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# RETARDATION EFFECTS ON THE PEIERLS PHASE

B. Horovitz

The Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem, Israel

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The mean field theory of the Peierls instability is extended to include the small momentum transfer interaction, which is shown to be a retarded interaction. The Peierls transition temperature is shown to depend significantly on the bare phonon frequency. A positive isotope shift parameter is predicted, with values in the range 0–0.5.

It is also argued that the ratio of the zero temperature gap to the transition temperature is larger than the BCS value of 3.5.

RECENT EXPERIMENTS have shown the occurrance of a Peierls instability in quasi one-dimensional ($1d$) conductors.[1,2] The Peierls instability is usually described in terms of the electron–phonon interaction with momentum transfer of $2p_F$, where $p_F$ is the Fermi wavevector. The mean field (MF) theory of this interaction leads to a BCS type equation and has been extensively studied.[3,4] In particular the region of validity of the MF theory, using an interchain coupling, has been examined.[4]

In the present work the MF theory is extended to include the small momentum transfer interaction which is shown to be a retarded interaction. This leads to a significant dependence of the Peierls transition temperature ($T_p$) on the bare phonon frequency ($\omega_0$). A positive isotope shift is predicted, and may be observed experimentally if $\omega_0 \gtrsim 2\pi T_p$.

The present formalism is also able to demonstrate that the electronic gap $\Delta$ at temperatures $T < T_p$ is larger than the BCS value. In particular $2\Delta(T=0)/T_p$ is larger than 3.5, which may account for experimental evidence.[5]

The essential property which leads to a Peierls instability is the existence of a Fermi surface with two opposite sheets and an electron dispersion which satisfies for $Q = 2p_F$[4]

$$\epsilon_{p+Q/2} = -\epsilon_{p-Q/2} \quad (p \simeq -p_F) \tag{1}$$

The important electron–phonon couplings $g_q$ which involve electrons near the Fermi surface correspond to

$$s_1 = 2N(0)g^2_{2p_F}/\omega_0; \quad s_2 = 2N(0)g^2_0/\omega_0 \tag{2}$$

where $N(0)$ is the electron density of states at the Fermi level for both spins and $\omega_0$ is the bare phonon frequency. For an optical phonon or a 3-dimensional acoustic phonon[6] it is reasonable to assume a constant $\omega_0$ and $s_1 = s_2$.

It is useful to introduce the Nambu notation[7] in the Peierls space[8] defined by the field $\psi^+_p = (C^+_{p+Q/2}, C^+_{p-Q/2})$ where $C^+_p$ is the electron creation operator. Using the Pauli matrices $\tau_i$ and equation (1) the Frohlich Hamiltonian[3,4] can be written in the form

$$\begin{aligned} H = &\sum_p{}' \epsilon_{p+Q/2}\psi^+_p\tau_3\psi_p + \sum_q \omega_0 a^+_q a_q \\ &+ \tfrac{1}{2} i g_Q \sum_{p,p'}{}' (\phi_{Q+p-p'} - \phi_{-Q+p-p'})\psi^+_p\tau_1\psi_{p'} \\ &+ \tfrac{1}{2} i g_Q \sum_{p,p'}{}' (\phi_{Q+p-p'} + \phi_{-Q+p-p'})\psi^+_p i\tau_2\psi_{p'} \\ &+ i \sum_{p,p'}{}' g_{p-p'}\phi_{p-p'}\psi^+_p 1\psi_{p'} \end{aligned} \tag{3}$$

where $\phi_q = a_q + a^+_{-q}$ and $a^+_q$ is the phonon creation operator. The prime on $\Sigma$ denotes $|p|, |p'| < p_F$ and the important states have $|p|, |p'| \ll p_F$. The phonon operators which multiply the $\tau_1, \tau_2$ terms are the phase and amplitude modes respectively[8,9] with propagators $D_{\Phi,R}(i\nu_n, q)$ ($\nu_n = 2\pi Tn$). These modes are non-degenerate only below $T_p$. The last term of (3) involves the small momentum phonons with the propagator $D(i\nu_n, q)$.

