Quasi-one-dimensional systems undergoing a Peierls transition

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A model of a quasi-one-dimensional system undergoing a Peierls structural transition is analyzed on the basis of the Ginzburg–Landau one-dimensional model. The electronic-state density with a pseudogap is derived for a strictly one-dimensional system, in which there is no true transition. The pseudogap arises because of fluctuations in the short-range order corresponding to a Peierls lattice distortion. The dielectric properties of the system turn out to occupy an intermediate position between those of metals and dielectrics. An analysis is also made of the role of fluctuations below the temperature of the true transition, which is stabilized in a three-dimensional system. These fluctuations lead to the formation of a pseudogap in the state density, so that measurements of the electronic characteristics of the system cannot reveal the point at which the true transition occurs.

Quasi-one-dimensional systems having a metallic conductivity have recently been the object of considerable experimental work.[1,2] Study of crystals based on TCNQ and platinum complexes [of the type $K_2Pt(CN)_4Br_{0.33}3H_2O$] has spurred interest in the familiar Peierls arguments regarding the instability of a one-dimensional metal with respect to a change in the lattice constant.[3] According to x-ray structural[4,5] and neutron-diffraction[6] data, a Peierls transition actually occurs in the compound $K_2Pt(CN)_4Br_{0.33}3H_2O$, so that at temperatures $T \lesssim 80°K$ the initial lattice constant is increased by a factor of 6, while at higher temperatures there is a pronounced softening of the frequency of phonons having a quasimomentum $\approx 2p_0$ (p_0 is the Fermi momentum of the electrons). It is also highly probable that a Peierls transition has been observed in the compound[7] TFF–TCNQ, although as yet there is no direct evidence for a doubling of the lattice constant in this system.

Below we describe a model for systems of this type under conditions such that the correlation length for the fluctuations in the order parameter corresponding to the deformation of the lattice with the new lattice constant is much longer than the interatomic distance. We analyze the one-electron spectrum and the state density of the system. We then turn to the dielectric constant corresponding to the reaction to an electric field oriented parallel to the metallic chains, and we analyze the conductivity along the chains at high frequencies. The properties of this system turn out to occupy an intermediate position between typical metallic and typical semiconducting properties, implying that there are certain unique features in quasi-one-dimensional systems in which the fluctuations of the order parameter near a second-order phase transition are extremely important.

We begin from the Hamiltonian

$$H = \sum_p \xi_p a_p^+ a_p + \sum_q \omega_q b_q^+ b_q + \frac{1}{\sqrt{N}} \sum_{pq} g_q a_{p+q}^+ a_p (b_q + b_{-q}^+), \qquad (1)$$

where ξ_p is the free-electron energy, reckoned from the Fermi level; ω_q is the phonon spectrum; g_p corresponds to the electron–phonon interaction; and a_p and b_p are the electron and phonon annihilation operators. Theory has already been worked out[8–10] for a Peierls transition in the self-consistent-field approximation in a strictly one-dimensional system; it is also known[11] that fluctuations of the self-consistent field in a one-dimensional system are extremely important and rule out the possibility of phase transitions altogether in a strictly one-dimensional system. Account of the three-dimensional nature of a real system can help stabilize the true transition (or suppress fluctuations). We are essentially adopting the Peierls-transition model proposed by Lee et al.,[12] which is based on the one-dimensional Ginzburg–Landau model, which has been analyzed in detail.[13] Although there is no true transition according to this model, the correlation radius for short-range order becomes macroscopic at a certain temperature $T_p \approx 1/4T_c$ (T_c is the transition temperature in the self-consistent-field approximation). We are interested in the temperature range $T \sim T_p$, in which this radius is quite large. If the true (three-dimensional) transition is stabilized at a certain temperature, i.e., if long-range order appears, the analysis must be modified. However, fluctuations are also important in the neighborhood of the true transition. The corresponding calculations are given in the Appendix.

