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Mean-field solution of the continuum Fröhlich problem at finite temperature

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The temperature behavior of the charge-density-wave (CDW) state in one-dimensional conductors is studied within the framework of a mean-field approach using the exact solution of the self-consistent equations. The properties of the CDW condensate are found to be dependent on the value of the dimensionless parameter which includes an electron-phonon coupling constant and the density of electrons. The thermal behavior of the CDW is shown to be similar to that of the Bardeen-Cooper-Schrieffer (BCS) superconducting condensate only at sufficiently weak electron-phonon coupling or relatively high electron density. In the case of comparatively strong coupling or sufficiently low electron density, the correct mean-field consideration leads to violation of the BCS relation between the phase transition temperature and electronic gap at $T=0$, and also to a variation of the CDW period, which decreases with increasing temperature.

I. INTRODUCTION

Recent years have witnessed extensive exploration of materials with quasi-one-dimensional properties. These are, for example, conducting polymers $(CH)_x$, organic superconductors $(TMTSF)_2PF_6$ (TMTSF is tetramethyltetraselenafulvalene), and organic tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) and inorganic $NbSe_3$, TaS_3, and $K_{0.03}MoO_3$ compounds in which the charge-density-wave (CDW) state is realized. The CDW is a self-consistent state of the electrons and the lattice distortion and has been widely investigated both theoretically and experimentally (see, e.g., the reviews in Ref. 1). Fröhlich[2] pointed out that the CDW phase would not be fixed relative to the laboratory frame in an ideal model (translational invariance) and that it would be possible for the CDW and the associated lattice distortion to move along the chain, giving rise to current.

At present there are a lot of theoretical works which have stressed various aspects of the Peierls-Fröhlich problem, in particular using the mean-field theory.[3–5] According to the Peierls theorem and following Fröhlich,[2] the CDW is often described as a harmonic wave with the wave vector $Q=2k_F$ (k_F is the Fermi wave number). In this case, the thermodynamics of the CDW state closely resembles that of a superconducting ground state.[1,5] At the same time, it has been established that in the adiabatic approximation some Peierls-Fröhlich models have exact analytical solutions.[3,4,6] The Fröhlich continuum model[2] is classified among such exactly solvable models.[3,6,7] The exact solution of the self-consistent equations shows that the CDW is essentially a nonlinear wave and makes it possible to understand more intimately the CDW properties and to explain some experimental observations without requiring additional mechanisms.[7] Therefore, it is of interest to consider the temperature properties of the CDW using the exact solution.

Belokolos and Pershko[3] attempted to carry out this consideration. In their paper the minimum of a thermodynamic functional at a given chemical potential is studied. In the present paper the self-consistent state of a one-dimensional electron-phonon system with a given number of electrons is investigated in the framework of the mean-field approach. It is shown that at sufficiently low electron density or comparatively strong electron-phonon interaction the CDW wave vector depends on temperature, and the BCS relation is violated.

Of course, it is necessary to keep in mind that the mean-field treatment of the Peierls transition is not entirely correct, since it neglects the important role of one-dimensional fluctuations. Due to fluctuations, the transition temperature is severely reduced as compared to the mean-field value.[8]

II. SELF-CONSISTENT STATE AT FINITE TEMPERATURE

Let us consider a simple one-dimensional chain of length $L=Na$ (a is the lattice constant). Without allowance for the Coulomb interaction, the state of electrons, interacting with atom oscillations, is described by the Fröhlich Hamiltonian

$$H=\sum_{k\sigma}E(k)a_{k\sigma}^{\dagger}a_{k\sigma}+\frac{1}{\sqrt{N}}\sum_{qk\sigma}\chi(q)a_{k\sigma}^{\dagger}a_{k-q\sigma}(b_q+b_{-q}^{\dagger})+\sum_{q}\hbar\Omega_q b_q^{\dagger}b_q\ , \tag{2.1}$$

where $a_{k\sigma}^{\dagger}$ ($a_{k\sigma}$) are the Fermi creation (annihilation) operators of an electron with the wave number $k=2\pi n/L$ $[n=0,\pm1,\ldots,\pm(\frac{1}{2}N-1),\frac{1}{2}N]$ and the spin $\sigma=\pm\frac{1}{2}$, $b_q^{\dagger}$ (b_q) are Bose creation (annihilation) operators of a phonon with the wave number q and the frequency Ω_q, $E(k)$ describes the dispersion law for electrons in the conduction band, and the function $\chi(q)$ is specified by the short-range deformation interaction between electrons and atomic displacements from their equilibrium positions. Since the simple chain is under consideration, the

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acoustic phonon mode corresponds to harmonic oscillations of the lattice. When the main role belongs to wave numbers small compared to the vector of a reciprocal lattice, $k \ll \pi/a$, one can use the long-wave approximation

$$E(k)=\frac{\hbar^2k^2}{2m}\ , \quad \Omega_q=V_a|q|\ ,$$
$$\chi(q)=2i\chi a\left[\frac{\hbar}{2M\Omega_q}\right]^{1/2} q\ , \tag{2.2}$$

where m is the effective mass of electrons in the conduction band, $V_a=a\sqrt{w/M}$ is the sound velocity in the chain with the elasticity coefficient w and the atom mass M, and χ is the parameter of electron-phonon interaction.

The Hamiltonian (2.1) commutes with the operators of the total momentum of the system,

$$\mathcal{P}=\sum_{k\sigma}\hbar k a_{k\sigma}^{\dagger}a_{k\sigma}+\sum_{q}\hbar q b_q^{\dagger}b_q\ , \tag{2.3}$$

and with the total number of electrons

$$\mathcal{N}_e=\sum_{k\sigma}a_{k\sigma}^{\dagger}a_{k\sigma}\ . \tag{2.4}$$

The state of thermodynamic equilibrium at a given value of the momentum $P=\langle\mathcal{P}\rangle$ and a given electron number $N_e=\langle\mathcal{N}_e\rangle$ corresponds to the minimum of the thermodynamic potential

$$F=\langle H-\mu\mathcal{N}_e-V\mathcal{P}\rangle-TS\ , \tag{2.5}$$

which has the meaning of free energy in the reference frame moving with velocity V, where μ is the chemical potential and S is the entropy.

The basic approach used for the treatment of the self-consistent state of quasiparticles which is described by the Hamiltonian (2.1) is the adiabatic Born-Oppenheimer approximation. Hence, the wave function (the state vector) of the system is assumed to be representable in the multiplicative form in terms of the phonon and electron variables[2-7]

$$|\Psi\rangle=|\Psi_{\text{ph}}\rangle|\Psi_e\rangle\ , \quad |\Psi_{\text{ph}}\rangle=U|\{\nu_q\}\rangle\ . \tag{2.6}$$

Here the unitary operator

$$U=\exp\left[\frac{1}{\sqrt{N}}\sum_q(\beta_q b_q^{\dagger}-\beta_q^{*}b_q)\right] \tag{2.7}$$

describes the lattice ground-state rearrangement caused by the electron-phonon interaction and $|\Psi_e\rangle$ is the ket vector of electron states in the deformed chain. The given approximation implies smallness of the kinetic-energy operator of lattice oscillations in the Hamiltonian (2.1), and the function (2.6) is an eigenfunction of the Hamiltonian H_0 corresponding to (2.1) without the operator of the atomic kinetic energy.

At the finite temperature T the system can be in any possible state (for both electrons and phonons) with the probabilities $w(\{\mathcal{E}_e\},\{\nu_q\})$ described by the Hibbs distribution. Using the known inequality for the free energy (2.5), we write down

$$F\le\langle H-\mu\mathcal{N}_e-V\mathcal{P}\rangle_0-TS_0\ . \tag{2.5$'$}$$

Here the averaging is carried out with the density matrix

$$\rho_0=\sum w(\{\mathcal{E}_e\},\{\nu_q\})U|\{\nu_q\}\rangle|\Psi_e\rangle\langle\Psi_e|\langle\{\nu_q\}|U^{\dagger}\ , \tag{2.8}$$

where ν_q is the phonon occupation number, and summation is performed over all possible states of both phonons $\{\nu_q\}$ and electrons $\{\mathcal{E}_e\}$. Using the explicit form (2.8) we find

$$F\le\sum w(\{\mathcal{E}_e\},\{\nu_q\})\langle\Psi_e|\tilde{\mathcal{H}}_e+\tilde{W}+\sum_q\hbar(\Omega_q-Vq)\nu_q|\Psi_e\rangle-TS_0\ , \tag{2.9}$$

where

$$\tilde{W}=\frac{1}{N}\sum_q\hbar(\Omega_q-Vq)|\beta_q|^2\ , \tag{2.10}$$

$$\tilde{\mathcal{H}}_e=\sum_{k\sigma}\left\{[E(k)-\hbar Vk-\mu]a_{k\sigma}^{\dagger}a_{k\sigma}+\frac{1}{N}\sum_q\chi(q)(\beta_q+\beta_{-q}^{*})a_{k\sigma}^{\dagger}a_{k-q\sigma}\right\}\ . \tag{2.11}$$