I proceed in a similar way to the derivation of the Elisahberg equations for superconductivity[7,10] The electron self mass is written in the form[8] ($i\omega_n = i\pi T(2n+1)$)

$$\sum(i\omega_n, p) = i\omega_n[1 - Z_n(p)]\ 1 + \chi_n(p)\tau_3 + \Delta_n(p)\tau_2 \tag{4}$$

and is evaluated using Figs. 1 (a and b). These diagrams imply phonon self mass corrections such as those in Figs. 1(c–e) which should be included in the full phonon propagators. In particular Fig. 1(c) leads to the usual description of the Peierls instability as phonon softening.[3,4]

The nonretarded limit of the present formalism has been treated previously.[11] In this limit it should be noted that the Parquet sum[12] leads to different results due to inclusion of the Cooper pair instability in the Peierls channel [i.e. Fig. 1(f)]. However the interchain coupling has a different effect on various parquet diagrams. For electron hopping between chains the system is still effectively $1d$[4] for diagrams 1(c and d), leading to singularities $(\ln \xi)^2$ in second order, where $\xi \to 0$ is an energy cutoff. However diagram 1f is less singular, leading to $\ln \xi \ln \eta$ where $\eta$ measures the interchain coupling. Also interchain Coulomb interaction may give a finite $T_p$, while the Cooper pair instability stays at $T = 0$.[13]. Thus the 3-dimensionality of the system ($T_p$ is finite) decouples the Cooper and Peierls channels to a large extent. Summation of the leading singularities reduces the Parquet sum to the present formalism if an interchain coupling is introduced.

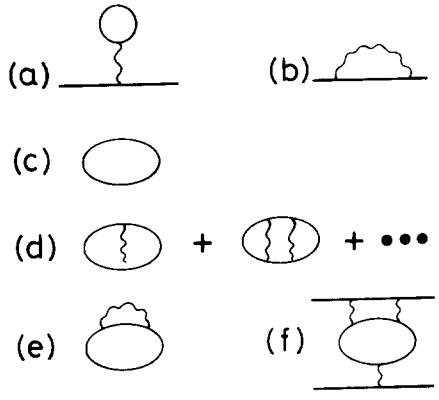


Fig. 1. Electron self mass corrections in the Nambu space: (a) Direct term, (b) Exchange term. (c, d and e) Phonon self mass corrections. (f) A parquet insertion.

By iterating Figs. 1(a and b) it is seen that the phonon self mass corrections are already included in Fig. 1(a), so that the direct term involves just the bare phonon propagator $D_0(i\nu_n, q) = -2\omega_0/(\nu_n^2 + \omega_0^2)$.

Evaluating Figs. 1(a and b) and comparing coefficients of 1 and $\tau_3$ with equation (4) gives the renormalizing functions $Z_n(p)$, $\chi_n(p)$, which represent normal processes such as in Fig. 1(e). These corrections involve the soft mode and diverge as $T \to T_p$ for a $1d$ system. In this sense $Z_n$ and $\chi_n$ represent fluctuation effects which are beyond the MF theory. However for large enough interchain coupling these corrections become small[14] and I assume $Z_n = 1, \chi_n = 0$.

Comparing the coefficients of $\tau_2$ gives the Peierls gap equation

$$\Delta_n(p + Q/2) = T \sum_{p',m} \frac{\Delta_m(p' + Q/2)}{\omega_m^2 + \epsilon_{p'+Q/2}^2 + \Delta_m^2(p' + Q/2)}$$

$$\{-2g_Q^2 D_0(0, Q)$$

$$-\tfrac{1}{2}g_Q^2 D_\phi(i\nu_{m-n}Q + p' - p) + \tfrac{1}{2}g_Q^2 D_R(i\nu_{m-n}Q + p' - p)$$

$$+ g_0^2 D(i\nu_{m-n}p - p')\}.$$

For $T \geqslant T_p$ the $\Phi$ and $R$ terms cancel and the exchange term contributes only with small momentum phonons. This corresponds to Fig. 1(d) where the phonons on the ladder cannot have momentum $\sim Q$ for $T \geqslant T_p$.[4]

The phonon renormalizations are important mainly for phonons with momentum $Q$,[4] so that for small momentum phonons the bare propagator may be used.

