ELECTRON SELF-LOCALIZATION, SOLITONS, AND PERIODIC SUPERSTRUCTURES IN QUASI ONE-DIMENSIONAL ELECTRONIC SYSTEMS: PEIERLS INSULATOR, FROHLICH STATE, CHARGE DENSITY WAVE

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Abstract

Most quasi one-dimensional conductors at low temperatures go over into an insulating state via a symmetry breaking transition. The theory of this state, which is characterized by periodic lattice deformations, in other words by charge-density waves (CD W), can be constructed on the basis of the Peierls model. Interest in this model has especially increased in connection with the study of doped polymers, and of the CDW motion.

The stationary states of charge and spin carriers in a Peierls insulator differ substantially from those of ordinary semiconductors. The reason lies in the strong self-trapping effect, which leads to self-localization of the electrons at a depth on the order of the width of the forbidden band. The result is the creation of solitons with the features of intermediate-radius tight-binding polarons, but having anomalous quantum numbers. Their classification depends on the band filling and symmetry breaking. For systems of the trans-polyacetylene type produced from a metal with half-filled band as a result of lattice dimerization, the majority carriers are solitons of the domain-wall type, having either a charge ±e or a spin 1/2. For systems with non-integer number of electrons per unit cell in the metallic phase, only spin uncharged solitons remain. In systems without a metallic phase whatever, such as polymers, spinless bipolarons with charge ± 2e can exist. Self-localization of thermally activated electrons, the carriers, can be suppressed only by strong coupling between the chains, but the extrinsic carriers form in this case, too, deeply localized clusters. The weak coupling between the chains does not alter the internal structure of the soliton, but exerts a strong influence on statistical properties of their ensembles. In the three-dimensionally ordered phase, the solitons are bound into pairs, and when the temperature is raised they are organized into flat domain walls.

When the electron density changes, or when they become redistributed among different chains or bands, periodic superstructures of the soliton-lattices type are produced. Excitations of the type of envelope solitons also exist against the background of these lattices; they carry a bound single-electron state, have a spin 1/2, but a non-integer electric charge. One-dimensional models are theoretically investigated by solving exactly a self-consistency equation based on the mathematical theory of finite-band potentials. The results explain a number of general and detailed properties of quasi one-dimensional electronic materials as they were on agenda in 1980's.

The literature update to 2000's can be found in short reviews
http://arxiv.org/abs/0709.2296v1 and http://arxiv.org/abs/0908.4249 and on the web site
http://lptms.u-psud.fr/membres/brazov/

I Introduction

§1 Quasi-One-Dimensional Compounds with Metal-Insulator Transition

More than a hundred materials with quasi-one-dimensional properties are known at present. The initial spur and a constant stimulus to the search for new synthetic materials was Little's suggestion [1] that the superconducting transition can be higher in hypothetical conductors of organic origin than in ordinary metals and alloys. Although this problem has not yet been solved, the results of the search went far beyond the framework of the initial idea.

The substances investigated are divided into several classes having entirely different chemical nature. With respect to the physical properties they can be insulators, semiconductors, metals, and even low-temperature *superconductors*, can have a magnetically ordered state, and so on.* Quasi-one-dimensional conducting materials contain as their basic elements chains of molecules with partially filled valence-electron bands. It was therefore to be expected that the substances would have the properties of metals. Most materials turn out, however, at least at low temperatures, to be insulators. An almost universal property of these substances is the presence of *lattice superstructures* that lead to formation of a *gap in the density of state* on the Fermi surface and to a finite activation energy in the spectra of *single-electron states* and *spin excitations*.**

Many substances are metallic at room temperature and have no *lattice superstructure*. However, when the temperature is lowered, a *structural phase transition* is observed into the dielectric state, which is

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*Within the framework of the present survey we are unable to discuss the detailed properties of concrete substances. The most investigated materials are described, for example, in the reviews [2–4]. However, modern experimental data, particularly on polymers, can be found so far only in original papers or in review articles presented at recent conferences [5–8].

**These three definitions of the dielectric gap are substantially different both with respect to the experimental data and in accordance with the theoretical premises advanced below.

characterized by lattice deformations with wave vector **Q** whose projection $Q_{\|}$ along the chains is close to the diameter $2p_F$ of the almost plane Fermi surface in the metallic phase. This phenomenon is called the *Peierls effect* [9] and the low-temperature phase with spontaneous lattice deformations is known as the *Peierls–Fröhlich state* [10].*

The different classes of quasi-one-dimensional conductors contain also materials that should have dielectric properties by the very nature of their basic structure, without formation of lattice superstructures.

In these substances, the chemical formula and the crystal structure are such that the plane *Fermi surfaces* lie from the very beginning on the boundaries of the Brillouin zone, as a result of which a gap E_g is produced at the *Fermi level* even in the absence of the *Peierls effect*. It is remarkable, however, that the values of E_g frequently turn out to be of the same order as in substances of the same class that manifest a *metal-insulator structural transition*. This observation, and also a number of concrete experimental data and the theoretical premises presented below, allow us to assume that the interaction between the electrons in the lattice exerts a substantial influence on the properties of the dielectric state in these substances, although it is not its only cause as in the *Peierls dielectrics*. Such quasi-one-dimensional substances will be called *combined dielectrics*, to distinguish them from *Peierls dielectrics* and from the opposite limit of dielectrics with a rigid band structure.

Thus, the most prevalent low-temperature phase of quasi-one-dimensional conductors is the dielectric state. Prior to 1978 it was regarded most frequently as a vexing obstacle to stabilization of the metallic state. However, detailed experimental and theoretical investigations have revealed unique properties of the nonmetallic state of quasi-one-dimensional conductors, which remain to this day the subject of intense study.

Both the experimental properties and the theoretical models of quasi-one-dimensional conductors depend substantially on the average number ρ of electrons per unit cell (usually, per molecule) in the metallic phase. It is remarkable that the quantity ρ, $0 < \rho < 2$, can

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*The frequently used designation "*Peierls dielectric*" is arbitrary, since these substances can be regarded at best as narrow-band semiconductors.

vary in a wide range. In stoichiometric compounds the change of ρ is discrete because of the changes in the chemical components that serve as donors or acceptors with respect to the conducting chain. Typical values here are $\rho = 1, 2/3, 1/2$, or similarly for $2 - \rho$.

A continuous variation of ρ is possible in non-stoichiometric compounds, e.g., in $(\mathrm{TTT})_2 I_{3+\delta}$ [11], where $\rho \approx 1/2$, in the KCP family [2–5, 12], where $\rho \approx 1/3$ or $2/3$, and in doped polymers, where $\rho \approx 1$ for *trans-polyacetylene* [13, 14] and $\rho \approx 2$ for other polymer semiconductors. Continuous variation of ρ under external action (pressure) takes place in substances with incomplete *charge transfer* between two types of conducting chains, e.g., in TTF-TCNQ, where $\rho \approx 1/3$ [4, 15], and in $\mathrm{TaS_3}$ and $\mathrm{NbSe_3}$, where $\rho \approx 1/2$ [16].

In all substances with non-integer values ρ, the values of E_g in the dielectric phase are small compared with the total width D of the valence band. For example, in inorganic conductors with *d*-electron bands, such as platinum complexes (KCP) and the compounds $\mathrm{NbSe_3}$ and $\mathrm{TaS_3}$, values $E_g \sim 10^{-1}$ eV are observed at $D \sim 1$ eV. In organic compounds with π-electron bands (TTF-TCNQ and others) we have $E_g \sim 10^{-2}$ eV at $D \sim 10^{-10}$ eV. However, in TCNQ salts with $\rho = 1$ (KTCNQ and others), the values observed already are $E_g \sim D \sim 10^{-1}$ eV, i.e., a strong interaction takes place. It is known that in the polymer trans-polyacetylene (trans-$(\mathrm{CH})_x$), where $\rho = 1$, we have $E_g = 1.5$ eV at $D \lesssim 10$ eV, i.e., the interaction is relatively weak. In the remaining polymers, regarded by us as *combined dielectrics* [17] or as systems with $\rho = 2$, the values of E_g are as a rule even higher: $E_g \approx 1.6$ eV in polydiacetylene $(\mathrm{C_3R})_x$, $E_g \approx 2$ eV in cis-$(\mathrm{CH})_x$, and $E_g \approx 3$ eV in polyphenylene $(\mathrm{C_6H_4})_x$. Obviously, tight binding already takes place in the latter case.

For substances with non-integer ρ, the most pronounced effects are anomalously high values of static *dielectric constant* $\epsilon \sim 10^2$–10^4 and nonlinear effects in anomalously weak electric fields $E \sim 1$ V/cm. These phenomena are frequently regarded as manifestations of the so-called *Fröhlich conductivity* (see the review [4]).

Another phenomenon common to many quasi-one-dimensional dielectrics is the strong difference between the values of the gap E_g determined from optical data, E_g^{opt}, and from the activation energies for the longitudinal $(E_a^{\|})$ and transverse $(E_a^{\perp})$ conductivity, and for the paramagnetic susceptibility E_a^{χ} (see, e.g., [18, 19]). These properties, while less pronounced than the *Fröhlich conductivity*, are very important in conjunction with the data presented below for *polyacetylene*.

It is tempting to regard dielectrics with $\rho = 1$ or 2, where which E_g is large and there are no Fröhlich effects, simply as semiconductors that differ in the anisotropic spectrum of the electrons, and frequently also of the phonons. However, the experimental data accumulated in recent years, as well as the theoretical results, make it necessary to revise the very nature of the electronic excitations of both the current carriers and the spin carriers in these substances. The most interesting data were obtained by investigating polyacetylene [13, 14, 21]. This quasi-one-dimensional material (see Fig. 1a, b) is unique for several reasons. The simple chemical structure, the possibility of reversible donor and acceptor doping, the wide temperature interval of the observation, the good separation of the different energy scales, the sufficiently weak interactions of the electrons with the lattice and with one another, and the weak coupling between the chains have made it possible to observe, for the first time ever, singular physical phenomena that, according to the prevailing theoretical concepts, should be in general typical of quasi-one-dimensional dielectrics.

By now, a large set of experimental data has been obtained for the electric (conductivity σ as a function of the temperature, frequency, and doping level), optical (absorption and Raman scattering in various ranges, photoconductivity, photoluminescence and nonlinear phenomena) have been obtained for polyacetylene. Of particular interest are experiments on the investigation of magnetic properties, such as the static susceptibility, EPR, NMR-relaxation and Knight shift, nonlinear effects in EPR and NMR coupling (dynamic nuclear polarization and Overhouser effect) [13, 21].

The conclusions drawn from these experimental investigations (albeit debatable [22]), can be formulated as follows.

1 Among the excitations of the system there exist long-lived deeply self-trapped states with electron levels in the region of the center of the forbidden band. They result from doping or optical pumping. These states are revealed by light absorption or by photoconductivity at frequencies $\hbar\omega \approx \Delta = E_g/2$ and by new lines of the Raman spectra and absorption in the region of the lattice-vibration frequencies $\omega \lesssim \omega_{ph}$.

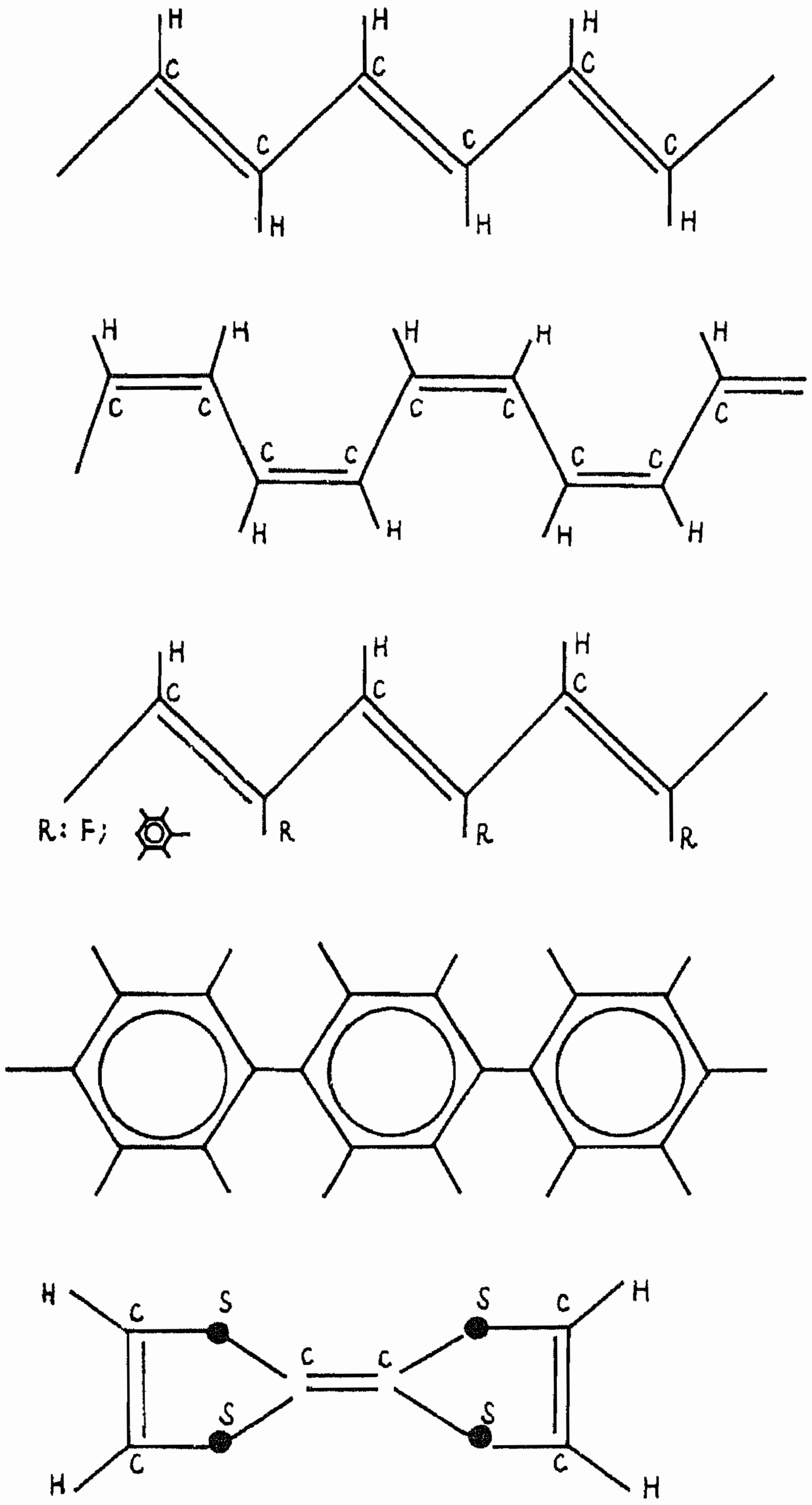

Figure 1

2 Undoped material contains *mobile spin carriers* that propagate exclusively along the $(CH)_x$ chain (the anisotropy of the diffusion coefficient, determined from measurements of the NMR relaxation time T_1 [21], amounts to $D_{\parallel}/D_{\perp} \sim 10^6$). These spin carriers have no electric charge and vanish when current carriers appear (as a result of doping).

3 In weakly doped material ($y < 0.005$) with hopping conductivity, the Curie law is not obeyed, i.e., the current carriers have no spin. In the intermediate doping region $0.005 < y < 0.05$, a state with metallic conductivity is observed. In this case, however, no paramagnetic properties, such as the Pauli susceptibility (neither static nor EPR) and the Knight shift, which are inherent in normal degenerate semiconductors and metals, are observed.

The foregoing groups 1–3 of the experimental data suggest that strong selflocalization of exciting electrons takes place in a quasi-one-dimensional dielectric. The resultant stationary elementary excitations are characterized by *anomalous quantum numbers*: they have either an electric charge or a spin, whereas in normal semiconductors the conductivity and the paramagnetism always accompany each other. This picture of the excitations, as well as the very origin of the dielectric state and of the *lattice superstructure*, can be naturally explained in the theory of the *Peierls–Fröhlich state*. The present review is in fact devoted to an exposition of the modern development of this theory.

1.1 Lattice Deformations or Coulomb Interaction?

A question that always arises in the interpretation of the properties of concrete quasi-one-dimensional materials is whether they are caused by lattice deformation, i.e., by the *Peierls effect*, or by interelectron interactions. For example, the properties of *polyacetylene* were initially interpreted [23] on the basis of the *Hubbard model* [24], which takes into account the repulsion of the electrons at one site, and recently [25] more frequently on the basis of the *Peierls model*, which takes into account the interaction of the electrons with the static deformations of the lattice. Lively discussions have taken place in connection with the interpretation of the properties of complexes based on TCNQ and other organic molecules. There is no doubt that both effects play an important role in most materials and one cannot count on determining the quantitative parameters by using some single model. However, there are qualitative differences between the predictions of the Peierls and Hubbard models, and these permit a direct comparison with experimental properties. Such properties are the relations between the activation energy E_a^χ for the magnetic susceptibility χ and the forbidden bands E_g, observable in optical (E_g^{opt}) and electric (E_g^{cond}) phenomena. The clearest picture can be regarded to be the one for systems with $\rho = 1$. In this case, both the lattice deformations and the interelectron repulsion lead to formation of gaps, E_g^{opt} and E_g^{cond}, with $E_g^{\mathrm{opt}} \gtrsim E_g^{\mathrm{cond}}$. Simultaneously, lattice deformations lead to the appearance of an activation energy E_a^χ in the magnetic susceptibility, $2E_a^\chi = E_g^{\mathrm{cond}}$.* The interelectron interactions, however, leave the system paramagnetic, $E_a^\chi = 0$, just as in the metallic region. The reason, roughly speaking, is that under the influence of the interaction there occurs not a charge (CDW) but a *spin* (*SDW*) *ordering*, and the system becomes an intrinsic antiferromagnet. This antiferromagnetic state can be stabilized by tunneling of electrons between the chains, as in $(\mathrm{TMTSF})_2X$ [15], or else a structural deformation of lattice somehow does take place and corresponds to the so-called *spin-Peierls transition* [28]. In the latter case, a finite E_a^χ appears and the system becomes qualitatively equivalent to a Peierls dielectric. Such an hierarchy of transitions is observed, e.g., in MEM(TCNQ)$_2$ [27]. Thus, if the relation

$$E_g^{\mathrm{opt}}, E_g^{\mathrm{cond}} \gg 2E_a^\chi \geqslant 0$$

holds, it can be concluded that *Coulomb interaction* predominates in the system. For a system with $\rho \neq 1$ it is possible to use with assurance in this criterion only E_g^{opt}, since E_g^{cond} can become small because of the Fröhlich conductivity effects [4, 10, 16, 28]. In complexes with charge transfer, both cases can apparently take place. In polyacetylene, the absence of paramagnetism indicates that this material must be described, at least qualitatively, by the Peierls model.

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*In experiment, E_g^{cond} can increase, $E_g^{\mathrm{cond}} \gtrsim 2E_a^\chi$, on account of addition of a mobility gap [18].

Thus, the Peierls model corresponds to materials that are dielectrics simultaneously with respect to the magnetic, optical and, with stipulation, electric properties.

§2 Models of Peierls Effect and Basic Results of the Theory of Solitons and Superstructures in the Peierls–Fröhlich State

We consider a one-dimensional dielectric with a narrow vertical forbidden band E_g. Its electronic properties can be described by the effective-mass method on the basis of the Hamiltonian

$$H = \begin{pmatrix} v\hat{k} & \Delta^+ \\ \Delta & -v\hat{k} \end{pmatrix}; \qquad k = -i\hbar\,\partial/\partial x; \qquad v = \text{const} \tag{1}$$

When using Eqs. (1) we are justified in assuming a slow dependence, compared with the atomic scale a, of the two-component wave function ψ and of the matrix element Δ on the coordinate x

$$\Delta = \Delta(x); \qquad \bar{\psi} = \bar{\psi}(x) = (\psi_1(x), \psi_2(x)) \tag{2}$$

The $\Delta(x)$ dependence is produced by the lattice deformations $\zeta(x)$. These deformations can be regarded as a classical field if the frequencies ω_{ph} of the corresponding phonons are low enough

$$\hbar\omega_{ph} \ll \delta E \tag{3}$$

where δE is the change of the electron energy on account of the stationary deformation $\Delta(x)$.

The ground state of the system and the stationary perturbations (*solitons*) can be determined, if the *adiabaticity criteria* are satisfied [3], from the condition that the total functional of the system energy

$$W = W\{\Delta\} = W_{el}\{\Delta\} + W_{lat}\{\Delta\} \tag{4}$$

be a minimum. The energy W_{el} of the electron subsystem takes in all cases the form

$$W_{\text{el}} = \sum_{E \leqslant \mu} E; \qquad E = E\{\Delta\} \tag{5}$$

where E is the eigenvalue of the Hamiltonian (1) and μ is the chemical potential. The lattice deformation energy W_{lat}, the class of the functions $\Delta(x)$, and the microscopic determination of the components of the wave function $\psi_{\pm}(x)$ depend substantially on the nature of the investigated system. One can single out three main phenomenological models A, B, and C, two crossover models AB and AC, and microscopic discrete models D.

2.1 A The Peierls–Fröhlich Model

The Peierls–Fröhlich model for substances in which the potential $\Delta(x)$ is produced by spontaneous lattice deformations $\zeta(x)$, with the characteristic wave vectors $Q \approx \pm 2k_f$ of the deformation $\zeta(x)$ far from the Brillouin-zone boundaries $Q_0 = \pm\pi/a$ of the main lattice: $2k_F \neq \pi/a$. Model A can be used to describe substances with $\rho \neq 1$ or 2. In this case the variables (2) determine the deformation $\zeta(x)$ and the wave function $\psi(x)$ of the electrons:

$$\zeta(x) \sim \Delta(x) e^{i2k_F x} + \Delta^*(x) e^{-i2k_F x} \tag{6}$$

$$\psi(x) = \psi_+ e^{ik_F x} + \psi_- e^{-ik_F x} \tag{7}$$

From the condition $\rho \neq 1, 2$ it follows that the points $\pm 2k_F = \pm\rho\pi/a$ are not equivalent in the Brillouin zone of the non-deformed phase. Consequently, $\Delta(x) = \Delta_1 + i\Delta_2$ is a complex field with independent components Δ_1 and Δ_2. The *incommensurability* of the deformation (6) causes also the effects of the interaction of the superstructure (6) with the main structure to be frequently insignificant: the pinning energy T_p is small in terms of the parameter [28, 29]

$$T_p/\Delta \sim (|\Delta|/D)^{n-2} \ll 1, \qquad n \geqslant 3 \tag{8}$$

if $\rho = m/n$ is an irreducible fraction. Consequently the lattice deformation energy $W_{\mathrm{lat}}\{\Delta\}$ should be invariant to a uniform shift of the superstructure (6) or, equivalently, to a constant shift of the phase of the field $\Delta(x)$ [30]:

$$\begin{gathered} \zeta \to \zeta(x + x_0); \qquad \Delta(x) \to \Delta(x) e^{ix0}, \qquad \psi_{\pm} \to \psi_{\pm} e^{\pm(1/2)x_0} \\ x_0 = 2k_F x_0 \end{gathered} \tag{9}$$

The deformation energy should therefore be of the form

$$W_{\mathrm{lat}}\{\Delta\} = \int \frac{|\Delta|^2}{g^2}\, dx \tag{10}$$

where the value of g corresponds to one of the standard definitions of the electron-phonon interaction constant.

The dynamics of the system is described in the adiabatic approximation by the Lagrangian [30] $\mathscr{L}\{\Delta\}$, $\Delta = \Delta(x, t)$:

$$\mathscr{L}\{\Delta\} = \int dx \frac{|\dot{\Delta}|^2}{g^2\bar{\omega}^2} - W\{\Delta\}, \qquad \dot{\Delta} = \frac{\partial \Delta}{\partial t} \tag{11}$$

where $W\{\Delta\}$ is the potential energy, defined by formulas (4), (5), and (10), and $\bar{\omega} = \omega_{ph}(2k_F)$ is the unrenormalized (bare) frequency of the phonons with wave vector $\pm 2k_F$.

The gauge invariance of (9) leads to a continuous degeneracy of the ground state with respect to the phase x,

$$\Delta = \Delta_0 e^{ix}; \qquad \Delta_0 \sim D \exp\left\{-\frac{1}{\lambda}\right\}; \qquad \lambda = \frac{g^2}{\pi 2_F^0} \tag{12}$$

The electrons in the ground state occupy the levels

$$E_k = -\left[(v_F k)^2 + \Delta_0^2\right]^{1/2}$$

Of importance in the phonon spectrum are two low-lying branches corresponding to the amplitude δ and phase χ oscillations

$$\begin{gathered} \omega_{s\delta}\omega_0\left[1 + \frac{1}{12}\zeta_0^2 k^2\right]^{1/2}; \qquad \zeta_0 = \hbar v_F/\Delta_0 \\ \omega_x = uk; \qquad \omega_0 = \frac{2^{3/2}\dot{u}\Delta_0}{\hbar v_F} = (2\lambda)^{1/2}\bar{\omega} \qquad k \ll \zeta_0^{-1} \end{gathered} \tag{13}$$

The total spectrum of the phonons for the case of quadrupling of the period, $\rho = 1/2$, is shown in Fig. 2a.

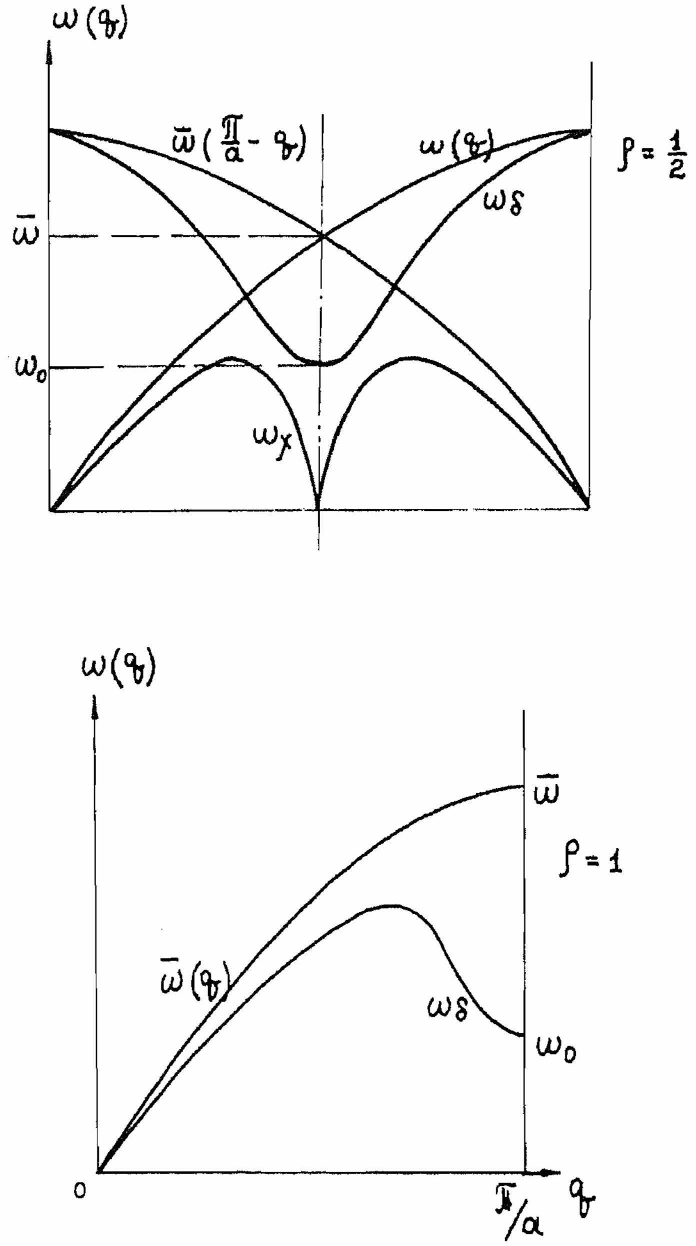

Figure 2

2.2 B The Peierls Model

The Peierls model for substances in which the potential $\Delta(x)$ is produced by spontaneous deformation $\zeta(x)$ corresponding approximately to doubling of the host-lattice period. Model B can be used to describe substances in which the metallic undeformed phase band is almost half-filled, $\rho \approx 1$. This case was investigated most intensively in connection with the theory of *trans-polyacetylene*, trans-$(CH)_x$, Fig. 1a. At $\rho \approx 1$ the quantity $4k_F = 2\pi\rho/a$ is close to the reciprocal-lattice period $2\pi/a$. As a result, the points $\pm 2k_F$ come closer together (accurate to $2\pi/a$) and their contributions to the deformation $\zeta(x)$ can no longer be separated as assumed in (6). For a correct description of the system we must now express $\zeta(x)$ in terms of the *envelope function* $\Delta(x)$ of the relatively rapid oscillations with a wave vector π/a corresponding to doubling of the period:

$$\zeta(x) \sim \Delta(x) e^{i\pi/a} + \Delta^* e^{-i\pi/a} = 2\tilde{\Delta}(x)\cos\left(\frac{\pi}{a}x + \varphi\right)$$

$$\Delta(x) = \tilde{\Delta}(x) e^{i\varphi}; \qquad \operatorname{Im}\tilde{\Delta}(x) = 0 \tag{14}$$

$$\psi(x) = \psi_+ \exp(i\pi/2a) + \psi_- \exp(-i\pi/2a)$$

Since the points $\pm\pi/a$ are equivalent, the functions $\Delta(x)$ and $\Delta^*(x)$ should agree accurate to a *constant* phase factor $\exp(i\varphi)$. The value of φ is determined by the details of the electron-phonon system. For example, for the deformations of the acoustic branch, observed in *polyacetylene*, we have $\varphi = \pi/2$, while for the intramolecular deformations $\varphi = 0$. In a theoretical investigation, the value of φ can be chosen arbitrary, by using the transformation (9). We shall assume everywhere in Chapters II–V that $\varphi = \pi/2$. The system dynamics is described, just as in the *model A*, by the Lagrangian (11), where the phase of the field $\Delta(x)$ is fixed [29] and $\bar{\omega} = \bar{\omega}(\pi/a)$ is the frequency of the phonons for the deformation $\zeta(x)$ on the boundary of the Brillouin zone. The phonon spectrum at $\rho = 1$ is shown in Fig. 1b.

2.3 AB Crossover Model

Crossover model for the investigation of effects of *weak double commensurability* [31]. It is suitable for the description of quasi-one-dimensional substances with total charge transfer from the singly valent ions to the conducting chains. These include the compounds of the type K(def)CP ($K_{1.75}Pt(CN_4) \cdot 1.5H_2O$) and the organic conductors of the type $(TTT)_2 I_{3+\delta}$, or $(TMTSF)_2 X$ with various monovalent acceptors X [11, 15], which are now most actively investigated.

In these substances the number of electrons ρ_0 per molecule (Pt, TTT, TMTSF) is fractional, so that the system might be approximately described by the model A. However, allowance for the weak modulation of the conducting chain by the field of the periodically disposed ions (K, X) increases the unit cell. If the ions are monovalent, their density is also equal to ρ_0. Consequently the quantity $4k_F = (2\pi/a)\rho_0$ coincides with the reciprocal vector of the large cell, i.e., the points $\pm 2k_F$ become equivalent. Therefore the expression for the free energy acquires additional terms

$$SW_{\mathrm{AB}} = \int \frac{dx}{2g^2}(B\Delta^2 + B^*\Delta^{*2}); \qquad W_{\mathrm{AB}} = W_{\mathrm{A}} + SW_{\mathrm{AB}} \quad (15)$$

where B is a constant complex quantity. Owing to the invariance of W_{A} to the transformation (9), the phase of the constant B can be chosen arbitrary. We shall assume that $\operatorname{Im} B = 0$. The condition that the lattice be stable without interaction with the electrons imposes the restriction $|B| < 1$.

2.4 C Combined-State Model

Combined-state model [17, 32, 33] for the description of substances that have no metallic phase, i.e., that would be dielectrics even without the effects of the interaction of the electrons with the lattice. It is convenient for the description of polymer semiconductor and, in conjunction with the AC model defined below, of compounds with total charge transfer from the chains of the divalent ions to the conducting chains. In the *C model* the matrix element $\Delta(x)$ of the Hamiltonian (1) consists of two parts

$$\Delta(x) = \Delta_e + \Delta_i(x)e^{i\varphi}; \qquad \Delta_e = \text{const}; \qquad \varphi = \text{const} \qquad \operatorname{Im}\Delta_i = 0; \quad (16)$$

The quantity Δ_e takes into account the interaction of the electrons with the potential of the rigid structure, and $\Delta_i(x)$ is determined by the local lattice deformations. In (16) we chose Δ_e and Δ_i to be real, and left out the constant phase shift φ. The value of φ is determined by the microscopic structure of the substance. For example, in the case of *cis*-$(CH)_x$ (see Fig. 2b), Δ_e is determined by the nonequivalence of the bonds that are located at the bases and the lateral sides of the trapezoids, and $\Delta_i(x)$ is also connected with the alternation of the bond lengths. Therefore for *cis*-$(CH)_x$ we should have $\varphi = 0$. The special case $\varphi = \pi/2$ can be realized in polyphenylacetylene and in the as yet uninvestigated polymer trans-$(C_2HF)_x$ (see Fig. 1c). In this case the quantity Δ_e is due to the non-equivalence of the carbon atoms that are bound to the hydrogen and fluorine. If the interaction of the electrons with the lattice deformations takes place, just as in trans-$(CH)_x$ via alternation of the bond lengths, then the case $\varphi = \pi/2$ should take place.

The lattice-deformation energy in the *model C* is determined obviously only by the component $\Delta_i(x)$

$$W^C_{\text{lat}} = \int \frac{\Delta_i^2(x)}{g^2}\, dx \tag{17}$$

$$L^C = \int \frac{\dot{\Delta}_i^2}{g^2 \bar{\omega}^2}\, dx - W^C \tag{18}$$

where $\bar{\omega}$ is the phonon frequency corresponding to the deformation Δ_i.

2.5 *AC Model of Combined Dielectrics*

Model of combined dielectrics close to the Peierls–Fröhlich state [33]. It can be used to describe materials with total charge transfer from the chain of divalent ions to the conducting chain. Examples are the organic compound $(DBTTF)_8(SnCl_6)_3$ [34] and the platinum complexes $M_x\,[Pt(C_2O_4)_2] \cdot 6H_2O$, where M = Mg, Co, and others, while $x = 0.6$ [5, 12]. Reasoning in anaology with the derivation of the *AB model*, we obtain

$$W_{\text{AC}} = W_{\text{AB}} + \int \left[C\Delta(x) + C^*\Delta^*(x) \right] dx \qquad C = \text{const} \tag{19}$$

2.6 D Discrete Models of the Peierls Effect

They are needed to derive the parameters of the continual models and to investigate the influence of the finite width and curvature of the electron band and the commensurability effects. The discrete models were effectively used (see the review [25]) in computer investigation of the statics and dynamics of solitons as applied to the theory of *trans*-$(\mathrm{CH})_x$. A class of exactly solvable discrete models [35, 36], which contain the continual *models A* and *B* as limiting cases, were recently found. The discrete model of *polyphenyl* [33, 37], Fig. 1d, also turned out to be exactly solvable.