With the unitary transformation

$$a_{k\sigma}=\sum_{\lambda}\tilde{\psi}_{\lambda}(k)A_{\lambda\sigma}\ , \tag{2.12}$$

we proceed to the new Fermi operators $A_{\lambda\sigma}^{\dagger}$ and $A_{\lambda\sigma}$ and require the operator (2.11) to be diagonal in the new representation,

$$\tilde{\mathcal{H}}_e=\sum_{\lambda\sigma}(\tilde{\mathcal{E}}_{\lambda}-\mu)A_{\lambda\sigma}^{\dagger}A_{\lambda\sigma}\ . \tag{2.11$'$}$$

To do this, the coefficients of the transformation (2.12) must satisfy the relations

$$\sum_k\tilde{\psi}_{\lambda'}^{*}(k)\left\{[E(k)-\hbar Vk]\tilde{\psi}_{\lambda}(k)+\frac{1}{N}\sum_q\chi(q)(\beta_q+\beta_{-q}^{*})\tilde{\psi}_{\lambda}(k-q)\right\}=\delta_{\lambda\lambda'}\tilde{\mathcal{E}}_{\lambda}\ . \tag{2.13}$$

To find the coefficients we introduce the functions

$$\tilde{\psi}_{\lambda}(x)=\frac{1}{\sqrt{L}}\sum_k\tilde{\psi}_{\lambda}(k)e^{ikx} \tag{2.14a}$$

of the continuous variable x. It should be noted that the function (2.14a) satisfies periodic boundary conditions, and if (2.14a) takes place then[9]

$$\tilde{\psi}_{\lambda}(k)=\frac{1}{\sqrt{L}}\int_{-L/2}^{L/2}\tilde{\psi}_{\lambda}(x)e^{-ikx}dx\ . \tag{2.14b}$$

Substituting (2.14b) into (2.13) and using the long-wave approximation (2.2), we find that (2.13) should be valid if

$$\tilde{\psi}_\lambda(x)=\exp\left[i\frac{mV}{\hbar}x\right]\psi_\lambda(x) \tag{2.15}$$

and the function $\psi_\lambda(x)$ satisfies the Schrödinger equation

$$\begin{gathered}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+u(x)\right]\psi_\lambda=\mathcal{E}_\lambda\psi_\lambda ,\\ \mathcal{E}_\lambda=\tilde{\mathcal{E}}_\lambda+\tfrac{1}{2}mV^2\end{gathered} \tag{2.16}$$

for electrons in the deformation potential

$$u(x)=\frac{1}{N}\sum_q \chi(q)(\beta_q+\beta^*_{-q})e^{-iqx} . \tag{2.17}$$

The electron operator form (2.11′) indicates that the ket vectors of electron states must be

$$|\Psi_e\rangle=\prod_{\lambda\sigma}(A^\dagger_{\lambda\sigma})^{n_{\lambda\sigma}}|0\rangle=|\{n_{\lambda\sigma}\}\rangle , \tag{2.18}$$

where $|0\rangle$ is the vacuum state, and $n_{\lambda\sigma}=0,1$ are the electron occupation numbers with spin σ of the energetic sublevel $\mathcal{E}_\lambda$. Then for the thermodynamic functional (2.9) we obtain

$$F\le\tilde{W}+\sum_{\lambda\sigma}\bar{n}_{\lambda\sigma}(\tilde{\mathcal{E}}_\lambda-\mu)+\sum_q\hbar(\Omega_q-Vq)\bar{\nu}_q-TS_0 , \tag{2.19}$$

where

$$\begin{gathered}\bar{n}_{\lambda\sigma}=\sum w(\{n_{\lambda\sigma}\},\{\nu_q\})n_{\lambda\sigma} ,\\ \bar{\nu}_q=\sum w(\{n_{\lambda\sigma}\},\{\nu_q\})\nu_q\end{gathered} \tag{2.20}$$

are the averaged occupation numbers of electrons and phonons, respectively.

The coefficients β_q are chosen from the minimality condition for the thermodynamic functional (2.19). This condition is equivalent to minimization of the system energy at the given entropy, which is inherently determined by the combinatory expression[10]

$$\begin{aligned}S_0=-k_B\Bigg\{&\sum_{\lambda\sigma}[\bar{n}_{\lambda\sigma}\ln\bar{n}_{\lambda\sigma}+(1-\bar{n}_{\lambda\sigma})\ln(1-\bar{n}_{\lambda\sigma})]\\ &+\sum_q[\bar{\nu}_q\ln\bar{\nu}_q-(1+\bar{\nu}_q)\ln(1+\bar{\nu}_q)]\Bigg\} ,\end{aligned} \tag{2.21}$$

where the first term is the electron entropy, the second one is the phonon entropy, and k_B is the Boltzmann constant. Hence, the mentioned condition is the minimal-energy condition at the given occupation numbers $\bar{n}_{\lambda\sigma}$ and $\bar{\nu}_q$, which are determined from the extremum condition for the same functional (2.19) (maximal entropy at given energy). This yields

$$\begin{gathered}\bar{n}_{\lambda\sigma}=\left[\exp\left[\frac{\tilde{\mathcal{E}}_\lambda-\mu}{k_BT}\right]+1\right]^{-1} ,\\ \bar{\nu}_q=\left[\exp\left[\frac{\hbar(\Omega_q-Vq)}{k_BT}\right]-1\right]^{-1} .\end{gathered} \tag{2.22}$$

From the minimality condition for the functional (2.19) with respect to the coefficients β_q in view of (2.10) and (2.13) we find

$$\beta_q=-\frac{\chi^*(q)}{\hbar(\Omega_q-Vq)}\sum_{\lambda\sigma k}\bar{n}_{\lambda\sigma}\tilde{\psi}^*_\lambda(k)\tilde{\psi}_\lambda(k+q) . \tag{2.23}$$

If we substitute (2.23) into (2.17) with allowance for (2.14b) and (2.2), we obtain the expression for the self-consistent deformation potential (2.17)

$$\begin{aligned}u(x)&=-\frac{4\chi^2a}{w(1-s^2)}\sum_{\lambda\sigma}\bar{n}_{\lambda\sigma}|\psi_{\lambda\sigma}(x)|^2\\ &=-\frac{4\chi^2a}{w(1-s^2)}\rho_1(x) ,\end{aligned} \tag{2.24}$$

where $s=V/V_a$ is the ratio of velocity V to the sound velocity V_a, and the function

$$\rho_1(x)=\sum_{\lambda\sigma}\bar{n}_{\lambda\sigma}|\psi_\lambda(x)|^2 \tag{2.25}$$

describes the spatial distribution of the electron density along the chain, since it is easy to verify that $\langle\mathcal{N}_e(n)\rangle/a=\rho_1(an)$, where

$$\mathcal{N}_e(n)=\frac{1}{N}\sum_{kk'\sigma}e^{-i(k-k')an}a^\dagger_{k\sigma}a_{k'\sigma}=\sum_\sigma a^\dagger_{n\sigma}a_{n\sigma}$$

is an operator of the electron number on the nth site of the chain.

Thus, to find the transformation coefficients (2.12) and to define the self-consistent one-electron states, it is necessary to solve the set of nonlinear equations

$$\frac{\hbar^2}{2m}\frac{d^2\psi_\lambda}{dx^2}+\frac{4\chi^2a}{w(1-s^2)}\sum_{\lambda'\sigma'}\bar{n}_{\lambda'\sigma'}|\psi_{\lambda'}|^2\psi_\lambda+\mathcal{E}_\lambda\psi_\lambda=0 . \tag{2.26}$$

The equations (2.26) in this form coincide with the ones given in Ref. 7. The exact solutions of the set (2.26) are expressed through elliptic functions.[6,7] The self-consistent potential (2.17) is shown to be the single-gap periodic Lamé potential,[3,7] whose spectrum has one forbidden band (the energetic gap) splitting the initial conduction band into two bands of allowed states. Therefore the quantum number λ labeling the electron states in (2.16) is a double quantum number,[7] $\lambda\equiv\{\nu,k\}$, which gives both the number of allowed bands, ν, and the states within these bands, namely, the wave number k in the space of the reciprocal lattice of the periodic potential (2.17).