Instead of the Ginzburg–Landau model we could adopt an interaction having a soft phonon mode near the transition point,[14] but in this case we would have to use specific models for the soft mode, and the range of applicability of these models is unclear. For the problem under consideration here the Landau free energy is[12]

$$F\{\psi_Q\} = a(T, 2p_0)|\psi_Q|^2 + b(T, 2p_0)|\psi_Q|^4 + c(T, 2p_0)(Q - 2p_0)^2 |\psi_Q|^2, \qquad (2)$$

where the order parameter $\psi_Q = g_Q \langle b_Q + b_{-Q}^+ \rangle$ is proportional to the Pierles lattice deformation. The expansion coefficients are

$$\left.\begin{aligned} a &= N_0 \frac{T - T_c}{T_c}, \quad T_c = \frac{2\gamma}{\pi} E_F \exp\left\{-\frac{\omega_{2p_0}}{g^2 N_0}\right\}, \\ b &= N_0 \left\{b_0 + (b_1 - b_0)\frac{T}{T_c}\right\} \frac{1}{T_c^2}; \quad c = N_0 \xi_0^2(T); \\ \xi_0^2(T) &= \frac{7\zeta(3) v_F^2}{16\pi^2 T^2}; \quad b_0 = \frac{1}{2}\frac{\gamma^2}{\pi^2}; \quad b_1 = \frac{7\zeta(3)}{16\pi^2}, \end{aligned}\right\} \qquad (3)$$

where $\ln\gamma = C$ is the Euler constant, N_0 is the free-electron state density at the Fermi level, E_F is the Fermi energy, and v_F is the Fermi velocity. Account of the electron-band structure in the strong-coupling approximation alters the constants in (3) only slightly.[15] In this model an electron is scattered in the static field of random fluctuations of the order parameter ψ_Q. The simplest eigenener-

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gy part of the one-electron Green's function is [12,16] [$\varepsilon_n = (2n+1)\pi T$]

$$\Sigma(\varepsilon_n, p) = \langle\psi^2\rangle \int \frac{dQ}{2\pi} S(Q) \frac{1}{i\varepsilon_n - \xi_{p+Q}}, \quad (4)$$

where $S(\beta)$ is the static structural factor for fluctuations of the order parameter, proportional to the Fourier transform of the two-point correlation function for the order parameter. For this model we have[12,13]

$$\frac{1}{2} S(Q) = \frac{\xi^{-1}(T)}{(Q-2p_0)^2 + \xi^{-2}(T)} + \frac{\xi^{-1}(T)}{(Q+2p_0)^2 + \xi^{-2}(T)}, \quad (5)$$

where $\xi(T)$ is the correlation length for fluctuations in the order parameter (the short-range correlation radius). At $T \approx 1/4T_e$ the length $\xi(T)$ increases exponentially with decreasing temperature.[14] Now assuming an electron having $p \sim +p_0$, we find

$$\Sigma(\varepsilon_n, p) = \langle\psi^2\rangle [i\varepsilon_n + \xi_p + iv_F\xi^{-1}(T)]^{-1} \approx \Delta^2 (i\varepsilon_n + \xi_p)^{-1}, \quad (6)$$

$$\Delta^2 = \langle\psi^2\rangle, \quad (7)$$

where we have used $\xi_{p-2p_0} = -\xi_p$ for the one-dimensional system.

The approximate equality in (6) holds [the corrections for the finite width of the S(Q) peak are small] under the conditions[17]

$$\left.\begin{aligned} \xi(T) &\gg |p - p_0|^{-1}, \\ v_F\xi^{-1}(T) &\ll 2\pi T. \end{aligned}\right\} \quad (8)$$

The first condition in (8) imposes a restriction on our analysis in the immediate vicinity of the Fermi level $T \sim 1/4T_c$, where $\xi(T)$ is large, the corresponding energy range is extremely narrow and of no particular interest. According to the data of ref. 5, we have ξ/a ($T = 300°K$) $> 10^2$, where a is the Pt–Pt distance in the compound $K_2Pt(CN)_4Br_{0.33}3H_2O$. Although the estimates of ref. 12 are less favorable, the values of $\xi(T)$ near the "transition" are undoubtedly very large and can reach hundreds of interatomic distances.