We consider a one dimensional chain of molecules located at the points x_n. For each N molecules we have $N_e = \rho N$ electrons, with $\rho \leqslant 2$. We shall assume that the electron spectrum is determined by the typical tight-binding Hamiltonian

$$H\psi_n = C_n\psi_{n+1} + C_{n-1}\psi_{n-1} + v_n\psi_n = E\psi_n$$

$$C_n = f(x_{n+1} - x_n) \tag{20}$$

where C_n are the integrals for the *electron hopping* between the nearest molecules, and v_n is the local potential of the possible intramolecular deformation. The ground state of the system is determined from the condition that the functional of the system energy

$$W = \sum_{E \leqslant \mu} E + U \tag{21}$$

be an extremum, where the energy levels of the electrons $E = E\{c_n, v_n\}$ are determined from (20), μ is the chemical potential of the electrons, and $U = U(x_n, v_n)$ is the energy of the potential interaction between the molecules and the intramolecular deformations.

Greatest interest attaches to the case of almost rigid lattices $x_n = na + u_n$, $|u_n| \ll a$, when the deformations v_n and the displacements u_n of the molecules under the influence of the electrons are small enough. It is then possible to confine oneself to a quadratic expansion of U in powers of u_n and v_n, and to a linear expansion of C_n in (20) in terms of $u_{n+1} - u_n$. Confining ourselves only to the potential interaction between the nearest molecules, we obtain

$$x_n \simeq na + u_n\,; \qquad C_n \simeq C_0\left[1 - \alpha(u_{n+1} - u_n)\right]$$
$$U = \sum_n \left[\frac{1}{2}K(u_{n+1} - u_n)^2 + \frac{1}{2}kv_n^2\right] \tag{22}$$

A linearized *lattice Peierls model*, defined by formulas (20)–(22) at $v_n = 0$, was investigated by Schrieffer and others [25, 37–42] as the model of *trans-polyacetylene* and of systems with $\rho = 1/3$. In the region where they are valid, the expressions (22) are not sensitive to the form of the total dependences of $f(x)$ and $U(x_n, v_n)$ in (20) and (21), and can be obtained from various model potentials. An exact analytic investigation of the *discrete model* is possible if the following relations hold for $C(x)$ and $V(x)$ [35, 36]:

$$C(x) = C_0 e^{-\alpha x}; \qquad f(x) = \kappa C_0^2 e^{-2\alpha x}$$
$$U = \sum_n \kappa\left[\frac{1}{2}v_n^2 + C_0^2 \exp\{-2(x_{x+1} - x_n)\}\right] \tag{23}$$

The formulas in (23) go over into (22) if the parameter α is small, or equivalently, if a is small. The functionals of the *models A or B* are obtained from (20)–(22) by substituting the expansions (6), (7), or (14) at $x = x_n = na$ after discarding the rapidly oscillating terms. The deformation $\zeta(x_n)$ can be taken to be either u_n or v_n.

The *model C* with $\varphi = \pi/2$ is obtained in the approximation of the *model B* by introducing a fixed dimerization with respect to v_n:

$$\zeta(x_n) = u_{n+1} - u_n\,; \qquad v_n = (-1)^n v_0\,; \qquad v_0 = \text{const}$$

The *model AC* is obtained in the approximation of the *model A*, likewise as fixed v_n corresponding to the potential of the periodically disposed ions

$$\zeta(x_n) = u_{n+1} - u_n\,; \qquad v_n = v_0\cos(\pi\rho n + \varphi_0)$$
$$v_0 = \text{const}; \qquad \varphi_0 = \text{const}$$

2.7 E Continual Model with Quadratic Dispersion

Besides the continual models A–C with linearized electron dispersion law, which leads to the Hamiltonian (1), interest attaches also to a continual model with quadratic dispersion. This model, which describes the electrons on a continuous deformable filament, is characterized by the functional

$$W = \sum_{E \leqslant \mu} E + \int \frac{U^2(x)}{g^2}\, dx \tag{23}$$

where E are the energy eigenvalues of the Schrödinger equation with potential $U(x)$:

$$\left(\frac{\hat{P}^2}{2m} + U(x)\right)\psi(x) = E\psi(x); \qquad \hat{P} = -i\hbar^{\partial}/\partial x \tag{24}$$

The model (24), (25) is obtained from the *discrete model* (20)–(22) at $\rho \ll 1$ when all the ψ_n, u_n, and v_n are slow functions of n:

$$n \rightarrow x, \qquad \psi_n \rightarrow \psi(x), \qquad \nu_n + m^{-1}(u_{n+1} - u_n) \rightarrow U(x) \qquad m = C_0^{-1}$$

An investigation of the model E makes it possible [43] to track the transition from the Peierls–Fröhlich state described by the model A to the system of loosely disposed bipolarons at $\rho \rightarrow 0$.

2.8 Principal Results of the Theory

Our understanding of the *Peierls state* has unexpectedly changed in recent years. It is interesting that the development of the theory followed two independent paths, on a completely different basis, but at one and the same time. One path, initiated by the study of Su, Schrieffer, and Heeger [37], was due to experiments on *polyacetylene* together with the general interest in the concepts of *topological solitons*. The other line, initiated by the paper of Brazovskii [41], was caused mainly by the internal needs of the theory of the *Peierls–*

Fröhlich state, and also by certain general but less clear experimental results for systems with *incommensurable charge density waves*.

From the point of view of semiconductor physics, the specifics of a *Peierls dielectric* can be explained by following [17, 30, 44]. In all semiconductors, the interaction of the electrons (e) and of the holes (h) with phonons leads to *polaron effects* and determines the structure of the *fundamental edge*. Among the three-dimensional substances, this interaction can lead to self-trapping, i.e., to formation of a tight-binding polaron [45], only in ionic and narrow-band dielectrics. A common feature of one-dimensional systems is that the *self-trapping* effects take place at any type of electron-phonon interaction, including also the case of a simple deformation potential [46], provided it is strong enough and satisfies the *adiabaticity condition* (3). It is important that in a one-dimensional system there is no barrier to *self-trapping*, so that the free electrons and holes are absolutely unstable. Among the one-dimensional dielectrics in general, a distinguishing feature of the *Peierls–Fröhlich state* is that for stationary interaction of the electron excitation with the amplitude and phase phonons, expressed in the scale $\Delta_0 = E_g/2$ for the energy and $\xi_0 = \hbar v_F/\Delta_0$ for the length, there is no small parameter. As a result, a polaron state is produced with a characteristic dimension $\sim\xi_0$ and the binding energy $\Delta_0 - E_s$ and the depth of the local level $\delta E_0 = \Delta_0 - E_0$ turn out to be of the order of Δ_0. The adiabaticity condition [45]

$$\alpha^4 = (\delta E_0/\hbar\omega_0)^2 \sim (\Delta_0/\hbar\omega_0)^2 \sim M_s/m^* \gg 1$$

where $m^* = \Delta_0/v_F^2$ is the mass of the free electron, M_s is the polaron mass, and ω_0 is the *frequency of the amplitude mode* (13), coincides with the region of applicability (3) of the *Peierls model* itself. Thus, the free electrons in a quasi-one-dimensional *Peierls–Fröhlich state* can be observed only in light-absorption effects when, according to the *Franck–Condon principle*, lattice deformations have low probability. All the excitations with lifetimes $\tau > \omega_0^{-1} \sim 10^{-12}$ sec, i.e., all the intrinsic thermally activated *charge* and *spin carriers* and the extrinsic carriers produced as a result of charge transfer, doping, injection, or optical pumping should be regarded as stationary states of a system with a deformed superstructure. They should be determined from the condition that the system energy have a local minimum when account is taken of the interaction of the electrons with the lattice deformations. In view of the deep self-trapping, in both analytic and computer theoretical investigations it is necessary to start out with the complete many electron problem, which takes into account also the delocalized states of the valence electrons. It was found that all the basic continual *models A*, *B*, *C*, *and E*, and some *discrete models* of the *Peierls effect*, admit of an exact analytic investigation of their static properties [17, 32, 35–37, 43, 44, 47–52]. The dynamics of the self-trapping phenomena was investigated with computers in [25, 39, 40] in the discrete model D with parameters corresponding to the continual model B; the conclusions of all the investigations are in full agreement. They show that the results of *self-trapping* differ strikingly in many cases from normal *polarons*. The resultant states have the character of *topological solitons* that join various equivalent ground states of the system $\Delta(-\infty) \neq \Delta(+\infty)$. These solitons have *anomalous quantum numbers* that result from total or partial cancellation of the charge density of the localized electrons, and from local perturbation of the electron density of the nonlocalized electrons of the continuous spectrum. The basic types of solitons are listed in the table (page 119), with the exception of the most nontrivial objects with *non-integer electric charge*, which arise in the *model C* with $\varphi = \pi/2$ (chapter II, §4) and in *model B* with a finite number of electrons, $\rho \neq 1$ (chapter IV). The soliton state is characterized by a *charge* e_s, by a *spin S*, by a *total energy* E_s, by a *local energy level* E_b, and by a number ν_0 of electrons on this level. *Non-topological solitons—polarons* and *bipolarons*—have two levels $\pm E_b$ and are characterized by occupation numbers $\nu_+ = \nu_e$ and $\nu_- = 2 - \nu_h$, where ν_e and ν_h are the numbers of electrons and holes participating in the self-trapping. The last two lines of the table indicate the physical manifestations of the solitons in the *one-dimensional regime* ($T > T_{3d}$) and the *three-dimensional ordered phase*.

In the first line of the table are indicated the chapter and paragraph of the review where the corresponding theory is presented.

Carriers are regarded as intrinsic if their activation energy is a minimum. They predominate in the absence of electron sources. Extrinsic carriers are considered to be those with minimum energy per electron. They predominate at low temperatures in the presence of sources (doping, optical, pumping, injection, or surface phenomena).

Table Basic Elementary Excitations for Different Types of the *Peierls–Fröhlich State*

Model §§	A, B, AB II, §2, 3	B II, §3	B, C II, §3, 4	C II, §4	C II, §4	AB II, §3	AC II, §4
Type	Amplitude kinks		Polaron	Bipolaron	Exciton	π-phase kink	2π-phase kink
ν_0 or $\nu_e = \nu_+$ $\nu_h = 2 - \nu_-$	$\nu_0 = 1$	$\nu_0 = 2, 0$	$\nu_e = 1, 0$ $\nu_h = 0, 1$	$\nu_e = 2, 0$ $\nu_h = 0, 2$	$\nu_e = 1$ $\nu_h = 1$	$\nu_0 = 2, 0$	$\nu_0 = 2, 0$
S	$1/2$	0	$1/2$	0	0, 1	0	0
e_s	0	$e, -e$	$e, -e$	$\pm 2e$	0	$e, -e$	$2e, -2e$
$E_0, E_\pm$	0	0	$\Delta > \lvert E_\pm \rvert \geqslant \frac{\Delta^*}{\sqrt{2}}$	$\Delta > \lvert E_\pm \rvert > 0$	$\Delta > \lvert E_\pm \rvert > 0$	$E_0 \approx -\Delta, \Delta$	$E_0 \approx -\Delta, \Delta$
E_s	$\frac{2}{\pi}\Delta$	$\frac{2}{\pi}\Delta$	$\Delta > E_s > \frac{2^{3/2}}{\pi}\Delta$	$2\Delta > E_s > \frac{4}{\pi}\Delta$		$E_s \ll \Delta$	$E_s \ll \Delta$
Manifestations at $T > T_{3d}$	ISC in absence of ESC	ISC	B: ISC in presence of ESC (IV, §4)	ESC	luminescence	ESC	ISC
Manifestations $T < T_{3d}$	B: only on defects A, AB: ISC acquire charge (VI, §1)	in the form of bound pairs (VI, §2)	similarly $T > T_{3d}$	similarly $T > T_{3d}$	similarly $T > T_{3d}$	ISC bound in 2π kinks	similarly $T > T_{3d}$

ISC—intrinsic carriers of charge (spin)
ESC—extrinsic carriers of charge (spin)
*equality takes place for model B.

II Self-Trapped States in One-Dimensional Models of the Peierls Effect

It was shown in §1 that in a *Peierls dielectric* there is realized a specific strong interaction of electronic excitations near the edge of the forbidden band $E = \Delta_0$ with phonons corresponding to deformations of the *lattice superstructure*. As a result, the edge of the optical spectrum $E_g = 2\Delta_0$ becomes smeared out and strong self-trapping of the electrons takes place with a lifetime $\tau > \omega_0^{-1}$ on the chain.

Stationary excited states should have the properties of tight-binding *polarons* (with respect to the parameter $\alpha^2 = \Delta_0/\hbar\omega_0 \gg 1$) of intermediate radius ($l \sim \xi_0 = \hbar v_F/\Delta_0$) with respect to motion along the chains, and of small radius $a_\perp$ for hops between the chains. The *self-trapping energy* δE_s and the depth δE_0 of the electron level should be of the order of Δ_0

$$\delta E_s = \Delta_0 - E_s\,; \qquad \delta E_0 = \Delta_0 - E_0\,; \qquad \delta E_s \sim \delta E_0 \sim \Delta_0$$

Detailed properties of this state call for an exact solution of the problem; this is presented in §§2–4.

In §2 we investigate the *self-trapping states* in the *Peierls–Fröhlich state* for *incommensurate systems*. It is shown that in the corresponding model A (I, §3) such a state takes the form of an *amplitude soliton* with energy $E_s = (2/\pi)\Delta_0$, spin $S = 1/2$, but zero charge $e_s = 0$. The soliton produces a *localized electron state* with energy E_b at the center of the band; this state should be singly occupied, $\nu_0 = 1$. The *soliton energy* turns out to be fully delocalized. The influence of various factors that distinguish real systems from the model A on the electroneutrality properties of the spin carrier is investigated. It is shown that inclusion of interelectron interactions preserves the property $e_s = 0$. A small *local charge*

$$e_s \sim e\xi_0^{-1} \frac{\partial}{\partial q} \ln \omega_{ph}(q)\bigg|_{q=2P_F} \sim e\Delta_0/\epsilon_F$$

appears on account of the *phonon dispersion*. The *commensurability effects* of odd order n lead to the appearance of a *fractional charge* ($e_s = e/3$ for $n = 3$) concentrated in the *soliton tails* whose length is

$l \sim \hbar v_F / T_p \gg \xi_0$, where $T_p \sim (\Delta_0/\epsilon_F)^{n/2-1}$ is the "pinning temperature."

In §3 are investigated systems with *doubly commensurate charge density wave*. It is shown that in the model B (I, §3) the amplitude soliton has a broader spectrum of the quantum numbers $s = 1/2$, $e_s = 0$, and $s = 0$, $e_s = \pm e$, corresponding to filling of the central level $\nu_0 = 1$ and $\nu_0 = 0$ and 2, with the same shape and energy as in *model A*. In addition to such *kink-type solitons* there is also a *polaron* with normal quantum numbers: $s = 1/2$, $e_s = \pm e$, and $E_s = 2\sqrt{2}\,\Delta_0/\pi$.

For systems with *weak double commensurability* (model AB, I, §3) there are *spin neutral solitons* described in §2, and also shallow solitons of the sine-Gordon type with $s = 0$, $e_s = \pm e$, and $E_s \ll \Delta_0$.

In §4 are considered electronic excitations in *combined dielectrics* (model C, I, §3). In this case kink-type solitons are strongly bound into pairs. As a result, excitations exist in the form of *polarons* with $s = 1/2$ and $e_p = \pm e$, *bipolarons* with $s = 0$ and $e_{bp} = \pm 2e$, and *excitons* (*non-Coulomb*) with $s = 0$ or 1 and $e_{ex} = 0$. On the basis of these results we compare the properties of polymer semiconductors belonging to types B and C. The possible existence of *Bose condensation of a bipolaron gas* is suggested.

§1 Electron-Phonon Interactions and Polaron Effect in the Peierls–Fröhlich State

1 As indicated in chapter I, a quasi-one-dimensional gas of non-interacting electrons on a system of deformable chains at zero temperature T is in the ground Peierls–Fröhlich state. With the exception of transition regions near $\rho = 0$, 1, and 2, it is characterized by a lattice deformation $\zeta(x)$ in the form

$$\zeta(x) = \zeta_0 \cos(2p_F x + \varphi) \tag{1}$$

where x_0 is the coordinate along the chains, p_F is the Fermi momentum for the electrons in the metallic phase. The phase φ of the charge density wave must be regarded as fixed, $\varphi = \text{const}$ in the model B for systems with $\rho = 1$ and can be regarded as arbitrary, neglecting weak *pinning effects*, in the *model A* for the system with $|\rho - 1| \gg \Delta_0/\epsilon_F$ (see chapter I, §2). The electrons occupy negative-energy states $E_k = -\epsilon_k$, where

$$\epsilon_k = \sqrt{(\hbar v_F k)^2 + \Delta_0^2}\ ; \qquad \Delta_0 = q\zeta_0 \sim \epsilon_F \exp(-1/\lambda) \tag{2}$$

where v_F is the Fermi velocity, g is the electron-phonon interaction constant, and $\lambda = g^2/\pi\hbar v_F$.

The ground state of the system, obtained in the *self-consistent-field approximation*, was determined correctly on account of the *adiabaticity parameter* (Brazovskii, Dzyaloshinskii [30])

$$\frac{m}{M} = \left(\frac{u}{v_F}\right)^2 = \frac{\lambda}{4}\,\frac{\hbar^2\bar{\omega}^2}{\Delta_0^2} \ll 1 \tag{3}$$

where m and M are the *band mass* and the so-called effective *charge-density-wave mass*, u is the *phase velocity* of the charge-density wave, $\bar{\omega} = \omega(2p_F)$ is the nonrenormalized phonon frequency.

The elementary excitations of the system contain, first, phonon modes (two for *model A* and one for *model B*), which are conveniently defined at low temperatures as the *amplitude and phase modes* δ and φ,

$$\begin{gathered} \zeta(x,t) \sim \operatorname{Re}\Delta(x,t) \\ \Delta(x,t) = \left[\Delta_0 + \delta(x,t)\right]\cos(2p_F x + \varphi(x,t)) \end{gathered} \tag{4}$$

with dispersion laws

$$\begin{gathered} \omega_\varphi(q) = uq; \qquad \omega_\delta(q) = \omega_0\left(1 + \tfrac{1}{12}\xi_0^2 q^2\right)^{1/2} \\ \omega_0 = 2\sqrt{2}\,\Delta_0 u/\hbar v_F\ ; \qquad \xi_0 = \hbar v_F/\Delta_0 \end{gathered} \tag{5}$$

This picture can be justified both for a system that is three-dimensional with respect to the phonons, and for a one-dimensional system, regardless of the presence of long-range order [30]. The thermal and quantum fluctuations of δ and φ lead to a smearing of the parameter Δ_0. In structure measurements, the value of Δ_0 is determined accurate to

$$\langle \delta^2 \rangle^{1/2} \sim \Delta_0 \max\left\{ \left(\frac{T}{\Delta_0} \right)^{1/2}; \left(\frac{\hbar\omega}{\Delta_0} \right)^{1/2} \right\}$$

but the picture of the smearing of the electron spectrum (2) turns out to be much more complicated.

We consider the electron and hole excitations that determine the properties of the system as a narrow-gap semiconductor. If, as is usually understood, the lattice state is assumed fixed ($\Delta(x) = \Delta_0 = \text{const}$), then the electron-hole excitations are constructed in the same way as the particles (2) of the ground state, namely linear combinations of the waves $|\pm p_F + k\rangle$ with a dispersion law $\pm \epsilon_k$. However, the excitations defined in this manner are not renormalized and should be modified to some degree under the influence of the interaction with the phonon modes—the *polaron effect*. As shown by Brazovskii [41], this effect is specifically strong in a one-dimensional *Peierls–Fröhlich system* and leads to a radical restructuring of the picture of the electronic excitations of the system. The reason is that the electron or hole excited initially in a state with momentum $k \ll \xi_0^{-1}$ and energy $\epsilon_k = \Delta_0$ interacts with the deformations of the superstructure (CDW)—renormalized phonons. Following [44], we shall show in this section that in the units v_F, Δ_0, and ξ_0 this interaction, for a quasi-one-dimensional phonon spectrum, does not contain any parameters whatever except the *adiabaticity parameter* (3). As a result, a distinction must be made between two types of electronic phenomena, depending on the relation between the *electron lifetime* τ and the characteristic phonon frequency ω_0.

i States with $\tau\omega_0 \ll 1$ are determined at a fixed spontaneous lattice configuration. These include real states with $\tau \sim \hbar\Delta_0^{-1}$, which are responsible for optical transitions across the gap, and virtual states, which determine the renormalization of the phonon spectrum and the specific *dielectric constant* [30] in a system with $\rho = 1$

$$\epsilon_0(q) = \frac{\hbar^2\omega_p^2}{\sigma\Delta_0^2 + (\hbar v_F q)^2}; \qquad \omega_p = \infty \frac{e^2}{\hbar v_F} \frac{\xi_0^2}{S_\perp} \qquad |q| \ll \xi_0^{-1} \quad (6)$$

(ω_p is the *plasma frequency*). Obviously belonging to the same type are states that determine the system energy and consequently the value of Δ_0. For all these *short-lived states* we can assume a spectrum $\pm\epsilon_k$ smeared out by certain amount $\sim\epsilon_1$; $\epsilon_1 \ll \Delta_0$ (see formula (13) below). The value of ϵ_1 is determined by the thermal and quantum fluctuations of the amplitude $\delta(x,t)$.

ii *Long-lived excitations* with $\tau \gg \omega_0^{-1}$ must already be investigated as stationary states of the electron-phonon system. In this case the phonon frequency, if the condition (3) is satisfied, drops out of the theory and the problem no longer has any small parameters at all.

2 We attempt now to describe the states of both types (with $\tau \gg \omega_0^{-1}$ and with $\tau \ll \omega_0^{-1}$), assuming that the scale ξ of the significant changes of δ and φ and of the wave functions of the electrons ψ is large compared with ξ_0, and the value of δ and the depth of the electron level $\epsilon = E - \Delta_0$ are small compared with Δ_0:

$$\xi \gg \xi_0 ; \qquad |\epsilon| \sim |\delta(x)| \ll \Delta_0$$

The *interaction* of the electron e or of the hole h with the *amplitude* δ or *phase* φ *phonons* (5) is determined by the Lagrangian

$$\mathscr{L}\{\delta,\varphi,\psi\} = \mathscr{L}_\delta + \mathscr{L}_\varphi - \mathscr{H} \tag{7}$$

where

$$\mathscr{L}_\delta = \int dx \frac{2}{\hbar v_F \hbar}\left[\frac{\dot{\delta}^2}{\omega_0^2} - \delta^2\right] \tag{8}$$

$$\mathscr{L}_\varphi = \int dx \frac{\hbar v_F}{4\pi}\left[\frac{\dot{\varphi}^2}{u^2} - \varphi'^2\right] \tag{9}$$

$$\mathscr{H} = \int dx\, \psi^*(x)\hat{H}\psi(x); \qquad \hat{H} = \frac{\hat{p}^2}{2m} + \Delta_0 + \delta \pm \frac{\hbar v_F}{2}\varphi' \tag{10}$$

(the ± signs correspond to e and h).

The functionals (7)–(10) were rigorously derived in [30] and used to describe *virtual states* and to determine the region of applicability of the *Peierls model*. Their form obviously corresponds to a definition of the function $\delta(x,t)$ as the local change in the forbidden gap width

$2\Delta(x,t)$ and of the function $(1/2)v_F\varphi'(x,t) = v_F\delta p_F(x,t)$ as the local shift of the Fermi level. The terms with the time derivatives $\dot{\delta}$ and $\dot{\varphi}$ in (8) and (9) are obtained by substituting (4) in the term $\sim|\dot{\Delta}|^2$ in the general Lagrangian (1.2.11) of *model A*.

3 We consider the state with $\tau \gg \omega_0^{-1}$. In this case the fluctuations of δ and φ' constitute for the electron a random potential of the Gaussian-white-noise type. Its action is determined by the correlations at coincident instants of time, which can be easily calculated on the basis of the Lagrangians (8), (9). Confining ourselves to the low-temperature region, $T \ll \hbar\omega_0$, when only quantum fluctuations are of importance, we obtain for the Fourier component with respect to the coordinate

$$\langle \delta_k(t)\delta_{-k}(t)\rangle = \frac{\pi}{8}\hbar v_F\omega_0 \tag{11}$$

$$\begin{aligned}\langle \delta\mu_k(t)\delta\mu_{-k}(t)\rangle &= \frac{\hbar^2 v_F^2 k^2}{4}\langle \varphi_k(x,t)\varphi_{-k}(x,t)\rangle \\ &= \frac{\pi}{8\sqrt{2}}\hbar v_F\omega_0\xi_0 k \end{aligned} \tag{12}$$

The extra power of k in (12) causes the contribution of the fluctuations of the phase (i.e., of the Fermi level) to be small in comparison with the contribution δ in terms of the parameters $\xi_0/\xi \ll 1$. The *state density* $N(E)$ for the Hamiltonian (10) in a random potential with distribution (11) is known from Halperin's paper [59]. For $N(\Delta_0 - \epsilon)$ we have the following asymptotic expression [30]

$$N(\Delta_0 - \epsilon) \approx \frac{32\epsilon}{\pi\hbar^2 v_F\omega_0}\exp\left[-(\epsilon/\epsilon_1)^{\nu_1}\right] \tag{13}$$

where

$$\nu_1 = 3/2; \qquad \epsilon_1/\Delta = \frac{1}{2}\left(\frac{3}{4}\frac{\omega_0}{\Delta_0}\right)^{2/3}; \qquad \omega_0 \ll \epsilon_1 \ll \Delta_0$$

We see that $\epsilon_1/\hbar\omega_0 \sim (\Delta_0/\hbar\omega_0)^{1/3} \gg 1$, thus confirming the correctness of the *adiabatic approximation* not only in the tail (13) of the state density, but also in the region $|\epsilon| \sim \epsilon_1$ where the edge is smeared. The general conclusion is that the strong *smearing of the fundamental edge* in a *Peierls dielectric* is a particularly pronounced *Urbach phenomenon* and is not specially connected with the absence of long-range order in the one-dimensional system.

The violation of the long-range order in a system with $\rho = 1$ (model B) means that the gas contains the solitons investigated in §3, at a concentration

$$C \sim \exp\left\{-\frac{E_s}{T}\right\}\left(\frac{T}{\Delta_0}\right)^{1/2}\frac{\hbar v_F}{\max(\hbar\omega_0 T)}\;; \qquad E_s = \frac{2}{\pi}\Delta_0$$

According to the results of the investigation of the optical absorption (chapter III, §3), it leads to broadening of the *fundamental edge* $2\Delta_0$ by an amount $(\hbar v_F n)^2/\Delta_0$. The loss of the *long-range order* in an *incommensurate system* (*model A*) on account of phase fluctuations, as indicated above, is inessential for *short-lived states*.

It is of interest to note that the possibility of treating *quantum fluctuations* of the displacements adiabatically, as a random potential, is unique to one-dimensional systems. In fact, a similar approach for a d-dimensional system would yield a formula of the type (13) in which ν_1 and ϵ_1 are generalized to

$$\nu_d = 2 - \frac{d}{2}\;; \qquad \left(\frac{\epsilon_d}{\Delta_0}\right)^{2-(d/2)} \sim \left(\frac{\Delta_0}{\epsilon_F}\right)^{d-1}\left(\frac{\hbar\omega_0}{\Delta_0}\right)$$

whence

$$\frac{\epsilon_2}{\omega_0} \sim \left(\frac{\Delta_0}{\epsilon_F}\right) \qquad \frac{\epsilon_3}{\omega_0} \sim \left(\frac{\Delta_0}{\epsilon_F}\right)^4\left(\frac{\hbar\omega_0}{\Delta_0}\right) \tag{14}$$

It is seen from (14) that at $d = 3$ we have $\epsilon_3/\hbar\omega_0 \ll 1$ even if a small parameter exists for the static electron-lattice coupling, expressed in (14) in the form Δ_0/ϵ_F. Thus, the adiabaticity condition is satisfied at $d = 1$, is violated at $d = 2$, and the problem becomes in principle dynamic at $d = 3$.

4 A *long-lived excited electron* causes static distortion of the lattice. It can be seen from (8) and (10) that we have a typical polaron problem. It is known [46] that in the one-dimensional case a *self-*

trapped state exists also in the case of a short-range interaction of the deformation-potential type, as in (8) and (10). Inasmuch as for a *polaron* at rest the parameter ω_0 drops out of the problem, the binding energy is $\epsilon_b = \Delta_0 - E_b \approx \Delta_0$, i.e., we encounter the deep-level problem which is outside the scope of the approximation (8), (10). At any rate it can be stated that the polaron size $\sim\xi_0 = \hbar v_F/\Delta_0$, its mass is $m_p \sim m^*\Delta_0^2/\hbar\omega_0^2$, and the coupling constant defined in polaron theory [45] as $\alpha^2 \sim \epsilon_0/\hbar\omega_0$ is of the order of $\alpha \sim (\Delta_0/\hbar\omega_0)^{1/2} \gg 1$. An investigation of such a strongly *self-trapped state* calls for an exact solution, which will be described in the following sections.

In the approximation (8), (10) we encounter *the problem of total screening of the charge*. An extremum solution for (8) and (10) yields

$$\varphi'(x) = -\pi 4^*(x)\psi(x); \qquad \varphi(+\infty) - \varphi(-\infty) = -\pi, \tag{15}$$

so that it follows from the properties of the phase [30, 55] that a charge that screens completely the charge of the introduced electron is produced in the deformed *CDW*. This result is confirmed by the exact solution investigated in §2.

The intensity I_p of the optical excitation of a pair of *self-trapped states* can be estimated by interpolating equation (13). We obtain

$$I_p \sim \exp\left\{-(\epsilon_0/\epsilon_1)^{3/2}\right\} = \exp\{-C\Delta_0/\hbar\omega_0\}; \qquad C \sim 1 \tag{16}$$

Inasmuch as frequently $\Delta_0/\hbar\omega_0 \approx 10$, the polaron lines should be practically invisible. In analogy with (16), the probability of the pure electronic mechanism for the transition of a polaron between chains should be small. The *polaron effect* explains the usual lowering of the activation energies and of the longitudinal conductivity compared with E_a for the transverse conductivity and with the value of $E_g/2$ determined from the optical absorption edge E_g.

To conclude this section, we shall bring to light the difference between the picture of electron-phonon interactions in related three-dimensional systems. The *Peierls state* can be regarded as a particular case of a three-dimensional dielectric of the exciton-insulator type [60] produced as a result of a structural phase transition from the metallic phase with a Fermi surface having the property

$$\epsilon(\mathbf{p} + \mathbf{Q}) = -\epsilon(p)$$

at a certain **Q**. The ground state of such a system is also described by the BCS theory. The Hamiltonian of the electron-phonon interaction in the dielectric phase also takes the form (10), where $\hat{p}$ should be understood as the operator of the three-dimensional momentum, and dx should be replaced by $d^3\mathbf{r}$. In the Lagrangian (7), however, dx will be replaced by $(p_F^2/\pi)d^3\mathbf{r}$, owing to the appearance of the area factor of the Fermi surface $4\pi p_F^2/(2\pi)^2$. This factor obviously leads also to a small electron-phonon interaction constant

$$q^* \sim (p_F\xi_0)^{-2} \sim (\Delta_0/\epsilon_F)^2 \ll 1$$

Consequently, in a non-one-dimensional BCS dielectric the electrons are well-defined excitations near the edge $E \approx \Delta_0$ of the band.

§2 Spin Solitons in the Peierls–Fröhlich Model for the Incommensurate State (Model A)

2.1 Single-Soliton Solution for an Isolated Filament

We consider a system of noninteracting electrons on a deformable filament in the *Peierls–Fröhlich ground state*. We add to the system $\nu_0 \leqslant \nu$ electrons, where ν is the *degeneracy multiplicity* of the initial band. ($\nu = 2$ for spin degeneracy). As a result of the interaction of these electrons with the deformation of the *superstructure* $\Delta(x)$, the system goes over into a certain stationary state, ground or excited. As shown in §1, one can expect self-trapping of the additional electrons in the region $\sim\xi_0$ at a binding energy $\epsilon_B \sim \Delta_0$. Since $\epsilon_B/\hbar\omega_0 \sim \Delta_0/\hbar\omega_0 \gg 1$, the problem can be solved in an approximation quasi-classical in the lattice degrees of freedom and corresponding to the tight-binding polaron theory [45]. As applied to one-dimensional problems, this theory was expounded in the papers of E. I. Rashba [46]. In the zeroth approximation in the parameter $\hbar\omega_0/\epsilon_B$ in the localization region, as well as in the parameter $\hbar\omega_0/\Delta_0$ outside this region [30], the lattice deformation can be regarded as a classical quantity

$$\zeta(x) = \frac{1}{g}\left[\Delta(x)e^{i(2p_Fx+x)} + C.C.\right]$$

where $\Delta(x) = \Delta_1(x) + i\Delta_2(x)$ is a complex function, and $x = \text{const}$ is an arbitrary phase. Far from the localization region $|x| \gg \zeta_0$ the system should go over into one of the possible ground states, i.e.,

$$\Delta(x) \xrightarrow[x\to\pm\infty]{} \Delta_\pm = \text{const}; \qquad |\Delta_\pm| = \Delta_0 \tag{1}$$

We write the electron wave functions $\psi(x)$ in the field $\Delta(x)$ in the form

$$\psi_E(x) = \sqrt{2}\left[u_E(x)\cos(p_F x + x) + iv_E(x)\sin(p_F x + x)\right] \tag{2}$$

Any stationary state of the system, including the ground state, is determined from the condition that the functional of the system energy $W\{\Delta(x), \psi_E(x)\}$ be an extremum. Assuming the spectrum of the electrons near the Fermi points $\pm p_F$ to be linear, we can use the functional of the energy of the model A, formulated in I, §2:

$$\begin{aligned} &W\{\Delta_1(x), \Delta_2(x); u_E(x), v_E(x)\} \\ &= \frac{\Delta_1^2(x) + \Delta_2^2(x)}{g^2} + \sum_E \{-i[u_E^*(x)v_E'(x) + v_E^*(x)u_E'(x)] \\ &\qquad + \Delta_1(x)[u_E^*(x)u_E(x) - v_E^*(x)v_E(x)] \\ &\qquad + i\Delta_2(x)[v_E^*(x)u_E(x) - u_e^*(x)v_E(x)]\} \end{aligned} \tag{3}$$

where $f'(x) \equiv df/dx$ and the summation extends over all the occupied states. The first term in (5a) is the lattice-deformation energy. We assume that $v_F = 1$.

Varying (3) with respect to $u_E(x)$ and $v_E(x)$ we obtain equations of the Dirac type for the eigenfunctions corresponding to the energies E:

$$u_E' - \Delta_2 u_E - i(E + \Delta_1)v_E = 0 \tag{4}$$

$$v_E' + \Delta_2 v_E - i(E - \Delta_1)u_E = 0 \tag{5}$$

Varying (3) with respect to $\Delta_1(x)$ and $\Delta_2(x)$ we obtain the self-consistency conditions,

$$\frac{\delta W}{\delta \Delta_1} = 2\frac{\Delta_1}{g^2} - \sum_E \left(u_E^* u_E - v_E^* v_E \right) = 0 \tag{6}$$

$$\frac{\delta W}{\delta \Delta_2} = 2\frac{\Delta_2}{g^2} + \frac{1}{i}\sum_E \left(u_E^* v_E - u_E v_E^* \right) = 0 \tag{7}$$

Equations (4)–(7) correspond to the *self-consistent field approximation* for an inhomogeneous state of the system or, strictly speaking, to the zero-order quasiclassical approximation. Their applicability, as indicated above, is based on the existence of the *adiabaticity parameter* $v_F/u \gg 1$. There is also another known physical system describable by approximately equivalent equations. This is the model, investigated in [61], of two-dimensional relativistic field theory with a large number of interacting fermions $\nu \gg 1$. The large parameter ν was necessary to be able to use the quasiclassical approach.