The equation for $T_p$ is obtained by linearizing equation (5). Using $\Delta(\omega_m) = \Delta(-\omega_m)$ and integrating $\epsilon_p$ gives

$$\Delta_n = \sum_{m=0}^{\infty} a_m [s_1 - s_2 b_{n,m}] \Delta_m \tag{6}$$

$$a_m = \frac{2\tan^{-1}(E_c/\omega_m)}{\pi(2m+1)}$$

$$b_{n,m} = -[D_0(i\nu_{m-n}) + D_0(i\nu_{m+n+1})] \cdot \omega_0/8$$

where $E_c$ is the electronic cutoff energy.

For $s_2 = 0$ the equation is of the BCS type, and using (for $T \ll E_c$)

$$\sigma \equiv \sum_{m=0}^{\infty} a_m = \tfrac{1}{2} \ln (1.13E_c/T) \tag{7}$$

the usual transition temperature[3,4] $T_p^0 = 1.13E_c \exp(-2/s_1)$ is obtained. In the limit $\omega_0/T \to 0$ the repulsive $s_2$ term is minimal and $T_p$ gets close to $T_p^0$. In this limit $b_{n,m} = \frac{1}{4}\delta_{n,m}$ and for $s_2 \lesssim 1$ the solution is

$$T_p^1 \simeq T_p^0 \cdot \exp\left(-\frac{\pi^2}{16} s_2\right). \tag{8}$$

In the nonretarded limit $\omega_0 \to \infty$, $b_{n,m} \to \frac{1}{2}$ and the solution is again of the BCS type[11]

$$T_p^2 = 1.13E_c \exp[-2/(s_1 - \tfrac{1}{2}s_2)]. \tag{9}$$

The actual $T_p$ lies between the two limits of equations (8) and (9). Due to the large cutoff $E_c$ it is advantageous to use equation (7). By iterating equation (6) a gap equation of the form $\sum_{m=0}^{\infty} A_{n,m}\Delta_m = 0$ is obtained, with

$$A_{n,m} = (\delta_{n,m} + s_2 a_m b_{n,m})(1 - s_1\sigma)$$

$$+ s_1 s_2 a_m \sum_{k=0}^{\infty} a_k b_{k,m}. \tag{10}$$

$T_p$ is the solution for det $(A) = 0$. The results are shown in Fig. 2 for $s_1 = s_2 = s$. The overall change in $T_p$ is a factor of $\sim \exp(2/s)$ which is very large if $s$ is small. The drop in $T_p$ becomes important for $\omega_0 \gtrsim 2\pi T_p$.

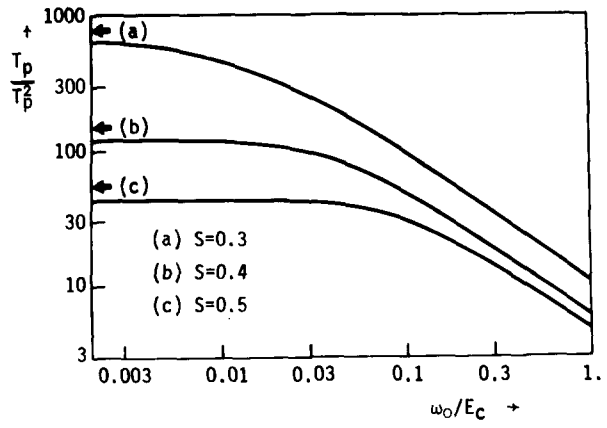


Fig. 2. $T_p$ for $s_1 = s_2 = s$. For $\omega_0 \gg E_c$, $T_p$ approaches the non-retarded value $T_p^2$ [equations (9) and (11)]. The arrows show the transition temperature for $s_1 = s, s_2 = 0$.