Using approximation (6) in the higher-order diagrams, we can sum all[1)] the important diagrams by the perturbation-theory method proposed in ref. 17. Scalapino et al.[13] analyzed the contribution of only the simplest diagram in (6), but the higher-order approximations are extremely important. Carrying out the summation, we find[17] the one-electron Green's function to be

$$G(\varepsilon_n, p) = \int_0^\infty d\zeta e^{-\zeta} \frac{i\varepsilon_n + \xi_p}{(i\varepsilon_n)^2 - \xi_p^2 - \zeta\Delta^2} \equiv \langle G_{\zeta\Delta^2}(\varepsilon_n, p, p)\rangle_\zeta, \quad (9)$$

where

$$G_{\Delta^2}(\varepsilon_n, p, p) = \frac{i\varepsilon_n + \xi_p}{(i\varepsilon_n)^2 + \xi_p^2 - \Delta^2} \quad (10)$$

is the normal Green's function of an ideal Peierls insulator having an energy gap $|\Delta|$. It is easy to say that Eq. (9) is the Green's function of an electron in an external field $W\cos 2p_0x$ whose amplitude "fluctuates" with a distribution $P\{W\} = |W|/\Delta^2 e^{-(W^2/\Delta^2)}$. The integral in (9) denotes an averaging over these fluctuations.

After the standard analytic continuation to the real frequencies, we find the electronic-state density to be

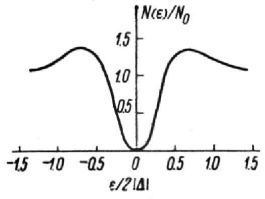

Fig. 1. Electronic density.

$$\frac{N(\varepsilon)}{N_0} = \left|\frac{\varepsilon}{\Delta}\right| \int_0^{\varepsilon^2/\Delta^2} d\zeta \frac{e^{-\zeta}}{\sqrt{\frac{\varepsilon^2}{\Delta^2} - \zeta}} = 2\left|\frac{\varepsilon}{\Delta}\right| e^{-\frac{\varepsilon^2}{\Delta^2}} \operatorname{Erfi}\left(\sqrt{\frac{\varepsilon}{|\Delta|}}\right), \quad (11)$$

where $\operatorname{Erfi} x = \int_0^x dx^{x^2}$. Figure 1 shows this state density, which contains a typical pseudogap having a width on the order of $|\Delta| \sim \langle\psi^2\rangle^{1/2}$. The temperature dependence of $\langle\psi^2\rangle$ was calculated in ref. 13; the asymptotic behavior is

$$\frac{N(\varepsilon)}{N_0} \to 1 \quad \text{as} \quad |\varepsilon| \to \infty; \quad \frac{N(\varepsilon)}{N_0} \approx 2\frac{\varepsilon^2}{\Delta^2} \to 0 \quad \text{as} \quad |\varepsilon| \to 0.$$

The vanishing of the state density in the middle of the pseudogap is nonphysical; our analysis is not valid in the immediate vicinity of the Fermi level because of restriction (8). Accordingly, in contrast with the situation in ref. 13, the summation of all the important diagrams leads to the existence of a pseudogap not only at $T \gtrsim 1/4T_c$ but also at $T < 1/4T_c$. A true gap does not arise even at low temperatures in the "dielectric" phase.[2)] As is shown in the Appendix, this result holds even in the case of a true phase transition (at $T \lesssim T_c$), so that, strictly speaking, measurements of the electronic characteristics of the system cannot reveal the transition point.