2 We seek a solution such that in the soliton region the function $\Delta(x)$ varies in the complex plane along a chord of the circle $|\Delta| = \Delta_0$. By properly choosing the phase χ in the definition (2), we can put $\Delta_1 = \text{const}$, $\Delta = \Delta_1 + i\Delta_2(x)$, as shown in Fig. 3a. We define now the parameters $0 \leqslant \theta \leqslant \pi$ and $k_0 \geqslant 0$ such that

$$\Delta_1 = \Delta_0 \cos\theta; \qquad k_0 = \sqrt{\Delta_0^2 - \Delta_1^2} = \Delta_0 \sin\theta$$

It can be seen from (4) and (5) that at $\Delta_1 = \text{const}$ there always exists a localized normalizable solution labeled hereafter by the index E_0:

a) if $\Delta_2(\pm\infty) = \mp k_0$, as shown by the arrow in Fig. 3a, then $E_0 = \Delta_1$, $v_0(x) = v_{E_0}(x) \equiv 0$,

$$u_0(x) = u_{E_0}(x) \sim \exp\left\{ \int_0^x \Delta_2(y)/dy \right\} \tag{8}$$

b) If $\Delta_2(\pm\infty) = \pm k_0$, then $E_0 = -\Delta_1$,

$$v_0(x) = v_{E_0}(x) \sim \exp\left\{ -\int_0^x \Delta_2(y)/dy \right\} \tag{9}$$

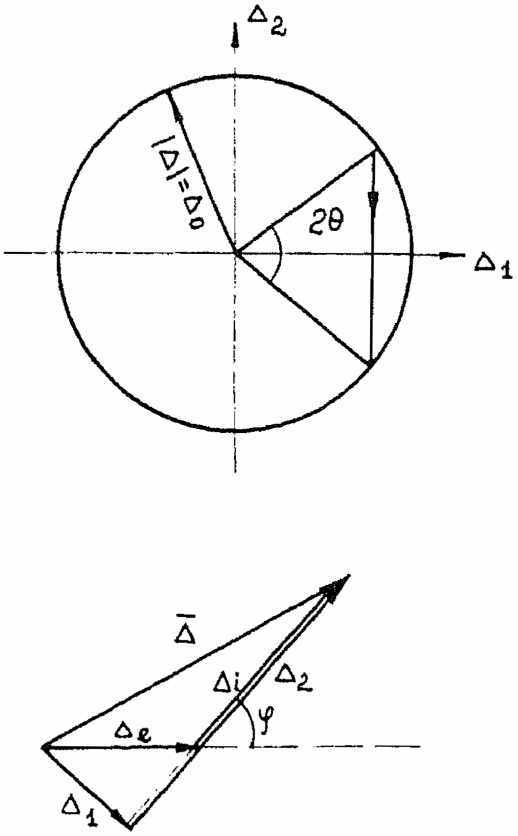

Figure 3

It is easy to verify that the cases a) and b) are charge-conjugated, i.e., they correspond to *electron* and *hole polarons*. For the sake of argument we shall consider hereafter the case a).

At $E \neq E_0$ it follows from (5) that

$$u_E(x) = \frac{v_E'(x) + \Delta_2(x) v_E(x)}{i(E - E_0)} \tag{10}$$

Substituting (10) in (6) and (7) we obtain

$$\frac{\delta W}{\delta \Delta_1} = 2\frac{\Delta_1}{g^2} + 2\sum_{E \neq E_0} v_E^* v_E - \rho(x) \tag{11}$$

where

$$\rho(x) = \sum_E (u_E^* u_E + v_E^* v_E) \tag{12}$$

is the *particle-number density* and

$$\frac{\delta W}{\delta \Delta_2} = 2\frac{\Delta_2}{g^2} + \sum_{E \neq E_0} \left(2\Delta_2 + \frac{d}{dx}\right) \frac{v_E^* v_E}{E - E_0} \tag{13}$$

Substituting (10) in (4), we obtain an equation for $v_E(x)$ at $E \neq E_0$:

$$v_E'' + \left[\Delta_2' - \Delta_2^2 - E_0^2 + E^2\right] v_E = 0 \tag{14}$$

We consider first the self-consistency condition (13) jointly with Eq. (14) for the set of functions v_E. As follows from the results presented in III. §4, the functional equations (13) and (14) reduce to algebraic ones and can be solved if the function $\Delta_2(x)$ satisfies the equation

$$\Delta_2''' - 6\Delta_2^2\Delta_2' - A\Delta_2' = 0; \qquad A = \text{const} \tag{15}$$

The *single-soliton solution* of Eq. (15) in case a) takes the form

$$\Delta_2(x) = -k_0 \operatorname{th}(k_0 x) \tag{16}$$

Substituting (16) in (8), (10), and (14) we obtain the complete set of the electronic states in the field $\Delta(x)$

$$\begin{aligned} &E_0 = \Delta_0 \cos\theta; \qquad v_0(x) = 0, \\ &u_0(x) = \frac{\sqrt{k_0/2}}{\operatorname{ch}(k_0 x)} \\ &E = -\epsilon_k: \qquad v_k(x) = \frac{1}{\sqrt{N_k L}} e^{ikx} \\ &u_k(x) = \frac{1}{\sqrt{N_k L}} \frac{-k + ik_0 th(k_0 x)}{E_0 + \epsilon_k} \end{aligned} \tag{17}$$

where

$$N_k = 2\epsilon_k/(E_0 + \epsilon_k) \tag{18}$$

We substitute (16)–(18) in Eqs. (11)–(13). In the summation we should regard the states with $E = -\epsilon_k$ as ν-multiply occupied states, those with $E = +\epsilon_k$ as unoccupied, and ascribe to the localized states $E = E_0$ an arbitrary *occupation number* ν_0 that is so far arbitrary: $0 \leqslant \nu_0 \leqslant \nu$.

We obtain

$$\frac{\delta W}{\delta \Delta_2} = 2\Delta_2(x)X \tag{19}$$

and

$$\frac{\delta W}{\delta \Delta_1} = 2E_0X + \frac{k_0}{2\,\mathrm{ch}^2(k_0x)}\left[\nu_0 - \frac{\nu}{L}\sum_k \frac{k_0}{\epsilon_k(E_0 + E_k)}\right] \tag{19a}$$

where

$$X = \frac{1}{g^2} - \frac{\nu}{L}\sum_k \frac{1}{2\epsilon_k} \tag{20}$$

At equilibrium we should have $X = 0$. For the ground state ($\theta = 0$, $\nu_0 = 0$) this condition determines the equilibrium value of the gap parameter

$$\Delta_{00} \sim \epsilon_F \exp\{-1/\lambda\}$$

in the absence of a soliton, the sum in (20) changes by an amount $\sim O(1/L)$ as a result of the change in the state density because of the presence of scattering phase shifts in $u_k(x)$ and as a result of the refinement of the normalization (18). We therefore always have

$$X = X(\theta) = O(1/L)$$

The sum in (19a) can be calculated to order $O(1)$, since it enters with a factor that is integrable with respect to x. We obtain

$$\frac{\delta W}{\delta \Delta_1} = \frac{\Delta_0 k_0}{2\,\mathrm{ch}^2(k_0x)}\left\{\nu_0 - \nu\frac{\theta}{\pi}\right\} + 2E_0X \tag{21}$$

In the equilibrium position

$$\delta W/\delta\Delta_1 = \delta W/\delta\Delta_2 = 0$$

and we have from (19) and (21)

$$\Delta_0 = \Delta_{00} + O(1/L); \qquad \theta = \theta_0 - \nu_0\pi/\nu, \quad \text{or} \quad \theta = 0.$$

We determine the total excitation energy $W(\theta)$ from the relation

$$\frac{dW}{d\theta} = \int dx\left[\frac{\delta W}{\delta\Delta_1}\frac{d\Delta_1}{d\theta} + \frac{\delta W}{\delta\Delta_2}\frac{d\Delta_2}{d\theta}\right] \tag{22}$$

whence

$$\frac{dW}{d\theta} = \int dx\left[\sin 2\theta\frac{xth(k_0x)}{\mathrm{ch}^2(k_0x)}X(\theta) + \frac{k_0^2}{2\,\mathrm{ch}^2(k_0c)}\left(\nu\frac{\theta}{\pi} - \nu_0\right)\right] \tag{22a}$$

The quantity $X(\theta)$ enters in (22a) with a factor integrable with respect to x, i.e., it can be assumed, with accuracy $O(1)$, that $X(\theta) = 0$. We obtain

$$\frac{dW}{d\theta} = \Delta_0\left(\nu\frac{\theta}{\pi} - \nu_0\right)\sin\theta \tag{22b}$$

Integrating (22b) with the boundary condition $W(0) = \nu_0\Delta_0$, corresponding to electrons at the momentum $k = 0$ for an *undeformed superstructure*, we obtain, in accordance with the results of [56, 62]*:

$$W(\theta) = \Delta_0\left[\left(\nu_0 - \nu\frac{\theta}{\pi}\right)\cos\theta + \frac{\nu}{\pi}\sin\theta\right] \tag{23}$$

$$W_s = W(\theta_0) = \frac{\Delta_0\nu}{\pi}\sin\left(\frac{\pi\nu_0}{\nu}\right); \qquad \theta_0 = \frac{\pi\nu_0}{\nu} \tag{23a}$$

As seen from (22b) and (23), the positions $\theta = 0$ and $\theta = \theta_0$ corre-

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*The presented derivation of the energy enables us to avoid the more laborious direct energy calculation in [61].

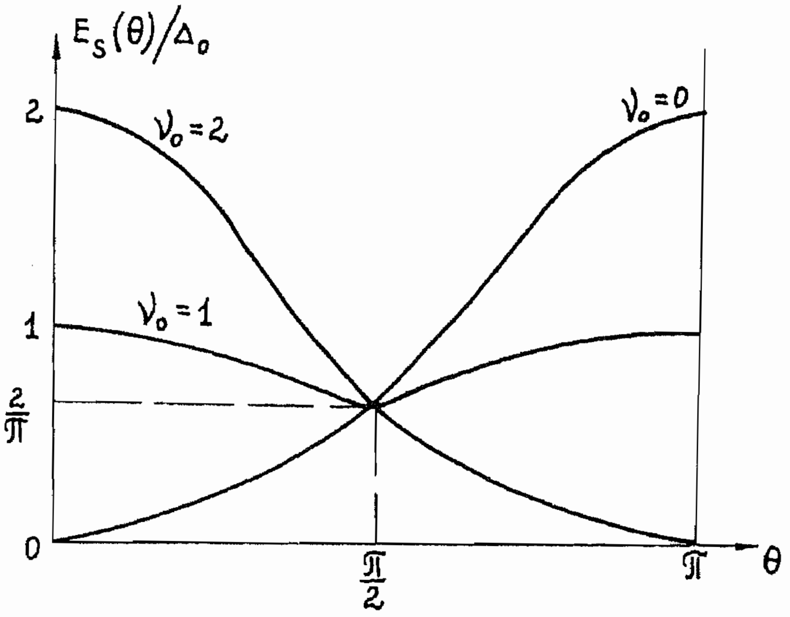

Figure 4

spond to the maximum and minimum energy of the system. Plots of $W(\theta)$ at $\nu = 2$ and $\nu_0 = 0$, 1, and 2 are shown in Fig. 4.

We consider the following different cases of *occupation numbers*

a) $\nu_0 = 0; \quad \theta_0 = 0; \quad W_s = 0; \quad k_0 = 0.$

We have an undeformed system in the ground state.

b) $\nu_0 = 2; \quad \theta_0 = \pi; \quad W_s = 0; \quad k_0 = 0.$

We have an undeformed system with an additional occupied level in the ground state.

We conclude that there are no singlet ($\nu_0 = 0$ and $\nu_0 = 2$) stationary excited states. *Any excited pair of electrons or holes will be absorbed in the ground state without a barrier after a time* $\tau \sim \omega_0^{-1}$. This *nonradiative recombination*, in accordance with the qualitative analysis given in §1, goes through intermediate *nonstationary polaron states.*

We consider now the case of one electron. We have here an already nontrivial stationary state:

$$\nu = 2; \quad \nu_0 = 1; \quad \theta_0 = \frac{\pi}{2}; \quad k_0 = \frac{\Delta_0}{\hbar v_F}; \quad E_0 = \Delta_1 = 0; \quad W_s = \frac{2}{\pi}\Delta_0 \tag{24}$$

which we shall in fact investigate hereafter. We note that this solution with $\theta_0 = \pi/2$ has electron-hole symmetry, i.e., self-trapping of either an electron or a hole leads to the same result.

We shall show that the total electron density remains homogeneous and that the local charge of the soliton is zero. It follows from (17) and (18) that the distributions of the densities $\rho_E(x)$ in the states $E = E_0$, and $E = \epsilon_k$ are equal:

$$\rho_0(x) = \frac{1}{2\,\mathrm{ch}^2(k_0 x)}\,; \qquad \rho_k(x) = -\frac{\rho_0(x)k_0}{L\epsilon_k(E_0 + \epsilon_k)}$$

The total change of the density in the system takes the form

$$\delta\rho(x) = \nu_0\rho_0 + \nu\sum_k \rho_k(x) = \left(\nu_0 - \nu\frac{\theta}{\pi}\right)\rho_0(x) \tag{25}$$

At equilibrium $\theta = \pi\nu_0/\nu$ and we find from (25) that

$$\delta\rho(x) = 0 \tag{25a}$$

Thus, exact compensation of the local charges took place. This property can be attributed to the *Fröhlich-conduction phenomenon.* It will be shown in §4 that the effects of the coupling between the chains, as well as the *commensurability* facts, produce again a local charge around the soliton, but at distances $l \gg \xi_0$. The obtained property can be established also without resorting to the explicit form of the solution. We differentiate (12) with respect to x and use Eqs. (4)–(7). We obtain

$$\frac{1}{2}\frac{d\rho}{dx} = \Delta_1\frac{\delta W}{\delta\Delta_2} - \Delta_2\frac{\delta W}{\delta\Delta_1} \tag{26}$$

It follows therefore that at equilibrium $\rho(x) = \text{const}$ and we arrive at (24a). A similar investigation for the more general model is carried out in §3.

We show now that the total energy of the soliton is delocalized. We have the lattice part of the energy density

$$w_{\text{lat}} = \frac{\Delta^2(s)}{g^2} - \frac{\Delta_0^2}{g^2} = -\frac{k_0^2}{g^2\mathrm{ch}^2(k_0 x)}$$

The energy density of the bound state

$$w_b = E_0 \rho_0(x)$$

as well as of the continuous-spectrum states

$$w_c(x) = -\sum_k \epsilon_k \rho_k(x) = -\frac{\theta}{\pi} E_0 \rho_0(x) + O(1/L)$$

The total *energy density* is

$$\begin{aligned} w(x) &= w_{\mathrm{lat}} + \nu_0 w_b + \nu w_c \\ &= \Delta_0 \rho_0(x)(\nu_0 - \nu\theta/\pi)\cos\theta + O(1/L) \end{aligned} \tag{27}$$

We see from (27) that at equilibrium, for $\theta = \theta_0 = \pi\nu_0/\nu$ we get $w(x) \sim 1/L$, and comparing with (23) we get

$$w(x) = \frac{2}{\pi}\Delta_0 \frac{1}{L}$$

Thus, the local changes of the electron and lattice energies cancel each other completely. The total energy of the soliton (23a), $E_s = (2/\pi)\Delta_0$, is determined by volume effects of the change of the density of states (18), although the equilibrium conditions (19a) and (20b) are locally determined.

The kinetic energy of a soliton moving with velocity $v \ll u$ is determined, just as for tight-binding polarons, mainly by the inertia of the lattice. The electronic contribution to the mass M_s is small in the ratio $\sim(u/v_F)^2 \ll 1$. We have

$$W_{\mathrm{kin}} = \int dx \frac{|\dot{\Delta}(x,t)|^2}{g^2 \bar{\omega}^2}; \qquad \dot{\Delta}(x,t) \equiv \frac{\partial \Delta(x,t)}{\partial t} \tag{28}$$

Neglecting the change of *the shape of the soliton* when it moves with low velocity v, we can substitute in (28) $\Delta(x,t) = \Delta_0 \mathrm{th}[(x - t)/\xi_0]$. We obtain

$$W_{\mathrm{kin}} = \frac{1}{2} M_s v^2; \qquad M_s = \frac{4}{\pi} \frac{\Delta_0^3}{\lambda \bar{\omega}^2 v_F^2 \hbar^2} = \frac{1}{\pi} \frac{\Delta_0^2}{\hbar^2 \omega_0^2} m^*; \qquad m^* = \frac{\Delta_0}{v_F^2}$$

2.2 *Effect of Perturbations on the Local Charge of the Soliton*

It was shown above with the framework of the one-dimensional *Peierls–Fröhlich model* that the charge and energy of the system remain homogeneous in the presence of a soliton. As a result, the solitons should not contribute to the electric conductivity and thermal conductivity of the system. Their only kinetic manifestation would be spin diffusion. In real systems, one might expect a substantial change in the local properties of the soliton. It is particularly important to take into account the interelectron interaction, which is usually not weak. In addition, we must investigate the effects of coupling between chains, the influence of phonon dispersion, of *commensurability*, as well as the effect of motion of the *soliton*. The *delocalization of the energy* is probably an accidental property of the simple model and should vanish when account is taken of the correlation energy. The *charge delocalization* was connected with the electron-hole degeneracy of the solution, and can be preserved also for a more complicated system. In this part we consider the question of the local charge of a *self-trapped excitation* for a sufficiently general model of a quasi-one-dimensional system of electrons on a deformable lattice. It turns out that its investigation can be carried out in general form on the basis of the equations of motion, without having the explicit form of the solution for the complicated model.

2 We consider a quasi-one-dimensional system of conducting filaments with transverse coordinates $\mathbf{R}_n$. We shall assume that there are no electronic transitions between the filaments. Let the electrons on one of the different filaments interact via long-wave phonon fields $\Phi_{i,n} = \Phi_i(x, \mathbf{R}_n, t)$, including the Coulomb potential $\Phi_c(x, \mathbf{R}_n)$ and the short-wave fields

$$B_\alpha(x, \mathbf{R}_n, t)e^{i2p_F x} + B_\alpha^+(x, \mathbf{R}_n, t)e^{-i2p_F x}$$

which transmit the backward scattering of the electrons. These fields are characterized by the parameters $g_{mn}^{(i,\alpha)}(x_m, x_n)$ for interaction with electrons and

$$D_{mn}^{(\lambda)}(x_m - x_n) = \sum_{k,\mathbf{k}_\perp} \frac{\overline{\omega}_\lambda^2 \exp\left[i\{ k(x_m - x_n) + \mathbf{k}_\perp(\mathbf{R}_m - \mathbf{R}_n)\} \right]}{\omega^2 - \omega_\lambda^2(k, \mathbf{k}_\perp)} \qquad (29)$$

for interaction with the unrenormalized Green's functions ($\lambda = i$ or

$\lambda = \alpha$). We assume for the sake of argument that the frequency of the short-wave phonons ($\lambda = \alpha$) at small k, i.e., near $\pm 2p_F$, can be written in the form

$$\omega_\alpha^2(k, \mathbf{k}_\perp) \approx \omega_\alpha^2(k) + \Omega_\alpha^2(\mathbf{k}_\perp) \tag{29a}$$

where

$$\omega_\alpha^2(k) \approx \bar{\omega}_\alpha^2 + 2\bar{\omega}_\alpha s_\alpha k$$

$$\Omega_\alpha^2(\mathbf{k}_\perp) = \sum_m I_{mn}^{(\alpha)} \exp\{i\mathbf{k}_\perp(\mathbf{R}_m - \mathbf{R}_n)\}$$

We introduce the operators for the creation $\psi_n^+(x)$, annihilation $\psi_n(x)$, density $\rho_n(x)$, and current $j_n(x)$ of the particles on the chain n, as well as the operators of the charge-density wave components $\eta_n^+(x)$ and $\eta_n(x)$

$$\left.\begin{array}{ll} \rho_n = \psi_n^+ \hat{I} \psi_n\,; & j_n = \psi_n^+ \hat{\sigma}_z \psi_n \\ \eta_n = \psi_n^+ \hat{\sigma}_- \psi_n\,; & \eta_n^+ = \psi_n^+ \hat{\sigma}_+ \psi_n \end{array}\right\}$$

where $\hat{\sigma}_z, \hat{\sigma}_\pm = \sigma_x \pm i\sigma_y$, and $\hat{I}$ are the Pauli matrices and the unit matrix. In terms of these variables, the system described is characterized by the Lagrangian

$$\begin{aligned} \mathscr{L} = \sum_{m,n,i,\alpha} \int dx \Big\{ & \frac{1}{2} \bar{\Phi}_{im} \left(D_{mn}^{(i)}\right)^{-1} \bar{\Phi}_{in} + B_{\alpha m}^+ \left(D_{mn}^{(\alpha)}\right)^{-1} B_{\alpha m} \\ & - \left[\Phi_{im} g_{mn}^{(i)} \rho_n + \Phi_{im} \tilde{g}_{mn}^{(i)} j_n + \Delta_n \eta_n^+ + \Delta_n^+ \eta_n\right] \\ & + \psi_n^+ \left(i\hat{I} \frac{\partial}{\partial t} + i\hat{\sigma}_z \frac{\partial}{\partial x} \right) \psi_n \Big\} \end{aligned} \tag{30}$$

where

$$\Delta_n(x, t) = \sum_{m,\alpha} g_{nm}^{(2)} B_{\alpha m}(x, t) \tag{30a}$$

is the field conjugate to the *charge-density wave density* $\eta_n(x)$. In the zeroth approximation for the *Peierls–Fröhlich model,* the operator $\Delta_n(x,t)$ goes over into the classical gap function $\Delta_n(x)$.

We assume that in the model considered, just as in the particular case of the *Peierls–Fröhlich model,* there exist self-trapped stationary excited states. The *adiabatic approximation* developed in §3, which corresponds to the theory of *tight-binding polarons,* means in the general case that at least some of the modes B_α have frequencies $\bar{\omega}_\alpha$ that are small compared with the *soliton binding energy.* On the other hand, as will be seen subsequently, a significant influence on the *soliton charge* is exerted only by modes with a considerable dispersion $\bar{s}, I_{mn}$. Both conditions lead us to practically the same modes—the *acoustic-branch phonons* $\alpha = a$. In the principal adiabatic approximation $B_a(x)$ can be regarded as classical local deformations. The remaining modes requires quantum mechanical averaging $\langle \cdots \rangle_a$ for specified $B_a(x)$. In the Feynman formulation this means that the path integral over the fields $B_a(x,t)$ is calculated by the saddle-point method (see [30]), but exact integration is assumed over the remaining fields $B_\alpha(x,t)$ with $\alpha \neq a$.

3 Assume the presence of an *isolated moving self-trapped excited state* of the system in the vicinity of the chain $n = 0$. Since the energy and the charge of the excitation must be finite, the characteristic perturbations of the quantities $\rho_n(x), j_n(x)$, and $\Delta_n(x)$ should decrease rapidly enough with increasing number n of the chain. We can therefore determine the summarized perturbations

$$\rho(x,t) = \sum_n \langle \rho_n(x,t) \rangle_a\,; \qquad J(x,t) = \sum_n \langle j_n(x,t) \rangle_a$$

We determine also the *effective gap parameter*

$$\Delta(x,t) = |\Delta(x,t)| \exp\{ i\chi(x,t) \}$$

in accordance with the formulas

$$|\Delta(x,t)|^2 = \sum_n \langle \Delta_n^+ \Delta_n \rangle_a$$

$$|\Delta(x,t)|^2 \frac{\partial \chi(x,t)}{\partial t} = \frac{1}{2i} \sum_n \langle \Delta_n^+ \frac{\partial}{\partial t} \Delta_n - \Delta_n \frac{\partial}{\partial t} \Delta_n^+ \rangle_a \tag{31}$$

$$\lim_{x \to \pm\infty} |\Delta(x,t)| = \Delta_0$$

The function $\Delta(x,t)$ goes over into the solution

$$\Delta(x) = \Delta_0 th(x/\xi_0)$$

for a *soliton* at rest, in the model considered in part II.

We use the equation of motion, introduced in Appendix I, which connects the operators ρ_n, j_n, and Δ_n. We average Eq. (A.10) at fixed perturbations $B_a(x,t)$ and substitute expressions (31). We obtain an equation that connects the perturbed distributions

$$\begin{aligned}&\frac{\partial}{\partial t}\left[J - \frac{\nu}{2\pi}\frac{|\Delta|^2}{\Delta_0^2 u^2}\frac{\partial x}{\partial t}\right]\\ &\quad + \left[\frac{\partial\rho}{\partial x} - \omega_p^2\int_0^x \rho(y)\,dy + \sum_i a\frac{\partial^2}{\partial x^2}\left(\frac{\partial^2}{\partial x^2} - s_i^{-2}\frac{\partial^2}{\partial t^2}\right)^{-1}\frac{\partial\rho}{\partial x}\right]\\ &\quad + \frac{1}{g^2}\frac{\bar{s}}{\overline{\omega}}\frac{\partial|\Delta|^2}{\partial x} = 0 \qquad (32)\end{aligned}$$

where

$$u^2/v^2 = \lambda\hbar^2\overline{\omega}_a^2/4\Delta_0^2\,; \quad \lambda = g^2/\pi\hbar v_F\,; \quad \omega_p^2 = \frac{8e^2 v_F}{\hbar S_\perp}\,; \quad |q| \ll \xi_0^{-1}$$

and the *effective electron-phonon interaction* constant g^2 is defined in (A.8a).

We consider now a perturbation moving with a constant velocity $v \neq s_i$. We then obtain from (A.5) $J = v$ and $\partial/\partial t = -v(\partial/\partial x)$. From (32) we get

$$\left[\frac{d\rho}{dx} - \kappa^2\int_0^x \rho(y)\,dy\right] = \frac{df}{dx}$$

where

$$\begin{aligned}f(x) &= \frac{\bar{s}}{\overline{\omega}}\frac{|\Delta|^2 - \Delta_0^2}{\hbar^2 b v_F^2} + \frac{\nu}{2\pi b}\frac{v_F^2}{u^2}\frac{|\Delta|^2}{\Delta_0^2}\frac{d\chi}{dx}\\ b &= 1 - \frac{v^2}{v_F^2} - \sum_i \frac{a}{1-(v/s_i)^2}\,; \qquad \kappa = \frac{1}{\sqrt{b}}\frac{\omega_p}{v_F}\end{aligned} \qquad (33)$$

It follows from (33) that

$$\rho(x)=\frac{1}{2\kappa}\int f''(y)\exp\{-\kappa|x-y|\}\,dy \tag{34}$$

or

$$\rho(x)=f(x)+\frac{\kappa}{2}\int f(y)\exp\{-\kappa|x-y|\}\,dy \tag{34b}$$

Since actually $\hbar\omega_p \gg \Delta_0$ and $f(y)$ changes over a length not shorter than $\xi_0=\hbar v_F/\Delta_0 \gg 1/\kappa$, we obtain from (34a)

$$\rho(x)\approx(1/\kappa^2)f''(x)$$

Since $f(y)\to 0$ as $y\to\pm\infty$, we obtain from (34a) the exact result, namely that the *soliton charge* e_s and the dipole moment P_1 are equal to zero, while the quadrupole and higher moments are finite:

$$e_s=0;\qquad P_1=0;\qquad P_2=e\int\rho(x)x^2\,dx=\frac{2e}{\kappa^2}\int f(y)\,dy \tag{35}$$

We introduce the *characteristic soliton length* ξ and the *gap-deformation amplitude* δ. We then have from (33)–(35)

$$\begin{aligned}\rho(x)&\sim\frac{1}{\lambda}\left(\frac{\Delta_0}{\epsilon_F}\right)^3\left(\frac{\epsilon_F}{\omega_p}\right)^2\frac{\delta}{\Delta_0}\,\frac{\xi_0}{\xi^2}\,;\qquad x\lesssim\xi\\ P_2&\sim\frac{e}{\lambda}\left(\frac{\Delta_0}{\epsilon_F}\right)^3\left(\frac{\epsilon_F}{\omega_p}\right)^2\frac{\delta}{\Delta_0}\,\xi_0\xi\end{aligned} \tag{36}$$

For the model considered in §2 we have exactly

$$\begin{aligned}f(x)&=\frac{4}{\pi\lambda}\,\frac{\bar{s}}{\bar{\omega}}\,\frac{\Delta_0^2}{\hbar^2v_F^2}\,\frac{1}{\mathrm{ch}^2(x/\xi_0)}\,;\qquad P_2=\frac{16}{\pi}\,\frac{e\Delta_0^2\bar{s}}{\lambda\hbar^2\omega_p^2\bar{\omega}}\,\xi_0\\ \rho(x)&\approx\frac{8}{\pi\lambda}\,\frac{\Delta_0^2\bar{s}}{\hbar^2\omega_p^2\bar{\omega}\xi_0^2}\,\frac{3\,th^2(x/\xi_0)-1}{\mathrm{ch}^2(x/\xi_0)}\end{aligned} \tag{37}$$

We see that the *local charges* are small in terms of the parameter $\Delta_0/\hbar\omega_p \ll 1$.

The exact *compensation of the charge*, which was established above, takes place because of long-range three-dimensional Coulomb fields. At a large distance and *a weak coupling between the chains*, the screening takes place with participation of a large number of chains. In kinetic phenomena, however, an important role is played by *local charges*, particularly on the central chain $n = 0$, where the localized electron is placed.

We consider Eq. (A.19), neglecting all *the couplings between the chains*, i.e., $I_{mn} = 0$. We obtain for J_0 and ρ_0 the equations (32) and (33) with $\kappa = 0$ and $\omega_p = 0$. The solution of (33), according to (34b) is $\rho_0(x) = f(x)$. As a result, the charge e_s and the even moments P_{2n} will differ from zero, with

$$e_s \sim \frac{e\delta}{\epsilon_F}\,\frac{\xi}{\xi_0}$$

Substituting in (33) the solution derived in Part II, we obtain in first order in the dispersion s/v_F

$$\rho(x) = \frac{4}{\pi}\,\frac{\bar{s}}{b\lambda\bar{\omega}\xi_0^2}\,\frac{1}{\mathrm{ch}^2(x/\xi_0)}\,; \qquad e_s = \frac{8e\bar{s}\Delta_0}{\pi b\lambda v_F\hbar\bar{\omega}} \tag{38}$$

For a moving soliton it is necessary to consider the second term in expression (33) for $f(x)$. When the zeroth solution is substituted it vanishes, since $\Delta(x)$ varies in the complex plane along a straight line passing through the origin. Generally speaking, motions with allowance for dispersion deforms the *soliton*. It can be shown, however, that the general character of the solution does not change also in next order of perturbation theory in $(v/u)^2$. We cannot exclude the possibility that $e_s(v) - e_s(0) \sim (v/u)^{2n}$ at $n \geqslant 3$.

We shall show in chapter IV that effects of proximity to the *twofold commensurability point* lead to the appearance of a charge in the *spin soliton*. The value of this charge depends on the shift $2k_F - \pi/a$. In chapter VI we shall show that the soliton charge can be restored on account of *interaction effects between the chains* in a *three-dimensionally ordered phase*.

2.3 *Perturbations That Violate the Gauge Invariance of the Model A*

All the perturbations that lower the degeneracy of the ground state of the model exert a strong influence on the *soliton structure.* For model A, such perturbations are the *commensurability effects* and the *interactions between the chains.* The role of these perturbations manifests itself at large distances $|x| \gg \xi_0$, where account need be taken of only the change of the phase φ_α of the field $\Delta_\alpha(x)$, where α is the chain index. The state of the system outside the *core* ($|x| \lesssim \xi_0$) of the *amplitude soliton* can be determined from the condition that the energy functional be a minimum (see, e.g., [4, 29, 55])

$$\mathscr{H} = \mathscr{H}\{\varphi_\alpha(x)\}$$

$$= \int dx \left[\sum_\alpha \left(\hbar v_F \frac{\varphi_\alpha'^2}{4\pi} + \frac{T_n^2}{\hbar v_F} \cos n\varphi_\alpha \right) + \sum_{\alpha,\beta} C T_c^2 \cos(\varphi_\alpha - \varphi_\beta) \right] \tag{39}$$

$$T_c\,, T_n \ll \Delta_0\,; \qquad C \sim 1$$

where T_c is the *temperature of the three-dimensional ordering* of the system, T_n is the *pinning temperature* [29], α and β are the indexes of the neighboring chains. The most important cases are $n = 1, 2, 3$:

Model AC: $n = 1$, $T_1^2 \sim \Delta_0 C/\lambda$

Model AB: $n = 2$, $T_2^2 \sim \Delta_0^2 B/\lambda$

Systems with $\rho = 2/3, 4/3$: $n = 3$, $T_3^2 \sim \Delta_0^3/D$.

The Hamiltonian (39) determines the structure of the system for self-trapping of two particles, distorting the term $\nu_0 = 2$, Fig. 5, in the region $\theta \approx \pi$. In place of a new homogeneous state expanded to cover two particles, we obtain now *a set of solitons* than connect equivalent states with $\varphi = 2k\pi/n$, $k = 0, 1, \ldots$. The *soliton charge* is [55]

$$e_s = \frac{e}{\pi}\left[\varphi(+\infty) - \varphi(-\infty)\right] = \frac{2}{r} e$$

Phase solitons with $n \neq 1$ can exist only in the interval $T_n > T > T_c$ and when the strengthened adiabaticity condition $\Delta_0/\hbar\omega_0 < n^2$ is satisfied, something that can apparently occur only in substances with

$n \leqslant 3$. At $n = 2$, in the *AB model*, solitons with $e_s = \pm e$ are possible and go over continuously, with increasing parameter B, into *the amplitude charged solitons* of the *model B* (§3). An analysis of the experimental data for $K(\text{def})CP$ as an example is given in [31].

In the disordered phase, $T < T_c$, the solitons are preserved only at $n = 1$. In the remaining cases they are bunched into "*phase-slip centers*," where the phase of one chain changes by 2π relative to the surrounding ones. The charge of the center is $e_s = 2e$ and its energy is $E_s \sim \max(T_c, nT_n)$. These excitations probably determine the small low-temperature activation energies and conductivities observed in many materials with $\rho \neq 1$ or 2.

