal state; regime
II: 'polaron-like' normal state; regime III: 'polaron-like' normal state; regime II cross-over, as defined from
$P(r)$ and $\rho(\omega)$ as discussed in text below. Left inset: $T_{co}$ vs $\lambda$ on
logarithmic scale Right inset: gap to transition temperature ratio.

Fig. 1 shows our calculated phase diagram. Where
there is overlap (roughly $\lambda > 0.8$) our results are in agree-
ment with those of Ciuchi and de Pasquale [14] if we scale
$T \to T/W$ and $\lambda \to \lambda/(2W)$ with $W = 2$. From the
left inset we see that the BCS approximation (dashed line)
overestimates $T_{c}$ by a constant factor, but a differ-
et 'modified BCS' approximation (open circles) agrees...
well with the small $\lambda$ numerical results. From the right inset of Fig. 1 we see that only for $\lambda = 0$ is the BCS value is obtained.

$$\lambda = 2.40 \quad \lambda = 4.00$$

**Fig. 2** Distribution of local distortions $P(r)$ for three different coupling strengths $\lambda$, for $T = 0$ (vertical line), $T \approx 0.93 T_{co}$ (light lines) and $T = 0.125 >> T_{co}$ (heavy lines). For $T < T_{co}$ solid line: A sublattice; dashed line: B-sublattice.

We next consider the phonon probability distribution $P(r)$ and the local electron spectral function $\rho(\omega) = -\frac{1}{\pi} \text{Im} G_{A/B}(\omega)$, shown in Figs 2 and 3 for several couplings and temperatures.

$$\lambda = 1.44 \quad \lambda = 2.40 \quad \lambda = 4.00$$

**Fig. 3** Spectral function of electrons $\rho(\omega)$ for three different coupling strengths $\lambda$, for $T = 0$ (vertical line), $T \approx 0.93 T_{co}$ (light lines) and $T = 0.125 >> T_{co}$ (heavy lines). For $T < T_{co}$ solid line: A sublattice; dashed line: B-sublattice.

For a weakly coupled fermi liquid (left panels, Figs 2,3; region I of figure 1) $P(r)$ is sharply peaked about its mean value $r = 0$ and $\rho(\omega)$ takes approximately the non-interacting form (in our case, a semicircle). For a very strongly coupled system (right panels, Figs 2,3; region III, Fig. 1) one should think of the excitations as polaron, strongly bound electron-phonon complexes. In this situation $P(r)$ displays two broad peaks (corresponding to distortions on occupied sites and antdistortions on unoccupied sites) and $\rho(\omega)$ has a two peak structure corresponding to bound and empty sites. The crossover between regions I and III occurs for couplings near $\lambda_c = 3\pi/4 \approx 2.356$ at which the weak coupling theory predicts a $T = 0$ transition to a charge-disordered polaron insulator (this transition is preempted by the charge ordering transition). We have defined the left-hand boundary of the cross-over region as the locus of points at which $P(r)$ loses its maximum at $r = 0$ and the right-hand boundary as the locus of points at which $\rho(\omega)$ gains a minimum at $\omega = 0$. The point $\lambda_c$ sits approximately in the center of region II.

We now examine the weak coupling limit of $T_{co}$ analytically. We first assume the equations have been solved with $T > T_{co}$, yielding a mean field function $c_n$. Just below the transition temperature the two effective fields $a_n$ and $b_n$ differ only slightly from each other or from the $T > T_{co}$ result, thus $a_n = c_n + \epsilon_n$, $b_n = c_n - \epsilon_n$. Expanding the equations for the effective fields to linear order in $\epsilon_n$ we get the matrix equation for $\epsilon_n$

$$\epsilon_n = -\frac{W^2}{4} \begin{bmatrix} G_n^2 & \sum_{m \neq n} \left( G_n G_m + \frac{G_m - G_n}{\epsilon_m - \epsilon_n} \right) \epsilon_m \end{bmatrix}$$

(7)

with $G_n = \frac{1}{\beta} \int dt e^{-i\omega_n t} \rho_{c_n c_n}(t)$. $T_{co}$ is the temperature at which Eq. (5) has a solution. As written it is general; in the weak coupling limit $G_n = \frac{1}{\beta} \int dt e^{-i\omega_n t} \rho_{c_n c_n}(t) + O(T^2 \lambda^2)$

with $\epsilon_n^0 = (G_n^0)^{-1} = \frac{1}{2} \left( i \omega_n - \sqrt{(i \omega_n)^2 - W^2} \right)$ and

$$\bar{\lambda} = \lambda / \left( 1 + \frac{\lambda W}{\beta} \sum_n \frac{1}{(\epsilon_n^0)^2} \right) \equiv \left( \lambda^{-1} - \lambda_c^{-1} \right)^{-1}$$

(8)

From the form of $G_n$ we see that the expansion parameter is $T \bar{\lambda}$ rather than $\lambda$. The factor $T$ is the classical analogue of the Migdal parameter $\omega_D$ while the presence of $\bar{\lambda}$ rather than $\lambda$ indicates that proximity to the polaronic instability strongly renormalizes the coupling. Inserting $G_n$ into (7) and rearranging leads, after lengthy calculation to the weak-coupling $T_{co}$-equation

$$1 = -\frac{1}{\beta} \sum_n \frac{G_n^0}{i \omega_n - 2 \lambda T_{co} G_n^{-1}}.$$  

(9)

Eq.(4) may be evaluated to logarithmic accuracy by replacing $G$ by its $\omega = 0$ values $\pm W$, yielding $\frac{\lambda}{T_{co}} = \frac{\pi}{2} + \frac{\pi}{2} \frac{\lambda}{1 - \lambda_c} \gamma \approx 1.78107$, showing explicitly the deviations from BCS.