We turn now to the reaction of the system to a longitudinal electric field directed parallel to the metallic chains. A variation $\delta\varphi_{q\omega}$ (q is the wave vector along the chain and ω is the frequency of the external field) causes a variation in the one-electron Green's function:

$$\frac{\delta G(\varepsilon, p)}{\delta\varphi_{q\omega}} = G(\varepsilon, p)\Gamma(\varepsilon, p, \varepsilon+\omega, p+q)G(\varepsilon+\omega, p+q), \quad (12)$$

where $\Gamma(\varepsilon, p, \varepsilon+\omega, p+q)$ is the corresponding vertex part. In this model the variational derivative in (12) can be calculated immediately;[17] we find

$$\begin{aligned} \frac{\delta G(\varepsilon, p)}{\delta\varphi_{q\omega}} &= -e\langle G_{\zeta\Delta^2}(\varepsilon, p, p) G_{\zeta\Delta^2}(\varepsilon+\omega, p+q, p+q)\rangle_\zeta \\ &- e\langle G_{\zeta\Delta^2}(\varepsilon, p, p-2p_0) G_{\zeta\Delta^2}(\varepsilon+\omega, p-2p_0+q, p+q)\rangle_\zeta, \end{aligned} \quad (13)$$

where e is the electronic charge, $G_{\Delta^2}(\varepsilon, p, p)$ is given in (10), and

$$G_{\Delta^2}(i\varepsilon_n, p, p-2p_0) = \frac{\Delta}{(i\varepsilon_n)^2 - \xi_p^2 - \Delta^2} \quad (14)$$

is the anomalous Green's function of a Peierls dielectric, which describes the flipping $p \to p-2p_0$. Accordingly, averages over binary products of anomalous Green's functions arise in the theory, while the anomalous functions themselves do not, in correspondence with the absence of long-range order in the system.

The polarization operator is ($\omega_m = 2\pi mT$)

$$\Pi(q\omega_m) = -\int_0^\infty d\zeta e^{-\zeta} 2T \sum_n N_{0?} \times$$

$$\times\int_{-\infty}^{\infty} d\xi_p \{G_{\zeta\Delta^2}(\varepsilon_m, p, p)\, G_{\zeta\Delta^2}(\varepsilon_n+\omega_m, p+q, p+q) \qquad (15)$$

$$+ G_{\zeta\Delta^2}(\varepsilon_n, p, p-2p_0)\, G_{\zeta\Delta^2}(\varepsilon_n+\omega_m, p+q, p-2p_0+q)\} \equiv \langle \Pi_{\zeta\Delta^2}(q, \omega_m)\rangle_\zeta,$$

where $\Pi_{\Delta^2}(q, \omega_m)$ is the polarization operator of a Peierls dielectric, and ρ is the density of the metallic chains in a cross section of the sample (here we are interested in the response of a unit volume of the system). The analysis continues as in ref. 17. The dielectric constant along the metallic chains is

$$\varepsilon(q, \omega) = 1 + \frac{4\pi e^2}{q^2}\Pi(q\omega) = \langle \varepsilon_{\zeta\Delta^2}(q\omega)\rangle_\zeta, \qquad (16)$$

where

$$\varepsilon_{\Delta^2}(q\omega) = 1 + \frac{4\pi e^2}{q^2}\Pi_{\Delta^2}(q, \omega) \qquad (17)$$

is the dielectric constant of a Peierls dielectric.

We consider first the case $\omega = 0$; then for this model we find[17]

$$\varepsilon(q, 0) \approx 1 - \frac{v_F^2\varkappa^2}{6\Delta^2}\exp\frac{v_F^2q^2}{6\Delta^2}\,\mathrm{Ei}\left(-\frac{v_F^2q^2}{6\Delta^2}\right), \qquad (18)$$

where $\varkappa^2 = 8\pi^2 N_0\rho$ is the inverse square of the Debye screening radius, and Ei(−x) is the integral exponential function. Hence, with $v_Fq \gg |\Delta|$, we find $\varepsilon(q, 0) \approx 1 + (\varkappa^2/q^2)$. For $v_Fq \ll |\Delta|$ we find

$$\varepsilon(q, 0) \approx 1 - \frac{v_F^2\varkappa^2}{6\Delta^2}\ln\gamma\frac{v_F^2q^2}{6\Delta^2}. \qquad (19)$$

This $\varepsilon(q, 0)$ behavior occupies an intermediate position between the behavior characteristic of metals and that characteristic of dielectrics.