The amplitude solitons take the system out of the equilibrium

$$\varphi_\alpha = \frac{2k+1}{n}\pi = \text{const}; \qquad k = 0; \pm 1; \ldots$$

determined by the minimum of the Hamiltonian (39), with the exception of the case of even n. This leads to equalization of the phase in a region of dimensions $l \sim \hbar v_F / T_c$; $\hbar v_F / T_n$, $l \gg \xi_0$, on the tails of the soliton. The electron density becomes perturbed in this region, and as a result a *spin soliton* can acquire an electric charge [47]. This phenomenon is investigated in detail in chapter VI, §1, with the interaction between chains as the example. The *commensurability effects* are investigated similarly. The plots of the complex function $\Delta(x)$ are shown in Fig. 5b for $n = 3$ and in Fig. 5c for $n = 1$. A change in $\Delta(x)$ takes place near the surface of the cylinder $|\Delta(x)| = \Delta_0$ at $|x| \gg \xi_0$, and near its diametral plane at $|x| \ll l$. At $n = 3$ we have $\varphi(\pm\infty) = \pm\pi/3$, and at $n = 1$ we have $\varphi(\pm\infty) = \pm\pi$. In the vicinity of the core of the *amplitude soliton* $\varphi(x) = (\pi/2)\operatorname{sgn}(x - x_0)$ *the charge of the soliton* is

$$e_s = \frac{e}{\pi}\left[(\varphi(+\infty) - \varphi(x_0 + 0)) + (\varphi(x_0 - 0) - \varphi(-\infty))\right]$$

We obtain

$$n = 1: \quad e_s = 2e; \qquad n = 3: \quad e_s = \tfrac{1}{3}e$$

A *fractional charge* was obtained *for spin solitons* at $n = 3$ in [47]. This effect was recently investigated in a discrete model in [40, 41].

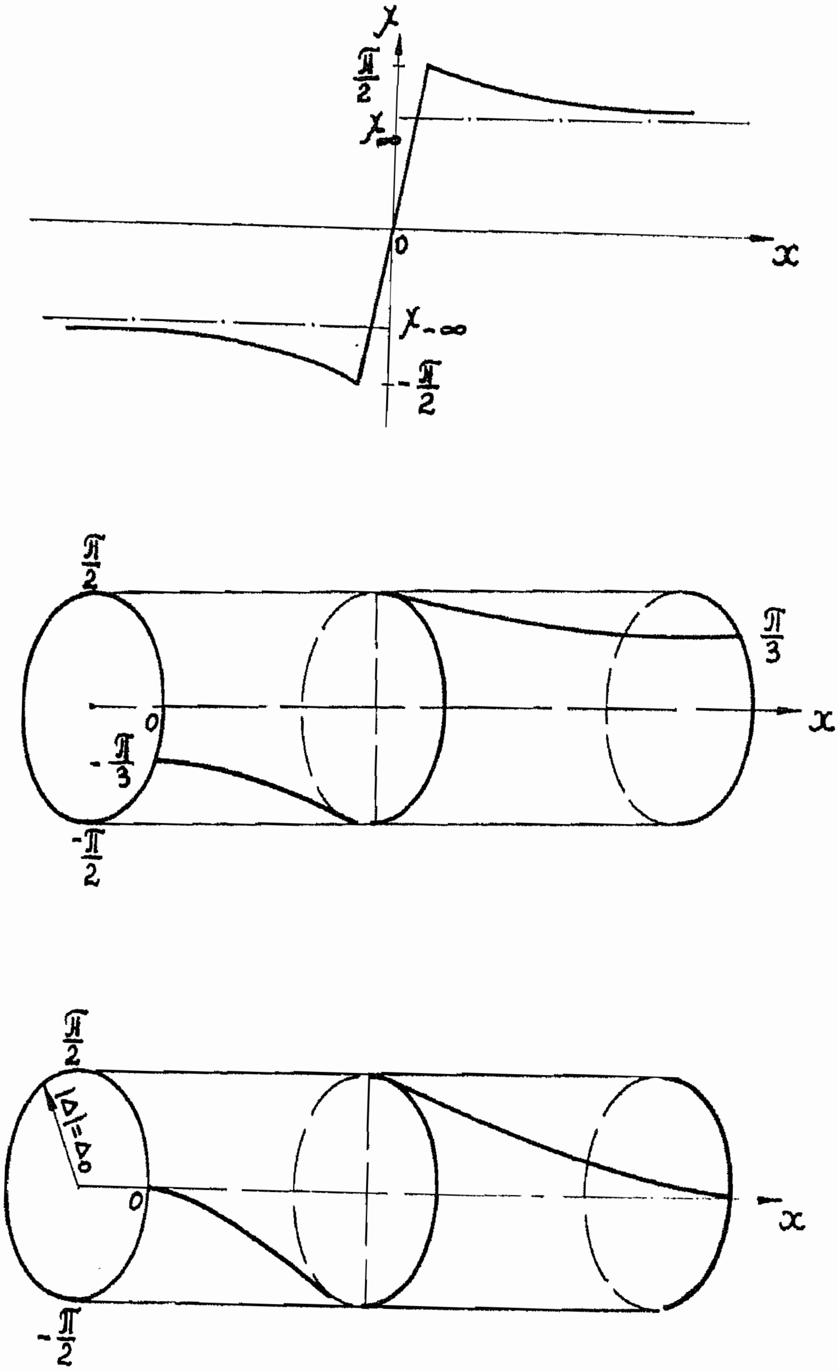
χ
$\frac{\pi}{2}$
χ_{∞}
0
x
$\chi_{-\infty}$
$-\frac{\pi}{2}$
$\frac{\pi}{2}$
$\frac{\pi}{3}$
0
x
$-\frac{\pi}{3}$
$-\frac{\pi}{2}$
$\frac{\pi}{2}$
$|\Delta|=\Delta_0$
0
x
$-\frac{\pi}{2}$

Figure 5

§3 Spin and Charge Solitons in the Peierls Model for Systems with Double Commensurability

In this section we consider systems in which the number of electrons ρ per unit cell in the metallic phase is equal to unity, $\rho = 1$, i.e., the initial band is almost half-filled. In this case $2p_F = \pi/a$, meaning that the period of the *superstructure* in the *Peierls states* is doubled compared with the period of the main structure. These are precisely the systems on which interest was focused in both the experimental and theoretical investigations. As shown in chapter I, §2, the stationary states of such a system are extrema of the energy functional of the *model B*

$$W\{\Delta\} = \sum_{E \leqslant \mu} E\{\Delta\} + \int dx \frac{\Delta^2}{g^2} \tag{1}$$

$$\hat{H}\bar{\psi} = E\bar{\psi}; \qquad \hat{H} = -i\hbar v_F \frac{\partial}{\partial x}\hat{\sigma}_z + \Delta\hat{\sigma}_y \tag{2}$$

$$\bar{\psi} = (\psi_+, \psi_-); \qquad \psi(x) = \psi_+ \exp\left\{\frac{i\pi}{2a}x\right\} + \psi_- \exp\left\{-\frac{i\pi}{2a}x\right\} \tag{3}$$

The extrema of the functional (1) obviously correspond to the extrema of the functional (2.3) of *model A* on the class of functions $\Delta(x)$ such that $\Delta_1 \equiv 0$ and $\Delta = i\Delta_2$. Therefore, by varying the functional (1) we obtain Eqs. (2.4, 5) and (2.7) at $\Delta_1 \equiv 0$. Now, however, we must not take into account Eq. (2.6) and its corollaries (2.19a) and (2.21), which are the results of varying the functional (2.3) with respect to $\Delta_1(x)$. In the upshot we obtain all the results described in Chapter II, §2, items 1–9, with the exception of the connection (2.23a) between θ_0 and ν_0. (Inasmuch as only the field amplitude $\Delta(x)$ changes now, we have $\theta = \pi/2$ at any ν_0).

We arrive at the conclusion that in *model B* the soliton can carry an arbitrary number of bound states $\nu_0 = 0; 1; 2$, and its shape and energy do not depend on ν_0. The corresponding *soliton charge* will be $e_s = -e$, 0, or $+e$, and the spin $s = 0$, $1/2$, or zero. Obviously, allowance for the Coulomb interaction should lift the *soliton energy degeneracy with respect to the charge* e_s. In first order in $e^2/\hbar v_F$ we should have

$$W_s = \frac{2\Delta_0}{\pi}\left[1 + C\frac{e_s^2}{\hbar v_F}\right]; \qquad C\sim 1 \tag{4}$$

The determination of the coefficient C is difficult because of the need for taking into account the variance of the dielectric constant $E(q)$ (1.6), which is substantial at $q\sim\xi_0^{-1}$. The appearance of solitons with $\nu_0 = 0$ and 2 can be attributed to the *topological stability* in a system with *discrete degeneracy of the ground state* ($\Delta\to -\Delta$) compared with the case of continual symmetry ($\Delta\to\Delta e^{i\chi}$). In the latter case, which was considered in §2, the *stability of the soliton with* $\nu_0 = 1$ was caused only by energy factors. However, the coincidence of the *shape and energy of the solitons* at all $\nu_0 = 0$, 1, and 2 is an unexpected property of the *Peierls model.*

Besides *topological solitons*, which bind different vacuum states of the system $\Delta(+\infty) = -\Delta(-\infty)$, there exist also *nontopological self-trapped states*, for which $\Delta(-\infty) = \Delta(+\infty)$. Their form can be obtained from Eq. (2.15), which under the symmetrical asymptotic conditions

$$\Delta(\pm\infty) = \Delta_0$$

takes the form

$$(\Delta')^2 = (\Delta - \Delta_0)^2(\Delta^2 + 2\Delta_0\Delta + \tilde{A}) \tag{5}$$

In analogy with the parameter θ_0 in §2, the constant $\tilde{A}$ in (5) must be determined from the *self-consistency equation* (2.7) or, in simpler manner, from the energy-minimum condition.

The electron spectrum in the presence of symmetrical deformation, $\Delta(x)$, defined by Eq. (5), has two local levels $\pm E_b$. As a result of simple calculations we find that the *symmetrical soliton* is stable only if the local levels $\pm E_b$ are so occupied that the total spin of the electrons is $S = 1/2$. This condition means either that the level $-E_b$ is doubly filled and the level $+E_b$ is singly filled, or else that the level $+E_b$ is empty and the level $-E_b$ is singly filled. The *soliton charge* is accordingly $e_s = +e$ or $e_s = -e$. In this case $A = 1 + 3/(2\sqrt{2} + 3)$, and from (5) we obtain the soliton shape

$$\Delta(x) = \Delta_0\left[1 - \frac{1}{1 + \sqrt{2}\,\mathrm{ch}\left(\sqrt{2}\,x/\xi_0\right)}\right] \tag{6}$$

The *total energy of the soliton* E_s and of the local level E_b are equal to

$$E_s = \frac{2\sqrt{2}}{\pi}\Delta_0 \approx 0.9\Delta_0\,; \qquad E_b = \frac{\Delta_0}{\sqrt{2}}$$

The *distribution of the charge* $\rho(x)$ and *of the spin* $\sigma(x)$ *in the soliton* now coincide and are determined only by the bound-state wave function $\psi_b(x)$

$$\rho(x) = 2\sigma(x) = |\psi_b(x)|^2 = 2^{-3/2}\xi_0^{-1}\left[1 - \Delta_0^{-2}\Delta^2(x)\right]$$

$$\psi_b(x) = \frac{1}{2^{5/4}\Delta_0\xi_0^{1/2}}\left(-\left(\Delta_0^2 - \Delta^2 - \Delta^1\right)^{1/2}, i\left(\Delta_0^2 - \Delta^2 + \Delta^1\right)^{1/2}\right)$$

Thus, a symmetrical soliton is perfectly analogous to a normal electron or hole polaron. We note that despite the deep self-trapping of the electron, the *total polaron energy* hardly differs numerically from the energy of the free electron or hole.

It must be borne in mind that the small value of the total self-trapping energy of one electron

$$\delta E = \Delta_0 - E_p \approx 0.1\Delta_0$$

can cause the polaron (6) to become a metastable state in real matter. The stability of this particle will be particularly sensitive to *electron hops between the chains*. In a system of ordered chains, the minimum energy will be possessed not by the polaron, but by the electron in the band state with energy $\Delta_0 - t_\perp$, where $t_\perp$ is the *integral of the hopping between the chains*.

Equivalent states were known in the *Gross–Neveu model* [61]. For the *Peierls model* they were first obtained by computer simulation of the self-trapping of one electron by Su and Schrieffer [39], and analytically by Brazovskii and Kirova [17, 32] and later by Bishop and Campbell [63].

A classification of the electronic excitations in the Peierls *model B* for the case of *double commensurability* is given in the table of §2 of chapter I. We have *polarons* with quantum numbers corresponding to normal electrons and holes: $s = 1/2$, $e_p = \pm e$, as well as *solitons* with *anomalous quantum numbers*: $s = 0$ and $e_s \pm e$, or else $s = 1/2$ and $e_s = 0$.

We emphasize once more that in the *incommensurate Peierls–Fröhlich model A* there is only one type of excitation, shown in the first column of the table of §2, chapter I. The problem of the crossover between such different electronic spectra of electronic excitations is solved in chapter IV.

§4 Elementary Excitations in Combined Dielectrics: the Bipolaron Problem

Generally speaking, there is no degeneracy of the ground state in combined dielectrics. Therefore the existence of single solitons such as kinks is impossible even in an isolated chain. In a weak field of external dimerization, Δ_e, however, (see I, §2, model C), the general arguments of §1 concerning strong self-trapping remain in force. Therefore the excited or injected electrons or holes, as well as particle pairs, will form *deep polarons*. The lattice deformation Δ_i should have identical asymptotic values $\Delta_i(+\infty) = \Delta_i(-\infty)$ as for the polaron in *model B*. An exception is the case of "*orthogonal external dimerization*," $\varphi = \pi/2$ (see I, §2), when the ground state of the system is doubly degenerate. In this case, self-trapping of a pair of particles would produce two *solitons of the kink type* (II.2.16) with energy (II.2.23) at a fixed value of θ (see Fig. 3a):

$$\varphi = \frac{\pi}{2}: \quad \Delta_1 = \Delta_e ; \qquad \Delta_2(x) = \Delta_i(x); \qquad th\theta = \frac{|\Delta_i(\infty)|}{\Delta_e}$$

In the continual *model C*, the energy functional of the system is of the form (I.2.12). For the homogeneous state $\Delta_i = \text{const}$, $E =$

$-\sqrt{(\hbar v k)^2 + |\Delta|^2}$ we obtain

$$\frac{W}{L} = \frac{|\Delta|^2}{\pi\hbar v}\left[\lambda^{-1} - \ln\frac{D}{|\Delta|} - \frac{1}{2}\right]$$
$$- \frac{2\Delta_e \cos\varphi}{g^2}\left(|\Delta|^2 - \Delta_e^2 \sin^2\varphi\right)^{1/2} + \frac{\Delta_e^2}{g^2}\cos 2\varphi \qquad (1)$$

where $\lambda = g^2/\pi\hbar v$ and D is an energy of the order of the width of the electron band. At equilibrium $(\partial W/\partial\Delta_i)_{\Delta e,\varphi} = 0$ we have $|\Delta| = \bar{\Delta}$ at $\Delta_i = \delta_\infty$ (see Fig. 3b), whence

$$\left(\frac{\bar{\Delta}^2}{\Delta_e^2} - \sin^2\varphi\right)^{1/2} \ln\frac{\bar{\Delta}}{\Delta_0} = \frac{\cos\varphi}{\lambda}$$
$$\bar{\Delta} = |\Delta| = \left[(\Delta_e \sin\varphi)^2 + (\delta_\infty + \Delta_e \cos\varphi)^2\right]^{1/2} \qquad (2)$$

Here $\Delta_0 \sim D\exp(-1/\lambda)$ is the gap in the limit $\Delta_e = 0$ (*model B*). The absolute minimum of (1), according to (2), is always located at $\bar{\Delta} > \Delta_0$, $\Delta_e \sin\varphi$ and $\bar{\Delta} > \Delta_e$, so long as $\Delta_e \ll D$. In the limit $\varphi = \pi/2$ we obtain $|\bar{\Delta}| = \max\{\Delta_e, \Delta_0\}$, i.e., $\Delta_i = \pm\sqrt{\Delta_0^2 - \Delta_e^2}$ at $\Delta_e < \Delta_0$, and there is no spontaneous dimerization, $\Delta_i = 0$, at $\Delta_e > \Delta_0$. At $\varphi \neq \pi/2$ we always have $\Delta_i \neq 0$. In the case of cis-CH$_x$ we can expect both Δ_e and Δ_i to result mainly from the change of the lengths of the bonds, which corresponds to $\varphi = 0$. In the isomers of (CH)$_x$ we have $2\bar{\Delta} = 2$ eV and $2\Delta_0 = 1.5$ eV, i.e., in cis-(CH)$_x$ we have $\Delta_i/\Delta_e = 3/\lambda - 1 = 5$, and the dimerization remains mainly spontaneous. Altogether we see from (2) that $\Delta_i > \Delta_e$ already at $\bar{\Delta} < (\Delta_0 D)^{1/2}$, i.e., in semiconducting polymers there is always a wide range of parameters for which the effect of spontaneous Peierls dimerization Δ_i is comparable with or exceeds the external effect Δ_e.

The *inhomogeneous self-trapped states*, which are stationary carriers of the charge and (or) of the spin, are also extremals of the functional of *model C*, defined by formulas (1.1.1, 4, 16, 17).* At a small number

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*All the necessary formulas can be obtained in the limit of low density, $n \to 0$, from the general periodic solution of the problem for *model C*, obtained in III, §4.

of trapped fermions (electrons ν_e or holes ν_h)

$$\nu = \nu_e + \nu_h = 0; 1; 2$$

the exact solution for $\Delta_i(x)$ is of the form

$$\Delta_i(x) = \delta_\infty \left\{ 1 - \left[th\left(\frac{x}{\xi} + \frac{\alpha}{2} \right) - th\left(\frac{x}{\xi} - \frac{\alpha}{2} \right) \right] \right\} - \Delta_e \cos \varphi$$

$$\delta_\infty = \left(\bar{\Delta}^2 - \Delta_e^2 \sin^2 \varphi \right)^{1/2}; \qquad \xi = \xi_\infty cth \alpha, \tag{3}$$

where α is a parameter to be determined. At $\alpha \ll 1$

$$\frac{\Delta_i - \delta_\infty}{\delta_\infty} \approx \frac{-2\alpha^2}{1 + \mathrm{ch}\, \dfrac{2\alpha^2 x}{\xi_\infty}}$$

and (4) describes a *shallow polaron*. At $\alpha \gg 1$ we have $\xi \approx \xi_\infty$ and (4) takes the form of two domain walls separated by a distance $d = \xi_\infty \alpha$ (Fig. 6a). The energy of the local states is

$$\pm E_b = \pm \sqrt{\Delta_e^2 \sin^2 \varphi + \delta_\infty^2 \mathrm{ch}^{-2} \alpha}$$

and their occupation numbers are $\nu_+ = \nu_e$ and $\nu_- = 2 - \nu_h$,

$$\nu_e + \nu_h = 2 + \nu_+ - \nu_- = \nu$$

The total excitation energy is

$$E_\nu = \frac{4}{\pi} \bar{\Delta} \left[\left\{ \frac{\pi}{4} \nu \cos \beta + \sin \beta - \beta \cos \beta \right\} + \gamma(\alpha - th\alpha) \right] \tag{4}$$

where

$$\cos \beta = \frac{E_b}{\bar{\Delta}}; \qquad \gamma = \Delta_e \cos \varphi / \lambda \bar{\Delta}$$

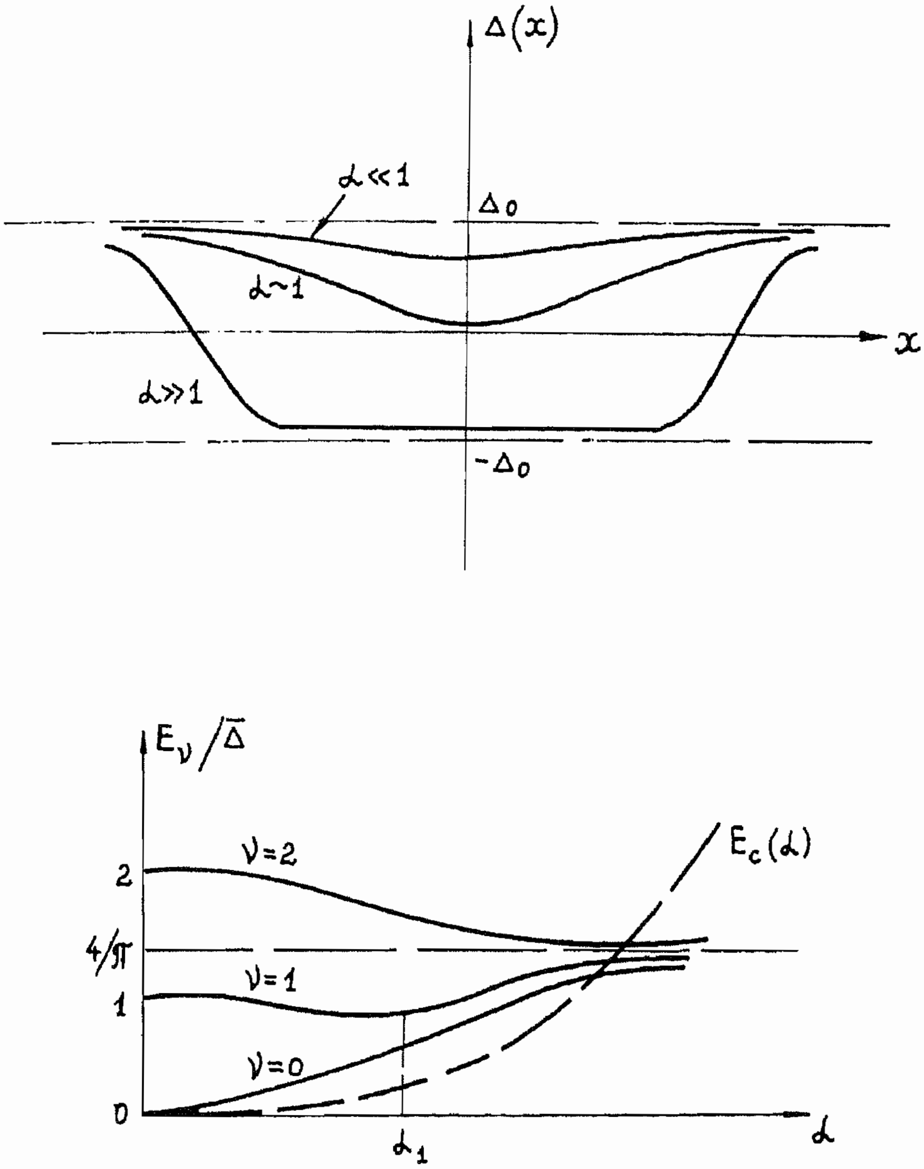

Figure 6

$E_\nu(\alpha)$ reaches a minimum $E_\nu = E_\nu(\alpha_\nu)$ at $\alpha = \alpha_\nu$, determined from the equation

$$\left(\delta_\infty^2/\bar{\Delta}^2 - \sin^2\beta\right)\left(\nu - \frac{4\beta}{\pi}\right) = 4\gamma \sin\beta \cos\beta$$
$$\beta = \beta(\alpha) \qquad (5)$$

The charge and the dipole moment of the excitation are equal to

($P_\nu \neq 0$ whenever $\varphi \neq 0$)

$$e^* = (\nu_e - \nu_h)e$$

$$P_\nu(\alpha) = e\xi_\infty \alpha \left(\frac{4}{\pi} \beta - \nu \right) \frac{\sqrt{1 - \sin^2\beta cth^2\alpha}}{th\alpha \cos \beta} \tag{6}$$

$$\alpha = \alpha_\nu , \qquad \beta = \beta(\alpha_\nu)$$

The terms $E_\nu(\alpha)$ are shown in Fig. 6b by solid lines in the limit $\gamma = 0$ (*model B*). The dashed curve is a plot of the additional term in (4) $E_c(a) \sim \gamma$, which differs from zero for systems described by *model C* at $\varphi \neq \pi/2$. If $\gamma \ll 1$, then $\alpha_2 \gg 1$ and the excitation can be regarded as a bound state of two domain walls. In this case

$$E_2(\alpha) = \mathscr{F} d, \qquad d = \alpha\xi, \qquad \text{where} \quad \mathscr{F} = 4\gamma\bar{\Delta}/\pi\xi_\infty$$

$\mathscr{F}$ is the distance-independent attraction force between the walls. According to (6), the charges of remote walls are equal to

$$(\nu_3 - 2\beta_\infty/\pi)e \quad \text{and} \quad -(\nu_h - 2\beta_\infty/\pi)e$$

where $\sin \beta_\infty = \delta_\infty/\bar{\Delta}$, which agrees with the results of §2.

In the absence of excited states of the particles (the lower curve, $\nu = 0$) the domain walls are attracted already at $\gamma = 0$, so that the gap becomes homogeneous, $\Delta(x) \equiv \bar{\Delta}$. For one fermion (the middle curve $\nu = 1$), a polaron state is produced, which goes over in the limit as $\gamma \to 0$ into the polaron of model B of §3. Its properties do not change qualitatively on going from model B ($\gamma = 0$) to model C. In contrast to the isolated *domain walls* for model B, the *polaron* carries both a charge $\pm e$ and a spin 1/2.

For the fermion pair $e + e$, $e + h$, or $h + h$ (the upper curve, $\nu = 2$) two domain walls that repel each other at $\gamma = 0$ are produced. At $\gamma \neq 0$, however, a bound state is formed, with $\alpha = \alpha_2(\gamma)$ determined from (5). We note that according to (2) we cannot have $\gamma \gg 1$. At $\gamma \sim 1$, the Coulomb repulsion

$$U_Q \sim e^2/\epsilon\xi$$

(ϵ is the low-frequency *dielectric constant*), which was not taken into account, assumes a greater role, whereas according to (4) we have at $\alpha \ll 1$

$$E_2 \approx \bar{\Delta}\xi_\infty^2/4\xi^2$$

A rough estimate yields

$$E_2 > U_Q \qquad \text{at} \quad \gamma < \frac{\epsilon\hbar v_F}{e^2} \sim \frac{\xi_\infty^2}{S_1}$$

In the opposite case, the neutral pair $\nu_e = \nu_h = 1$ will be a *Mott exciton*, and the charged pair (*bipolaron* $\nu_e = 2$, $\nu_h = 0$ or $\nu_e = 0$, $\nu_h = 2$) breaks up into two *polarons* $(\nu = 2) \to 2(\nu = 1)$.

The results enable us to interpret a number of experimental data [20], namely: the large photoresponse time in *trans*-$(CH)_x$ is attributed to the formation, after a time $\tau \sim \omega_{ph}^{-1} \sim 10^{-13}$ sec, of *domain walls* that move apart. The potential barrier of the repelling walls prevents intersection of the localization regions of e and h, thus delaying their recombination. The exponential growth of the *photoconductivity* in the region from 1.1 eV to 1.5 eV can be attributed [44] *to fluctuational Urbach absorption* (§1) from the threshold of the production of the separated domain walls ($(4/\pi)\Delta = 1.0$ eV) to the production of free $e - h$ pairs. The absence of recorded *photoconductivity* and, on the contrary, the observation of *luminescence* in cis-$(CH)_x$ agrees with the *confinement principle*. A strong electron-phonon interaction manifests itself in experiments on *Raman scattering* near $2\bar{\Delta}$. The absence of paramagnetism in doped *polyphenylene* $(C_6H_4)_x$ [see Fig. 1d)] can be evidence of the existence of *bipolarons*. The microscopic theory of polyphenylene as a combined dielectric was developed by Brazovskii, Kirova, and Matveenko (unpublished). It was found that the role of $\Delta_i(x)$ is played by the *libronic mode* of the rotation of the benzene rings around the molecule axis. The large width of the forbidden band $\sim$3 eV does not make it possible to employ quantitatively the continual *model C*. It was found, however [33], that a realistic model of polyphenylene admits of an exact solution in analogy with the *discrete Peierls model* (III, §2).

Formation of *tight-binding polarons* might be revealed by the suppression of their direct optical excitation and by the strong anisotropy of the diffusion registered in accord with NMR data for the spin components (polarons with $\nu = 1$). The absence of photoconductivity at a pronounced absorption peak may be evidence of *self-trapping of e-h pairs*. The growth of the conductivity upon doping or upon injection, without an increase of a paramagnetic response, in systems described by model C, can point to formation of *e-e* (or *h-h*) *bipolarons*. Since the bipolarons are spinless ($S = 0$) charged ($e_{bp} = \pm 2e$) particles, their gas with concentration $c \ll \xi_\infty^{-1}$ can become superconducting. The transition temperature T_c can be estimated with the aid of the results of [64]

$$T_c/\delta_\infty \sim C\xi_\infty \left(\frac{\hbar\omega_{ph}}{\delta_\infty} \right)^{2-2b} \left(\frac{\hbar\omega_\perp}{\delta_\infty} \right)^{b}$$

where ω_{ph} is the frequency of a phonon corresponding to the deformation Δ_i, $\omega_\perp$ is the frequency of the bipolaron jumps between the filaments, and $b \approx 2/3$. It is recognized here that the *bipolarons* form a *quasi-one-dimensional Bose gas* with strong repulsion between the particles on one chain. The particle density C is assumed to be high enough for the collision frequency $\tau^{-1} \sim \hbar n^2/M_{bp}$ to be large compared with $\omega_\perp$. $M_{bp} \sim \bar{\Delta}/(\xi_\infty \omega_{ph})^2$ is the bipolaron mass.

III Periodic Superstructure in One-Dimensional Models of the Peierls Effect

In this chapter we consider in detail the ground state of a one-dimensional *Peierls system*. In the previously investigated models it was regarded as homogeneous, $\Delta(x) = \text{const}$. This, however, no longer holds even in continual models when the atomic concentration ρ of the electrons changes in the vicinity of $\rho = 1$. In a discrete model that takes into account both the superstructure and the host lattice, the ground state cannot be regarded at all as homogeneous.

In §1 we investigated the ground state of the *model B* in a wide range of ρ, bounded only by the condition $|\rho - 1| \ll 1$. We investigate *the evolution of the superstructure* $\Delta(x)$ from a *lattice of solitons* of the type of II, §3, at $\rho \approx 1$, to an almost *sinusoidal superstructure* at $|\rho - 1| \gg \Delta$. We obtain the changes of the electronic spectrum and of the thermodynamic functions. We solve thereby the problems of the *commensurability effects* near the point $\rho = 0$ and of the *crossover from the model B to model A* with change of ρ.

In §2 we present the results of a solution of the *discrete Peierls model* (1.2.20, 21, 23), which takes into account the effects of the finite width and of the curvature of the electronic band and the compressibility of the host lattice. These results show that for physical quantities considered at constant pressure the conclusions of the continual model are applicable in the case of weak binding.

In §3 we consider the *optical absorption* for the band structure obtained in §1. We investigate transitions between different singular points of the electron spectrum. We show that all the direct transitions located above the first absorption threshold are dipole-forbidden. We shall consider the restoration of the transitions when the long-range order of the periodic structure is destroyed. We obtain the *broadening of the fundamental edge* when the soliton lattice melts in the limit as $\rho \to 1$. We show that the qualitative change of the *absorption spectrum as* $\rho \to 1$ is due to the coming together of the sequence of transitions in which *umklapp processes* take part.

In §4 we consider the periodic structure for the ground state in the model C, which corresponds to a doped *combined dielectric*. A complete description of the problem is presented, based on a simple hypothesis but without resorting to the special mathematical formalism used in the complete solution. In various limiting cases the results give the relations used in chapters II and III.

§1 Ground State of One-Dimensional System Near the Double Commensurability Point

We consider a one-dimensional system in which the number of electrons per unit cell of the undeformed (metallic) phase is close to unity, $\rho \approx 1$, meaning that the initial band is almost half-filled. The study of such systems was carried out quite actively in connection with experimental investigations of doped polyacetylene, trans-$(CH)_x$.

From the viewpoint of the theory we can point independently to a number of problems that call for a special investigation of the region $\rho \approx 1$. First, as mentioned in chapter I, §2, the system states with $\rho = 1$ and with $|\rho - 1| \sim 1$ are described by different *models*, *B and A*, having different electron as well as phonon properties. The homogeneous state $\Delta = \text{const}$ in the *complex-field model A* is strongly inhomogeneous from the point of view of the model of the real field: if $\Delta_A \approx$ const, then

$$\Delta_B \approx \Delta_A \sin\left[\frac{\pi}{a}(\rho - 1)(x - x_0)\right], \qquad 1 \gg |\rho - 1| \gg \frac{\Delta_A}{D} \tag{1}$$

Second, as shown in chapter II, §3, introduction of additional electrons in *Peierls dielectrics* with $\rho = 1$ leads to formation of *solitons* with a local level lying at the center of the forbidden band. Consequently, as $\rho \rightarrow 1$ the deformation should take the form of a *soliton lattice* that goes over at $|\rho - 1| \sim 1$ into the *sinusoidal structure* (1). In this case the midgap state of the soliton gives rise to a new allowed band located symmetrically relative to the center of the metal band $E = 0$. The width of the new band E_- turns out to be comparable with Δ_1 when the distance between solitons is of the order of $\xi_1 = \hbar v_F/\Delta_1$, i.e., at an electron density $n = |\rho - 1|/a \sim \xi_1^{-1}$

$$\Delta_1 = \Delta_B(x)|_{\rho = 1} = \text{const}$$

An investigation of this crossover region calls for an exact solution of the problem of the ground state of the *model B*, §1.2, at arbitrary ρ. This solution was first obtained by Brazovskii, Gordyunin, and Kirova [49], and independently by Horovitz [50]. A number of the results of [49] were later derived anew in [51].

A more convenient form of the results was obtained in a paper by Brazovskii, Dzaloshinskii, and Kirova [52] as a particular case of the solution of the more general problem expounded in chapter IV. The first results on the behavior of the *model B* as $\rho \rightarrow 1$ were obtained by Kotani [66] on the basis of numerical methods. An attempt by Rice and Timonen [67] to investigate the problem on the basis of the phenomenological Ginzburg–Landau model for $\Delta(x)$ led to an incorrect result namely that the deformation vanishes at a certain critical ρ. We present below the main results of an exact solution.