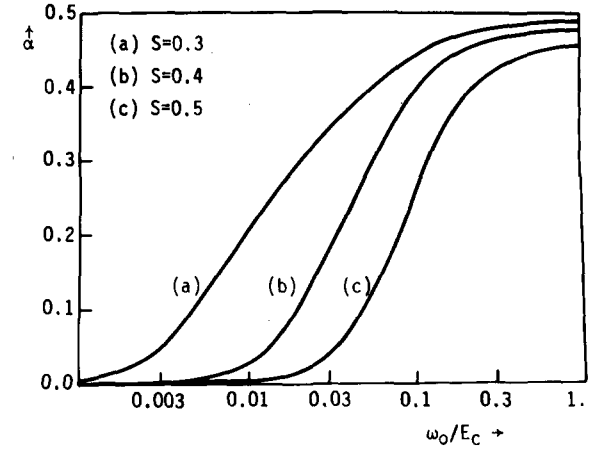


Fig. 3. Isotope shift parameter for $s_1 = s_2 = s$. For $\omega_0 \gg E_c$ the curves approach $\alpha = \frac{1}{2}/(1 + \omega_0/E_c)$.

The isotope shift parameter is defined by $\alpha = \mathrm{d} \ln T_p / \mathrm{d} \ln M$ where $M$ is the ion mass and $\omega_0 \sim M^{-1/2}$. Evidently $\alpha > 0$ and can be rather large for $\omega_0 \gtrsim 2\pi T_p$, as shown in Fig. 3.

For $\omega_0 \gtrsim E_c$ it is more practical to consider the gap equation on the real axis. Using the same procedure as for superconductivity[10] and asuming a frequency independent gap gives

$$T_p = T_p^2 (1 + E_c/\omega_0)^{s_2/(2s_1 - s_2)}. \qquad (11)$$

Thus the non-retarded limit is obtained only for $\omega_0 \gg E_c$.

Finally the gap $\Delta_0$ at $T = 0$ is considered. Using equation (8) I obtain for small $\omega_0$

$$2\Delta_0/T_p \simeq 3.5 \exp\left(\frac{\pi^2}{16} s_2\right) \quad (\omega_0 \ll T_p). \qquad (12)$$

In the nonretarded limit of high $\omega_0$ the gap has the form $\Delta_0 = 2E_c \exp[-2/(\tilde{s}_1 - \frac{1}{2} s_2)]$ with

$$\tilde{s}_1 = s_1 \left[1 - \left(\frac{\omega_0}{2\omega_R}\right)^2 + \left(\frac{\omega_0}{2\omega_\phi}\right)^2\right] \quad (\omega_0 \gg E_c) \qquad (13)$$

where $\omega_\phi$, $\omega_R$ are average phase and amplitude frequencies. Since $\omega_\phi < \omega_R$[9] the ratio $2\Delta_0/T_p^2$ in this limit can be much larger than 3.5.

The same effect is demonstrated by equation (5) for all termperatures $T < T_p$. As $T/T_p$ becomes smaller, the difference between the phase and amplitude propagators becomes larger. Since this difference is attractive, the gap becomes larger than the gap of the BCS type equation.

It is known experimentally that $2\Delta_0/T_p$ is in the range 8–10.[5] This is usually ascribed to thermal fluctuations which reduce $T_p$ but not $\Delta_0$. However this result can be accounted for by either the $s_2$ interaction [equation (12)] or by the non-degeneracy of the phase and amplitude modes [equation (13)]. Both effects are fully consistent with $T_p$ as a solution of equation (6) which does not involve fluctuation effects.

In conclusion, the importance of the small momentum phonons was shown. $T_p$ is a decreasing function of $\omega_0$ and the isotope shift is positive. This general feature is a consequence of two factors: (a) The $s_1$ interaction is attractive while $s_2$ is repulsive. (b) Retardation affects only the $s_2$ term. The factor (a) is true also in the exactly soluble case of the non-retarded interaction.[15] The factor (b) is related to the fact that $s_1$ couples a static deformation with the electrons and this coupling should not involve dynamical effects. On the other hand $s_2$ couples only virtual phonons [like in Fig. 1(d)] which are responsible for the frequency dependence. Thus it can be expected that the general feature of the results will not change even if higher order terms were included. (As needed if the interchain coupling is too small.)

Experimentally acoustic phonons would show a small isotope shift, since then $\omega_0 \sim T_p$.[1,2] However it was suggested[16] that high frequency bond vibrations are responsible for the Peierls instability in TTF–TCNQ. In such a case $\omega_0 \gg 2\pi T_p$ and an isotope shift measurement may check this suggestion.

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