Turning now to the case $\omega \neq 0$, $v_Fq \ll |\Delta|$, we find[17]

$$\mathrm{Re}\,\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{6\Delta^2}\mathrm{Ei}\left(-\frac{\omega^2}{4\Delta^2}\right) - \frac{\omega_p^2}{\omega^2}\left\{1 - e^{-\frac{\omega^2}{4\Delta^2}}\right\}, \qquad (20)$$

where $\omega_p^2 = v_F^2\varkappa^2$ is the square of the plasma frequency.

In the case $\omega \gg 2|\Delta|$ we have $\mathrm{Re}\,\varepsilon(\omega) \approx 1 - (\omega_p^2/\omega^2)$; in the case $\omega \ll 2|\Delta|$ we have

$$\mathrm{Re}\,\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{6\Delta^2}\ln\gamma\frac{\omega^2}{4\Delta^2}. \qquad (21)$$

Of particular interest is the behavior of the imaginary part of the dielectric constant, since it governs the absorption of electromagnetic energy in the system. The real part of the conductivity is

$$\mathrm{Re}\,\sigma(\omega) = \frac{\omega}{4\pi}\mathrm{Im}\,\varepsilon(\omega). \qquad (22)$$

By analogy with ref. 17 we have

$$\mathrm{Im}\,\varepsilon(\omega) = \frac{\pi}{2}\omega_p^2\frac{|\Delta|}{\omega^3}\int_0^{\frac{\omega^2}{4\Delta^2}} d\zeta e^{-\zeta}\frac{\zeta}{\sqrt{\frac{\omega^2}{4\Delta^2}-\zeta}}$$

$$= \pi\omega_p^2\frac{|\Delta|}{\omega^3}e^{-\frac{\omega^2}{4\Delta^2}}\left\{\frac{\omega^2}{4\Delta^2} - \frac{d}{d\alpha}\right\}\mathrm{Erfi}\left(\sqrt{\alpha}\,\frac{\omega}{2|\Delta|}\right)\Big|_{\alpha=1}. \qquad (23)$$

Asymptotically we find

$$\left.\begin{aligned}\mathrm{Im}\,\varepsilon(\omega) &\approx \pi\left(\frac{\omega_p}{\omega}\right)^2\left(\frac{\Delta}{\omega}\right)^2,\\ \mathrm{Re}\,\sigma(\omega) &\approx \frac{1}{4}\left(\frac{\Delta}{\omega}\right)^2\frac{\omega_p^2}{\omega}\end{aligned}\right\} \qquad (24)$$

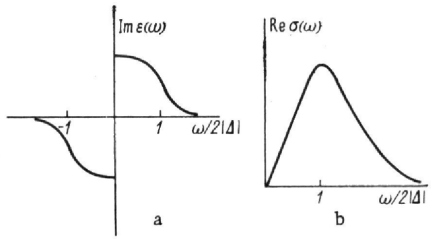

Fig. 2. Qualitative behavior of the imaginary part of the dielectric constant (a) and of the real part of the conductivity (b) as functions of the frequency of the external field.

for $\omega \gg 2|\Delta|$; for $\omega \ll 2|\Delta|$, we find

$$\left.\begin{aligned}\mathrm{Im}\,\varepsilon(\omega) &\approx \frac{\pi}{12}\frac{\omega_p^2}{\Delta^2},\\ \mathrm{Re}\,\sigma(\omega) &\approx \frac{1}{48}\left(\frac{\omega_p}{\Delta}\right)^2 \omega\to 0 \quad \text{for} \quad \omega\to 0.\end{aligned}\right\} \qquad (25)$$