We express the *lattice-deformation potential* $\Phi(x)$ and the electron wave functions $\psi(x)$ in the form

$$\Phi(x) = \Delta(x)\sin(\pi x/a);$$

$$\psi_E(x) = \sqrt{2}\left[U_E(x)\cos\frac{\hbar x}{a} + iV_E(x)\sin\frac{\pi x}{a} \right]$$

$\Delta(x) = \Delta_1 =$ const corresponds to *doubling of the period* at $\rho = 1$. The energy functional $W\{\Delta, U, V\}$ of the system is of the same form as in II.2.3 (here and hereafter $v_F = 1$) at $\Delta_1 = 0$ and $\Delta_2(x) = \Delta(x)$

$$W\{\Delta, U_E, V_E\} = \int dx\left[\frac{\Delta^2}{g^2} + \sum_{E \leqslant \mu} \left[-i(U_E^* V_E' + V_E^* U_E') + i\Delta(V_E^* U_E - U_E^* V_E) \right] \right] \qquad (2)$$

where the energy levels E and the chemical potential μ are reckoned from the center of the metallic-phase band. From (2) follow the Dirac equations for U and V

$$U_E' - \Delta U_E = iEV_E; \qquad V_E' + \Delta V_E = iEU_E \qquad (3)$$

or

$$U_E'' + \left[E^2 - P(x)\right]U_E = 0; \qquad V_E'' + \left[E^2 - Q(x)\right]V_E = 0$$
$$P(x) = \Delta^2 + \Delta' \qquad Q(x) = \Delta^2 - \Delta' \qquad (4)$$

and the *self-consistency condition*

$$\frac{\Delta}{g^2} = \frac{1}{2i} \sum_{E \leqslant \mu} (U_E^* V_E - V_E^* U_E) = -\sum_{E \leqslant \mu} \frac{1}{E}\left(\Delta + \frac{1}{2}\frac{d}{dx}\right)V_E^* V_E \qquad (5)$$

In contrast to the investigation carried out in II, §§2, 3, we must seek a periodic and not a solitary solution of the system (2)–(5). As will be shown* in III, §4, the periodic solution of the problem of finding the extremum of the functional (2) satisfies the equation

$$\Delta''' - 6\Delta^2\Delta' + A\Delta' = 0 \qquad \text{where} \quad P''' - 6PP' + AP' = 0;$$
$$Q''' - 6QQ' + AQ' = 0 \tag{6}$$

Choosing $A = \Delta_k^2(1 + k^{-2})$, $0 \leqslant k \leqslant 1$, we obtain

$$\Delta(x) = \Delta_t sn(\xi, k); \qquad \xi = x\Delta_k/k; \qquad k = k(P) \tag{6a}$$

The functions $\Delta(x)$, $P(x)$, and $Q(x)$ have a period $l = 4kK(k)/\Delta_k$, where $K(k)$ is a complete elliptic integral of the first kind [78]. It is known [57, 58] that the spectrum of the Schrödinger equation (4) with a potential satisfying Eq. (6) has only one forbidden band: $E_-^2 \leqslant E^2 \leqslant E_+^2$.

The following connection exists between the parameters k, Δ_k and E_+, E_-

$$k = \frac{E_+ - E_-}{E_+ + E_-}; \qquad \Delta_k = E_+ - E_-; \qquad \frac{E_-}{E_+} = r' = \sqrt{1 - r^2} = \frac{1-k}{1+k} \tag{7}$$

The *spectrum of the electronic states* consists of three allowed bands

$$Z_1:\ E \leqslant -E_+; \qquad Z_2:\ -E_- \leqslant E \leqslant E_-; \qquad Z_3:\ E_+ \leqslant E$$

which are separated by two forbidden bands

$$G_1:\ -E_+ \leqslant E \leqslant -E_-; \qquad G_2:\ E_- \leqslant E \leqslant E_+$$

as shown in Fig. 7.

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*All the results presented below follow from the formulas of Chapter III, §4 for *model C* in the limit

$$\Delta_e = \Delta_1 = E_1 = 0; \qquad E_2 = E_-; \qquad E_3 = E_+.$$

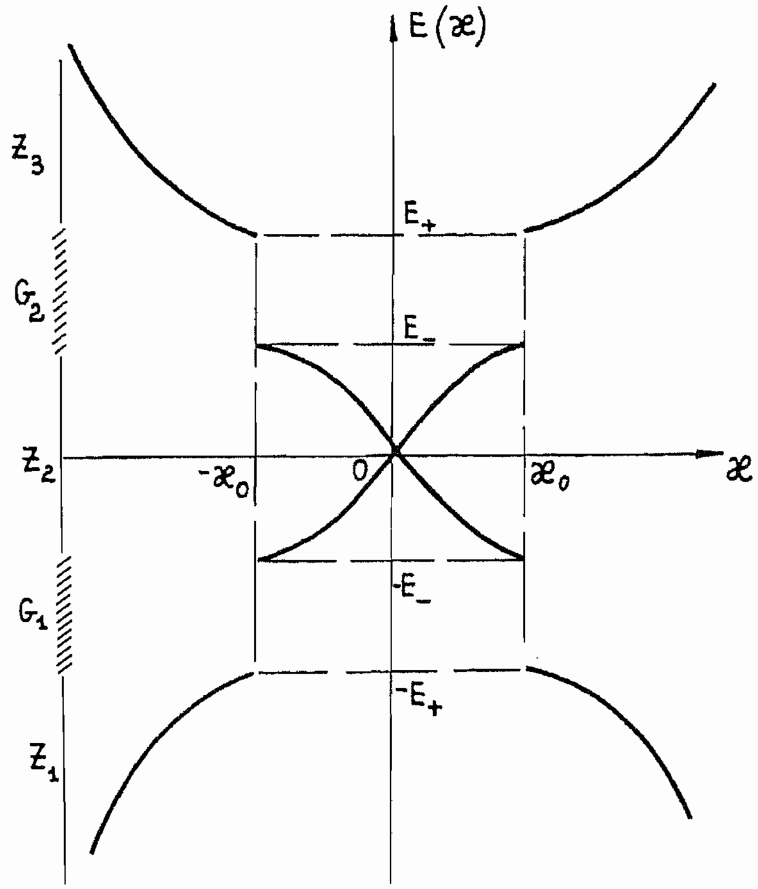

Figure 7

The *state density* in the allowed bands is equal to

$$\frac{1}{L}\,\frac{dN}{dE}=\frac{2}{\pi}\,\frac{|(E^2-S)|}{R^{1/2}(E)} \tag{8}$$

where*

$$R(E)=(E^2-E_+^2)(E^2-E_-^2) \tag{9}$$

$$\begin{gathered} 2S=-\overline{\Delta^2}+E_+^2+E_-^2=E_+^2\,E(r)/K(r) \\ r=\left[1-E_-^2/E_+^2\right]^{1/2}=2\sqrt{k}\,/(1+k) \end{gathered} \tag{10}$$

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* $K(r)$ and $E(r)$ are complete elliptic integrals of kind I and II, respectively [78].

The components of the electron wave function in the allowed bands can be written in the form

$$U_E = \left| \frac{p+b}{2L(b-S)} \right|^{1/2} \exp\left\{ \pm 2iR(E) \int_0^x \frac{dy}{P(y)+b} \right\}$$

$$V_E = \pm \left| \frac{Q(x)+b}{2L(b-S)} \right|^{1/2} \exp\left\{ \pm 2iR(E) \int_0^x \frac{dy}{Q(y)+b} \right\} \quad (11)$$

$$b = b(E) = 2E^2 - \Delta_k^2(1 + k^{-2})/2$$

They correspond to a wave vector κ equal to

$$\kappa = \pm 2R(E) \left\langle \frac{1}{P+b} \right\rangle \quad (12)$$

The $\pm$ sign in (11) coincides with the sign of the derivative $d\kappa/dE$. The *band boundaries* are located at $\kappa = \pm\kappa_0$, where

$$\kappa_0 = \frac{\pi}{l} = \frac{\pi}{4\hbar v_F} \frac{\Delta_k}{kK(k)} = \frac{1}{2\hbar v_F} \frac{E_+}{K(r)} \quad (13)$$

The *spectrum of the electronic state* is shown in Fig. 7.

The determination of the parameters E_+ and E_-, or equivalently of k and Δ_k, depends on the electron distribution in the quasi-one-dimensional system. We consider a situation wherein the electron density n on the chain is given, $n = |\rho - 1|/a$. In this case, as follows from the results of chapter IV, the central band Z_2 should be either empty if $\rho < 1$, or filled if $\rho > 1$. (We shall assume below, for the sake of argument, that $\rho < 1$). In addition to the rigorous result, this filling corresponds to intuitive notions concerning the formation of a soliton lattice at $|\rho - 1| \ll a/\xi_1$ with empty ($\rho < 1$) or doubly filled ($\rho > 1$) midgap state. At $|\rho - 1| \sim 1$, the forbidden band (G_1 at $\rho < 1$ or G_2 at $\rho > 1$) should coincide with the gap Δ at the Fermi points $\pm k_F$ for the Peierls–Fröhlich *model A*. The second gap, which is symmetric with respect to the center of the band, drops out in this case from the region where the model A is applicable.

The number of states in the central band Z_2, with account taken of the two branches of the spectrum and of the spin degeneracy, is

$$N_2 = 2 \cdot 2L \cdot \frac{2\kappa_0}{2\pi} = \frac{4}{\pi} L\kappa_0 \tag{14}$$

Accordingly, the *numbers of the states* in bands Z_1 and Z_3 decrease by

$$\delta N_1 = \delta N_3 = -\frac{1}{2} N_2 = \frac{2}{\pi} L\kappa_0 \tag{15}$$

This value should coincide with the change of the total number of particles relative to the case of a half-filled band. We obtain

$$n = \frac{|\rho - 1|}{a} = \frac{2}{\pi} \kappa_0 = \frac{E_+}{K(r)\hbar v_F} \tag{16}$$

The *self-consistency condition* (5) takes the form

$$\frac{\pi}{g^2} + \int_{E<-E_+} \frac{E\,dE}{\left\{(E^2 - E_+^2)(E^2 - E_-^2)\right\}^{1/2}} = 0 \tag{17}$$

The logarithmic divergence at the lower integration limit is eliminated by subtracting from (17) the analogous equation at $\rho = 1$, when

$$E_- = 0; \qquad E_+ = \Delta_1 \sim \epsilon_F e^{-1/\lambda}; \qquad \epsilon_F = \text{const} \tag{18}$$

As a result we obtain the simple self-consistency condition

$$E_+^2 - E_-^2 = \Delta_1^2 = \text{const} \tag{19}$$

Substituting (19) in (16) we obtain an equation for the dependence of the single parameter r on the density n:

$$rK(r) = \frac{\Delta_1}{n\hbar v_F}; \qquad r = r(n) \tag{20}$$

The remaining quantities can be easily expressed with the aid of Eqs. (7) in terms of r and of the constant Δ_1

$$E_+ = \frac{\Delta_1}{r}; \qquad E_- = \frac{\Delta_1\sqrt{1 - r^2}}{r}; \qquad \Delta_k = \Delta_1\sqrt{k}$$
$$k = (1 - r')/(1 + r') \tag{21}$$

The change of the energy of the system compared with $\rho = 1$ is

$$W_\rho - W_1 = W(E_+, E_-) - W(\Delta_1, 0) = \frac{\langle \Delta^2 \rangle}{g^2}$$

$$+ \int \frac{dE}{\pi} E \left[\frac{1}{\sqrt{(E^2 - E_-^2)(E^2 - E_+^2)}} - \frac{1}{E\sqrt{E^2 - \Delta_1^2}} \right]$$

$$= \frac{1}{2\pi\hbar v_F} \left[-E_+^2 - E_-^2 + 4E_+^2 \frac{E(r)}{K(r)} \right] \tag{22}$$

Substituting expressions (21) for E_1 and E_1, we obtain finally

$$W_\rho - W_1 = \delta W(n) = \frac{\Delta_1^2}{2\pi\hbar v_F} \left[1 - \frac{2}{r^2} + \frac{4}{r^2} \frac{E(r)}{K(r)} \right] \tag{23}$$

where $r = r(n)$ is determined from (20). The chemical potential of the electrons is

$$\mu = \frac{\partial W}{\partial n} = \frac{2}{\pi} \frac{\Delta_1}{r} E(r) \tag{24}$$

Expressions (11) for the wave functions enable us also to calculate the *local densities* $w(x)$ of the energy and $\rho(x)$ of the particle number. We have

$$w(x) = \frac{\Delta^2(x)}{g^2} + \int_{E \leqslant -E_+} E \frac{dN}{dE} \left[U_E^* U_E + V_E^* V_E \right] dE$$

$$= \Delta^2(x) \left[\frac{1}{g^2} + \frac{1}{\pi} \int_{E \leqslant -E_+} \frac{E\, dE}{\left[(E^2 - E_+^2)(E^2 - E_-^2) \right]^{1/2}} \right]$$

$$+ \sum E \tag{25}$$

The first term in (25) vanishes by virtue of the *self-consistency* *condition* (17). Consequently, $w(x) = W/L$, i.e., the energy of the system, just as in the case of one soliton, remains homogeneous.

For the *particle-number density* $\rho(x)$ we obtain at $\rho < 1$

$$\rho(x) - \rho = \sum_E \left(U_E^* U_E + V_E^* V_E - 1/L \right)$$

$$= \frac{1}{\pi \hbar v_F \Delta_1} r K(r') \left[\Delta^2(x) - \overline{\Delta^2} \right] \tag{26}$$

In the limit as $\rho - 1$ we obtain

$$\Delta(x) \simeq \Delta_1 th(\Delta_1 x); \qquad \rho(x) \sim -1/2\mathrm{ch}^2(\Delta_1 x) \tag{27}$$

$$\mu = E_s \left[1 + \frac{E_-^2}{2n\hbar v_F} + O(E_-^4) \right] \tag{28}$$

$$E_s = \frac{2}{\pi} \Delta_1$$

$$E_+ = \Delta_1, \qquad E_- \approx 4\Delta_1 \exp(-\Delta_1/n)$$

Equations (27) show that the lattice deformation and the charge distribution as $\rho \to 1$ correspond to the dilute lattice of *charged solitons* investigated in chapter II. The quantity E_s in (28) coincides with the soliton energy. The next term in (28) yields *the repulsion energy*, which decreases exponentially with distance between the solitons.

In the limit $n \gg \Delta_1/\hbar v_F$, $|\rho - 1| \gg \Delta_1 a/\hbar v_F$ we have

$$W(n) - W(0) = \frac{\pi}{4} n^2 \hbar v_F + \frac{\Delta_1^2 - \Delta^2(n)}{2\pi \hbar v_F} \tag{29}$$

where

$$\Delta(n) = (E_+ - E_-)/2 \approx \Delta_1^2 / 2\pi n \hbar v_F \sim \frac{D^2}{n\hbar v_F} e^{-2/\lambda}$$

$$E_+ = E_- \approx \frac{\pi}{2} n \hbar v_F \tag{30}$$

$E_g = 2\Delta(n)$ is the gap on the Fermi surface.

The connection (29) between $W(n)$ and $\Delta(n)$ corresponds to the *energy of a "homogeneous" Peierls–Fröhlich state in model A*. The first term is the change of the energy of the metallic phase compared with $\rho = 1$. The difference between the arguments of the exponentials in Eq. (30) for Δ and Eq. (18) for Δ_1 can be interpreted as a decrease, by a factor of 2, of the electron-phonon interaction constant λ on going through the region $n \sim \Delta_1$, owing to the suppression of the *umklapp processes*. Actually, however, there exists a strong pre-exponential dependence, so that we can write the interpolation formula

$$\Delta(n) \simeq \Delta_1^2/\max(\delta\epsilon_F, \Delta_1); \qquad \delta\epsilon_F = \frac{\pi}{2}\hbar v_F n \tag{31}$$

where $\delta\epsilon_F$ is the shift of the Fermi level in the metallic phase away from the center of the band.

§2 Results of Exact Solution of Discrete Peierls Models

In this section we present the results of an investigation of the exactly solvable discrete Peierls model formulated in chapter I, §2. A consistent solution together with the necessary results from the *spectral theory of Schrödinger difference operators* is given in the paper of Brazovskii, Dzyaloshinskii, and Krichever [35]. We recall that the model D, defined by formulas (I.2.20–23) in the weak-binding limit $\lambda = (\pi\kappa c)^{-1} \ll 1$ and at $|\rho - 1| \ll 1$ goes over approximately into the continual *model B* investigated in §1. At arbitrary λ and ρ we have the following results.

The ground state of the *model D* for the lattice $x_n = na + u_n$ is an *incommensurate doubly periodic structure*. It can be regarded as a superposition of two sublattices with even and odd n, shifted relative to each other, and with periods

$$N_\rho = 2/|\rho - 1|:$$

$$u_n = u(n - n_0) = \frac{1}{2}\ln\frac{\theta((n - n_0 - 1)/N_\rho + (-1)^n/4)}{\theta((n - n_0 + 1)/N_\rho + (-1)^n/4)} \tag{1}$$

$$\theta(\xi) = \theta_4(\xi, \tau); \qquad \tau = iK'/K; \qquad K' = K(k')$$

where θ_i are the *elliptic Weierstrass functions* and K and K' are *elliptic integrals* [78].

We note that n_0 in (1) is an arbitrary, generally speaking, integer so that the ground state is continuously degenerate with respect to *translation of the superstructure*, despite the absence of translational invariance in the energy functional (I.2.20–23). This result, of course, is the consequence of the special degeneracy of the model and is closely connected with its exact integrability.

The deformations (1) are accompanied by the appearance of *charge density waves*, defined as the local *electron-density distribution*:

$$\rho_n = 2 \sum_{E \leqslant \mu} |\psi_n(E)|^2 = \rho + \frac{N_0}{4} \frac{K'}{K} \frac{\partial}{\partial n_0} u(n - n_0) \tag{2}$$

The parameters $\tau = \tau(\rho)$ or $k = k(\rho)$ are determined from the *self-consistency condition*

$$\begin{gathered} \frac{K(r)}{cnu} \frac{\theta(0)}{\theta^2(|\rho - 1|/2)} = \pi\kappa\bar{c}; \qquad r = dnu \\ u = K(k)|\rho - 1|; \qquad \bar{c} = e^{-a} \end{gathered} \tag{3}$$

where $cnu = cn(u, k)$ etc. (dnu, snu) are the *Jacobi elliptic functions* [78].

At arbitrary $\rho \neq 0$, 1, or 2 the *electronic spectrum* consists of three allowed bands $(-E_m, -E_+)$, $(-E_-, E_-)$, and (E_+, E_m). The chemical potential lies in one of the forbidden bands $(-E_+, -E_-)$ or (E_-, E_+), depending on whether $0 < \rho < 1$ or $1 < \rho < 2$. The band edges E_-, E_+, and E_m are defined by the following expressions:

$$E_m = 2\bar{c} \frac{\theta\left(\frac{1 - |\rho - 1|}{2}\right) \theta\left(\frac{|\rho - 1|}{2}\right)}{\theta\left(\frac{1}{2}\right) \theta(0)}; \qquad \frac{E_+}{E_m} = snu \tag{4}$$

$$\frac{E_-}{E_+} = \frac{k'}{dnu}$$

The ground-state energy $W_0(\rho, a)$ (per molecule) is equal to

$$N^{-1}W_0 = \frac{K^2(r)}{\pi^2\kappa}\left[1 + \frac{sn^2u\,dn^2u}{cn^2u} - 4\frac{E(r)}{K(r)} - \frac{snu}{K(k)}\,\frac{\theta'(1/2 - |\rho - 1|/2)}{\theta(1/2 - |\rho - 1|/2)}\right] \tag{5}$$

For the pressure $P(\rho, a)$ we obtain

$$P = N^{-1}\left(\frac{\partial W_0}{\partial a}\right)_\rho = \frac{2}{\pi^2}\,\frac{K(r)}{\kappa}\left[1 + \frac{sn^2u\,dn^2u}{cn^2u} - 2\frac{E(r)}{K(r)}\right] \tag{6}$$

The parameters k, u, and r in expressions (4)–(6) must be determined from the relations (3).

In the weak-interaction limit

$$\lambda_\rho = \left[\pi\kappa\bar{c}\cos\left(\frac{\pi}{2}|\rho - 1|\right)\right]^{-1} \ll 1$$

$$|\rho - 1| \gg e^{-1/\lambda_1}$$

we obtain from (3) and (4)

$$\begin{aligned} &E_m \approx 2\bar{c}; \qquad E_+/E_m \approx E_-/E_m \approx \sin(\pi|\rho - 1|/2) \\ &E_+^2 - E_-^2 = \Delta_\rho^2\cos^2(\pi|\rho - 1|/2); \qquad \Delta_\rho = 8\bar{c}e^{-1/\lambda_\rho} \end{aligned} \tag{7}$$

The approximate relations (7) are a generalization of the results obtained for the *continual Peierls–Fröhlich models* in §1. They must be refined when the ground state of the system acquires the character of a *soliton lattice*. This occurs in fact at $\rho \to 1$, $\rho \to 0$, and $\rho \to 2$.

At $\rho(2 - \rho) \ll 1/\kappa c$ we arrive at the limit of the isolated *self-trapped state—bipolaron*. The problem of the transition of the *Peierls–Fröhlich state* into a *dilute polaron lattice* was solved by Belokolos [43] for the continual *model E*.

In the case of interest to us, $\rho \approx 1$ and $|\rho - 1| \ll \exp\cdot(-1/\lambda_1)$, we have a *loose lattice of kinks*. For an isolated *kink* we obtain from (1) and (2)

$$u_{2n} = \frac{1}{2}\ln\frac{\mathrm{ch}\left[\alpha(n-n_0-1/2)\right]}{\mathrm{ch}\left[\alpha(n-n_0+1/2)\right]}$$

$$u_{2n+1} = \mathrm{const}$$

$$\rho_{2n} - \rho = \frac{1}{2}\left[th(\alpha(n-n_0-1/2)) - th(\alpha(n-n_0+1/2))\right]$$

$$\rho_{2n+1} = \rho; \qquad \sum_n \rho_{2n} = 1$$

$$\alpha = \tfrac{1}{2}e^{-1/\lambda_1}$$

We note that for an isolated kink only every other site takes part in the deformation and in *the redistribution of the charge.*

For the *electron spectrum* we obtain

$$E_m \approx 2\bar{c}, \qquad E_+ \approx \Delta_1; \qquad E_- = 4\Delta_1 \exp\{-8\alpha/|\rho-1|\} \qquad |\rho-1| \ll \alpha \tag{8}$$

We consider in the same limit expressions (3)–(6), leaving out terms $\sim O(E_-/\Delta_1)$, which are exponentially small when the distances between the solitons are $N_\rho = 2|\rho-1|^{-1}$. This approximation corresponds to the limit $k \to 1$, $|\tau| \to |\rho-1|$ in expressions (3)–(6). We obtain:

$$rK(r)\left(\frac{1+r'}{r}\right)^{|\rho-1|} = \pi\kappa\bar{c} \tag{9}$$

$$w_0 = \frac{K^2(r)}{\pi\kappa}\left[2 - r^2 - 4\frac{E(r)}{K(r)} + 2r'|\rho-1|\right] \tag{10}$$

$$P = \frac{2}{\pi^2\kappa}K^2(r)\left[2 - r^2 - 2\frac{E(r)}{K(r)}\right] \tag{11}$$

Using (9)–(11) we obtain the following: an expression for the system energy $w_0(\rho)$ at a given length either pressure

$$w_0(\rho) = w_0(1) + E_s|\rho - 1| + O\left(\frac{E_-}{\Delta_1}\right) \tag{12}$$

where $E_s = |\mu|$ is the *soliton energy*.

We note that

$$\left(\frac{\partial \mu}{\partial \rho}\right)_P = O(\exp\{-8\alpha/|\rho - 1|\})$$

just as for the continual model B, §1. In contrast to Horovitz's calculations [50], we find that $\partial\mu/\partial\rho > 0$, i.e., the system is thermodynamically stable.

In the *weak-interaction limit* we obtain $E_s = (2/\pi)\Delta_1$.

We note that Eq. (9) leads to a linear dependence of the average length on the concentration $|\rho - 1|$.

§3 Optical Absorption and Dielectric Constant in a State with Periodic Superstructure

The *band structure* of *the electron spectrum* in a *Peierls dielectric*, described in §§1 and 2 of this chapter, can be experimentally investigated by optical methods. An investigation of the optical properties is particularly important for a substance with *a weak coupling between the chains*, when the spectrum of *the single-particle state* of the system differs substantially, as a result of the *self-trapping effects*, from the band states at a fixed deformation $\Delta(x)$.

The investigations of the kinetic and thermodynamic properties can in this case yield information only on solitons. For *optical absorption*, however, owing to the condition $\Delta \gg \hbar\omega_{ph}$, the *Franck–Condon principle* holds, according to which light absorption takes place at a fixed lattice configuration. Therefore, by studying the light absorption we can obtain information on the band structure of the ground state. Naturally, for a *Peierls dielectric* greatest interest attaches to an investigation of the region $\rho \approx 1$, where qualitative changes of the band structure take place.

In this region we must trace the manner in which the fundamental absorption edge $\hbar\omega = 2\Delta_1$ and the absorption threshold on the local

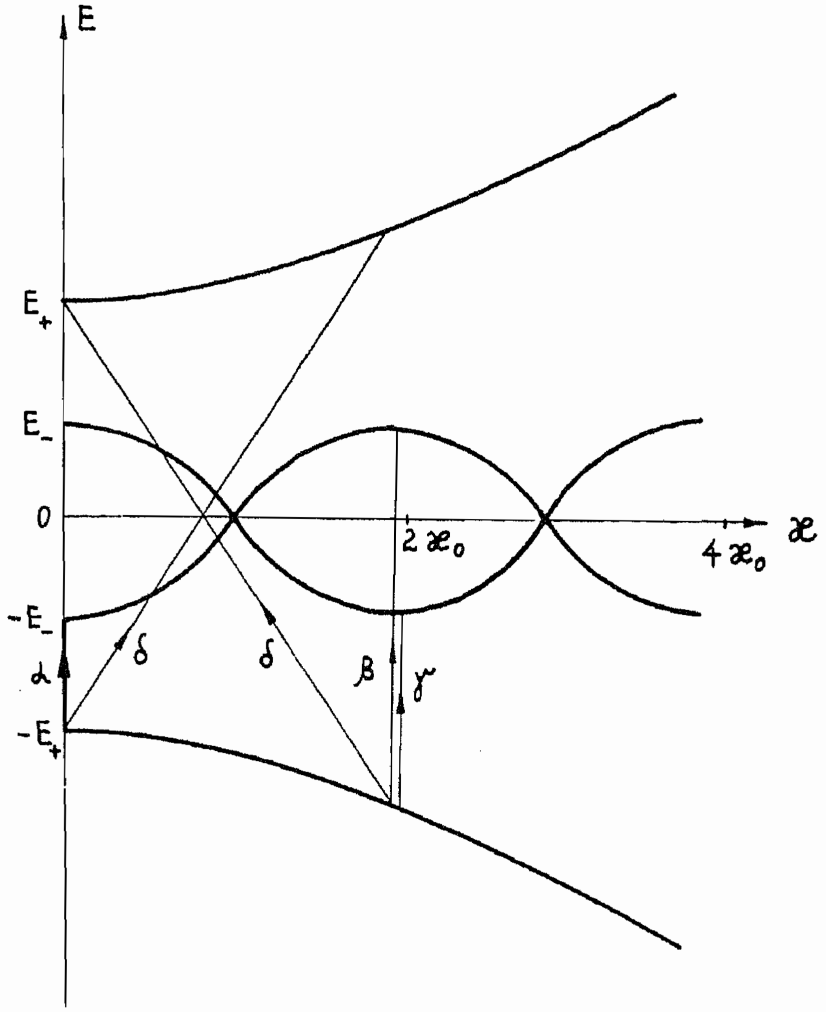

Figure 8

level of the soliton $\hbar\omega = \Delta_1$ go over as $\rho \to 1$ into the fundamental edge $\hbar\omega = 2\Delta(\rho)$ for *model A* at $|\rho - 1| \sim 1$. It is also of interest to us to ascertain whether the second (G_2 at $\rho < 1$) forbidden band can be optically observed (Fig. 8).

From among the low-frequency optical properties, of principal interest is the process of the establishment of the *Fröhlich conductivity* from the *dielectric constant* (II.1.6) for *model B*. This problem can be solved in the long-wave limit with the aid of the thermodynamic functions obtained in §§1 and 2 for the Peierls model.

To calculate the optical absorption we use the usual expression for the imaginary part of the dielectric constant in the dipole approximation

$$\epsilon_2(\omega) = \frac{4\pi}{\omega^2 S_\perp L} \sum_{1,2} |J_{12}|^2 \delta(E_2 - E_1 - \omega\hbar) \tag{1}$$

where L is the length of the system, $S_\perp$ is the cross section per chain, J_{12} is the matrix element of the current operator $\hat{J}$. In the (ψ_+, ψ_-) representation we obviously have $\hat{J} = ev_F \cdot \hat{\sigma}_z$. Consequently, in the representation (1.2) we have

$$J_{12} = ev_F \int \tilde{\psi}_1^* \hat{\sigma}_x \tilde{\psi}_2 \, dx, \qquad \tilde{\psi} = (U, V) \tag{2}$$

It is obvious that optical transitions proceed with conservation of the quasimomentum, and the total momentum κ is conserved, generally speaking, accurate to within the reciprocal-lattice vector: $\kappa_2 - \kappa_1 = 2\kappa_0 m$.* Equation (1) takes the form

$$\epsilon_2(\omega) = \frac{4\pi e^2 v_F^2}{\omega^2 S_\perp} \sum_{m=0,\pm 1,\ldots} \int \frac{d\kappa}{2\pi} \delta(E_2(\kappa + 2\kappa_0 m) - E_1(\kappa) - \omega) \cdot \left| \int (U_2^*(\kappa + 2\kappa_0 m) V_1(\kappa) + V_2^*(\kappa + 2\kappa_0 m) U_1(\kappa) \, dx \right|^2 \tag{3}$$

We consider now the principal optical transitions, assuming that $\rho < 1$.

3.1 *Absorption from Z_1 into Z_3 (Transition d in Fig. 8)*

For a direct transition with $m = 0$ we obtain with the aid of (III.1)

$$J_\delta^{(0)} = 2ev_F \int U_2^* U_1 \left[i\Delta(x) \left(\frac{E_1}{b_1 + P} - \frac{E_2}{b_2 + P} \right) - \frac{R_1}{b_1 + P} + \frac{R_2}{b_2 + P} \right] dx \tag{4}$$

where $R_i = R(E_i)$ is defined in (1.9). Since $E_2 = -E_1$, $R_2 = R_1$, and $b_2 = b_1$, we obtain as a result of (1.11)

$$J_\delta^{(0)} = \frac{ev_F E_2}{(\bar{P} + b_2) L} \int \Delta(x) \, dx = 0 \tag{5}$$

Consequently, this transition is forbidden in the dipole approximation for an ideal periodic system, i.e., there is no absorption threshold at $\hbar\omega = 2E_+$.

---

* Everywhere in this paragraph m, m_1, m_2 are integers.

For transitions with $m \neq 0$, we write down the matrix element in a form that is more convenient for our case. As a result of (1.11) we have

$$J_\delta^{(m)} = \frac{ev_F L}{l} \int_0^{l/2} dx \left\{ (U_2^* V_1 + V_2^* U_1) + \left[(\pm U_2^*)(\pm V_1) + (\pm V_2^*)(\pm U_1)\right] \times \exp\left\{ \frac{i\kappa_0 m^l}{2} \right\} \right\} \tag{6}$$

For transitions at $\kappa_1 \kappa_2 > 0$ we obtain from (6)

$$J_\delta^{(m)} = \frac{ev_F L}{l} \int_0^{l/2} (U_2^* V_1 + V_2^* U_1)\, dx \left[1 - (-1)^m\right]$$

Consequently, transitions with $m = 2m_1$ are forbidden. For transitions with $\kappa_1 \kappa_2 < 0$ we find similarly that transitions with $m = 2m_1 + 1$ are forbidden.

We consider now allowed transitions. Let $\kappa_1 \kappa_2 > 0$ and $\kappa_1 - \kappa_2 = (2m + 1)2\kappa_0$. Substituting expressions (1.11) in (6) we obtain after simple transformations

$$J_\delta^{(m)} = \frac{2ev_F}{\left[(\bar{P} + b_1)(\bar{Q} + b_2)\right]^{1/2}} \int_0^{l/4} \frac{dx}{l} \{ f(P, Q) - f(Q, P) \} \tag{7}$$

$$f(q, p) = \frac{1}{\left[(q + b_1)(p + b_2)\right]^{1/2}} \times \cos\left(2\epsilon_2 R_2 \int_0^x \frac{dy}{q + b_2} - 2\epsilon R_1 \int_0^x \frac{dy}{p + b_2} \right)$$

$$\epsilon_i = |E_i|$$

Transitions with $m \neq 0$ are most significant in the limit $\rho \to 1$ $\xi_1 \kappa_0 \ll 1 \xi_1 = \hbar v_F / \Delta_1$, when the transition frequencies become close in value.

In this limit we have for $0 < x < l/4$

$$\Delta \approx \Delta_1 th \frac{x}{\xi_1}, \quad P \approx \Delta_1^2; \quad Q \approx \Delta_1^2(1 - 2\,\mathrm{ch}^{-2}x/\xi_1)$$

$$\epsilon \approx \Delta_1\left[1 + \frac{1}{2}(\xi_1 \delta\kappa)^2\right] \quad \delta\kappa = \kappa - \kappa_0, \quad b = \Delta_1^2 + 2(\delta\kappa)^2; \quad R \approx \Delta_1 \delta\kappa$$

$$2\epsilon R \int_0^x \frac{dy}{Q + b} \approx \delta\kappa x + \frac{\pi}{2}; \quad 2\epsilon R \int_0^x \frac{dy}{P + b} \approx \delta\kappa x \tag{8}$$

Substituting (8) in (7) we obtain for the transitions ($Z_{1,\pm} \rightarrow Z_{3\mp}$)

$$J_\delta^{(2m+1)} = 4ev_F \int_0^{l/4} \frac{dx}{l}\, th \frac{x}{\xi_1} \sin\left[(\kappa_2 - \kappa_1)x\right] \approx \frac{ev_F}{\pi(2m + 1)} \tag{9}$$

Analogously, for the transitions ($Z_{1\pm} \rightarrow Z_{3\pm}$) we obtain

$$J_\delta^{(2m)} \approx ev_F / 2\pi m \tag{10}$$

Substituting (9) and (10) in (3) we obtain

$$\begin{aligned}\epsilon_2(\omega) &= \frac{\hbar^2\omega_p^2}{\Delta_1^2} + \sum_n \int \frac{d\kappa\, \hbar v_F}{(4\pi m)^2}\, \delta\left[2\Delta_1 - \hbar\omega + \frac{\Delta_1 \xi_1^2}{2}\left\{(\delta\kappa_1)^2 + (\delta\kappa_2)^2\right\}\right] \\ &= \frac{\hbar^2\omega_p^2}{32\pi^2\Delta_1^2} \sum_m \frac{\Delta_1 \theta\left[\omega\hbar - 2\Delta_1 - \dfrac{(\xi_1\kappa_0)^2\Delta_1}{2} - \dfrac{(\kappa_0\xi_1)^2(1 + 2m)^2\Delta_1}{2}\right]}{m^2\left[\Delta_1(\omega\hbar - 2\Delta_1) - \Delta_1^2(2m\xi_1\kappa_0)^2\right]^{1/2}}\end{aligned} \tag{11}$$

where $\theta(x)$ is the *Heaviside function*.

It follows from (11) that the *fundamental absorption edge* splits into a series of thresholds $\hbar\omega - 2\Delta_1 \approx 2(2m^2 + 2m + 1)(\kappa_0\xi_1)^2\Delta_1$, $m \geqslant 1$, with an intensity that decreases like $1/m^2$. At $\Delta_1 \gg \hbar\omega - 2\Delta_1 \gg (\kappa_0\xi_1)^2\Delta_1$, calculation of the sum in (11) leads to the expression

$$\epsilon_2(\omega) \approx \frac{\hbar^2\omega_p^2\theta(\hbar\omega - 2\Delta_1)}{16\Delta_1\left[\Delta_1(\hbar\omega - 2\Delta_1)\right]^{1/2}} \tag{12}$$

which agrees with the result for the absorption in a homogeneous *Peierls dielectric*. Thus, *umklapp processes* ensure continuity of the averaged *optical absorption* as $n \to 0$, even though the direct optical transition is forbidden.