Using the results obtained previously in Ref. 7, we can write the solution of the set (2.26) as

$$\begin{gathered}\psi_\lambda(x)\equiv\psi_{\nu,k}(x)=e^{ikx}u_{\nu,k}(x) ,\\ u_{\nu,k}(x)=C_\nu(k)e^{-\eta'\lambda_\nu}\frac{\sigma(x+\omega'+\lambda_\nu)}{\sigma(\lambda_\nu)\sigma(x+\omega')}\exp\left[-\frac{\eta}{\omega}\lambda_\nu x\right] ,\end{gathered} \tag{2.27}$$

where

$$\lambda_\nu\equiv\lambda_\nu(\alpha)=i\alpha+\omega\nu \tag{2.28}$$

is a solution parameter. Here the number ν takes the values 0 and 1, α is a real parameter, and $C_\nu(k)\equiv C_\nu(\alpha)$ are the normalization constants.

Henceforth we employ the standard notation of elliptic function theory,[11] namely, $\wp(z)$, $\sigma(z)$, and $\zeta(z)$ are the two-parametric Weierstrass functions on the complex plane. As the parameters there, we can use either the invariants g_2 and g_3 defining the differential equation

$$\begin{aligned}\wp'^2(z)&=4\wp^3(z)-g_2\wp(z)-g_3\\&=4(\wp-e_1)(\wp-e_2)(\wp-e_3)\ ,\end{aligned}$$

or the half-periods ω and ω' of the double-periodic Weierstrass elliptic function $\wp(z)=\wp(z+2m\omega+2n\omega')$. In the case under consideration the period 2ω is a real number specifying the spatial periodicity of the solution (2.27), and $2\omega'=i2\tilde{\omega}$ is a purely imaginary number connected with the periodicity in space of the reciprocal lattice.[7] Often one draws on the symmetrical notations for the half-periods

$$\omega_1=\omega\ ,\quad \omega_2=-\omega-\omega'\ ,\quad \omega_3=\omega'\ .$$

Standard constants of elliptic function theory are the values $\wp(\omega_j)=e_j$ $(j=1,2,3)$ where e_j are the roots for the right-hand side of the differential equation for $\wp(z)$, i.e., $\wp'(\omega_j)=0$, with $e_1>e_2>e_3$, $e_1>0$, $e_3<0$, and $e_1+e_2+e_3=0$. $\zeta(\omega_j)=\eta_j$, i.e., $\eta_1=\zeta(\omega)\equiv\eta$ is a real number, and $\eta_3=\zeta(\omega')\equiv\eta'$ is a purely imaginary one.

The wave function (2.27) satisfies the Bloch theorem $u_{\nu,k}(x+2\omega)=u_{\nu,k}(x)$. In this case the number k has the meaning of the wave number and is related to the parameter α by[7]

$$k=i\left[\zeta(\lambda_\nu)-\frac{\eta}{\omega}\lambda_\nu\right]\ . \tag{2.29}$$

For the functions (2.27) the following formulas exist:

$$|\psi_{\nu,k}(x)|^2=(-1)^{\nu+1}|C_\nu(k)|^2[\wp(\lambda_\nu)-\wp(x+\omega')]\ , \tag{2.30a}$$

$$\frac{d^2\psi_{\nu,k}}{dx^2}=[\wp(\lambda_\nu)+2\wp(x+\omega')]\psi_{\nu,k}\ . \tag{2.30b}$$

Substituting the functions (2.27) into Eq. (2.26) and bearing in mind (2.30a) and (2.30b), we obtain the eigenvalues $\mathcal{E}_\lambda=\mathcal{E}_\nu(\alpha)\equiv\mathcal{E}_\nu(k)$:

$$\mathcal{E}_\nu(\alpha)=\frac{\hbar^2}{2m}\left[-2A-\wp(\lambda_\nu)\right]\ , \tag{2.31}$$

where

$$A=\kappa\sum_{k\nu\sigma}(-1)^{\nu+1}\bar{n}_{\nu\sigma}(k)|C_\nu(k)|^2\wp(\lambda_\nu)\ . \tag{2.32}$$

Here the notation

$$\kappa=\frac{4m\chi^2a}{\hbar^2w(1-s^2)} \tag{2.33}$$

is introduced. Due to nonlinearity of Eqs. (2.26), the normalization coefficients $C_\nu(k)$ should satisfy the relation

$$\sum_{\sigma\nu k}(-1)^{\nu+1}\bar{n}_{\sigma\nu}(k)|C_\nu(k)|^2=\frac{1}{\kappa}\ . \tag{2.34}$$

The expressions (2.31) together with (2.29) give the spectrum of one-electron states in the parametric form (through the parameter α). Restricting the values of the parameter α by the main domain

$$-\tilde{\omega}<\alpha\leq\tilde{\omega}\ ,\quad i\tilde{\omega}=\omega'\ , \tag{2.35}$$

we come to the broadened band scheme in the space of the wave vectors.[7] For the lower band, $\nu=1$, the values of the wave numbers are within the range of the first Brillouin zone of the periodic potential with the period 2ω: $-\pi/(2\omega)<k\leq\pi/(2\omega)$, and the energy (2.31) has values in the range

$$\frac{\hbar^2}{2m}(-2A-e_1)\leq\mathcal{E}_1(k)\leq\frac{\hbar^2}{2m}(-2A-e_2)\ . \tag{2.36a}$$

The upper band, $\nu=0$, is defined by values of the wave numbers outside the first Brillouin zone $|k|\geq\pi/(2\omega)$, and its energy is

$$\mathcal{E}_0(k)\geq\frac{\hbar^2}{2m}(-2A-e_3)\ . \tag{2.36b}$$

Therefore, the lower band of width

$$\mathcal{L}=\frac{\hbar^2}{2m}(e_1-e_2) \tag{2.37}$$

is separated from the upper one by the energy gap

$$2\Delta=\frac{\hbar^2}{2m}(e_2-e_3)\ . \tag{2.38}$$

According to (2.25) and (2.30a) the distribution of the electron density along the chain is a periodic function (the charge density wave) with period 2ω:

$$\rho_1(x)=\frac{1}{\kappa}[A-\wp(x+\omega')]\ . \tag{2.39}$$

The constant A can be found from the condition that the total number of electrons is equal to a given number N_e. Integrating (2.39) over the whole chain, we find

$$A=\frac{2\kappa k_F}{\pi}-\frac{\eta}{\omega}\ , \tag{2.40}$$

where $k_F=\pi n_e/(2a)$ is the Fermi wave number for the free electrons and $n_e=N_e/N$ is the concentration of electrons in the chain.

The relations (2.34) and (2.32) with allowance for (2.40) and the explicit form of coefficients $C_\nu(k)$ determined from the normalization condition of the wave function (2.27) give the self-consistent relations for determining the unknown parameters, namely, the chemical potential μ and the half-periods ω and ω'. However, to yield three unknown values, a third condition is necessary. This remaining indeterminacy is related to the fact that, in integrating the set (2.26), there appears an additional integration constant[7] involving the invariants g_2 and g_3. To determine this constant it is necessary to carry out an additional minimization of the free energy with respect to one of the parameters. For this purpose we write down the free energy (2.19) using the explicit form of the solution (2.27),

$$F\le\frac{\hbar^2}{2m}\left\{\frac{1}{\kappa}\left[\frac{1}{12}g_2-\frac{\eta^2}{\omega^2}\right]+\frac{4k_F}{\pi}\frac{\eta}{\omega}-\Sigma\right\}L$$

$$-\left[\mu+\frac{\hbar^2\kappa k_F}{\pi m}+\tfrac{1}{2}mV^2\right]N_e+\sum_q\hbar(\Omega_q-Vq)\bar{\nu}_q-TS_0, \tag{2.41}$$

where

$$\Sigma\equiv\sum_{\sigma\nu k}(-1)^{\nu+1}\bar{n}_{\sigma\nu}(k)|C_\nu(k)|^2\wp(\lambda_\nu)\left[\frac{\eta}{\omega}+\wp(\lambda_\nu)\right].$$

For minimization of (2.41) with respect to one of the parameters we use the method of Ref. 3 based on the homogeneity relations for the Weierstrass functions,[11]

$$\wp(tz|t\omega,t\omega')=t^{-2}\wp(z|\omega,\omega')\ ,$$

$$g_2(t\omega,t\omega')=t^{-4}g_2(\omega,\omega')\ ,$$

$$\eta(t\omega,t\omega')=t^{-1}\eta(\omega,\omega')\ .$$

Setting $\omega=t\varpi$ and $\omega'=t\varpi'$, consider the parameter t as a variational one. In this case the Jacobi parameter depending on the ratio ω'/ω remains unchanged. Then the part of the free energy (2.41) depending on the parameter t is

$$F\le\frac{\hbar^2}{2m}\left\{\frac{1}{\kappa t^4}\left[\frac{1}{12}\bar{g}_2-\frac{\bar{\eta}^2}{\varpi^2}\right]+\frac{4k_F}{\pi t^2}\frac{\bar{\eta}}{\varpi}-\frac{1}{t^4}\bar{\Sigma}\right\}+\cdots\ . \tag{2.41'}$$