Accordingly, the static conductivity vanishes in our approximation. Analogously, the static conductivity of a Peierls dielectric vanishes at zero temperature. Equation (23) describes a sort of interband absorption (Fig. 2), having a peak at $\omega \sim 2|\Delta|$. We also see that our model describes a substance whose properties are intermediate between those of metals and dielectrics: In a metal we would have $\mathrm{Im}\,\varepsilon(\omega) \sim 1/\omega$ as $\omega \to 0$, while in a dielectric we would have $\mathrm{Im}\,\varepsilon(\omega) = 0$ at $\omega = 0$. In our case the quantity $\mathrm{Im}\,\varepsilon(\omega)$ has a finite discontinuity at $\omega = 0$:

$$(\mathrm{Im}\,\varepsilon(\omega) = -\mathrm{Im}\,\varepsilon(-\omega)).$$

Strictly speaking, these equations do not hold at low frequencies, since the entire analysis breaks down near the Fermi level, according to the first condition in (8). Our calculation of the polarization operator holds only for

$$\omega \gg v_F\xi^{-1}(T). \qquad (26)$$

This condition has a clear meaning: Over the scale time for a change in the external field an electron moves a distance shorter than $\xi(T)$.

A Peierls system thus apparently represents a substance whose properties occupy an intermediate position between those of metals and dielectrics. An experimental search for absorption peaks at frequencies corresponding to the width of the pseudogap would be very interesting. The possible anomalous behavior of $\varepsilon(w)$ according to (21) and (25) at $\omega \lesssim 2|\Delta|$ emphasizes the importance of experiments in the rf range. No reliable experimental data are presently available.

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APPENDIX

A phase transition cannot occur in a strictly one-dimensional system because of the disruptive influence of fluctuations.[11] In particular, the self-consistent-field approximation does not have a range of applicability because of the large width of the critical region, $\Delta T/T_c \sim 1$ (ref. 13). However, since real systems are three-dimensional in nature, fluctuations can be suppressed in some manner (e.g., the fluctuation amplitude can be limited by a long-range Coulomb interaction between electrons of neighbor-

ing chains). Then a true phase transition is possible in the in the system at $T = T_c$. Apparently it is this case which occurs in $K_2Pt(CN)_4Br_{0,33}3H_2O$ (ref. 4), where the true (three-dimensional) transition stabilizes at $T_c \leqslant 80°K$. Then, at $T < T_c$, a long-range order arises, and the system can be described satisfactorily in the self-consistent-field approximation. However, the fluctuations of the order parameter, even though suppressed, can turn out to be important even at $T < T_c$. In this case we have[13]

$$\psi_Q = \Delta + \delta\psi_Q, \tag{A.1}$$

where

$$\Delta = \left(-\frac{a}{2b}\right)^{1/2} = \begin{cases} \sqrt{\frac{8\pi^2 T_c}{7\zeta(3)}}\sqrt{T_c - T} & \text{at} \quad T \leqslant T_c, \\ \frac{\pi}{\gamma} T_c & \text{at} \quad T = 0 \end{cases} \tag{A.2}$$

is the equilibrium value of the order parameter, and $\delta\psi_Q$ is its fluctuation. Here Δ plays the role of a coherent field, which transmits a momentum $2p_0$ and which leads to Bragg scattering of electrons by the boundaries of the new Brillouin zone, and $\delta\psi Q$ is the random field. In the diagram technique we find two types of interaction lines: lines of the coherent field Δ, which transmit a momentum $2p_0$, and lines of the random field, which are associated with the correlator $\langle \delta\psi_Q \delta\psi_{-Q} \rangle = \langle \delta\psi^2 \rangle S(Q)$. Here $S(Q)$ is again given by (5) (ref. 13). The equations for $\langle \delta\psi^2 \rangle$ and $\xi(T)$ derived on the basis of the self-consistent-field approximation[13] are now, generally speaking, inapplicable (because of the three-dimensional nature of the critical fluctuations), so that $\langle \delta\psi^2 \rangle$ and $\xi(T)$ are treated below as parameters of the theory. Near the transition point ($T \leqslant T_c$) the quantity $\xi(T)$ increases, so that we can again use an approximation like that in (6)-(8). Then the random-field lines also transmit a momentum $2p_0$. In the expansion of the one-electron Green's function a sequence of alternating Green's functions $\{i\varepsilon_l - \xi_p\}^{-1}$ and $\{i\varepsilon_l + \xi_p\}^{-1}$ dominates. In perturbation theory of order n there are 2n vertices, of which 2k are connected by random-field lines of the fluctuations, and with which factors $\delta\Delta^2 = \langle \delta\psi^2 \rangle$ are associated; at $2(n-k)$ vertices, single coherent-scattering lines arise, each of which is associated with a factor Δ. Then the expansion of the Green's function is