3.2 Absorption from the Band Z_1 to the Band Z_2

For a transition to the lower edge of the Z_2 band at $\kappa_1 = \pm\kappa_0$, $\kappa_2 = \mp\kappa_0$, $m = 1$ (transition α of Fig. 8) we easily obtain from (3)

$$J_\alpha^{(1)} = \frac{e v_F}{2L\left(\bar{P}^2 - \Delta_1^4\right)^{1/2}} \int \left[\left(P(x) - \Delta_1^2\right)\left(Q(x) + \Delta_1^2\right)\right]^{1/2} dx$$

$$\epsilon_2(\omega) = \frac{4}{\hbar\omega^2 S_1} J^2 \left(\frac{M^*}{\hbar\omega - (E_+ - E_-)}\right)^{1/2}; \qquad \frac{1}{M^*} = \frac{1}{M_+} + \frac{1}{M_-} \tag{13}$$

The effective masses $M_\pm$ on the edges of the bands $E_\pm$ are therefore equal to, as a result of (1.8),

$$M_\pm = \frac{\Delta_1^2}{2v_F^2}\left(\frac{E(k)}{K(k)} - 1 \pm 1\right) \Big/ (1 \pm k)$$

At $n \gg \xi_1^{-1}$ we obtain from (13) an expression of the type (12), but with Δ_1 replaced by $\Delta_k/2$. This formula corresponds to absorption through a gap $E_g = \Delta_k$ in *model A* for the *Peierls–Fröhlich limit.*

For the transition to the upper edge of the band (transition β of Fig. 8) we obtain, using (6), at $m = 1$

$$J_\beta^{(i)} = 0$$

Consequently, in the dipole approximation the transition $\beta(Z_1 \to Z_2)$ is forbidden at all frequencies, i.e., there is no absorption threshold at $\hbar\omega = E_+ + E_-$. At low densities, just as for the $Z_1 \to Z_3$ transitions, processes with quasimomentum nonconservation become significant. We consider transitions from Z_1 and Z_2 with momentum change $\kappa_2 - \kappa_1 = 2\kappa_0 m$; $m > 1$. For the transitions $Z_\pm \to Z_\pm$ (transition γ of

Fig. 8) we obtain

$$J_{\gamma}^{(m)} = \frac{ev_F L}{l} \int_0^{l/2} (U_2^* V_1 + V_2^* U_1)(1 + (-1)^n)\,dx$$

i.e.,

$$J_{\gamma}^{(2n+1)} = 0$$

For the transitions $Z_{\pm} - Z_{\mp}$, on the contrary, $J_{\alpha}^{(2m)} = 0$. For the transitions γ with even n, $\kappa_2 - \kappa_1 = 2\kappa_0 2m$ we obtain in analogy with (12)

$$J_{\gamma}^{(2m)} = \frac{2ev_F}{l} \int_0^{l/4} \frac{dx}{\left[|(\bar{P} + b_2)(\bar{Q} + b_1)| \right]^{1/2}} \{ f(P, Q) - f(Q, P) \} \tag{14}$$

$$f(q, p) = \left[|(q + b_1)(p + b_2)| \right]^{1/2} \cos\left(2 \int_0^x dy \left[\frac{\epsilon_2 R_2}{|q + b_2|} - \frac{\epsilon_1 R_1}{|p + b_1|} \right] \right)$$

$$\epsilon_i = |E_i|$$

In the limit $n\xi_0 \ll 1$, $k \to 1$ we can calculate (14) by using approximate equations (18) and equations similar to them for the Z_2 band:

$$2\epsilon_2 R_2 \int_0^x \frac{dy}{|P + b_2|} \approx \delta\kappa x + \frac{\pi}{2}\,; \qquad 2\epsilon_2 R_2 \int_0^x \frac{dy}{|Q + b_1|} \approx \delta\kappa x$$

$$b_2 \approx -\Delta_1^2\,; \qquad M^* = M_+ \approx \frac{\Delta_1}{v_F^2}\,; \tag{15}$$

From (14) and (15) we obtain $J_{\gamma}^{(2m)} \approx \pi e v_F (n\xi_1)^{1/2}$, i.e., as $n \to 0$ the matrix element depends weakly on m. The same results are obtained by calculating the matrix elements $J_{\alpha}^{(m)}$ and $J_{\beta}^{(m)}$. Just as for absorption from Z_1 into Z_3, Eq. (11), we obtain a series of thresholds at $\hbar\omega - \Delta_1 \approx m^2(\xi_1\kappa_0)^2\Delta_1/2$. At $\Delta_1 \gg \hbar\omega - \Delta_1 \gg (\xi_1\kappa_0)^2\Delta_1$ we obtain in analogy with (12)

$$\epsilon_2(\omega) = \frac{\pi^2}{16}\,\xi_1 \frac{\hbar^2\omega_p^2}{\Delta_1^2} \left(\frac{2\Delta_1}{\hbar\omega - \Delta_1} \right)^{1/2} \theta(\hbar\omega - \Delta_1) \tag{16}$$

Equation (16) describes the *threshold of midgap absorption* by dilute solitons. We emphasize that it can be obtained only when account is taken of the quasimomentum nonconservation, whereas a strictly vertical transition disappears in the presence of a soliton [13].

3.3 Change of the Optical Properties Upon Violation of the Periodic Structure

In a real system there are always perturbations that cause its state, stationary or instantaneous, to differ from the periodic structure investigated above. These perturbations influence the optical properties of the system, particularly the transitions forbidden for an ideal periodic structure. We consider below the influence of the inhomogeneities on the absorption in the region of the edge ($\hbar\omega \approx 2E_+$) of the transitions from Z_1 into Z_3.

A distinction can be made between two characteristic inhomogeneity cases. The first is typical of high densities $n\xi_1 \gg 1$ and corresponds to smooth perturbations of the phase of the complex field Δ in *model A*. The second case is important for the limit of low densities $n\xi_1 \ll 1$, when strong disordering of the *lattice of loose solitons* is possible. Its results from thermal melting, quantum fluctuations, and, most importantly for the description of *polyacetylene*, from interaction with the doping impurities.

In the first case the long-range order may be violated, the correlation radius R_c becomes finite, but the short-range order is preserved. We can therefore use the same expressions for the current matrix elements (2) as for the ideal structure, but in expression (3) for the *dielectric constant* it is necessary to average over the long-range perturbations.

We consider a direct transition from Z_1 into Z_3 with $m = 0$ at $n\xi_1 \gg 1$. From (4 and 5) we obtain

$$\left\langle \left(J_\delta^{(0)}\right)^2 \right\rangle = \frac{e^2 v_F^2 E^2}{(\bar{P}+b)^2 L^2} \left\langle \int \Delta(x)\,\Delta(y)\,dy\,dx \right\rangle$$

$$= \frac{e^2 v_F^2 E^2 \int K(z)\,dz}{(\bar{P}+b)^2 L}\,; \qquad K(z) = \langle \Delta(z,t)\Delta(0,t) \rangle \quad (17)$$

where $\langle \ldots \rangle$ denotes averaging over all the perturbations due to impurities or to thermal or quantum fluctuations. From (17) and (1) we obtain at $\hbar\omega - 2E_{+} \ll \Delta_1$

$$\epsilon_2(\omega) = \frac{4\pi}{\omega^2 S_{\perp}\hbar}\left\langle \left(J_{\delta}^{(0)}\right)^2 \right\rangle \left(\frac{M_{+}}{\hbar\omega - 2E_{+}} \right)^{1/2} \tag{18}$$

In the limit when $n\xi_1 \gg 1$ and $k \ll 1$, which corresponds to the *Fröhlich model*, we have

$$\Delta(x) = \Delta_k \sin(2\kappa_0 x + \varphi(x)); \qquad 2\kappa_0 = \pi$$

Consequently

$$\left\langle \left(J_{\delta}^{(0)}\right)^2 \right\rangle = \frac{2E^2\Delta_k^2 e^2 v_F^2}{L(\bar{P}+b)^2} S(2\kappa_0); \qquad S(q) = \int \langle e^{i\varphi(x) - \varphi(y)} \rangle e^{iq(x-y)}\, dy \tag{19}$$

where $S(q)$ is the *structure factor*. It can be seen from (18) and (19) that $\epsilon_2(\omega) \sim L^{-1}$, i.e., even when inhomogeneities are taken into account there exists a threshold on $\hbar\omega = 2E_{+}$ only in a system of finite length. Since $S(q)$ is also very small, it can be concluded that the absorption considered is practically unobservable. Other causes that lead to a finite value of the matrix element of the direct transition from Z_1 to Z_3 may be the account of the nonzero light momentum and the higher multipole terms.

We consider now the case of low densities, when the system is a set of *randomly disposed solitons*. For a dilute system of solitons, the function $\Delta(x)$ can be approximately represented in the form

$$\Delta(x) = \Delta_1 \prod_{j=1}^{N} th\left\{ \frac{x - x_j}{\xi_1} \right\}; \qquad 0 \leqslant x < L \tag{20}$$

In (20) we have neglected corrections $\sim \exp(-1/n\xi_1)$, which are due to the soliton interaction. The wave functions U and V of the electrons are obtained with the same accuracy from (II.2.18).

For the states of the continuous spectrum

$$\begin{aligned} U_{2j,k}(x) &= \frac{\hbar k v_F + i\Delta_1 th \dfrac{x - x_{2j}}{\xi_1}}{\sqrt{2L}\, E_k} \exp\{ikx + i\varphi(2j-1)\} \\ V_{2j,k}(x) &= \frac{1}{\sqrt{2L}} \exp\{ikx + i\varphi(2j-1)\} \end{aligned} \qquad (21)$$

$$\frac{x_{2j} + x_{2j-1}}{2} < x < \frac{x_{2j} + x_{2j+1}}{2}$$

$$\begin{aligned} U_{2j-1,k}(x) &= \frac{1}{\sqrt{2L}} \exp\{ikx + i\varphi 2(j-1)\} \\ V_{2j-1,k}(x) &= \frac{\hbar k v_F + i\Delta_1 th \dfrac{x - x_{2j-1}}{\xi_1}}{\sqrt{2L}\, E_k} \exp\{ikx + i\varphi 2(j-1)\} \end{aligned} \qquad (22)$$

$$\frac{x_{2j-2} + x_{2j-1}}{2} < x < \frac{x_{2j-1} + x_{2j}}{2}$$

where $\exp(i\varphi) = (kv_F\hbar + i\Delta_1)E_k$; $E_k = \pm\epsilon_k = \pm\sqrt{\hbar^2 v_F^2 k^2 + \Delta_1^2}$, and U_j and V_j are functions of $U(x)$ and $V(x)$ in the vicinity of the jth soliton. For localized states with $E = 0$, the wave functions can be obtained in the *tight-binding approximation*

$$\begin{aligned} V_\alpha &= \sum_{j=1} \frac{A^\alpha_{2j-1}}{\sqrt{2\xi_1}\, \mathrm{ch}[(x - x_{2j-1})/\xi_1]} \\ U_\alpha &= \sum_{j=1} \frac{A^\alpha_{2j}}{\sqrt{2\xi_1}\, \mathrm{ch}[(x - x_{2j})/\xi_1]}\,; \qquad \sum_{j=1}^{N} A_j^\alpha (A_j^{\upsilon 1})^* = \delta_{\alpha\alpha} \end{aligned} \qquad (23)$$

$\alpha = 1, 2, \ldots, N$ where N is the number of *solitons*.

When substituting expressions (21) in (1) and (2) it must be borne in mind that owing to the inhomogeneity of the system the optical transitions will take place with arbitrary change of the momentum $p_1 \neq p_2$.

In the region of the *fundamental edge* $\hbar\omega = 2\Delta_1$ we obtain from (1), (2), and (21)

$$
\begin{aligned}
J(p_1, p_2) = \frac{ev_F}{2L} \sum_{j=1}^{N} e^{i(\varphi_1-\varphi_2)(j_1-j_2)}
&\times \left\{ \left[\exp\left(\frac{i}{2}(p_1-p_2)(x_{j+1}+x_j) \right) \right. \right. \\
&\left. - \exp\left(\frac{i}{2}(p_1-p_2)(x_j+x_{j-1}) \right) \right] \frac{i\hbar v_F}{p_1-p_2} \left(\frac{p_1}{\epsilon_{p_1}} - \frac{p_2}{\epsilon_{p_2}} \right) \\
&- \left[\exp\left(\frac{i}{2}(p_1-p_2)(x_j+x_{j+1}) \right) \right. \\
&+ \exp\left(\frac{i}{2}(p_1-p_2)(x_j+x_{j-1}) \right) \\
&\left. - \frac{\pi\hbar v_F(p_1-p_2)\exp(i(p_1-p_2)x_j)}{\Delta_1 \operatorname{sh}\left\{ \dfrac{\pi(p_1-p_2)}{2\Delta_i} \right\}} \right] \\
&\left. \times \frac{1}{p_1-p_2} \left(\frac{\Delta_1}{\epsilon_{p_2}} + \frac{\Delta_1}{\epsilon_{p_1}} \right) \right\} \qquad (24)
\end{aligned}
$$

where $\varphi_1 = \varphi(p_1)$, $\varphi_2 = \varphi(p_2)$; $x_0 = -x_1$; $x_{N+1} = 2L - x_N$, and $\epsilon_{p_i} = |E_{p_i}|$. Since, in the main, $p_1 - p_2 \sim n \ll \xi_1^{-1}$, we obtain from (24)

$$
\begin{aligned}
J(p_1, p_2) &= J(p, q) \\
&= \frac{ev_F^2\hbar}{2L\epsilon_p} \sum_{j=1}^{N} (-1)^{j-1} \\
&\quad \times \Bigg\{ i\big[\exp(iq(x_{j+1} + x_j)) - \exp(iq(x_j + x_{j-1}))\big] \\
&\quad - \frac{2\Delta_1}{\hbar v_F q}\big[\exp(iq(x_{j-1} + x_j) + \exp(iq(x_j + x_{j+1})) \\
&\quad - 2\exp(i2qx_j)\big]\Bigg\}; \\
&q = (p_1 - p_2)/2; \qquad p = (p_1 + p_2)/2
\end{aligned}
\tag{25}
$$

The first term in (25) vanishes at $q = 0$, and therefore makes no singular contribution to $\epsilon_2(\omega)$. Retaining in (25) the principal second term, we obtain

$$
J^2(q, p) = \frac{e^2\Delta_1^2 v_F^2}{\epsilon_p^2 q^2 L^2} \sum_{j,l} (-1)^{j+1} \exp(i2q(x_j - x_l)) \tag{26}
$$

Expression (26) must be averaged over the coordinates x_j. We shall assume that under the influence of the random fields of the impurities and of the thermal and quantum motion of the *solitons*, the coordinates x_j are randomly distributed and that their correlation is inessential. Then, using the Poisson distribution, we obtain at large N

$$
J^2(p, q) \approx \frac{e^2 v_F^2}{L^2(4c^2 + q^2)} \tag{27}
$$

It follows from (1) at $\hbar\omega \approx 2\Delta_1$ that

$$\epsilon_2(\omega) = \frac{4\pi e^2 L}{\hbar^2\omega^2 S_\perp} \int \frac{dq}{(2\pi)^2} \frac{\Delta_1 |J(p,q)|^2}{\left[\Delta_1(\hbar\omega - 2\Delta_1) - (\hbar v_F q)^2\right]^{1/2}} \tag{28}$$

Substituting (27) in (28) we obtain finally

$$\epsilon_2(\omega) = \frac{\hbar^2\omega_p^2}{4\Delta_1^2} \frac{\theta(\omega - 2\Delta_1)}{\left[(\xi_1)^2 + (\hbar\omega/\Delta_1 - 2)^2\right]^{1/2}} \tag{29}$$

It can be seen from (29) that the absorption peak becomes smoothed out at $\hbar\omega - 2\Delta_s \sim (\xi_1 n)^2\Delta_1$. For the transition into the middle band, using (1), (2), (21), and (23), we have

$$\epsilon_2(\omega) = \frac{\pi^2\omega_p^2 n\xi_1\hbar}{8\omega\left(\hbar^2\omega^2 - \Delta_1^2\right)^{1/2}} \frac{1}{\operatorname{ch}\left[\pi\left(\hbar^2\omega^2 - \Delta_1^2\right)^{1/2}/2\Delta_1\right]} \tag{30}$$

Equation (28) shows that absorption into the middle band is proportional to the number of solitons, i.e., it takes place for each soliton independently.

3.4 Summary of Results on Optical Absorption

The band structure of a *Peierls dielectric* with $\rho \neq 1$ electrons per atom has eight *Van Hove singularities* location at the points of the wave vectors $\pm\kappa_0$ at energies $\pm E_-$ and $\pm E_+$ (Fig. 7). For an ideal periodic structure, the *optical absorption coefficient* should have a singularity $\epsilon_2(\omega) \sim (\omega - \omega_i)^{-1/2}$ for the following transitions (formula 13):

$$\alpha : \{\pm\kappa_0, -E_+\} \to \{\mp\kappa_0, -E_-\}; \qquad \hbar\omega_i = E_+ - E_- = \Delta_k$$

The remaining transitions between the singular points are dipole-forbidden. Allowed transitions with change of momentum, which occur between singular and nonsingular points (Figs. 8 and 9a) are:

$$\beta : \{ \pm(\kappa_0 + (2m_1 - 1)2\kappa_0), E < -E_+ \}$$

$$\rightarrow \{ \mp \kappa_0, E_- \}; \qquad \hbar\omega_i > E_+ - E_-$$

$$\gamma : \{ \pm(\kappa_0 + 4m_1\kappa_0), E < -E_+ \}$$

$$\rightarrow \{ \pm \kappa_0, -E_- \}; \qquad \hbar\omega_i > E_+ - E_-$$

$$\delta : \{ \pm(-\kappa_0 + 2m_2\kappa_0), E < -E_+ \}$$

$$\rightarrow \{ \pm(2m_1 + 4m_2 - 3)\kappa_0, E > E_+ \}; \qquad \hbar\omega_i > 2E_+$$

where $m_1, m_2 = 1, 2, \ldots$

Near the transitions β, γ, and δ the absorption coefficient should have a threshold.

As $\rho \rightarrow 1$, $E_- \rightarrow 0$, and $\kappa_0 \rightarrow 0$ the transition frequencies δ with different m_1 and m_2 come closer together. As a result, the sum of transitions of type δ leads to the normal singularity $\epsilon_2(\omega) \sim (E - E_g)^{-1/2}$, $E_g = 2\Delta_1$, which is typical of *fundamental absorption* for the *Peierls state* with $\rho = 1$.

The frequencies of the transitions α, β, and γ also come closer together and lead to the singularity $\epsilon_2(\omega) \sim (1 - \rho)(\hbar\omega - \Delta_1)^{-1/2}$, which corresponds to transitions from the valence band $E < -\Delta_1$ to the local levels $E = 0$ of solitons with concentration $n = (1 - \rho)/a$. In the limit $n\xi_1 \gg 1$, the transition α assumes a form peculiar to the *fundamental absorption edge* for a *Peierls dielectric*.

The forbiddenness of the direct ($\kappa_0 \rightarrow \kappa_0$) dipole transitions is lifted when the periodic structure is disturbed. At $n\xi_1 \ll 1$, in a real system, the periodic structure should go over into a system of *randomly disposed solitons*. In this case (Fig. 9b) the transition δ becomes allowed, but the absorption peak becomes smeared out in the region $\hbar\omega - 2\Delta_1 \sim (n\xi_1)^2\Delta_1$. At $n\xi_1 \gg 1$, the structure becomes disturbed only at large distances $x \gg \hbar v_F / E_g$, on account of thermal and quantum fluctuations and under the influence of random potentials. As a

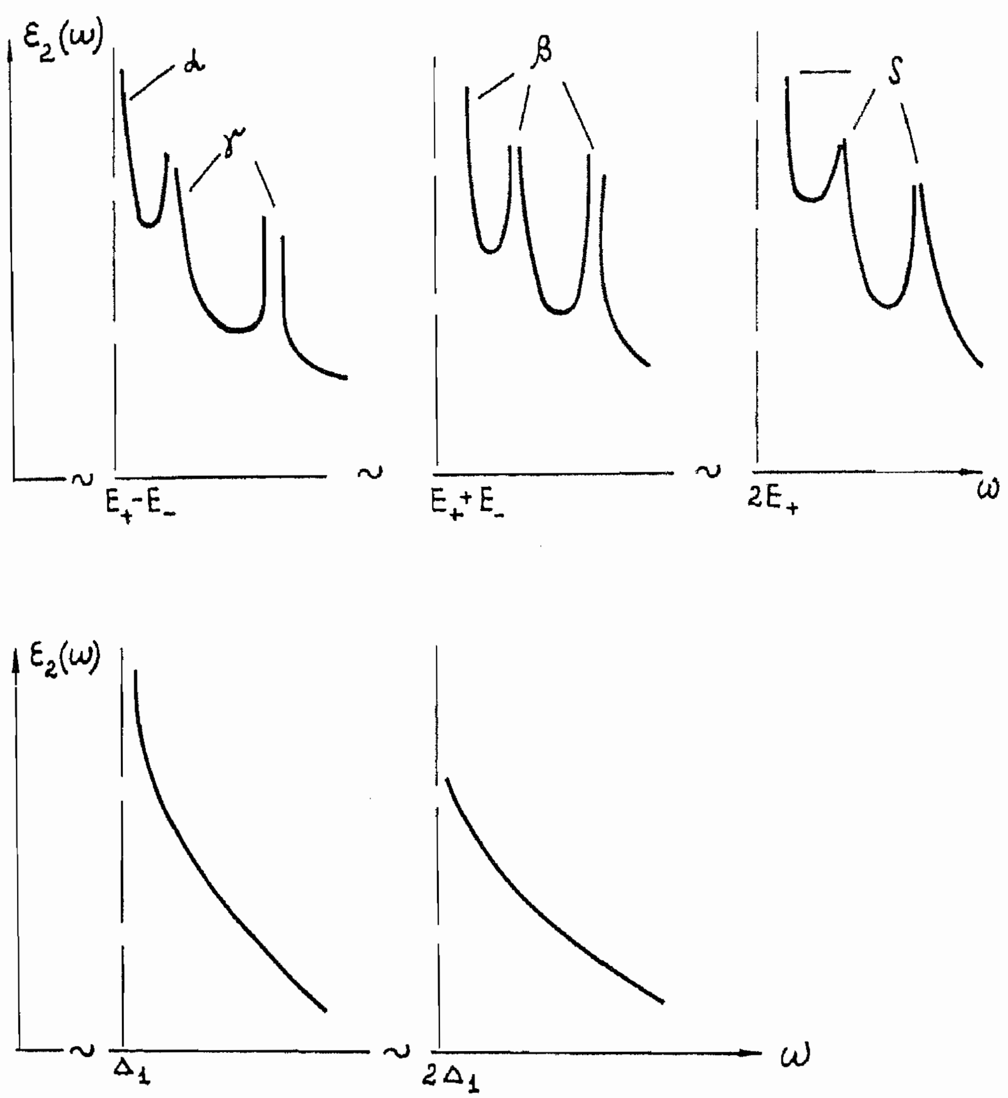

Figure 9

result, the transition δ becomes allowed (18) in the finite fluctuating system, but with a very small *oscillator strength*.

Absorption on loosely disposed solitons was investigated in [13, 68–70]. In [13] was obtained absorption from the lower band Z_1 to the soliton level, and it was also noted that the strictly vertical transition at $\hbar\omega = 2\Delta_1$ from Z_1 into Z_3 vanishes in the presence of one soliton. Nonetheless, the absorption remains finite on account of transitions with nonconservation of the momentum. At a finite density, approximate calculations were performed in [68] and [69] respectively for periodic and random arrangements of the *solitons*. It was found that the *oscillator strength* for transitions with $\hbar\omega \approx 2\Delta_1$ decreases because of the appearance of absorption with $\hbar\omega \approx \Delta_1$. However, in view of uncontrollable approximation, all the nontrivial effects were left out, namely, the forbiddenness of vertical optical transitions at $\hbar\omega \approx 2\Delta_1$ for a periodic arrangement of the solitons, and the suppression of the singularity at $\hbar\omega = 2\Delta_1$ for the random arrangement. The systematic investigation reported in this section was carried out by Brazovskii and Matveenko [71].

3.5 Low-Frequency Dielectric Constant and Establishment of Fröhlich Conductivity*

The results of §1 enable us to determine the nondissipative dielectric constant $\epsilon_1(q, \omega)$ at $\omega \ll \omega_0$ and $q \ll n$. In the long-wave limit we can use the relations obtained in §1 for $\Delta(X)$ and $w(n)$, assuming $X = X(x,t)$ and $n = n(x,t)$. The local changes δn of the electron density are connected with X by the relation

$$\delta n = \frac{2}{l}\,\frac{\partial X}{\partial x} = \frac{1}{n\pi}\,\frac{\partial \varphi}{\partial x}\,; \qquad \varphi = 2\pi\frac{X}{l}\,; \quad l = \frac{2}{n}$$

Here l is the local period of the superstructure $\Delta(x)$, and φ corresponds to the usual definition of the phase of a *charge-density wave.*

Substituting $\Delta(X(x,t))$ from (III.1.6a) and $w(n(x,t))$ from (III.1.23) in (I.2.11) we obtain the Lagrangian for the perturbations of $X(x,t)$. In the presence of an external electric potential $\Phi(x,t)$, this Lagrangian is of the form

$$\mathscr{L}(X) = \frac{1}{2}\rho_{\mathrm{CDW}}\left[\left(\frac{\partial X}{\partial t}\right)^2 - u^2\left(\frac{\partial X}{\partial x}\right)^2\right] - \frac{en}{S_\perp}\,\frac{\partial X}{\partial x}\,\Phi \tag{31}$$

where

$$\rho_{\mathrm{CDW}} = \frac{4\langle(\Delta')^2\rangle}{n\pi\omega_0^2 v_F} = \frac{32}{3\pi}\,\frac{\Delta_1^4}{\hbar^3 v_F^3\omega_0^2}\left[\left(1 - \frac{r^2}{2}\right)\frac{E(r)}{K(r)} - 1 + r^2\right] \tag{32}$$

---

*These results are published here for the first time.

is the "*charge-density-wave mass density*" and

$$u^2 = \frac{8}{\rho_{\mathrm{CDW}} l^2} \frac{\partial^2 \omega}{\partial c^2} = \frac{16 \hbar V_F}{\rho_{\mathrm{CDW}} l^2 \pi} \frac{(1 - r^2) K^3(r)}{E(r)} \tag{33}$$

where u is the *phase velocity of the charge density wave.*

For $\epsilon_1(q, \omega)$ we obtain from (31)

$$\begin{aligned} \epsilon_1(q, \omega) &= \epsilon_0 + \frac{\omega_p^{*2}}{u^2 q^2 - \omega^2}; \\ \omega_p^{*2} &= \frac{4\pi e^2}{S_\perp} \frac{n^2}{\rho_{\mathrm{CDW}}}; \end{aligned} \tag{34}$$

At $n\xi_1 \gg 1$, Eq. (34) goes over into the expression for the Fröhlich dielectric constant [4, 10, 28, 30]. At $n\xi_1 \ll 1$ and $\rho_{\mathrm{CDW}} \sim n$ the effective plasma frequency ω_p^* vanishes—the *Fröhlich conductivity* vanishes together with the *soliton lattice.*

The phenomenon considered here explains possibly the behavior of *trans*-$(CH)_x$ in the concentration region $0.002 < na < 0.05$, where metallic conductivity without spin paramagnetism is observed [13, 14].

§4 Periodic Superstructure in Dielectrics of the Combined Type. Exact Solution for the General Model C

In this section we investigate the ground state of a combined type dielectric at an arbitrary electron density. The results obtained for model C in different limiting cases will be given by relations previously employed in the study of *models A and B*. We present here an elementary derivation of the solution, without resorting to special mathematical data. A complete study will be published by Brazovskii, Kirova and Matveenko in [33].

The energy functional for model C, defined by formulas (I.2.1, 16,

17) can be written in the form (we assume in (I.2.1) a constant $v = 1$)

$$W\{\Delta_i(x)\}$$

$$= \int dx \left[\frac{\Delta_i^2(x)}{g^2} + \sum_E \bar{\psi}^* \left(-i \frac{\partial}{\partial x} \sigma_z + \Delta(x)\sigma_+ + \Delta^*(x)\sigma_- \right) \bar{\psi} \right] \tag{1}$$

$$\Delta(x) = \Delta_e + \Delta_i(x) e^{i\varphi}$$

where σ_z and $\sigma_\pm = 2^{-1}(\sigma_x \pm i\sigma_y)$ are Pauli matrices. We introduce the following parameters and functions

$$\Delta_1 = \Delta_e \sin\varphi; \qquad \Delta_2(x) = \Delta_i(x) + \Delta_e \cos\varphi \tag{2}$$

$$\Delta(x) = \left[\Delta_2(x) - i\Delta_1(x) \right] e^{i\varphi} \tag{3}$$

$$\psi_\pm(x) = 2^{-1/2}(u(x) \pm v(x)) e^{\pm i\varphi/2} \tag{4}$$

Relations (2) and (3) are illustrated in Fig. 3b. In terms of the variables $\Delta_2(x)$, $u(x)$, and $v(x)$, the functional (1) takes the form

$$W\{\Delta_2(x), u(x), v(x)\}$$

$$= \frac{\Delta_e^2 \cos^2\varphi}{g^2} L + \int dx \left\{ \frac{\Delta_2^2(x)}{g^2} - \frac{2}{g^2} \cos\varphi \Delta_e \Delta_2(x) \right.$$

$$+ \sum_{E<\mu} \left[-i(u^* v' + v^* u') + \Delta_1(u^* u - v^* v) \right.$$

$$\left. \left. + i\Delta_2(x)(v^* u - u^* v) \right] \right\} \tag{5}$$

Variation of the functional (5) with respect to the components of the wave functions $u(x)$ and $v(x)$ yields the equations

$$u' - \Delta_2 u = i(E + \Delta_1)v \tag{6a}$$

$$v' + \Delta_2 v = i(E - \Delta_1)u \tag{6b}$$

or

$$u'' + \left(E^2 - \Delta_1 - p\right)u = 0 \qquad p = \Delta_2^2 + \Delta_2' \tag{7a}$$

$$v'' + \left(E^2 - \Delta_1 - q\right)v = 0 \qquad q = \Delta_2^2 - \Delta_2' \tag{7b}$$

With the aid of (6a) and (6b) we can easily obtain separate normalization conditions

$$\frac{1}{L}\int u_E^* u_E \, dx = \frac{1}{2} + \frac{\Delta_1}{2E} \tag{8a}$$

$$\int v_E^* v_E \, dx = \frac{1}{2} - \frac{\Delta_1}{2E} \tag{8b}$$

Variation of the functional (5) with respect to $\Delta_2(x)$ yields a *self-consistency condition* that can be expressed with the aid of (6b) in the form

$$-\frac{2\Delta_e \cos\varphi}{g^2} + \frac{2\Delta_2(x)}{g^2} + \sum_{E<\mu} (E - \Delta_1)^{-1}\left(2\Delta_2(x) + \frac{d}{dx}\right)F_E(x) = 0 \tag{9}$$

$$F_E(x) = v_E^*(x) v_E(x)$$

The function $F_E(x)$ satisfies, as a result of (7b), the equation

$$F_E''' + 4(E^2 - \Delta_1 - q)F_E' - 2q'' F_E = 0 \tag{10}$$

and the normalization condition (8b).

The self-consistency condition (9) jointly with equations (10) and (8b) is a functional equation for the set of functions $F_E(x)$ and $\Delta_2(x)$. We stipulate that it be reducible to an algebraic equation. In the simplest case this means that for each E the following relation holds

$$\left(2\Delta_2(x) + \frac{d}{dx}\right)F_E(x) \equiv A_E\Delta_2(x) + B_E \tag{11}$$

where A_E and B_E do not depend on x. with the aid of (10) we can exclude F_E from this equation and obtain a single equation for the function $\Delta_2(x)$:

$$\Delta_2''' - 6\Delta_2^2\Delta_2' - \alpha\Delta_2' = 0 \tag{12}$$

where α is an arbitrary constant.

As a result of (12), the potentials $p(x)$ and $q(x)$ satisfy the equation

$$U''' - 6UU' - \alpha U' = 0, \qquad U = p(x), q(x) \tag{13}$$

When (13) is satisfied, we easily find from (10) and (11) that

$$F_E(x) \sim \left(E^2 - q(x) + \text{const}\right) \tag{14}$$

We can now determine, integrating Eqs. (12) and (13), the explicit relations for the deformation $\Delta_2(x)$ and for the potentials $p(x)$ and $q(x)$. Expression (14) yields the modulus of the wave function, while its phase can be determined in elementary fashion from Eq. (7b). It is convenient to write the result of these simple calculations by introducing the parameters E_1, E_2, and E_3 and a function $\gamma(x)$ such that

$$\begin{gathered} q(x) = E_1^2 + E_2^2 + E_3^2 - 2\gamma(x) - \Delta_1^2 \\ E_1^2 \leqslant E_2^2 E_3^2; \qquad E_2^2 \leqslant \gamma(x) \leqslant E_3^2 \end{gathered} \tag{15}$$

From (13) and (15) we get the equation

$$\begin{gathered} \gamma'(x) = \pm 2\sqrt{-R(\gamma(x))} \\ R(\gamma) = (\gamma - E_1^2)(\gamma - E_2^2)(\gamma - E_3^2) \end{gathered} \tag{16}$$

From (16) we obtain

$$\gamma(x) = E_3^2 - r^2k^2 sn^2(kx, r) \tag{17}$$

$$r = \sqrt{\frac{E_3^2 - E_2^2}{E_3^2 - E_1^2}}\ ; \qquad k = \sqrt{E_3^2 - E_1^2} \tag{17a}$$

For the normalized wave function we obtain

$$v_E(x) = \sqrt{\frac{(E - \Delta_1)}{2E} \frac{(E^2 - \gamma(x))}{A_E}}$$

$$\times \exp\left\{ \pm i\sqrt{R(E^2)} \int^x \frac{dy}{E^2 - \gamma(y)} \right\} \tag{18}$$

$$A_E = L|E^2 - \langle\gamma(x)\rangle| = L\left[E^2 - E_1^2 - k^2 E(r)/K(r)\right] \tag{19}$$

The spectrum of the wave functions (18) has three forbidden bands G and four allowed bands Z

$$\begin{aligned} G:&\quad E^2 < E_1^2; \qquad E_2^2 < E^2 E_3^2\,; \\ Z:&\quad E_1^2 < E^2 < E_2^2\,; \qquad E_3^2 < E^2 \end{aligned} \tag{20}$$

as shown in Fig. 10. The potentials $p(x)$ and the functions $u_E(x)$ are defined by expressions of the type (15) and (17), with the substitutions

$$\Delta_1 \to \Delta_1\,; \qquad \gamma(x) \to \gamma(x + x_0); \qquad x_0 = \text{const} \tag{21}$$

The parameter x_0 can be determined by comparing the definitions of $\Delta_2(x)$ from (6a) and (6b)

$$\Delta_2(x) = -\left.\frac{v_E'(x)}{v_E(x)}\right|_{E=-\Delta_1} = \left.\frac{u_E'(x)}{u_E(x)}\right|_{E=\Delta_1} \tag{22}$$

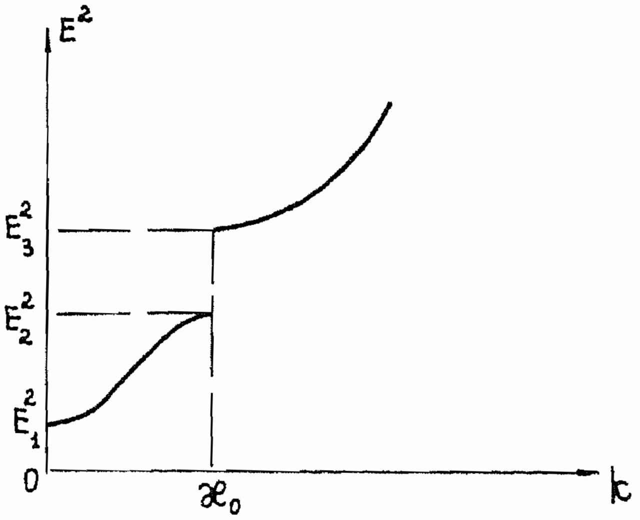

Figure 10

With the aid of (17), (18), and (21) we obtain from (22)

$$x_0 = \frac{1}{k} F\left[\arcsin\frac{k}{\sqrt{E_3^2 - \Delta_1^2}}\,;r\right] \tag{23}$$

$F(\xi, r)$ is an *incomplete elliptic integral of the first kind* [78].

$$\Delta_2(x) = \left\{E_1^2 + \left(E_2^2 - E_3^2\right)\left[sn^2(kx,r) - cn^2(k(x+x_0),r)\right]\right\}^{1/2} \tag{24}$$

The momentum $p(E^2)$ can be easily determined from (18) with the aid of (16)

$$P(E^2) = \left\langle \frac{\left[R(E^2)\right]^{1/2}}{E^2 - \gamma(x)} \right\rangle = k\left\{E(\nu, r') + \left(\frac{E(r)}{K(r)} - 1\right)F(\nu, r')\right\} \tag{25}$$

$$\nu = \nu(E) = \arcsin\sqrt{\frac{E^2 - E_1^2}{E_2^2 - E_1^2}}\;; \qquad r'^2 = 1 - r^2$$

The spectrum of $E^2(p)$ is shown in Fig. 10. For the density of state we can obtain from (25)

$$\frac{dp}{dE^2} = \frac{A_E}{2L\sqrt{R(E^2)}} \tag{26}$$

where A_E is defined in (19).