Here the overbar marks the quantities depending only on ϖ and ϖ'. In general, the dependence on the parameter t is also inherent in the average occupation numbers $\bar{n}_{\sigma\nu}(k)$ which are determined through $\mathcal{E}_\nu(\alpha)$. However, by virtue of (2.22) $\partial F/\partial\bar{n}_{\sigma\nu}=0$. Differentiating (2.41′) with respect to t and equating the derivative to zero, we obtain the condition

$$\sum_{\sigma\nu k}(-1)^{\nu+1}\bar{n}_{\sigma\nu}(k)|C_\nu(k)|^2\wp(\lambda_\nu)\left[\frac{\eta}{\omega}+\wp(\lambda_\nu)\right]$$

$$=\frac{1}{\kappa}\left[\frac{1}{12}g_2-\frac{\eta^2}{\omega^2}+\frac{2k_F\kappa}{\pi}\frac{\eta}{\omega}\right]. \tag{2.42}$$

Then we use the normalization condition

$$\int_{-L/2}^{L/2}|\psi_{\nu k}(x)|^2dx=1\ ,$$

giving the normalization coefficients

$$|C_\nu(\alpha)|^2=\frac{1}{L}\frac{(-1)^{\nu+1}}{\eta/\omega+\wp(\lambda_\nu)}\ . \tag{2.43}$$

Substituting (2.43) into (2.32), (2.34), and (2.42) with allowance for (2.40), we obtain after some simple transformations the three self-consistent relations

$$\frac{1}{L}\sum_{\sigma\nu k}\frac{\bar{n}_{\sigma\nu}(k)}{\eta/\omega+\wp(\lambda_\nu)}=\frac{1}{\kappa}\ , \tag{2.44}$$

$$\frac{1}{L}\sum_{\sigma\nu k}\bar{n}_{\sigma\nu}(k)=\frac{2k_F}{\pi}\ , \tag{2.45}$$

$$\frac{1}{L}\sum_{\sigma\nu k}\bar{n}_{\sigma\nu}(k)\frac{\wp''(\lambda_\nu)}{\eta/\omega+\wp(\lambda_\nu)}=0\ , \tag{2.46}$$

where

$$\wp''(z)\equiv\frac{d^2\wp}{dz^2}=6\wp^2(z)-\tfrac{1}{2}g_2\ .$$

Having solved Eqs. (2.44)–(2.46) for μ, ω, and ω', we can determine all characteristics of the CDW state, both the energetic ones, for example, (2.37) and (2.38), and the form of the charge-density wave itself (2.39) in the moving reference frame. Using the representation in terms of Jacobi Θ functions,[11] the expression (2.39) can be represented in terms of two equivalent expansions

$$\rho_1(x)=\frac{n_e}{a}\left\{1+\frac{\pi}{2\kappa k_F}\left[\frac{\pi}{\omega}\right]^2\sum_{n=1}^{\infty}\frac{n}{\sinh(\pi\tilde{\omega}/\omega)n}\cos\frac{\pi nx}{\omega}\right\}$$

$$=\frac{n_e}{a}\left[1-\frac{\omega_0\tilde{\omega}_0}{\omega\tilde{\omega}}\right] \tag{2.47a}$$

$$+\frac{\tilde{\omega}_0}{\tilde{\omega}}\sum_{n=-\infty}^{\infty}\frac{\pi/2\tilde{\omega}}{\cosh^2(\pi/2\tilde{\omega})(x+2\omega n)}\ , \tag{2.47b}$$

where

$$\omega_0=\frac{\pi}{2k_F}\ ,\quad\tilde{\omega}_0=\frac{\pi}{2\kappa} \tag{2.48}$$

are the values of the half-periods ω and $\tilde{\omega}$ at absolute zero temperature.[7] The first expansion (2.47a) is the Fourier series, and it is useful for analyzing the spectrum of the current oscillation caused by the CDW motion,[7] and the second one (2.47b) shows that the CDW is a lattice of solitons having the width $2\tilde{\omega}$ and spaced by 2ω.

Now let us analyze the relations (2.44)–(2.46) and investigate the temperature behavior of the CDW in some limiting cases.

III. CDW STATE AT LOW TEMPERATURE

In the relations (2.44)–(2.46) there are functions depending explicitly on the parameter α. Therefore, it is convenient to proceed from summation over the states to integration over this parameter. Having summed over the spins, we can write down the relations of self-consistency in the following first form:

$$\int_0^{\tilde{\omega}}\bar{n}_1(\alpha)d\alpha+\int_{\tilde{\omega}}^0\bar{n}_0(\alpha)d\alpha=\frac{\pi}{2\kappa}\ , \tag{3.1}$$

$$\int_0^{\tilde{\omega}}\bar{n}_1(\alpha)\left[\frac{\eta}{\omega}+\wp(i\alpha+\omega)\right]d\alpha$$

$$+\int_{\tilde{\omega}}^0\bar{n}_0(\alpha)\left[\frac{\eta}{\omega}+\wp(i\alpha)\right]d\alpha=k_F\ , \tag{3.2}$$

$$\int_0^{\tilde{\omega}}\bar{n}_1(\alpha)\wp''(i\alpha+\omega)d\alpha+\int_{\tilde{\omega}}^0\bar{n}_0(\alpha)\wp''(i\alpha)d\alpha=0\ , \tag{3.3}$$

where

$$\bar{n}_\nu(\alpha)=\left[\exp\left[\frac{\mathcal{E}_\nu(\alpha)-\mu}{k_B T}\right]+1\right]^{-1} \tag{3.4}$$

and $\mathcal{E}_\nu(\alpha)$ is given by the expression (2.31) with allowance for (2.40). Below we confine ourselves to the case of the CDW at rest, $V=0$, with $\tilde{\mathcal{E}}_\nu(\alpha)=\mathcal{E}_\nu(\alpha)$.

Since the average occupation numbers (3.4) are functions of the energy of one-electron states, it is useful to proceed to integration over energy. Then the expressions (3.1)–(3.3) are transformed to the second form

$$\int_0^{\mathcal{L}}\frac{\bar{n}(\mathcal{E})}{\sqrt{P(\mathcal{E})}}d\mathcal{E}-\int_J^{\infty}\frac{\bar{n}(\mathcal{E})}{\sqrt{P(\mathcal{E})}}d\mathcal{E}=\frac{\pi}{\sqrt{\mathcal{E}_s}}\ , \tag{3.5}$$

$$\int_0^{\mathcal{L}}\bar{n}(\mathcal{E})\frac{JE/K-\mathcal{E}}{\sqrt{P(\mathcal{E})}}d\mathcal{E}+\int_J^{\infty}\bar{n}(\mathcal{E})\frac{\mathcal{E}-JE/K}{\sqrt{P(\mathcal{E})}}d\mathcal{E}=2\sqrt{\mathcal{E}_F}\ , \tag{3.6}$$

$$\int_0^{\mathcal{L}}\bar{n}(\mathcal{E})\frac{d\sqrt{P(\mathcal{E})}}{d\mathcal{E}}d\mathcal{E}-\int_J^{\infty}\bar{n}(\mathcal{E})\frac{d\sqrt{P(\mathcal{E})}}{d\mathcal{E}}d\mathcal{E}=0\ , \tag{3.7}$$

where

$$P(\mathcal{E})=\mathcal{E}[\mathcal{E}^2-(J+\mathcal{L})\mathcal{E}+J\mathcal{L}]=\begin{cases}\mathcal{E}(\mathcal{L}-\mathcal{E})(J-\mathcal{E}) & \text{at } 0\le\mathcal{E}<\mathcal{L}\\ \mathcal{E}(\mathcal{E}-\mathcal{L})(\mathcal{E}-J) & \text{at } \mathcal{E}\ge J\ ,\end{cases} \tag{3.8}$$

$$J=\mathcal{L}+2\Delta=\frac{\hbar^2}{2m}(e_1-e_3)\ , \tag{3.9}$$

$$\mathcal{E}_F=\frac{\hbar^2 k_F^2}{2m}\ ,\quad \mathcal{E}_s=\frac{\hbar^2\kappa^2}{2m}\ . \tag{3.10}$$

The energy in (3.5)–(3.7) is calculated from the bottom of the lower band $\mathcal{E}_1(0)$ and

$$\bar{n}(\mathcal{E})=\left[\exp\left[\frac{\mathcal{E}-\mu_1}{k_B T}\right]+1\right]^{-1}\ ,\quad \mu_1=\mu-\mathcal{E}_1(0)\ . \tag{3.11}$$

Since the Eqs. (3.5)–(3.7) explicitly contain the spectrum characteristics $\mathcal{L}$ and Δ given by the expressions (2.37) and (2.38), it is reasonable to solve these equations for the quantity J given by (3.9) and the parameter

$$k^2=\frac{2\Delta}{J}=\frac{e_2-e_3}{e_1-e_3}\ , \tag{3.12}$$

which has the meaning of the elliptic integral modulus.[11] The half-periods ω and $\tilde{\omega}$ are then defined as

$$\omega=\sqrt{\hbar^2/2mJ}\,K\ ,\quad \tilde{\omega}=\sqrt{\hbar^2/2mJ}\,K'\ . \tag{3.13}$$

Here, as in (3.6), $K=K(k)$ and $E=E(k)$ are the total elliptic integrals of the first and second kind, respectively, $K'=K(k')$, $E'=E(k')$, and $k'^2=1-k^2$.