$$G(\varepsilon_l, \xi_p) = \sum_{n=0}^{\infty} \sum_{k=0}^{n} B_n^k(\varepsilon_l, \xi_p), \tag{A.3}$$

where

$$B_n^k = \tag{A.4}$$

$$|\Delta|^{2(n-k)} \left[\frac{n!}{k!(n-k)!}\right]^2 |\delta\Delta|^{2k} k! \{i\varepsilon_l - \xi_p\}^{-n} \{i\varepsilon_l + \xi_p\}^{-n} \{i\varepsilon_l - \{\xi_p\}^{-1}.$$

Actually, an electronic line has 2k vertices, to which random-field lines are attached; of these vertices, k have an outgoing line, which goes to the remaining k vertices in any of k! methods. Here $[n!/k!(n-k)!]^2$ is the number of arrangements of single coherent-field lines at any $2(n-k)$ vertices taken from the total of 2n vertices; the circumstance that the momentum $2p_0$ "enters" half of these vertices and "exits" from the other half is taken into account. We use the identity $(1+x)^n(1+y)^n = \sum_{k_1 k_2 = 0}^{n} x^{k_1} y^{k_2} C_n^{k_1} C_n^{k_2}$, where we have set

$$x = \zeta \frac{\delta\Delta}{\Delta} = |\zeta| e^{i\varphi} \frac{\delta\Delta}{\Delta}; \quad y = x^*;$$

$$\int_0^{2\pi} \frac{d\varphi}{2\pi} \left(1 + \zeta \frac{\delta\Delta}{\Delta}\right)^n \left(1 + \zeta^* \frac{\delta\Delta}{\Delta}\right)^n = \sum_{k=0}^{n} |C_n^k|^2 |\zeta|^{2k} \left(\frac{\delta\Delta}{\Delta}\right)^{2k}.$$

Using $\int_0^{\infty} d|\zeta|^2 |\zeta|^{2k} e^{-|\zeta|^2} = k!$, we find

$$G(\varepsilon_l, \xi_p) = \int_0^{\infty} d|\zeta|^2 e^{-|\zeta|^2}$$

$$\times \int_0^{2\pi} \frac{d\varphi}{2\pi} \frac{i\varepsilon_l + \xi_p}{(i\varepsilon_l)^2 - \xi_p^2 - \Delta^2 \left[1 + |\zeta|^2 \left(\frac{\delta\Delta}{\Delta}\right)^2 + 2|\zeta| \frac{\delta\Delta}{\Delta} \cos\varphi\right]}$$

$$= \frac{1}{\pi} \int d^2\zeta e^{-|\zeta|^2} \frac{i\varepsilon_l + \xi_p}{(i\varepsilon_l)^2 - \xi_p^2 - \Delta^2 \left|1 + \zeta \frac{\delta\Delta}{\Delta}\right|^2}, \tag{A.5}$$

where

$$\int d^2\zeta \ldots \equiv \int d\,\mathrm{Re}\,\zeta\, d\,\mathrm{Im}\,\zeta \ldots = \int_0^{\infty} d|\zeta| |\zeta| \int_0^{2\pi} d\varphi \ldots$$