The boundaries of the forbidden bands are located at $E = \pm E_1$ and at $E = \pm E_2, \pm E_3$,

$$\Delta_1 < E_1 < E_2 < E_3; \qquad p(E_1^2) = 0; \qquad p(E_2^2) = p(E_3^2) = p_-$$

The quantity p_- can be easily determined from (25) and we obtain for the *total number of states* (with allowance for the spin) in each of the separated bands (E_1, E_2) and $(-E_2, -E_3)$

$$n = \frac{2}{\pi} p_- = \frac{k}{K(r)}; \tag{27}$$

From Eq. (27), with allowance for (17a), we obtain the first relation between the three free parameters E_1, E_2, and E_3. The two other relations can be obtained from the *self-consistency conditions*. Substituting (15) and (18) in (9) and using (12) and (13) we obtain, in accordance with condition (11), the equation

$$J_1\gamma(x) + J_2 = 0 \tag{28}$$

where

$$J_1 = \frac{1}{g^2} + \sum_{E<\mu} \frac{E^2 - \Delta_1^2}{EA_E} \tag{29}$$

$$J_2 = \frac{\Delta_e \cos\varphi}{g^2} + \sum_{E<\mu} \frac{\sqrt{R(\Delta_1^2)}}{EA_E} \tag{30}$$

From (28) follow the *self-consistency conditions* $J_1 = J_2 = 0$.

Equation (30) contains logarithmically diverging sums. We regularize this equation by subtracting a similar equation at

$$E_1 = E_2 = \Delta_1 = 0; \qquad E_3 = \Delta_0 {\sim} D\exp\{-1/\lambda\} \qquad \lambda = g^2/\pi\hbar v \tag{31}$$

This limit corresponds to the homogeneous state in *model B*, i.e., the quantity Δ_0 is the gap in the *Peierls dielectric* with the dimetization, at the same coupling constant λ as in the considered *combined dielectric*. Changing over in (29) and (30) from summation to integration, we obtain after simple calculations

$$F(\beta,t) - \frac{\Delta_e \cos\varphi}{\lambda}\,\frac{E_2\left(E_3^2 - E_1^2\right)^{1/2}}{\left[-R\left(\Delta_1^2\right)\right]^{1/2}} = 0 \tag{32}$$

$$\begin{aligned}&\left(E_3^2 - \Delta_1^2\right)F(\beta,t) - \left(E_3^2 - E_2^2\right)\Pi(\beta,r',t)\\&\quad + \frac{1}{2}E_2\left(E_3^2 - E_1^2\right)^{1/2}\ln\frac{\Delta_0^2}{E_3^2 + E_2^2 - E_1^2} = 0^{*}\end{aligned} \tag{33}$$

where

$$\beta = \arcsin\frac{E_2}{E_3}\,; \qquad t = \frac{E_3}{E_2}r'; \qquad r' = \sqrt{\frac{E_2^2 - E_1^2}{E_3^2 - E_1^2}}$$

Equations (27), (32), and (33) determine the parameters of the spectrum E_1, E_2, and E_3 in terms of the constants Δ_0, Δ_e, φ, and λ as functions of the electron density n.

The ground-state energy W_0 is defined as the value of the functional (5) when relations (27), (32), and (33) are satisfied. The calcula-

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* $F(\beta,t)$, $E(\beta,t)$, and $\Pi(\alpha,n,r)$ are *incomplete elliptic integrals* of the first, second, and third kind, respectively, $K(r) \equiv F(\pi/2,r)$; $E(r) \equiv E(\pi/2,r)$ [78].

tions are carried out in analogy with the *self-consistency conditions* (29) and (30). The calculation procedure is the same as in chapter IV for the doubly periodic state in *model B*. We obtain

$$W = \frac{1}{\pi} \frac{F(\beta,t)}{E_2\left(E_3^2 - E_1^2\right)^{1/2}}$$

$$\times\left[E_1^2E_2^2 - \Delta_1^2\left(E_3^2 + E_2^2 - E_1^2\right) + 2\Delta_1^2\left(E_3^2 - E_1^2\right)^{1/2} E(r) R\right]$$

$$+ \frac{1}{\pi} E_2\left(E_3^2 - E_1^2\right)^{1/2} E(\beta,t) + \frac{2n}{\pi}\left(E_3^2 - E_1^2\right)^{1/2} E(r)$$

$$- \frac{2}{g^2} \frac{\Delta_e \cos\varphi}{K(r)} \frac{\left(-R\left(\Delta_1^2\right)\right)^{1/2}}{E_3^2 - \Delta_1^2} \Pi\left(\frac{\pi}{2}, \frac{E_3^2 - E_1^2}{E_3^2 - \Delta_1^2}; r\right)$$

$$+ \frac{1}{2\pi}\left(3E_1^2 - 3E_2^2 - E_3^2\right) + \text{const} \tag{34}$$

The *electric-charge density distribution*

$$\sigma(x) - \bar{\sigma} = e \sum_{E<\mu} \left[u_E^* u_E + v_E^* v_E - \frac{1}{L} \right]$$

can also be easily calculated with the aid of (18) and (26). We obtain

$$\sigma(x) - \bar{\sigma}$$

$$= \frac{e}{\pi} kK(r')r^2 \left[sn^2(kx,r) + sn^2(k(x+x_0),r) - \frac{2}{r^2}\left(1 - \frac{E^2(r)}{K(r)}\right)\right]$$

$$+ \frac{e}{\pi} \frac{\Delta_e \cos\varphi}{\lambda} \frac{\Delta_1 k^2 r^2}{\sqrt{-R\left(\Delta_1^2\right)}} \left[sn^2(kx,r) - sn^2(k(x+x_0)r\right] \tag{35}$$

The first term in (35) yields the *charge distribution* and the second yields the *distribution of the dipole moment*. The relations obtained above go over into the formulas of chapter II, §4 for the *bipolaron*, $\nu = 2$. To this end they must be investigated in the limit $n \to 0$, when

$$E_3 \to \bar{\Delta}, \qquad E_2 \to E_1 \to E_b = \bar{\Delta} \cos \beta = \bar{\Delta}\left[\Delta_1^2 + \left(\bar{\Delta}^2 - \Delta_1^2\right)/\mathrm{ch}^2\alpha\right]^{1/2}$$

The corresponding results are given in chapter II, §4.

IV Doubly Periodic Superstructures, Spin Excitations, and One-Electron States in the Peierls Model

In this chapter we consider *doubly periodic solutions* in the one-dimensional continual Peierls model, and solve the problem of *spin excitations* and of one-electron states at an arbitrary number ρ of electrons per atom. We investigate the ground state of the system as a function of ρ and of the spin angular momentum m. We obtain for m a dependence on the external field h, characterized by a critical value $H_c \neq 0$ such that at $H > H_c$ an angular momentum m is produced in the system and a second period appears in the lattice deformation. For $m \to 0$ we consider, against the background of the periodic structure, *solitons* that carry *localized electronic states*. These solitons correspond to states of the system with one extra electron. The triplet and singlet excitations are sums of two *single-particle states*. We find that the *soliton charge*, in contrast to the spin, is partially screened at $\rho \neq 1$, so that in the *Fröhlich limit* at $|\rho - 1| \gg \Delta_1/D$ the *local charge* q vanishes like $q \sim e\Delta/\delta\mu$, where $\Delta = \Delta(\rho)$ is the gap on the Fermi surface and $\delta\mu = \mu(\rho) - \mu(1)$ is the Fermi level measured from the center of the band.

The results are applicable also to the problem of the ground state and of elementary excitations of a system of two coupled chains which is relevant to a model of TaS_3. In this case the *integral* $f_\perp$ *of electron hopping* between chains plays the role of the magnetic field h, and the difference between the occupation numbers of the symmetrized and antisymmetrized orbitals plays the role of the magnetization m.

§1 Peierls Model in a Magnetic Field or the Problem of Two Chains

The investigations of continual models, reported in the preceding chapters, show that the wave vector $2\pi/\lambda$ of the *superstructure* $\zeta(x)$ is equal to the diameter $2k_F$ of the Fermi surface in a metallic phase, with accuracy to the wave vector $2\pi/a$ of the main-structure reciprocal lattice. Such a superstructure can be regarded as singly periodic. At the same time, a number of physical problems call for the investigation of quasiperiodic lattice deformations characterized by *incommensurate wave numbers* $Q_i = 2\pi/\lambda_i$. Different periods λ_i can appear in the ground state of the system in the case when the metallic phase contained several groups of electrons characterized by different Fermi momenta $k_F^{(i)}$. Such a problem is obviously encountered for a system in a strong magnetic field, in which we have in the metallic phase $k_F\uparrow \neq k_F\downarrow$ for different spin projections $\sigma_z = \uparrow$ and $\downarrow$.

More pressing is the equivalent problem of a system consisting of two chains in which the electron wave functions overlap. In the case of a *strong elastic coupling between the chains*, the deformations of both chains should coincide: $\Delta^{(1)}(x) \equiv \Delta^{(2)}(x) \equiv \Delta(x)$, and the system energy functional can be written in the form (II:3.1–3) with an electron Hamiltonian

$$H = H_0 I + t_\perp \tau_x\,; \qquad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad \tau_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

where H_0 is the Hamiltonian (II.3.2) for one chain and $t_\perp$ is the *integral of the electron transition between chains*. The matrices I and τ_x act on the spinor $(\bar{\psi}^{(1)}; \bar{\psi}^{(2)})$, $\bar{\psi}^{(\alpha)} = (\psi_+^{(\alpha)}, \psi_-^{(\alpha)})$, where the index $\alpha = 1$ or 2 numbers the chains. Changing over to the components $\psi_{\uparrow\downarrow} = 2^{-1/2}(\bar{\psi}^{(1)} \pm \bar{\psi}^{(2)})$, we obtain the Hamiltonian of one chain in an effective magnetic field $h = \mu_B H = t_\perp$.* By way of an important example we cite a molecule of the TTF type, in which the stacks make up many quasi-one-dimensional compounds (Fig. 1e). In this case $\psi^{(\alpha)}$ are the upper molecular π orbitals for each of the two rings, and $t_\perp$ is the *overlap integral* between the rings along the C=C bond. Another possibility can be realized in organic conductors with complex mole-

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*The same role plays a potential energy shift between two nonequilibrium sets of chains, like in monoclinic TaS_3 or $NbSe_3$.

cules that usually contain a large number (M) of π electrons. In these compounds, the appearance of several unfilled bands can occur at $M \gtrsim T/t_{\parallel}$, where T and $t_{\parallel}$ are the respective hopping integrals between neighboring atoms in the molecule and between neighboring molecules in the conducting chain. Typically, $T \approx 2$ eV, $t_{\perp} \lesssim 0.5$ eV, and $M \sim 10$–30, i.e., the condition for the existence of many bands can indeed be satisfied.

Quasiperiodic solutions are also a convenient means of finding *solitons* against the background of periodic structures by going to the limit of infinite periods $\lambda_i \to \infty$, $i > 1$ at a fixed fundamental period λ_1 of the structure. An investigation of the solitons is essential for the determination of the electronic excitations in the system (see the review [58]). This limiting transition yielded the *charged spinless excitations* at $\rho = 1$ (chapter III) and $\rho = 0$ in the *E model* [43]. To determine the spectrum of the spin excitations at arbitrary ρ it is necessary already to use *doubly periodic structures.*

The most interesting changes of the properties of the system take place in the concentration region $|\rho - 1| \ll 1$ adjacent to the limit of the half-filled band at $\rho = 1$. We recall that at $\rho \approx 1$ the essential wave vectors of the lattice deformations lie near the Brillouin-zone boundaries $\pm\pi/a$, as a result of which it is necessary to take accurate account of lower (second) order umklapp processes in the electron-phonon interaction (Brazovskii, Dzyaloshinskii, Obukhov [29]). At the same time we can neglect higher-order umklapp processes ($k > 2$) which arise at $\rho \neq 1$ and whose amplitudes have a relative smallness $(E_g/\epsilon_F)^{k-2} \ll 1$, $k > 2$. As a result we arrive at a continual model that contains the real field of the deformations of $\Delta(x)$:

$$\zeta(x) \sim \Delta(x)\cos(\pi x/a); \qquad \Delta(x)| = \Delta_1 = \text{const} \qquad \rho = 1 \tag{1}$$

where the function $\Delta(x)$ varies slowly over distances of the order of the interatomic distance a. At a large value of the concentration

$$n = \frac{|\rho - 1|}{a} \gg \Delta_1 |\hbar v_F\,; \qquad |\rho - 1| \gg \Delta_1 | D \tag{2}$$

when v_F is the Fermi velocity at the center of the metal band, the *Fröhlich limit* is reached, wherein the influence of the host lattice becomes insignificant. In this limit it is possible (chapter II) to describe the system by the complex $\tilde{\Delta}(x)$ field:

$$\zeta(x) \sim \operatorname{Re} \tilde{\Delta}(x) \exp(i2k_F x) \tag{3}$$

where $\tilde{\Delta}(x)$ varies slowly over distances of the order of

$$l = 2\pi/Q; \qquad Q = |2k_F - \pi/a| = |\rho - 1|\pi/a$$

As shown in chapter III, the transition between two limits is realized continuously via evolution of the $\Delta(x)$ *superstructure* in (1) from a *soliton lattice* to the *almost sinusoidal deformation* (3).

We recall that the *elementary electronic excitations* cannot be band states in the potential of the superstructure $\Delta(x)$ of the ground state because of the strong *self-trapping effect* (II, §1). At $\rho = 1$ there exist (II, §2) *spinless* ($s = 0$) *excitations* with charge $q = \pm e$, or else *uncharged* ($q = 0$) with spin $s = 1/2$, of the domain-wall type

$$\Delta_s(x) = \Delta_1 th(x/\xi_1); \qquad \xi_1 = \hbar v_F/\Delta_1; \qquad E_s = \frac{2}{\pi}\Delta_1 \tag{4}$$

with energy $E_s < \Delta_1$, and *symmetrical polarons* (bound states of an electron and two walls), which carry both a charge $\pm e$ and a spin $1/2$, with energy E_p:

$$\begin{gathered} \Delta_p(x) = \Delta_1\left[1 - \sqrt{2}/\left(\operatorname{ch}\left(x\sqrt{2}/\xi_1\right) + \sqrt{2}\right)\right] \\ E_p = 2\sqrt{2}\,\Delta_1/\pi \end{gathered} \tag{5}$$

We note that $E_s < E_p < \Delta_1$.

In the *Fröhlich-model* limit (2) and (3) there are electronic excitations of only one type (II, §2), which carry a spin but are not charged:

$$\begin{gathered} s = 1/2; \qquad q = 0, \qquad \tilde{\Delta}(x) = \Delta_\rho e^{i\varphi} th\frac{x - x_0}{\xi}; \qquad \xi = \frac{\hbar v_F}{\Delta_\rho} \\ E_s = 2\Delta_\rho/\pi \end{gathered} \tag{6}$$

where E_s is the (*soliton*) excitation *energy*, while φ and x_0 are arbitrary constants.

Thus, the question arises of the change of the excitation spectrum with changing ρ. The question of charge excitations is relatively simple to solve. From the results of chapter III, §1 it follows that at $\rho \neq 1$ *charged solitons* (4) with $e_s = \pm e$ and $s = 0$ cannot be regarded as excitations of the system, since they form the periodic structure of the ground state $\Delta(x)$. They are replaced by gapless excitations of the electron density, which constitute sound in the *soliton lattice* (III.3.34) at $n \ll \xi_1^{-1}$, and go over into *Fröhlich conduction* at $n \gg \xi_1^{-1}$.

The question of spin excitations is more complicated. It follows from the results of chapter II, §4, that the soliton (4) with $e_s = 0$ and $s = 1/2$ cannot be stable in the presence of another *soliton* with $e_s = \pm e$ and $s = 0$. Two solitons of the type (4), with $s = 0$ and $s = 1/2$, could merge into a *polaron* (5), with an energy gain

$$\delta E = 2E_s - E_p = 4\Delta_1/\pi - 2\sqrt{2}\,\Delta_1/\pi > 0$$

It is therefore natural to assume that with increasing n a gradual change takes place in the character of the *single-electron excitations*, from the type (5) at $n \ll \xi_1^{-1}$ to the type (6) at $n \gg \xi_1^{-1}$. As can be seen from (5) and (6), in this case a qualitative change takes place in the form of the soliton, from an *isolated polaron* (5) to an *enveloping soliton* against the background of a rapidly oscillating structure (6), Figs. 11a and b. Even more substantial is the change in the quantum

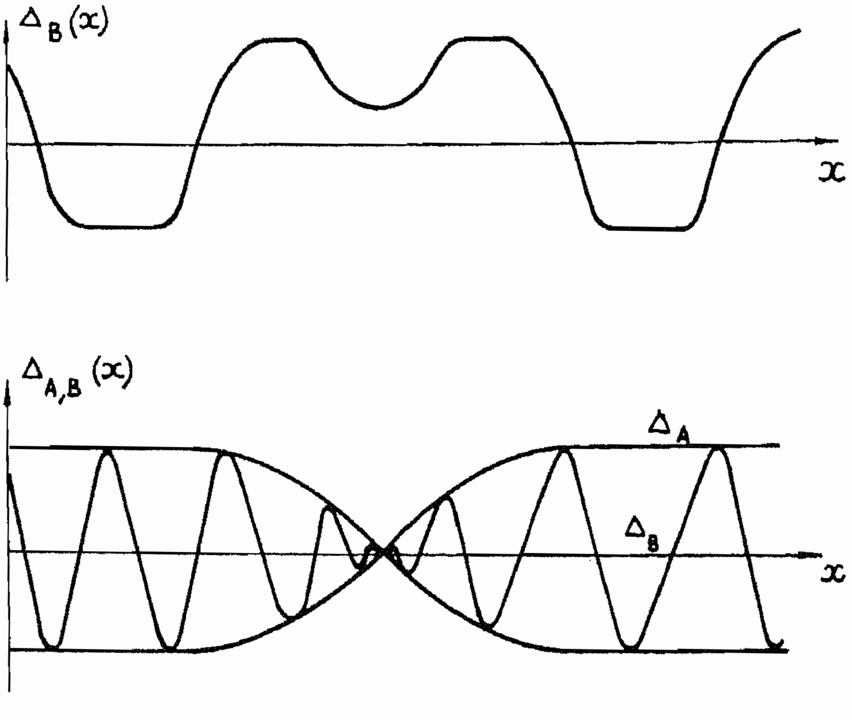

Figure 11

numbers of the *spin soliton*, from $q = \pm e$ at $n \ll \xi_1^{-1}$ to $q = 0$ at $n \gg \xi_1^{-1}$. We shall show that this change proceeds continuously, i.e., the *spin excitation*, at $\rho = 1$ is connected with a *non-integer local charge*.

Solution of this problem makes it also possible to determine the change of the system energy $W(N)$ when the number N of the electrons is changed by unity, i.e., to find the work function of the electron $A = W(N+1) - W(N)$, which does not equal the chemical potential $\mu = \partial W / \partial N$. We shall obtain simultaneously the *spin triplet excited state* of the system.

In this chapter we construct *doubly periodic solutions* in the one-dimensional continual *Peierls model*, in which the number ρ of electrons per atom satisfies the condition $|\rho - 1| \ll 1$. We obtain the system ground-state energy $W(n, m)$ as a function of the concentration of the *total number of particles* $n = n\uparrow + n\downarrow = |\rho - |/a$ and of the spin angular momentum $m = n\uparrow - n\downarrow$, where $n\uparrow$ and $n\downarrow$ are the concentrations of electrons with different spin projections on the magnetic-field direction. We investigate the function $m(H)$, which is characterized by a critical value $H = H_c$ such that a spontaneous

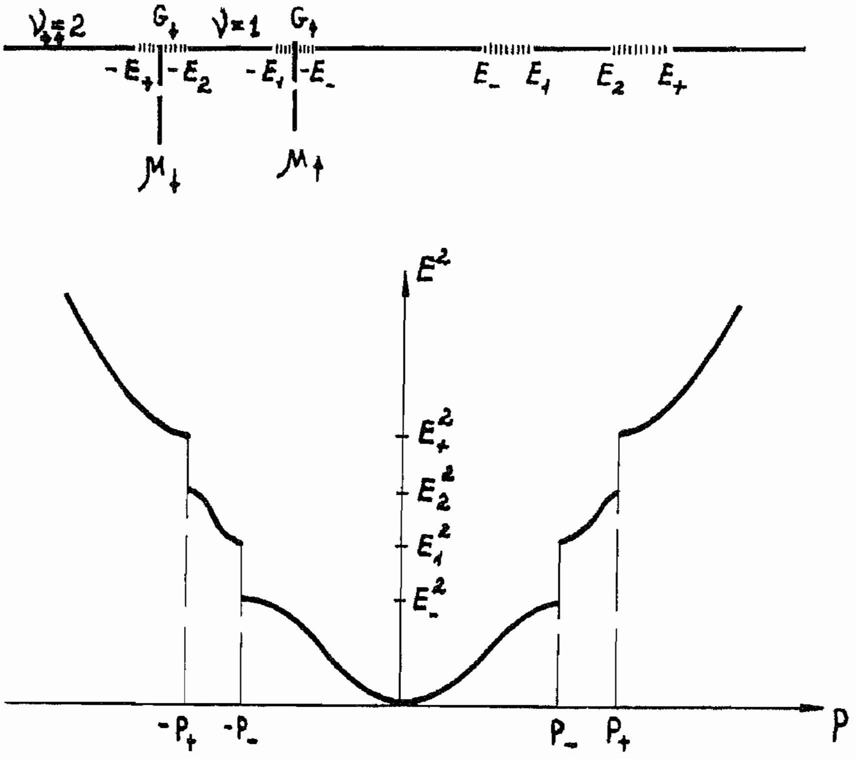

Figure 12

angular momentum $m \neq 0$ is produced in a system at $H > H_c$. At $m \neq 0$ the *superstructure* of the lattice becomes *doubly periodic*, and additional bands, one forbidden and one allowed, appear in the vicinity of the Fermi level (Fig. 12).

We consider, as $m \to 0$, solitons against the background of a *singly periodic superstructure*, which carry localized spin states. We investigate the *soliton-charge screening*, which is found to be negligible at $n \ll \xi_1^{-1}$ and almost complete at $n \gg \xi_1^{-1}$, in accordance with (4) and (6).

§2 Doubly Periodic Structures and Finite-Band Potentials

We write down the wave functions $\Psi(x)$ of the electrons in the form

$$\Psi(x) = 2^{1/2}\left[u(x)\cos(\pi x/2a) + iv(x)\sin(\pi x/2a)\right] \tag{7}$$

The components of the spinor $\bar{\psi}(u, v)$ as well as the potential $\Delta(x)$ from (1) are related by the equation for the eigenvalues of the energy E of the electrons

$$u_E' - \Delta u_E = iEv_E\,; \qquad v_E' + \Delta v_E = iEu_E \tag{8}$$

(the prime denotes derivatives with respect to x). Here and elsewhere the Fermi velocity is equal to unity. We obtain from (8) the equivalent equations

$$\begin{aligned} &u_E'' + (E^2 - p)u_E = 0 \qquad p = \Delta^2 + \Delta' \\ &v_E'' + (E^2 - q)v_E = 0 \qquad q = \Delta^2 - \Delta' \end{aligned} \tag{9}$$

The energy functional W of the system is

$$W\{\Delta(x); f_\sigma(E)\} = \sum_{E,\sigma} f_\sigma(E)E + \int \frac{\Delta^2(x)}{g^2}\,dx \tag{10}$$

where $f_\sigma(E)$ are the *occupation numbers of the states* with energy E

and spin σ, which take on the values $f_\sigma(E) = 0$ and 1, while g is the electron-phonon interaction constant. The stationary state of the system is determined from the condition that the functional (10) be extremal with respect to the field $\Delta(x)$, given the *total particle numbers* $N_\sigma = n_\sigma L$, where L is the length of the system. We introduce the Fermi levels μ_σ and the thermodynamic potential $\tilde{W}(\mu_\sigma)$ that depends on them:

$$\tilde{W}(\mu_\sigma) = W - \sum_\sigma \mu_\sigma N_\sigma \,; \qquad \left(\frac{\delta \tilde{W}}{\delta \Delta(x)}\right)_{\mu_\sigma} = 0$$

$$\mu_\sigma = \mu \pm h; \qquad h = \mu_B H \tag{11}$$

where μ and H are the chemical potential and the external magnetic field, and μ_B is the Bohr magneton. The variation in (11) should be carried out at specified distribution functions $f_\sigma(E)$. These functions are determined next from the conditions that the free energy of the system $\tilde{\mathscr{F}} = \tilde{W} - TS$ be a minimum, where T is the temperature and S is the entropy of the system. Confining ourselves only to the limit $T = 0$, we should assume that

$$f_\sigma(E) = \begin{cases} 1; & E < \mu_\sigma \\ 0; & E > \mu_\sigma \end{cases}$$

For the variation of (10) with respect to $\Delta(x)$ we note that, according to (9),

$$\frac{\delta E^2}{\delta q(x)} = 2v^*(x)v(x); \qquad \frac{\delta q(x)}{\delta \Delta(y)} = \delta(x-y)\left[2\Delta + \frac{d}{dx}\right] \tag{12}$$

Account is taken here of the fact, which can be deduced from (8), that the components $u(x)$ and $v(x)$ can be independently normalized

$$\int u^*(x)u(x)\,dx = \int v^*(x)v(x)\,dx = 1/2 \tag{13}$$

With the aid of (12) we obtain from (10) and (11)

$$\frac{\delta \tilde{W}}{\delta \Delta(x)} = \frac{2}{g^2}\Delta(x) + \sum_{E,\sigma} E^{-1} f_\sigma(E)\left[2\Delta + \frac{d}{dx}\right] v_E^*(x) v_E(x) = 0 \tag{14}$$

It follows from (8) that

$$\begin{gathered}\Delta(x) = -v_0'(x)/v_0(x); \quad q(x) = v_0''(x)/v_0(x); \\ v_0(x) = v(x)|_{E=0}\end{gathered} \tag{15}$$

Using (15), we can rewrite (14) in the form

$$\frac{d}{dx} v_0^{-2}(x)\left[\sum_{E,\sigma} E^{-1} f_\sigma(E) v_E^*(x) v_E(x) + g^{-2}\right] = 0 \tag{16}$$

Equation (16) can be integrated, and the integration constant can be determined from the normalization condition (13). We obtain

$$\sum_{E,\sigma} E^{-1} f_\sigma(E)\left[|v_E(x)|^2 - v_0^2(x)\right] + \frac{1}{g^2}\left(1 - 2Lv_0^2(x)\right) = 0 \tag{17}$$

At the transformation from (14) to (17) we lose only the *self-consistency conditions* for the particular case of the homogeneous solution $|v_E(x)|^2 \equiv (2L)^{-1/2}$, which corresponds to $\rho = 1$.

Substituting (15) in the second equation of (9), we obtain

$$v_E''/v_E - v_0''/v_0 + E^2 = 0; \qquad v_0''/v_0 = q(x) \tag{18}$$

The system of equations (18) and (16) or (17), with allowance for the normalization condition (13), determines the sought set of wave functions. We shall show that this system has solutions in the class of so-called *finite-band potentials* $q(x)$. A theory of Schrödinger equations (18) whose spectrum has only a finite number of forbidden bands was developed by Novikov et al. [57, 58] in connection with solutions of *Korteweg–de Vries (KdV) equations* with respect to $q(x)$. The problem considered by us calls for taking additional account of the functional relations (16) and (17) between the solutions $v_E(x)$. It turns out that (17) reduces to an algebraic equation for *finite-band potentials.*

We shall consider specifically the case of interest to us, that of a spectrum with two forbidden bands $G_{1,2}$, but the derivation presented below can be generalized in elementary fashion to include the case of an arbitrary number of forbidden bands. We define the boundaries of the spectrum $E_\alpha = (E_-, E_1, E_2, E_+)$ as shown in Fig. 12, where the forbidden bands G_1 and G_2 are dashed

$$G_1:\quad E_-^2 < E^2 < E_1^2;\qquad G_2:\quad E_2^2 < E^2 < E_+^2$$

According to [57, 58], the two-band potential $q(x)$, its eigenfunctions $v_E(x)$, and the state density $dN(E^2)/dE^2$ are expressed in terms of two (in accordance with the number of forbidden bands) functions $\gamma_{1,2}$ which are defined in the regions of the forbidden bands $G_{1,2}$:

$$E_2^2 \leqslant \gamma_2(x) \leqslant E_+^2;\qquad E_-^2 \leqslant \gamma_1(x) \leqslant E_1^2$$

Namely,

$$\begin{aligned} v_E(x) &= \left[\left(E^2 - \gamma_1(x)\right)\left(E^2 - \gamma_2(x)\right)/2LA(E)\right]^{1/2} \\ &\quad \cdot \exp\left\{\pm i \int^x dx\, R^{1/2}(E^2)/\left(E^2 - \gamma_1(x)\right)\left(E^2 - \gamma_2(x)\right)\right\} \end{aligned} \tag{19}$$

where

$$\begin{aligned} R(\epsilon) &= \epsilon\left(\epsilon - E_-^2\right)\left(\epsilon - E_1^2\right)\left(\epsilon - E_2^2\right)\left(\epsilon - E_+^2\right) \\ A(E) &= \langle\left|\left(E^2 - \gamma_1(x)\right)\left(E^2 - \gamma_2(x)\right)\right|\rangle \end{aligned} \tag{20}$$

The angle brackets $\langle \cdots \rangle$ here and below denote averaging over the length of the system:

$$\langle F(x)\rangle = \frac{1}{L}\int_0^L F(x)\,dx$$

For the potential $q(x)$ and for the deformation $\Delta(x)$ we have

$$\begin{aligned} q(x) &= E_+^2 + E_-^2 + E_1^2 + E_2^2 - 2(\gamma_1(x) + \gamma_2(x)) \\ \Delta(x) &= -\frac{1}{2}\frac{d}{dx}\ln(\gamma_1(x)\gamma_2(x)) \end{aligned} \tag{21}$$

The number dN of states in the interval dE^2 is

$$dN = \frac{L\,dp}{2\pi} = \frac{L\,dE^2}{2R^{1/2}(E^2)}\left\langle\left|\left(E^2 - \gamma_1(x)\right)\left(E^2 - \gamma_2(x)\right)\right|\right\rangle \tag{22}$$

where

$$p(E^2) = \pm R^{1/2}(E^2)\left\langle\left\{(E^2 - \gamma_1(x))(E^2 - \gamma_2(x))\right\}^{-1}\right\rangle \tag{23}$$

is the wave vector of the function (19). With the aid of (20) we can rewrite (22) in the form

$$\frac{dN}{dE^2} = LA(E)/4R^{1/2}(E^2) \tag{24}$$

The following additional conditions are also in force:

$$\int_{G_i} dN(E^2) = 0 \tag{25}$$

Formula (25) ensures equality of the momenta $p(E^2)$ at the complementary edges of forbidden bands. We present also, for the sake of completeness, the differential equations that define the family of functions $\gamma_{1,2}(x)$

$$\gamma_i' = \pm 2iR^{1/2}(\gamma_i)/(\gamma_2 - \gamma_1)$$

Here $q(x)$ satisfies the second *KdV equation* [58]

$$q'''' - 5(q')^2 - 10qq' + 10q^3 + C_1 q = C_2\,; \qquad \begin{array}{l} C_1 = \text{const} \\ C_2 = \text{const} \end{array}$$

It is remarkable that in the subsequent calculations no use is made of the coordinate dependences or of the equations that must be satisfied by the functions $\gamma_{1,2}(x)$.

We substitute the expressions (19) in Eqs. (16) and (17). From (17) we obtain

$$\frac{1}{L}\sum_{E,\sigma}\frac{f_\sigma(E)}{E}\left[\frac{|(E^2-\gamma_1)(E^2-\gamma_2)|}{A(E)} - \frac{\gamma_1\gamma_2}{A(0)}\right] + \frac{1}{g^2}\left[1 - \frac{\gamma_1\gamma_2}{A(0)}\right] = 0 \tag{26}$$

Equation (26) is of the form

$$B_1 + B_2[\gamma_1(x) + \gamma_2(x)] + B_3\gamma_1(x)\gamma_2(x) = 0 \tag{27}$$

where B_1, B_2, and B_3 are constants. In analogy with (16) we obtain

$$\frac{d}{dx}\left[B_1\gamma_1^{-1}\gamma_2^{-1} + B_2(\gamma_1^{-1} + \gamma_2^{-1})\right] = 0$$

from which, with Equation (21) we obtain

$$B_1\Delta' + B_2(\Delta''' - 6\Delta^2\Delta') = 0 \tag{28}$$

The only solution that (28) can have in modified Korteweg–de Vries equation (*MKdV*) form is a *single-period potential* $\Delta(x)$ with a single forbidden band $E_-^2 < E^2 < E_+^2$, which was investigated in chapter III.