At the absolute zero temperature, when

$$\bar{n}(\mathcal{E})=\begin{cases}1 & \text{at } \mathcal{E}<\mu\\ 0 & \text{at } \mathcal{E}>\mu\ ,\end{cases}$$

it is convenient to use the first form of the self-consistent relations. In this case the integrals in (3.1)–(3.3) can easily be calculated. The condition (3.3) holds only in the case when the chemical potential μ is located in the forbidden band, i.e., $\bar{n}_1(\alpha)=1$ and $\bar{n}_0(\alpha)=0$. Then from (3.1) and (3.2) the values (2.48) follow at once. The case of $T=0$ was analyzed in detail previously.[7] Here it should only be noted that the CDW characteristics, for example, the relation between the gap width (2.38) and the width of the filled (condensate) band (2.37), depend on the value of the parameter

$$\tau=\frac{\tilde{\omega}_0}{\omega_0}=\frac{k_F}{\kappa}=\frac{\pi\hbar^2 w n_e}{8m\chi^2 a^2}\ . \tag{3.14}$$

This parameter is seen to define the ratio of the size of solitons in the expansion (2.47b) to the distance between them. The value $\tau>1$ corresponds to the Fröhlich limit and at $\tau<1$ the CDW is a lattice of bisolitons[12] sufficiently distant from each other.

From the standpoint of the one-electron spectrum, at $T=0$ the CDW state represents a semiconductor (dielectric) with a completely filled lower (valence) band and an empty upper conduction band. When the temperature T is finite, some of the electrons occupy the upper band. The appearance of electrons with the average occupation number $\bar{n}_e(\mathcal{E})=\bar{n}_0(\mathcal{E})$ in the conduction band is accompanied by the origination of holes in the lower valence band. Hence, one can consider the average occupation number of holes in the lower band,

$$\bar{n}_h(\mathcal{E})=1-\bar{n}_1(\mathcal{E})\ . \tag{3.15}$$

As is usually accepted in semiconductor theory, we calculate the electron energy from the bottom of the upper band $\mathcal{E}_0(\tilde{\omega})$ and the hole energy from the upper edge of the lower band $\mathcal{E}_1(\tilde{\omega})$, and introduce the chemical potentials of electrons μ_e and holes μ_h

$$\mu_e=\mathcal{E}_0(\tilde{\omega})-\mu\ ,\quad \mu_h=\mu-\mathcal{E}_1(\tilde{\omega})\ , \tag{3.16}$$

which are connected by the relation

$$\mu_e+\mu_h=2\Delta\ . \tag{3.17}$$

Then the self-consistent relations specifying the CDW parameters can be written in the third form

$$\frac{1}{2}\sqrt{\hbar^2/2m}\left\{\int_0^{\mathcal{L}}\frac{\bar{n}_h(\mathcal{E})}{\sqrt{P_h(\mathcal{E})}}d\mathcal{E}+\int_0^{\infty}\frac{\bar{n}_e(\mathcal{E})}{\sqrt{P_e(\mathcal{E})}}d\mathcal{E}\right\}=\tilde{\omega}-\frac{\pi}{2\kappa}\ , \tag{3.18}$$

$$\frac{1}{2}\sqrt{2m/\hbar^2}\left\{\int_0^{\mathcal{L}}\frac{\bar{n}_h(\mathcal{E})(\mathcal{L}-\mathcal{E})}{\sqrt{P_h(\mathcal{E})}}d\mathcal{E}+\int_0^{\infty}\frac{\bar{n}_e(\mathcal{E})(J+\mathcal{E})}{\sqrt{P_e(\mathcal{E})}}d\mathcal{E}\right\}=k_F-\frac{\pi}{2\omega}+\frac{2mJ}{\hbar^2}\frac{E}{K}\left[\tilde{\omega}-\frac{\pi}{2\kappa}\right]\ , \tag{3.19}$$

$$\int_0^{\mathcal{L}} \bar{n}_h(\mathcal{E}) \frac{d\sqrt{P_h(\mathcal{E})}}{d\mathcal{E}} d\mathcal{E} - \int_0^{\infty} \bar{n}_e(\mathcal{E}) \frac{d\sqrt{P_e(\mathcal{E})}}{d\mathcal{E}} d\mathcal{E} = 0 , \tag{3.20}$$

where

$$\bar{n}_{e,h}(\mathcal{E}) = \left[\exp\left[\frac{\mathcal{E}+\mu_{e,h}}{k_B T} \right] + 1 \right]^{-1} \tag{3.21}$$

and

$$P_h(\mathcal{E}) = \mathcal{E}(2\Delta+\mathcal{E})(\mathcal{L}-\mathcal{E}) , \quad P_e(\mathcal{E}) = \mathcal{E}(2\Delta+\mathcal{E})(J+\mathcal{E}) . \tag{3.22}$$

Let us consider the case of sufficiently low temperatures at which the following inequalities hold:

$$\frac{\mathcal{L}}{k_B T} \gg 1 , \quad \frac{\Delta}{k_B T} \gg 1 , \quad \frac{\mu_{e,h}}{k_B T} \gg 1 . \tag{3.23}$$

In this case the average occupation numbers (3.21) are small and can be represented in the form

$$\bar{n}_{e,h}(\mathcal{E}) \simeq e^{-\mu_{e,h}/k_B T} e^{-\mathcal{E}/k_B T} .$$

Then from the condition (3.20) we find

$$\mu_e - \mu_h = k_B T \ln \frac{I_e}{I_h} , \tag{3.24}$$

where

$$I_e = \int_0^{\infty} e^{-\mathcal{E}/k_B T} f_e(\mathcal{E}) d\mathcal{E} , \quad I_h = \int_0^{\mathcal{L}} e^{-\mathcal{E}/k_B T} f_h(\mathcal{E}) d\mathcal{E} . \tag{3.25}$$

Integrals similar to (3.25) arise also in (3.18) and (3.19). By virtue of the inequalities (3.23) we let, introducing a small error, the upper limit in the integrals I_h tend to infinity, and the integrand functions $f_{e,h}(\mathcal{E})$ can be expanded in powers of $\mathcal{E}/\mathcal{L}$, $\mathcal{E}/J$, and $\mathcal{E}/\Delta$. Then the integrals (3.25) can be expressed in terms of the expansions

$$\begin{gathered} I_{e,h} = \sum_{n=0}^{\infty} C_n^{(e,h)}(T) I_n , \\ I_n = \int_0^{\infty} e^{-x} x^{n-1/2} dx = \frac{(2n-1)!!}{2^n} \sqrt{\pi} \end{gathered} \tag{3.25'}$$

in powers of the small quantities $k_B T/\mathcal{L}$ and $k_B T/\Delta$.