We now compare Eq.4 to the result obtained from the divergence of the charge order susceptibility defined by
\[
\chi_{co} = \frac{1}{\beta T} \sum_{n,m} e^{-i \vec{Q} \vec{r}} \frac{\beta}{\theta} \int_0^\theta d\tau \left( \langle n_\tau \mid n_0 \rangle - \langle n_0 \mid n_0 \rangle \right)^2
\]
\[
\cong \left( \frac{1}{\beta T} \right)^2 \sum_{n,p} \chi_{np} \chi_{np} \text{ may be expressed in terms of an irreducible vertex function } \bar{\Gamma} \text{ which, within the dynamical mean-field approximation, is local}\]

\[
\chi_{np} = -\lambda_0^2 \delta_{np} - \chi_0 \beta \sum_m \chi_{nm} \chi_{mp} \text{ with } \chi_0 = -\lambda \sum_n \chi_{0n}^\dagger \chi_{0n} = -\lambda \sum_n \chi_{0n} \chi_{0n}^\dagger. \]  

This equation may be expressed diagrammatically; in the weak coupling limit, the terms are shown in Fig. 4, which is exact up to terms of order \((T\lambda)^2\).

\[\text{Fig. 4 } \text{Diagrammatic expansion of the one-particle self-energy}
\]
(a) of the irreducible vertex of the charge-order susceptibility (b) Heavy lines: full local Green’s function \(G_n\). Dashed lines: free phonon propagator \(D_\omega\). All not shown but possible diagrams are smaller by additional factors of \(T\).

We find \(\Sigma_n = \lambda^2 T\) and \(\bar{\Gamma}_{nm} = -\lambda + \lambda^\dagger \delta_{nm}\), with \(\lambda = \lambda / (1 + \lambda / 2 \sum \beta G_n^\dagger)\). Note, \(\lambda\) coincides with the previously introduced one if we replace \(G_n \rightarrow G_n^0\) which is correct at the order in \(T\) to which we work. Use of this \(\bar{\Gamma}\) yields \(\chi_{n,m}^{-1} = \chi_{n,m}^{-1} - \lambda\) with \(\chi_0 = \frac{1}{\beta} \sum_n \chi_{0n} \chi_{0n}^\dagger\). This diverges when Eq. 4 is fulfilled.

We can now interpret Eq. 4 on more physical grounds. In the BCS limit, the irreducible vertex is given by \(\lambda\) and \(\lambda_0\) by the convolution of two bare Green’s function. The leading effect of increased coupling is a \(T\)-dependent self-energy, corresponding to inelastic scattering of electrons by phonons. Insertion of self-energies into \(\chi_{n,m}\) increases the scale at which the logarithmic divergence is cut off, thereby reducing \(T_{co}\). This physics however does not operate at \(T = 0\); thus it does not reduce the gap. In a more realistic model including quantum phonons some inelastic scattering would be present at \(\omega > 0\) even at \(T = 0\), renormalizing the gap slightly, but it would be weak in comparison to the thermally generated scattering so \(T_{co}\) will be reduced more then \(\Delta\). Also in a more realistic quantum model the thermal scattering is negligible for temperatures lower than \(\Theta_D/3\) (\(\Theta_D\) is the Debye temperature); thus the effects we have described will be important only if \(T_{co} > \Theta_D/3\). In addition to the self-energy, there is a vertex correction, which acts just as the self-energy, to weaken the instability via inelastic scattering.

The ‘modified BCS’ result 4 is shown as the dashed line in Fig. 1 and is seen to break down at the boundary of region I, when \(\rho(\omega)\) and \(P(\tau)\) begin to acquire structure indicating polaronic features. This shows that in the weak coupling regime, inelastic scattering is the key issue, and that ‘pseudogap’ formation not easily described in terms of traditional diagrammatics leads to changes in behavior.

We finally discuss the relation of our results to the interesting proposal of McMillan [10] concerning phonon entropy effects. As can be seen from Fig. 2, at intermediate coupling thermal fluctuations of the phonon fields are crucial. If the fluctuations were negligible as in the BCS theory the widths of the peaks at \(T = 0.04\) would be negligible in comparison to their separation. However, as can also be seen the peaks either in the phonon distribution or the density of states do not shift appreciably until \(T\) becomes extremely close to \(T_{co}\). Thus the fluctuations, while strong, apparently do not feed back and reduce the mean value of the gap in the manner assumed by McMillan. However, the fluctuations do lead to a non-negligible probability of \(r \approx 0\), i.e., of regions with a very small local gap. Electronic excitations in these regions give rise to the non-vanishing low energy density of states at the chemical potential, and as the regions become more probable, cause the destruction of the ordered phase. Comparison of the middle and left panel of Figs. 2 and 3 shows that as the coupling is further increased, the physics crosses over smoothly to that expected in the very strong coupling limit.

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