We have obtained a normal Green's function with a gap which "fluctuates" around Δ as given by Eqs. (A.2). The equation for the anomalous Green's function is obvious. As $\Delta \to 0$, Eq. (A.5) converts into Eq. (9), and in the case $\delta\Delta \to 0$ we find (10), i.e., an ideal Peierls dielectric. Accordingly, the analysis above is valid for the case $T \gtrsim T_c$. Obviously, even in the case $T \leqslant T_c$ the fluctuations are extremely important. For the state density we have

$$\frac{N(\varepsilon)}{N_0} = \frac{|\varepsilon|}{\pi} \int d^2\zeta e^{-|\zeta|^2} \frac{\theta\left[\varepsilon^2 - \Delta^2 \left|1 + \zeta \frac{\delta\Delta}{\Delta}\right|^2\right]}{\sqrt{\varepsilon^2 - \Delta^2 \left|1 + \zeta \frac{\delta\Delta}{\Delta}\right|^2}}. \tag{A.6}$$

Omitting the lengthy details, we state that as $\delta\Delta \to 0$ (i.e., as $T \to 0$) we would have

$$\frac{N(\varepsilon)}{N_0} \to \begin{cases} \frac{|\varepsilon|}{\sqrt{\varepsilon^2 - \Delta^2}} & \text{for} \quad |\varepsilon| > \Delta, \\ 0 & \text{for} \quad |\varepsilon| < \Delta, \end{cases} \tag{A.7}$$

i.e., we find an ideal dielectric with a gap 2Δ. When $\delta\Delta$ is finite we always have $N(\varepsilon)/N_0 \neq 0$ for $|\varepsilon| < \Delta$.

For example, as $|\varepsilon| \to 0$ we would have

$$\frac{N(\varepsilon)}{N_0} \approx \frac{2}{\sqrt{\pi}} \frac{|\varepsilon|}{|\delta\Delta|} \cdot 1.68 \left\{1 - \mathrm{Erfc}\left(\frac{1}{2}\left|\frac{\Delta}{\delta\Delta}\right|\right)\right\}, \tag{A.8}$$

where $\mathrm{Erfc}\, x = 2/\sqrt{\pi} \int_0^x dx e^{-x^2}$. With $|\varepsilon| = \Delta$ we find

$N(|\varepsilon| = \Delta)/N_0 \approx \sqrt{\Delta/|\delta\Delta|}$.

Accordingly, we again find a state density having a pseudogap. In the case $|\delta\Delta| \ll \Delta$ the state density in the energy gap is of course small, but this is not generally true in the case $T \leqslant T_c$. We see that fluctuations of the order parameter are extremely important even in the case of a true phase transition. Near the transition, the state density has a pseudogap at both $T \gtrsim T_c$ and $T \leqslant T_c$. In this sense the transition point is not defined and cannot be determined from measurements of electronic characteristics of the system. In terms of their effects, the fluctuations turn out to be analogous to an internal disorder of the system, analyzed in ref. 18: They suppress the true transi-

tion and "smear" its effects on the electronic properties.

Note added in proof. D. B. Tanner recently reported [Phys. Rev. Lett., 32, 1303 (1974)] experimental data on IR absorption in TTF = TCNQ at 65 and 320°K. The results are qualitatively analogous to Fig. 2b, with Re σ ($\omega = 2|\Delta|$) $\simeq 5 \cdot 10^2$–$10^3\ \Omega^{-1} \cdot cm^{-1}$. Extrapolating (25) to $\omega = 2|\Delta|$ and using the experimental values $2|\Delta| = 0.14$ eV, and $\omega_p = 1.2$ eV, we find Re $\sigma(\omega = 2|\Delta|) \simeq 8 \cdot 10\ \Omega^{-1} \cdot cm^{-1}$.

[1)] We assume that all the higher-order correlators for the order parameter can be factored into binary correlators; this procedure is equivalent to taking only Gaussian fluctuations into account.

[2)] Account of non-Gaussian fluctuations could hardly have a qualitative effect on this result. The gap can appear only in the presence of a true long-range order.

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