From (3.24) and (3.17) we find

$$\begin{gathered} \mu_e = \Delta + \frac{1}{4} k_B T \ln \frac{\mathcal{L}+2\Delta}{\mathcal{L}} + \frac{3}{4} \frac{\mathcal{L}+\Delta}{\mathcal{L}(\mathcal{L}+2\Delta)} (k_B T)^2 + \cdots , \\ \mu_h = \Delta - \frac{1}{4} k_B T \ln \frac{\mathcal{L}+2\Delta}{\mathcal{L}} - \frac{3}{4} \frac{\mathcal{L}+\Delta}{\mathcal{L}(\mathcal{L}+2\Delta)} (k_B T)^2 - \cdots . \end{gathered} \tag{3.26}$$

Using these values in (3.18) and (3.19) and neglecting the quantities of the order of $k_B T/\Delta$ and $k_B T/\mathcal{L}$, we derive the set of equations for the parameters J and k:

$$\frac{2}{\pi} K' \sqrt{J/\mathcal{E}_F} = \tau \frac{J}{\mathcal{E}_F} + \left[\frac{\pi k_B T}{\mathcal{E}_F} \right]^{1/2} e^{-\Delta/k_B T} \frac{1+k'^2}{\pi k k'^{3/2}} , \tag{3.27a}$$

$$\left[\frac{J}{\mathcal{E}_F} \right]^{1/2} = \frac{2}{\pi} K \left[1 - \left[\frac{\pi k_B T}{\mathcal{E}_F} \right]^{1/2} e^{-\Delta/k_B T} \frac{k'^{1/2}}{k} \times \left[1 - \frac{E}{K} \frac{1+k'^2}{2k'^2} \right] \right] . \tag{3.27b}$$

Excluding the parameter J from (3.27a), we obtain the equation for the modulus

$$\begin{aligned} K' \left[1 + \left[\frac{\pi k_B T}{\mathcal{E}_F} \right]^{1/2} e^{-\Delta/k_B T} \frac{k}{2k'^{3/2}} \right] & \\ - \tau K \left[1 - \left[\frac{\pi k_B T}{\mathcal{E}_F} \right]^{1/2} e^{-\Delta/k_B T} \frac{2k'^{1/2}}{k} \right] & \\ = \left[\frac{\pi k_B T}{\mathcal{E}_F} \right]^{1/2} e^{-\Delta/k_B T} \frac{1+k'^2}{2kk'^{3/2}} (2\tau E + E') & . \end{aligned} \tag{3.28}$$

We now consider two limiting cases.

(i) At large values of the parameter τ, $\tau \geq 1.5$, the solution of (3.28) corresponds to small values of the modulus k, $k^2 \ll 1$. Using the expansion

$$\begin{gathered} K = \frac{\pi}{2}(1+\tfrac{1}{4}k^2) , \quad E = \frac{\pi}{2}(1-\tfrac{1}{4}k^2) , \\ K' = \ln \frac{4}{k} , \quad E' = 1 , \end{gathered}$$

we find from (3.28) and (3.27b)

$$\begin{gathered} J = \mathcal{E}_F(1+\tfrac{1}{2}k^2) , \\ k = k_0 - \left[\frac{\pi k_B T}{\mathcal{E}_F} \right]^{1/2} e^{-\Delta/k_B T} , \quad k_0 = 4e^{-\pi\tau/2} . \end{gathered} \tag{3.29}$$

Hence, for the characteristics of the one-electron spectrum of the CDW state at low temperatures we have

$$\begin{gathered} \Delta(T) = \Delta_0 \left[1 - 2 \left[\frac{\pi k_B T}{2\Delta_0} \right]^{1/2} e^{-\Delta_0/k_B T} \right] , \\ \Delta_0 \equiv \Delta(0) = 8\mathcal{E}_F e^{-\pi\tau} , \end{gathered} \tag{3.30a}$$

$$\begin{gathered} \mathcal{L}(T) = \mathcal{L}_0 \left[1 + 16 e^{-\pi\tau} \left[\frac{\pi k_B T}{2\Delta_0} \right]^{1/2} e^{-\Delta_0/k_B T} \right] , \\ \mathcal{L}_0 \equiv \mathcal{L}(0) = \mathcal{E}_F(1-8e^{-\pi\tau}) . \end{gathered} \tag{3.30b}$$

For the spatial characteristics of the CDW (for the half-periods ω and $\tilde{\omega}$) we obtain

$$\omega(T) \simeq \omega_0 = \frac{\pi}{2k_F} , \tag{3.31a}$$

$$\tilde{\omega}(T) = \tilde{\omega}_0 \left[1 + \frac{1}{\tau} \left[\frac{2k_B T}{\pi\Delta_0} \right]^{1/2} e^{-\Delta_0/k_B T} \right] . \tag{3.31b}$$

(ii) In the bisoliton limit when the parameter τ is small, $\tau \lesssim 0.5$, the solution of (3.28) corresponds to modulus values close to unity, i.e., $k'^2 = 1 - k^2 \ll 1$. Using the expansions

$$K \simeq \ln \frac{4}{k'}\ , \quad E = 1\ , \quad K' = \frac{\pi}{2}(1 + \tfrac{1}{4}k'^2)\ ,$$

$$E' = \frac{\pi}{2}(1 - \tfrac{1}{4}k'^2)\ ,$$

we find from (3.28) and (3.27b)

$$J = \mathcal{E}_s \left\{ 1 - \frac{\tau}{8\pi} e^{3\pi/4\tau} \left[\frac{\pi k_B T}{\mathcal{E}_F} \right]^{1/2} e^{-\Delta/k_B T} \right\}\ ,$$
$$k' = k'_0 + \left[\frac{\pi k_B T}{k'_0 \mathcal{E}_F} \right]^{1/2} e^{-\Delta/k_B T}\ , \quad k'_0 = 4e^{-\pi/2\tau}\ . \qquad (3.32)$$

In this case for the temperature dependences of the CDW energy and spatial characteristics we derive the expressions

$$\Delta(T) = \Delta_0 \left[1 - \frac{1}{\pi} e^{\pi/4\tau} \left[\frac{\pi k_B T}{\mathcal{L}_0} \right]^{1/2} e^{-\Delta_0/k_B T} \right]\ ,$$
$$\Delta_0 = \tfrac{1}{2}\mathcal{E}_s(1 - 8e^{-\pi/\tau})\ , \qquad (3.33a)$$

$$\mathcal{L}(T) = \mathcal{L}_0 \left[1 + \frac{1}{\tau} e^{\pi/4\tau} \left[\frac{\pi k_B T}{\mathcal{L}_0} \right]^{1/2} e^{-\Delta_0/k_B T} \right]\ ,$$
$$\mathcal{L}_0 = 16\mathcal{E}_s e^{-\pi/\tau}\ , \qquad (3.33b)$$

$$\omega(T) = \omega_0 \left[1 - \frac{1}{2\pi} e^{\pi/4\tau} \left[\frac{\pi k_B T}{\mathcal{L}_0} \right]^{1/2} e^{-\Delta_0/k_B T} \right]\ , \qquad (3.34a)$$

$$\tilde{\omega}(T) = \tilde{\omega}_0 \left[1 + \frac{1}{2\pi} e^{\pi/4\tau} \left[\frac{\pi k_B T}{\mathcal{L}_0} \right]^{1/2} e^{-\Delta_0/k_B T} \right]\ . \qquad (3.34b)$$

As can be seen from comparison between formulas (3.30a)–(3.31b) and (3.33a)–(3.34b), the temperature behavior of the CDW state, although to some extent similar in the bisoliton and Fröhlich limits, is, nevertheless essentially different. First, in the Fröhlich limit the CDW period (3.31a) is practically independent of temperature, whereas in the bisoliton limit this period (3.34a) decreases with increasing T. Secondly, at $\tau \gtrsim 1.5$ the temperature dependence of the energetic gap (3.30a) is more pronounced than that of the condensate bandwidth (3.30b), and at $\tau \lesssim 0.5$ the pattern is reversed. This difference lends itself to the following physical interpretation. In accordance with the expansion (2.47b) at $\tau \lesssim 0.5$, the CDW is a lattice of bisolitons sufficiently distant from each other. At finite temperature T the thermal dissociation of some of the bisolitons into solitons is possible. When the length of a chain is fixed, the appearance of new solitons decreases the average distance between them. With increasing temperature, the fraction of dissociated solitons increases; this leads to a decrease of the CDW period. Now let us take notice of the constant term in (2.47b) (vanishing at $T=0$) which can be interpreted as the density of the free electrons, which are uniformly distributed and not coupled into solitons. When we substitute (3.34a) and (3.34b) into this term, we see that its order of smallness exceeds the accuracy of obtaining the formulas (3.33a)–(3.34b). Thus, at low temperature in this limit, all electrons remain coupled with solitons whose number increases with increasing T. Since the electrons participate with equal probability in generating each soliton, the average number of electrons corresponding to one soliton decreases with increasing T. This leads to a self-consistent increase of the soliton width $2\tilde{\omega}$. Decrease of the distance between solitons increases the overlap integral between wave functions of electrons belonging to neighboring solitons. This fact affects, in the first place, the broadening of the electron band $\mathcal{L}$ (3.33b) generated due to the splitting of the soliton level $\mathcal{E}_s = \hbar^2\kappa^2/(2m)$.

In the Fröhlich limit, $\tau \gtrsim 1.5$, bisolitons are strongly overlapping and, figuratively speaking, there is no free space between them. Hence, the unique channel of thermal dissociation is the electron ejected into the band of free states. In this case, the CDW period is not changed and the constant term in (2.47b) is nonzero and increases with increasing T. The appearance of the free electrons is accompanied by decrease of the average number of electrons involved in generation of one soliton; this leads to the self-consistent increase of soliton size $2\tilde{\omega}$. With increase of the soliton diffuseness the amplitude of the periodic potential (2.24) decreases. In this case the potential shape is defined mainly by the first harmonic of the expansion (2.47a). The decrease of the amplitude $u(x)$ affects in the first place the decrease of the energetic gap 2Δ, whose value can be obtained from the solution of the Schrödinger equation (2.16) in the almost-free-electron approximation.

The general feature of the behavior of the CDW state is the decrease of the energetic gap $2\Delta(T)$, which tends to zero when the temperature approaches the value T_P of the Peierls phase transition.[13,14]

IV. THE TEMPERATURE OF THE PHASE TRANSITION

At the temperature T_P of the phase transition the energetic gap in the one-electron spectrum of the CDW state vanishes.[13] To determine the values T_P we use the self-consistent relations in the second form (3.5)–(3.7) setting $T = T_P$. Since $\Delta(T_P) = 0$ and $J(T_P) = \mathcal{L}(T_P)$ then the polynomial (3.8) is reduced to the form

$$P(\mathcal{E}) = \mathcal{E}(\mathcal{E} - \mathcal{L}_P)^2\ . \qquad (4.1)$$

For the critical temperature the relations (3.5)–(3.7) can then be written as

$$\int_0^\infty \frac{\bar{n}(\mathcal{E})\,d\mathcal{E}}{(\mathcal{L}_P - \mathcal{E})\sqrt{\mathcal{E}}} = \frac{\pi}{\sqrt{\mathcal{E}_s}}\ , \qquad (4.2)$$

$$\int_0^\infty \frac{\bar{n}(\mathcal{E})\,d\mathcal{E}}{\sqrt{\mathcal{E}}} = 2\sqrt{\mathcal{E}_F}\ , \qquad (4.3)$$

$$\int_0^\infty \bar{n}(\mathcal{E})\sqrt{\mathcal{E}}\,d\mathcal{E} = \tfrac{1}{3}\mathcal{L}_P\sqrt{\mathcal{E}_F}\ , \qquad (4.4)$$

where $\mathcal{L}_P \equiv \mathcal{L}(T_P)$ and $\mu_1 = \mu_1(T_P)$.

The relations (4.2)–(4.4) are a set of three equations for obtaining T_P, $\mathcal{L}(T_P)$, and $\mu_1(T_P)$. At an arbitrary value of the parameter $\tau = k_F/\kappa = \sqrt{\mathcal{E}_F/\mathcal{E}_s}$, the analysis of these equations requires numerical calculations. However, in the limiting cases one can obtain asymptotical solutions.

(i) The first limiting case corresponds to the assumption that at the temperature T_P the electrons in the system are strongly degenerate. The implication involved is that the inequalities

$$\mu_1(T_P)>0\ , \quad \frac{\mu_1(T_P)}{k_B T_P}\gg 1 \tag{4.5}$$

hold. In this case, using the known methods for the estimation of Fermi-Dirac integrals, from the relations (4.3) and (4.4) we find

$$\mu_1(T_P)=\mathcal{E}_F\left\{1+O\left[\left[\frac{k_B T_P}{\mu_1}\right]^2\right]\right\}, \tag{4.6a}$$

$$\mathcal{L}(T_P)=\mathcal{E}_F\left\{1+O\left[\left[\frac{k_B T_P}{\mu_1}\right]^2\right]\right\}. \tag{4.6b}$$

Using the values obtained in (4.2), taking into account the identity

$$(e^x+1)^{-1}=\frac{1}{2}\left[1-\tanh\frac{x}{2}\right]$$

and the intermediate integration by parts, we obtain the expression

$$\int_0^{\mathcal{E}_F}\frac{\ln[(\sqrt{\mathcal{E}_F}+\sqrt{\mathcal{E}_F-\mathcal{E}})/(\sqrt{\mathcal{E}_F}-\sqrt{\mathcal{E}_F-\mathcal{E}})]}{\cosh^2\mathcal{E}/2k_B T_P}\frac{d\mathcal{E}}{2k_B T} + \int_0^{\infty}\frac{\ln[(\sqrt{\mathcal{E}_F+\mathcal{E}}+\sqrt{\mathcal{E}_F})/(\sqrt{\mathcal{E}_F+\mathcal{E}}-\sqrt{\mathcal{E}_F})]}{\cosh^2\mathcal{E}/2k_B T_P}\frac{d\mathcal{E}}{2k_B T_P}=2\pi\tau \tag{4.7}$$

By virtue of the inequality (4.5) which can be written as $\mathcal{E}_F/(k_B T_P)\gg 1$, the basic contribution to the integrals (4.7) is given by the values of $\mathcal{E}$ that are considerably smaller than $\mathcal{E}_F$. Then the logarithmic functions in (4.7) can be expanded in the ratio $\mathcal{E}/\mathcal{E}_F$ and in the first approximation the known Kuper result[13] can be obtained:

$$k_B T_P=\frac{1}{\pi}e^{C}8\mathcal{E}_F e^{-\pi\tau}\ , \tag{4.8}$$

where $C=0.577$ is the Euler constant. Since in our calculations the inequality (4.5) has been used, the solution obtained is valid at $\tau\gtrsim 1.5$ only. In this case the phase transition temperature T_P and the energy gap Δ_0 at the temperature of absolute zero (3.30a) are related by the BCS relation[13,14]

$$\Delta_0=1.76k_B T_P\ . \tag{4.9}$$

(ii) The second limiting case, when analytical solution of Eqs. (4.2)–(4.4) is possible, corresponds to the assumption that the quasiparticles are nondegenerate at the temperature T_P. This means that at $T=T_P$ the chemical potential $\mu(T_P)$ is disposed below the edge of the one-electron states, i.e.,

$$\mu_1(T_P)=-\xi\ , \quad \frac{\xi}{k_B T_P}>1\ . \tag{4.10}$$

Then the Fermi distribution function (3.11) turns into the Maxwell-Boltzmann distribution of classical statistics

$$\bar{n}(\mathcal{E})=e^{-\xi/k_B T_P}e^{-\mathcal{E}/k_B T_P}\ . \tag{4.11}$$

Substituting (4.11) into (4.3) we find

$$\exp\left[-\frac{\xi}{k_B T_P}\right]=2\left[\frac{\mathcal{E}_F}{\pi k_B T_P}\right]^{1/2}\ . \tag{4.12}$$

and from (4.4) in view of (4.11) and (4.12) we obtain

$$\mathcal{L}(T_P)=\tfrac{3}{2}k_B T_P\ . \tag{4.13}$$

Using Eqs. (4.12) and (4.13) for (4.2), for the temperature of the phase transition we have

$$k_B T_P=\frac{4}{\pi}\sqrt{\mathcal{E}_F\mathcal{E}_s}\,\Phi(1,\tfrac{3}{2};-\tfrac{3}{2})=\frac{16}{\pi}\frac{\hbar^2\kappa k_F}{2m}\ , \tag{4.14}$$

where $\Phi(\alpha,p;z)$ is the degenerate hypergeometric function $\Phi(1,\tfrac{3}{2};-\tfrac{3}{2})=0.4$. Substituting (4.14) into (4.12) we obtain

$$\exp\left[-\frac{\xi}{k_B T_P}\right]=1.58\sqrt{\tau}\ . \tag{4.15}$$

From this with allowance for the inequality (4.10) it follows that the solution obtained is correct only at small values of the parameter τ; $\tau\ll 1$. According to (4.14) and (3.33a), in the soliton-type CDW limit, the temperature T_P and the energy gap Δ_0 at $T=0$ are related by

$$k_B T_P=\frac{3.2}{\pi}\tau\Delta_0\ . \tag{4.16}$$

V. DISCUSSION

As has been shown above, in the weak electron-phonon coupling case or at comparatively high electron density when the parameter τ is greater than 1.5, the phase transition temperature T_P and the electronic gap Δ_0 at $T=0$ are connected by the BCS relation. The well-known[5,13,14] similarity of the thermal behavior of the CDW condensate in the Fröhlich limit to that of the BCS superconducting condensate follows from the self-consistent relations (3.18)–(3.20). According to Sec. III the modulus $k(T)$ decreases with increasing T. Thus, at small $k(0)$

corresponding to the Fröhlich limit the inequality

$$\frac{\tilde{\omega}}{\omega}\geq 1.5 \tag{5.1}$$

is always valid and the Jacobi parameter $q=\exp(-\tau\tilde{\omega}/\omega)$ is small. Then, using the formulas of elliptic function theory[11] one can obtain the following expressions for (2.37) and (2.38):

$$\mathcal{L}=\frac{\hbar^2}{2m}\left[\frac{\pi}{2\omega}\right]^2\Theta_4^4(0,q)\simeq\frac{\hbar^2}{2m}\left[\frac{\pi}{2\omega}\right]^2 , \tag{5.2a}$$

$$\Delta=\frac{\hbar^2}{4m}\left[\frac{\pi}{2\omega}\right]^2\Theta_2^4(0,q)\simeq 8\mathcal{L}e^{-\pi\tilde{\omega}/\omega} , \tag{5.2b}$$

where $\Theta_j(v,q)$ are the Jacobi theta functions $(j=1,2,3,4)$.

With the inequality

$$\frac{k_BT}{\mathcal{L}}\ll 1 \tag{5.3}$$

valid up to the critical temperature, it is possible to expand the integrand functions of (3.18)–(3.20) in powers of $\mathcal{E}/\mathcal{L}$. Neglecting the terms of order $(k_BT/\mathcal{L})^2$ and $(2\Delta/\mathcal{L})^2$, we find that the condition (3.20) can be satisfied if

$$\mu_e=\mu_h=\Delta , \tag{5.4}$$

so that the relation (3.19) leads to

$$\omega(T)\simeq\omega_0=\frac{\pi}{2k_F} , \tag{5.5}$$

i.e., in this limiting case the chemical potential μ is located at the center of the gap, and the CDW period does not depend on temperature. According to (5.5) and (5.2a), the condensate bandwidth $\mathcal{L}$ is close to the Fermi energy $\mathcal{E}_F$. With allowance for (5.4), (5.5), and (5.2b), after changing the integration variable the condition (3.18) may be reduced to the well-known BCS relation[10] which determines the temperature dependence of the electronic gap $2\Delta(T)$:

$$\ln\frac{\Delta_0}{\Delta(T)}=2I(u) , \tag{5.6}$$

where $u=\Delta(T)/(k_BT)$ and

$$I(u)=\int_0^\infty\frac{dx}{\sqrt{x^2+u^2}\left(e^{\sqrt{x^2+u^2}}+1\right)} . \tag{5.7}$$

But when the parameter τ is less than unity Eqs. (5.4)–(5.6) must break down. According to the results obtained, when $\tau\ll 1$ the CDW period is a function of temperature, decreasing with increasing T, and tends to the limiting value

$$2\omega(T_P)=\pi\left[\frac{\hbar^2}{2m\mathcal{L}(T_P)}\right]^{1/2}\simeq 2\omega_0\sqrt{1.3\tau} . \tag{5.8}$$

In this case, according to Eq. (4.16), the relation between Δ_0 and T_P reads

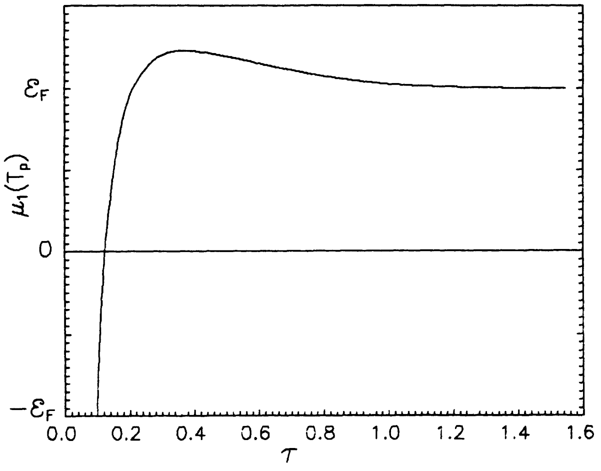

FIG. 1. Chemical potential $\mu_1(T_P)$ vs τ.

$$\frac{\Delta_0}{k_BT_P}=\frac{\pi}{3.2\tau} . \tag{5.9}$$

At an arbitrary value of the parameter τ the analysis of the relations (4.2)–(4.4) requires numerical calculations. The results are presented in Figs. 1 and 2. Figure 1 shows the value of $\mu_1(T_P)$ as a function of the parameter τ. It is shown that the chemical potential $\mu(T_P)$ coincides with the Fermi level $\mathcal{E}_F$ at $\tau\gtrsim 1$. At $\tau<0.2$ the value of $\mu_1(T_P)$ becomes less than $\mathcal{E}_F$, and at $\tau=0.123$ the chemical potential at T_P coincides with the bottom of the electron band. Thus, formulas (4.13), (4.16), (5.8), and (5.9) are valid for $\tau<0.123$.

In Fig. 2 the ratios $\Delta_0/(k_BT_P)$ and $2\omega(T_P)/(2\omega_0)$ versus the parameter τ are presented. It is shown that the mean-field approach leads to violation of the BCS relation at $\tau<1.2$. A significant variation of the CDW period with temperature may be observed at $\tau<0.8$.

As is mentioned in the Introduction, the mean-field treatment of the Peierls transition is not entirely correct and, strictly speaking, not valid near the phase transition temperature. First of all, the variational consideration of

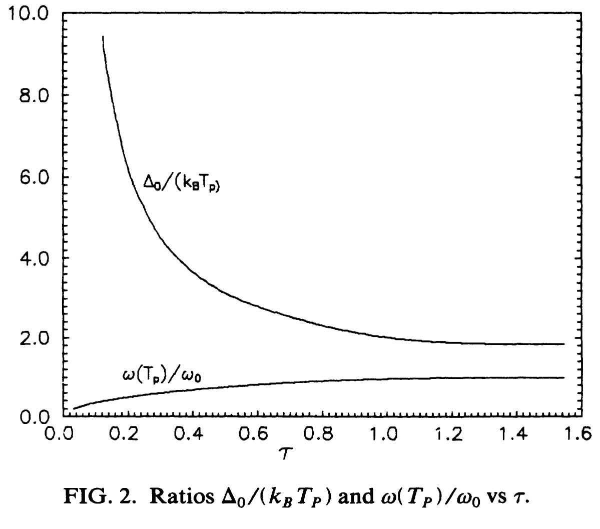

FIG. 2. Ratios $\Delta_0/(k_BT_P)$ and $\omega(T_P)/\omega_0$ vs τ.

the free-energy functional (2.5) neglects the important role of one-dimensional thermal fluctuations. Due to these fluctuations, no phase transition can occur in a purely one-dimensional system at finite temperature.[8,14] (For a system of coupled chains the phase transition is restored at $T \neq 0$.) Secondly, the adiabatic Born-Oppenheimer approximation (2.6) is valid only for a sufficiently wide electron band and under moderately strong electron-phonon coupling. When the electronic gap is less than the characteristic phonon frequency (under sufficiently weak coupling or near the phase transition temperature), the quantum fluctuations due to nonadiabatic terms in the Hamiltonian would destroy the gap and would lead to a normal-metal state in the chain. Probably fluctuations[8,15] are mainly responsible for the fact that the experimentally determined[16] ratio $\Delta_0/(k_B T_P)$ is significantly larger than the mean-field value. Note also that the adiabatic approximation (2.6) is not appropriate under extremely strong electron-phonon coupling, when the polaronic effect plays an important role and leads to a significant narrowing of the electron band (increasing the effective polaron masses) due to the Debye-Waller factor.

Finally, the long-wave (continuum) approximation will be justified only when

$$k_F a < 1 \ , \quad \kappa a < 1 \ . \tag{5.10}$$

This imposes constraints on both the concentration of carriers (electrons or holes) in the chain and the electron-phonon coupling constant. The maximal concentrations which may be considered correspond to a nearly quarter-filled (or nearly quarter-empty) band. With these maximal values of k_F, the continuum approximation is valid only at $\tau \gtrsim 1$ (for $\tau < 1$ it is necessary to take into consideration the discreteness of the chain).

The Fröhlich current-carrying sliding mode has been observed experimentally in CDW materials such as $NbSe_3$, TaS_3, $(TaSe_4)_2I$, and $K_{0.3}MoO_3$ (see, e.g., Ref. 1, and references therein). The electron configuration in these materials corresponds to just the same nearly quarter-filled band. As likely as not, the value $\tau \gtrsim 1$ is realized in these compounds. In most of them, temperature dependence of the CDW period is not observed,[17] and the temperature behavior of the gap $2\Delta(T)$ and the amplitude Δu of the periodic lattice deformation potential (2.24), $\Delta u = u(\omega) - u(0) = 4\Delta(T)$ [e.g., in $NbSe_3$ (Ref. 18)] are in agreement with a BCS-like formula.

The predicted peculiarities of the CDW thermal behavior at $\tau < 1$ may be observed in materials with lower carrier concentrations in the chains.

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