To obtain a potential with two forbidden bands it is necessary to stipulate $B_1 = B_2 = B_3 = 0$. As a result we obtain from (26) the three *self-consistency conditions*

$$B_1 = \frac{1}{g^2} + \frac{1}{L}\sum_{E,\sigma} f_\sigma(E)\frac{E^3}{A(E)}\operatorname{sign} R(E^2) = 0 \tag{29}$$

$$B_2 = \frac{1}{L}\sum_{E,\sigma} f_\sigma(E)\frac{E}{A(E)}\operatorname{sign} R(E^2) = 0 \tag{30}$$

$$B_3 = -\frac{1}{g^2 A(0)} + \frac{1}{L}\sum_{E,\sigma}\frac{f_\sigma(E)}{E}\left[\frac{\operatorname{sign} R(E^2)}{A(E)} - \frac{1}{A(0)}\right] = 0 \tag{31}$$

Using relations (19) we can find that Eqs. (29)–(31) are linearly dependent. We shall therefore use hereafter only two of them, (30) and (31).

The investigated state of the system is characterized by six parameters μ_σ, $\sigma = \uparrow, \downarrow$ and E_i, $i = 1, 2, +, -$. Equations (30) and (31) and the laws of conservation of the number of particles with each spin projection

$$N_\sigma = Ln_\sigma = \sum_{E_i} f_\sigma(E) \qquad (32)$$

impose on these parameters four constraints that determine, say, E_i in terms of μ_σ. The remaining two parameters are determined from the condition that the total energy of the system (1) be a minimum on the class of *two-band potentials*, or from the condition that it be extremal on a larger class of potentials.

We shall assume in the present paper that the Fermi levels μ_σ pass through the forbidden bands of the potential. This assumption is sufficient for an investigation of the single-electron states, when we must consider isolated *solitons* with local level E_0: $E_1 \to E_2 \to E_0$. In this case $E_+^2 > \mu_\uparrow^2 > E_0^2$ and $E_0^2 > \mu_\downarrow^2 > E_-^2$. This assumption seems natural also in strong fields $h \gg \Delta_1$, $m \gg \xi_1^{-1}$. In this limit, the deformations $2k_{F\uparrow}$ and $2k_{F\downarrow}$, and respectively the gaps $G_\uparrow = \{E_+^2, E_2^2\}$ and $G_\downarrow = \{E_1^2, E_-^2\}$ on the Fermi levels $\mu_\uparrow$ and $\mu_\downarrow$ should be approximately independent. A rigorous proof can be obtained in analogy with the investigation of the *discrete Peierls model* [35] or the Peierls model on an elastic filament [43].

We shall assume hereafter that $\rho < 1$, i.e., that the electron band as a whole is less than half-filled (the case $\rho > 1$ differs only in that the electrons are replaced by holes). This means that the bands $E > E_+$ and $E_- > E > -E_-$ are not filled, and $n_\sigma(E) = 0$ at $E > -E_-$. Furthermore, the band $E < -E_+$ is always filled for both spin components $n_\sigma(E) = 1$, $E < -E_+$, $\sigma = \uparrow;\downarrow$, i.e., each band state is doubly filled. The degree of filling of the additional band $-E_2 < E < -E_1$ can differ, depending on the arrangement of the levels μ_σ. For the multiplicity of the filling of the states of this band $\nu = n_\uparrow(E) + n_\downarrow(E)$, $-E_2 < E < -E_1$, we have

$$\nu = \begin{cases} 0 & \mu_\uparrow < -E_2; \qquad\qquad \mu_\downarrow > -E_+ \qquad (33a) \\ 1 & -E_1 < \mu_\uparrow < -E_-; \qquad -E_2 > \mu_\downarrow > -E_+ \qquad (33b) \\ 2 & -E_1 < \mu_\uparrow < -E_-; \qquad -E_- > \mu_\downarrow > -E_1 \qquad (33c) \end{cases}$$

We consider now the *self-consistency condition* (3) for an arbitrary value of ν. Transforming from summation over E to integration with the aid of (24) we obtain

$$-2\int_{E_+^2}^{\infty}\tilde{R}^{-1/2}(\epsilon)\,d\epsilon+\nu\int_{E_1^2}^{E_2^2}\tilde{R}^{-1/2}(\epsilon)\,d\epsilon=0 \tag{34}$$

where

$$\tilde{R}(\epsilon)=(\epsilon-E_+^2)(\epsilon-E_-^2)(\epsilon-E_2^2)(\epsilon-E_1^2) \tag{34a}$$

Calculating the integrals in (34), we obtain

$$\frac{E_2^2-E_-^2}{E_+^2-E_-^2}=sn^2\left(\frac{\nu}{2}K(p);\,p\right);\qquad p^2=\frac{(E_2^2-E_1^2)(E_+^2-E_-^2)}{(E_+^2-E_1^2)(E_2^2-E_-^2)} \tag{35}$$

From (35) we obtain the following results:

a) $\nu=0$; $E_2^2=E_-^2$, the empty additional band $\{-E_1,-E_2\}$ contracts and joins the empty band $\{-E_-,E_-\}$ located above it.

b) $\nu=2$; $E_2^2=E_+^2$, i.e., the completely filled additional band joins, preserving the finite width corresponding to the number of particles, the completely filled band $\{E<-E_+^2\}$ beneath it.

c) $\nu=1$: from (35) follows the relation

$$E_+^2+E_-^2=E_1^2+E_2^2\equiv 2E_0^2 \tag{36}$$

i.e., the bands have a common center designated E_0^2 in (36).

The results of items (a) and (b) show that in a single-band ($m=0$) Peierls state the Fermi level $\mu_\uparrow=\mu_\downarrow$ can be placed only in the forbidden band. Otherwise the system turns out to be absolutely unstable with respect to a discontinuity in the state density on the Fermi level, with subsequent merging of the equally filled bands. These results agree with the conclusion obtained in II, §2, that in the *Fröhlich limit* $|\rho-1|\sim 1$ there are no activation charge excitations, despite the presence of a gap in the state spectrum of the rigid potential. We note that the usual picture of degenerate semiconductors would correspond precisely to location of a Fermi level in a forbidden band.

We consider now the *self-consistency condition* (29) or (31). We subtract from (29) Eq. (30) multiplied by E_0^2, and change from summation to integration with the aid of (13). We obtain

$$\frac{1}{g^2} - \int_{-E_m}^{-E_+} \frac{E^2(E^2 - E_0^2)}{\pi R^{1/2}(E^2)}\, dE + \frac{1}{2}\int_{-E_2}^{-E_1} \frac{E^2(E^2 - E_0^2)}{\pi R^{1/2}(E^2)}\, dE = 0 \tag{37}$$

When account is taken of relations (36) it is easy to find that the last term in (37) vanishes. The logarithmic dependence on the *cutoff energy* E_m is eliminated by subtracting from (37) the same equation at $\rho = 1$, when $E_1 = E_2 = E_- = 0$ and $E_+ = \Delta_1$. The lower integration limit $(-E_m)$ can now be allowed to tend to $-\infty$. As a result we obtain from (37), subject to the condition (36), a second relation

$$(E_+^2 - E_-^2)^2 - (E_2^2 - E_1^2)^2 = \Delta_1^4 \tag{38}$$

It shows that the interval (E_+^2, E_-^2), which stems from the forbidden band of the *single-band potential*, becomes wider when the additional allowed band (E_1^2, E_2^2) is included. At $E_1 = E_2$, Eq. (38) goes over into the relation $E_+^2 - E_-^2 = \Delta_1^2$, which agrees with the result of chapter III. Relations (36) and (38) impose two constraints on the four parameters E_i, $i = +, -, 1, 2$. The free parameters of the band structure can be connected with the *particle density* n_σ or, in other words, with the *end-point* momenta p_+ and p_- of the bands (Fig. 12b)

$$\begin{aligned} n &= n_\uparrow + n_\downarrow = \frac{1}{\pi}(2p_- + p_+ - p_-) = \frac{1}{\pi}(p_+ + p_-) \\ m &= n_\uparrow - n_\downarrow = \frac{1}{\pi}(p_+ - p_-) \end{aligned} \tag{39}$$

where

$$p_- = \int_0^{E_-^2} \frac{dp}{dE^2}\, dE^2; \qquad p_+ - p_- = \int_{E_1^2}^{E_2^2} \frac{dp}{dE^2}\, dE^2 \tag{40}$$

We introduce the notation

$$z = E^2 - E_0^2\,; \quad 2a = E_+^2 - E_-^2; \quad 2b = E_2^2 - E_1^2\,; \quad \left(a^2 - b^2 = \Delta_1^4/4\right) \tag{41}$$

and use relation (36). Equation (24) then takes the form

$$\frac{dp}{dz} = \frac{z^2 + \frac{1}{2}\langle q\rangle z - A_0}{2Q^{1/2}(z)} \tag{42}$$

where

$$Q(z) = \left(z + E_0^2\right)\left(z^2 - a^2\right)\left(z^2 - b^2\right)$$

The quantities q and $A_0 = A(E_0)$ are defined in (11) and in (10a). The coefficients $\langle q\rangle$ and A_0 in (42) can be obtained from the conditions (25).

We define a family of *hyperelliptic integrals*

$$I_n^{\pm}(z_1, z_2) = \int_{z_1}^{z_2} \frac{z^n\,dz}{\left|\left(E_0^2 \pm z\right)\left(z^2 - a^2\right)\left(z^2 - b^2\right)\right|^{1/2}} \tag{43}$$

and introduce the abbreviated notation

$$I_n^{\pm}(b, a) = I_n^{\pm}\,; \qquad I_n^{\pm}(-b, b) = J_n^{\pm}\,; \qquad I_n^{\pm}(a, \epsilon) = \tilde{J}_n^{\pm} \tag{43a}$$

for the integrals over the forbidden ($I_n^{\pm}$) and allow ($J_n^{\pm}, \tilde{J}_n^{\pm}$) bands. Substituting (25) in (42) we obtain

$$A_0 = -\left\langle\left(E_0^2 - \gamma_1\right)\left(E_0^2 - \gamma_2\right)\right\rangle = \frac{I_2^- I_1^+ + I_2 + I_1^-}{I_0^- I_1^+ + I_0^+ I_1^-} \tag{44}$$

and

$$\langle q\rangle = \langle\Delta^2\rangle = 2\left(2E_0^2 - \langle\gamma_1 + \gamma_2\rangle\right) = 2\,\frac{I_2^- I_0^+ - I_2^+ I_0^-}{I_0^- I_1^+ + I_0^+ I_1^-} \tag{45}$$

Substituting (32) in (4) we obtain

$$p_+ - p_- = \frac{1}{2} J_2^+ + \frac{1}{4} \langle q \rangle J_1^+ + \frac{1}{2} A_0 J_0^+ \tag{46}$$

and

$$p_- = \tilde{J}_2^- / 2 + \langle q \rangle \tilde{J}_2^- \tag{47}$$

The equations (46) and (47), with allowance for (44), (45), and (39) and in conjunction with the constraints (36) and (38) determine completely the band boundaries E_i given the *particle numbers* $n_\uparrow$ and $n_\downarrow$.

We now derive general relations for the *densities of the energy* $w(x)$, of the *charge* $\rho(x)$, and of the *spin* $\sigma(x)$. By definition,

$$\begin{gathered} w(x) = \frac{\Delta^2(x)}{g^2} + \sum_{E,\sigma} f_\sigma(E) \bar{\psi}_E^*(x) \bar{\psi}_E(x) \\ \langle w(x) \rangle = W/L \end{gathered} \tag{48}$$

Using (8), (19), and (29), we transform (48) into

$$w(x) = \frac{1}{L} \sum_E A^{-1}(E) E^3 \left[E^2 - E_0^2 \right] \tag{49}$$

We find that, just as in the case of a *single-band potential* (chapter III) and in the limit of an *isolated soliton* (chapters II and III), the *total energy of the system* is delocalized, i.e., $w(x) = W/L = \text{const}$.

The summation in (49) diverges rapidly far from the Fermi levels. We can regularize it by subtracting the energy density of the *Peierls dielectric* w_1 at $\rho = 1$, when $E_1 = E_2 = E_- = 0$; $E_+ = \Delta_1$, $p_+ = p_- = 0$, and $w_1 = w_{\text{met}} - \Delta_1^2/2\pi$. Here w_{met} is the energy of a metal with $\rho = 1$ and without lattice deformation. Since the sum over E converges for $w - w_1$, we can calculate w and w_1 separately by introducing an arbitrary limiting momentum $p_m \gg p_1, p_-$. The value of p_m should be fixed in order that the changes of the particle densities n_σ be connected with the momenta $p_\pm$ by relations (39). The value of p_m

is connected with the energy E_m corresponding to this state by the relation (23). Since $E_m \gg E_i$; $i = 1, 2, +, -$, we obtain from (13)

$$p_m \approx E_m \left[1 - \frac{\langle q \rangle}{2E_m^2} + O\left(\frac{E_i^2}{E_m^2} \right) \right] \tag{50}$$

We can write down the condition $p_m = \text{const}$, according to (50) approximately as

$$E_m^2 - \langle q \rangle = \text{const} + O\left(\gamma_{1,2}/E_m^2\right) \tag{51}$$

This result is in fact not connected with the form of the potential $q(x)$, but follows directly from (9) at $E_m^2 \gg \langle q \rangle$.

For the case (33c), $\nu = 1$ of interest to us, expression (49) reduces, when account is taken of (24) and (36), to

$$w = \int_{E_1^2}^{E_2^2} dE^2 \frac{E^3\left(E^2 - E_0^2\right)}{2\pi R^{1/2}\left(E^2\right)} - \int_{E_+^2}^{E_m^2} dE^2 \frac{E^3\left(E^2 - E_0^2\right)}{\pi R^{1/2}\left(E^2\right)}$$

Calculating the integrals, we obtain

$$w = w(n, m) = \frac{E_0^2 - E_m^2}{\pi} = \frac{E_0^2 - \langle q \rangle}{\pi} + \text{const} \tag{52}$$

whence

$$\begin{gathered} w(n, m) - w(0, 0) = \frac{E_+^2 + E_-^2 + \Delta_1^2 - 2\langle \Delta^2 \rangle}{2\pi} \\ w(0, 0) = w_1 \end{gathered} \tag{53}$$

The quantity $\langle \Delta^2 \rangle$ as a function of E_i is given by Eq. (45). Equation (53) yields also the general form for the energy, which was used in the case of a *single-band potential*, in chapter III, §1.

The *particle-number density* $n(x)$ in the system is, by definition,

$$n(x) = \sum_{E,\sigma} f_\sigma(E) \bar{\psi}_E^*(x) \bar{\psi}_E(x)$$

Using (8), (19), (30), and (42) we obtain

$$n(x) = C\Delta^2(x) + D\Big[2\left(E_0^2 - \gamma_1\right)\left(E_0^2 - \gamma_2\right) - 1/4\left(4E_0^2\Delta' - 6\Delta^2\Delta' + \Delta'''\right)\Big] \qquad (54)$$

where

$$C = \left[-2I_1^+(a, \infty) + \nu J_1^+\right]/4\pi \qquad (54a)$$

$$D = \left[\nu J_0^+ - 2I_0^+(a, \infty)\right]/4\pi \qquad (54b)$$

The *particle spin density*, is, by definition,

$$\sigma(x) = \frac{1}{2}\sum_E \left[f_\uparrow(E) - f_\downarrow(E)\right]\bar{\psi}_E^*(x)\bar{\psi}_E(x); \qquad \langle\sigma(x)\rangle = \frac{m}{2}$$

In analogy with (54) we obtain

$$\sigma(x) = \frac{1}{2}\tilde{C}\Delta^2 + \frac{1}{2}\tilde{D}\Big[2\left(E_0^2 - \gamma_1\right)\left(E_0^2 - \gamma_2\right) - \frac{1}{4}\left(4E_0^2\Delta' - 6\Delta^2\Delta' + \Delta'''\right)\Big] \qquad (55)$$

where

$$\tilde{C} = \nu J_1^+/4\pi; \qquad \tilde{D} = \nu J_0^+/4\pi \qquad (55a)$$

Equations (36), (38), (39), (46), (47), and (53)–(55) enable us to investigate the principal static properties of the *Peierls model* at zero temperature. Simpler relations can be obtained in the limit of large n and in the limit of small m.

§3 The Fröhlich Limit. Phase Transition in a Magnetic Field

We consider the general relations of the theory on going to the *Fröhlich limit* $n \gg \xi_1^{-1}$, $E_0^2 \approx E_+^2 \approx E_-^2 \gg \Delta_1^2$; a; b. It is natural to express all the physical quantities in this limit in terms of the width

$E_g = E_+ - E_-$ of the gap between the doubly filled and unfilled states, and the width $E_b = 2\Delta_b = E_2 - E_1$ of the singly filled band, $E_g = E_+ - E_- \approx a/E_0$ and $E_b = E_2 - E_1 \approx b/E_0$. The results should not depend explicitly on the value of E_0, which now determines only the overall shift of the Fermi levels relative to the center of the band. The energy scale is defined by the quantity

$$\Delta_0 = \Delta|_{b=0} \approx \Delta_1^2/4E_0; \qquad E_q = 2\Delta; \qquad k = \Delta_0/\Delta < 1 \tag{56}$$

Expanding the integrals (43) up to terms $\sim E_0^{-3}$ inclusive, we obtain from (44) and (45)

$$\langle q \rangle = \langle \Delta^2(x) \rangle \approx 2\Delta^2(2-k^2) + 4\Delta^2 E(k)/K(k) \tag{57}$$

$$A_0 = -\left\langle \left(E_0^2 - \gamma_1\right)\left(E_0^2 - \gamma_2\right) \right\rangle \approx 4E_0^2\Delta^2 E(k)/K(k) \tag{58}$$

$K(k)$ and $E(k)$ are *complete elliptic integrals* of the first and second kind, respectively [78]. From (46), (47), (57), and (58) we obtain

$$m = (p_+ - p_-)/\pi \approx 2\Delta_0/kK(k)\hbar v_F \tag{59}$$

$$n = (p_+ + p_-)/\pi \approx \frac{2}{\pi}\frac{E_0}{\hbar v_F}\left[1 + \frac{\Delta^2}{E_0^2}\left(\frac{E(k)}{K(k)} - \frac{3}{2}\right) + \frac{3}{16}\frac{\Delta_0^2}{E_0^2}\right] \tag{60}$$

From (60) we can determine E_0 and substitute it together with (57) and (58) into the formula (53) for the energy. We obtain

$$w(n,m) - w(0,0)$$
$$= \frac{\pi\hbar v_F}{4}n^2 + \frac{\Delta_0^2}{2\pi\hbar v_F} + \frac{\Delta_1^2}{2\pi\hbar v_F} + \frac{\Delta^2}{\pi\hbar v_F}\left(2\frac{E(k)}{K(k)} - 1\right)$$

or

$$\begin{aligned} w(n,m) - w(n,0) &\approx \Delta_0^2 f(k)/\pi\hbar v_F \\ f(k) &= 1 - k^{-2}\left[1 - 2E(k)/K(k)\right] \end{aligned} \tag{61}$$

Equations (59) and (61) enable us to determine the *spin-excitation energy* in the *Fröhlich limit*. As $m \to 0$ we have according to (59) $k \to 1$, $\Delta \to \Delta_0$, and we obtain from (61)

$$\begin{aligned} w(n,m) - w(n,0) &\approx E_s m \\ E_s &= 2\Delta_0/\pi \end{aligned} \tag{62}$$

The quantity E_s is the *energy of the self-trapped state* (6) with spin $s = 1/2$ in the *Peierls–Fröhlich model*, which was investigated in chapter II, §1.

At high spin density $m \gg \Delta_0/\hbar v_F$ we have from (59) $k \to 0$, and we obtain from (61)

$$w(n,m) = \frac{\hbar v_F \pi m^2}{4} - \frac{\Delta_0^4}{\pi^3 m^2 (\hbar v_F)^3} \tag{63}$$

We have considered so far the system properties for given *particle numbers* $N_\uparrow$ and $N_\downarrow$, i.e., given n and m. We consider now the system properties in the case when only the *total number of particles* is given, $N_\uparrow + N_\downarrow = nL = \text{const}$. The *spin density* m should be determined from the condition that the free energy be a minimum,

$$\tilde{w}(n,h) = w(n,m) - mh\hbar v_F \tag{64}$$

at the specified magnetic field h. The investigation of expression (64) at arbitrary n is quite difficult. We confine ourselves to the *Fröhlich limit* considered above, $n \gg \Delta_1/\hbar v_F$. This region is of greatest interest, first, because it involves practically all the quasi-one-dimensional substances with structural dielectric transitions. Second, with increasing n the gap 2Δ decreases in proportion to n^{-1} in accordance with (56), and can become equalized with the attainable magnetic fields. Substituting (59) and (61) in (64) we obtain

$$\begin{aligned} \tilde{w}(n,m) - \tilde{w}(n,0) &= \frac{\Delta_0^2}{\pi\hbar v_F}\left[1 + \frac{1}{B_2}\left(2\frac{E(k)}{K(k)} - 1\right) - \frac{2}{k}\frac{h}{E_s}\right] \\ &= \frac{\Delta_0^2}{\pi\hbar v_F}\tilde{f}(k) \end{aligned} \tag{65}$$

where $k = \Delta_0/\Delta$ according to (56). From (65) we find

$$\frac{d\tilde{f}}{dk} = \frac{2E(k)}{K(k)} \frac{(h/E_s)k - E(k)}{k^3(1-k^2)} \tag{66}$$

where $E_s = 2\Delta_0/\pi$ according to (62). It can be seen from (66) that the function $f(k)$ has a minimum at $k = k_m < 1$ only at $h > h_c = E_s$

$$\frac{E(k_m)}{k_m} = \frac{h}{h_c} \tag{67}$$

Equations (67) and (59) determine the function $m(h)$. As $h \to h_c + 0$ we have

$$\frac{h}{h_c} \sim \frac{1-k^2}{2\ln(1-k^2)}; \qquad \frac{m\hbar v_F}{\Delta_0} \sim \frac{1}{\ln(1-k^2)}$$

whence

$$h \approx \frac{m\hbar v_F hc}{2\pi\Delta_0} \exp\left\{-\frac{\Delta_0}{m\hbar v_F}\right\} \qquad x^{-1} = \frac{\partial h}{\partial m} \approx \frac{\hbar v_F hc}{2\pi\Delta_0} \exp\left\{-\frac{\Delta_0}{m\hbar v_F}\right\} \tag{68}$$

At $h \gg h_c$, $k \to 0$ and

$$h/h_c \approx \pi/2k; \quad \hbar v_F m \approx h_c/k; \quad h = \frac{\pi}{2} m\hbar v_F; \quad \chi = \frac{2}{\pi\hbar v_F} = \chi_{\text{Pauli}}$$

We have found that at $h < h_c$ the system has no paramagnetic susceptibility: $m = 0$, $\chi = 0$. At $h > h_c$ the system becomes paramagnetic, and furthermore with a susceptibility χ that becomes infinite at $h = h_c$. At $h \gg h_c$, the value of χ coincides with the Pauli susceptibility χ_{Pauli} for a normal metal, despite the presence of gaps on the Fermi levels $\mu_\uparrow$ and $\mu_\downarrow$.

The results are applicable also to other systems with two bands overlapping if the Fermi velocities can be regarded as close. The field

h corresponds in this case to the difference between the Fermi momenta for the two groups of electrons in the metallic phase, while $\pi m/2$ corresponds to the difference between wave numbers $2p_+$ and $2p_-$ of the two interfering components of a CDW in the dielectric phase.

§4 Single-Electron States and Spin Excitations

We consider the limit of an infinitely small *spin density*, when the number of states, and the number of particles that is equal to it, in the band $\{-E_2, E_1\}$ tends to zero. The band itself contracts in this case into a local level $-E_0$

$$m \to 0; \qquad E_1 \to E_2 \to E_0\,; \qquad b \to 0; \qquad a \to \Delta_1^2/2; \qquad m \sim \ln(\Delta_1^2/b)$$

To calculate the effects of first order in m it suffices to separate in the integrals (43) the terms $\sim \ln(\Delta_1^2/b)$ and to neglect the corrections of higher power in b.

Assume that a small spin density $m = M/L \ll n$ is produced in the system, and the total density changes, $n \to n + \delta n$, where $\delta n \ll n$. The quantities m and δn determine the width b and the shift $\delta(E_0^2)$ of the center of the band $\{E_1^2, E_2^2\}$. From (46) and (47) we obtain in first order in δn and m

$$n = \frac{\Delta_1}{rK(r)\hbar v_F}\,; \qquad m \approx \frac{\Delta_1 Z\left(\frac{\pi}{4}, r\right)}{\hbar v_F r \ln(\Delta_1^2/b)} \tag{69}$$

$$m + \delta n \approx \frac{1}{2\Delta_1 \hbar v_F}\,\frac{rE(r)}{(1-r^2)K^2(r)}\,\delta\left(E_0^2\right) + mS(r)$$

$$S(r) = \frac{4}{\pi} K(r')\left[Z\left(\frac{\pi}{4}, r\right) - \frac{r^2}{2}\left(1 - \frac{r^2}{2}\right)^{-1/2} + 2\Lambda_0(\varphi, r')\right] \tag{70}$$

where

$$r = \frac{\Delta_1}{E_+}\,; \qquad r' = \frac{E_-}{E_+}\,; \qquad r^2_+ r'^2 = 1; \qquad \operatorname{ctg}\varphi = r'$$

$$Z(\theta, r) = E(\theta, r) - F(\theta, r)E(r)/K(r)$$

$$\Lambda_0(\varphi, r') = \frac{2}{\pi}\left[K(r')E(\varphi, r) - (K(r') - E(r'))F(\varphi, r)\right]$$

$Z(\theta, r)$ is the *Jacobi zeta function*, $\Lambda_0(\varphi, r')$ is the *Heuman lambda function*, $F(\theta, r)$ and $E(\theta, r)$ are *elliptic integrals* of the first and second kind, respectively ($K(r) \equiv F(\pi/2; r)$, $E(r) \equiv E(\pi/2, r)$).

We calculate $\delta\langle q\rangle$ from (45) and $\delta(E_0^2)$ from (70) and substitute in (53). We obtain the change of the system energy

$$\delta W = L\left[w(n + \delta n, m) - w(n, 0)\right] = \mu(\delta N - M) + E_s M \qquad (71)$$

In the limiting cases Eq. (71) takes the form

$$\delta W \simeq \frac{2}{\pi}\Delta_1(\delta n - m) + \frac{2\sqrt{2}}{\pi}\Delta_1 m; \qquad \hbar v_F n \ll \Delta_1\,. \qquad (72)$$

$$\delta W \simeq E_+\,\delta n + \frac{2}{\pi}\Delta m; \qquad 2\Delta = E_+ - E_-, \qquad \hbar v_F n \gg \Delta_1\,. \quad (73)$$

It follows from (71) that the change of the system energy is equal to $\delta W_s = 2\mu$ following the addition of a singlet pair ($\delta N = 2$, $M = 0$), to $\delta W_t = 2E_s$ following the addition of a triplet pair ($\delta N = M = 2$), to $W_t - W_s = 2(E_s - \mu) = 2E_a$ following the transition from the singlet to the triplet state, to $\delta W_{+1} = \mu_+ = E_s$ following the addition of one particle ($\delta N = M = 1$), to $\delta W_{-1} = \mu_- = 2\mu - E_s$ following the removal of one particle ($\delta N = -M = -1$), and to $E_g^* = \mu_+ - \mu_- = 2(E_s - \mu) = 2E_a$ upon excitation of an electron-hole pair.

We note that the *electron-hole* and *spin excitations* have the same activation energy E_a, while the single-particle chemical potentials are equal to $\mu_\pm = \mu \pm E_a$. These facts, as well as an investigation of the corresponding coordinate dependences, show that the two-particle state is simply an assembly of two distant solitons, each carrying one localized particle. At $n \gg \xi_1^{-1}$ it follows from (73) that $E_a \approx 2\Delta/\pi$, i.e., each *soliton* constitutes a *domain wall* (6).

At $n \ll \xi_1^{-1}$ it follows from (72) that $E_a \approx 2\Delta(\sqrt{2} - 1)/\pi$, i.e., the activation is effected via a transformation of the *spinless domain walls* (4) into *polarons* (5).

We consider the local properties of one soliton, namely charge and spin. To this end it is necessary to investigate the limit $m \to 0$ in Eqs. (54) and (55). Far from the soliton (as $x \to \pm\infty$) we have $\Delta(x) \to \Delta_{\pm\infty}(x)$, where $\Delta_{\pm\infty}(x)$ satisfies Eq. (28) with $B_1/B_2 = 4E_0^2$, while

$$\left(E_0^2 - \gamma_1(x)\right)\left(E_0^2 - \gamma_2(x)\right) = -A(B_0)|v_E(x)|^2 \to 0$$

inasmuch as $v_E(x)$ degenerates as $E_1 \to E_2$ into the wave function of a local level. The expression in the square brackets in (54) and (55) tends therefore to 0 as $x \to \pm\infty$. According to [73], the asymptotic *singly periodic solutions* $\Delta_{\pm\infty}(x)$ in the presence of one soliton differ exactly by half a period, from which it follows that $\Delta_{+\infty}(x) = -\Delta_{-\infty}(x)$. Taking these remarks into account, we obtain from (54) the soliton charge q_s:

$$\begin{aligned} q_s &= e \lim_{m \to 0} \left[\langle n(x) - n\infty(x)\rangle / m\right] \\ &= e \lim_{m \to 0} \Big\{ \Big[C\langle \Delta^2(x) - \Delta_\infty^2(x)\rangle \\ &\qquad + 2D\langle \left(E_0^2 - \gamma_1(x)\right)\left(E_0^2 - \gamma_2(x)\right\rangle \Big] / m \Big\} \end{aligned} \tag{74}$$

Calculating the coefficients C and D in (54a, b) as $b \to 0$, we obtain

$$\begin{aligned} C &= -\frac{K(r')}{\pi E_+} \\ D &= \frac{1}{\Delta_0^2 E_0}\left[3 - 2\frac{F\left(\frac{\pi}{4}, 4\right)}{K(r)} - \frac{4}{\pi} K(r') Z\left(\frac{\pi}{4}, r\right)\right] \end{aligned} \tag{75}$$

Calculating (44) and (45) as $b \to 0$, we obtain, taking (69) into account,

$$\langle \Delta^2(x) - \Delta_\infty^2(x)\rangle \simeq 4mE_+ Z\left(\frac{\pi}{4}, r\right); \qquad A_0 \approx \Delta_1^2 E_0 m \tag{76}$$

Substituting (75) and (76) in (74) we obtain ultimately

$$q_s = e\left[1 - 2\frac{F\left(\frac{\pi}{y}, r\right)}{K(r)}\right] \approx \begin{cases} 1 - \dfrac{n\hbar v_F}{\Delta_1}\ln\dfrac{\sqrt{2}+1}{\sqrt{2}-1}\,; & n \ll \Delta_1/\hbar v_F \\ \dfrac{2}{\pi^3}\,\dfrac{\Delta_1^2}{n^2\hbar^2 v_F^2}\,; & n \gg \Delta_1/\hbar v_F \end{cases} \tag{77}$$

Equation (77) shows that at $n \ll \xi_1^{-1}$ the *soliton charge* is close to the one-electron charge. With increasing n, partial screening of the soliton takes place on account of deformation of the periodic structure in the vicinity of the soliton.

In the *Fröhlich limit* $n \gg \xi_1^{-1}$ and $r \ll 1$ we obtain $q_s \to 0$, i.e., the charge is completely screened in accord with the results of II, §2. The residual charge $q_s \sim -e\Delta/E_+$ is a weak effect of a distant commensurability point and becomes lost when the approximate functional of the *Peierls–Fröhlich model* (II, §2) with complex field $\Delta(x)$ is used. Calculation of the *spin density* in accordance with formulas (55) and (55a) as $m \to 0$ leads to the obvious result that the spin of one soliton is $s = 1/2$.

V *Polarons* and *Domain Walls* in Systems with Strong Elastic Coupling Between Chains

In this chapter we consider the *Peierls state* in a system of chains with sufficiently strong elastic coupling, when the degree of anisotropy α of the *phonon frequencies* and of the electron-phonon interactions is not too large, $1 > \alpha > \lambda$. When this condition is satisfied, a strong change takes place in the picture of the *elementary excitations* and sometimes in the structure of the ground state.

In §1 is considered the *interaction of electrons with superstructure* *deformations*, for a system with small *integrals of electron transfer between chains*, $t_{\perp} \ll \Delta$. In this case the deformation covers a large number of chains, and the *polaron effect* for one electron turns out to be weak. The *self-trapping*, however, becomes strong, $\sim\Delta_0$, if several $(N \sim \alpha/\lambda)$ electrons participate in it. The results are droplets whose size is limited by *Coulomb repulsion*.

In §2 we consider the ground state of the system in which the electron spectrum is considerably three-dimensional. It will be shown that if the *tunnel integrals* $t_{\perp}$ in the *Peierls-dielectric phase* with doubling of the period increase, say because of an applied pressure, the dielectric phase becomes unstable with respect to formation of *soliton walls*, which are the combinations of *neutral solitons* investigated in chapter II, §§2, 3. Formation of a *periodic superstructure* of soliton walls leads to the appearance, in the dielectric phase, of Fermi surfaces that correspond to a new type of carrier. From the experimental point of view, at the instant when the *soliton walls* appear, the anisotropy of the conductivity acquires an unexpected character: the *conductivity transverse to the filaments* becomes larger than the *longitudinal conductivity* (at low temperatures). The reason is that when the distance between the walls is large metallic conductivity along the soliton wall immersed in the dielectric phase becomes predominant.

The conclusions obtained in §2, jointly with the results of chapter IV, can possibly explain the origin of the *incommensurate superstructure* and the residual metallization of $NbSe_3$.

The material of §1, based on [54], is published here for the first time. The material of §2 is based on [74, 75].

§1 Polarons and Electron Droplets in a System with One-Dimensional Electron Spectrum

The conclusion obtained in chapter II, concerning the *strong self-trapping* of the electronic states, and the results of chapter I, §§2–4 for different soliton forms, are applicable if under certain restrictions on the *transfer integral* $t_{\perp}$ of the electrons between the chains and on the transverse dispersion α of the *phonon spectrum* $\omega(2p_F, q_{\perp})$ and of the interaction constant $\lambda(q_\perp)$:

$$\alpha \sim \delta\omega^2(2p_F, q_\perp)/\omega^2(2p_F, 0) \sim \delta\lambda(q_\perp)/\lambda(0)$$

Namely, it is necessary to satisfy the inequalities

$$t_\perp \ll \Delta_0 \tag{1}$$

$$\alpha \ll \lambda \tag{2}$$

Whereas condition (1) on t_1 is certainly satisfied at least as a weak inequality, by virtue of the very existence of the *Peierls effect*, the condition (2) that the structural coupling be weak may not be satisfied at all.

The presence of *solitons* destroys the *correlation between the chains*. Therefore, even at $\alpha/\lambda \ll 1$ the *interaction between the chains* leads to attraction between solitons with a force independent of the distance

$$\mathscr{F} \sim (\alpha/\lambda)(\Delta_0/\xi_0); \qquad \xi_0 = \frac{\hbar v_F}{\Delta_0}$$

so that at low temperatures solitons of one filament can be bound into pairs, or else domain walls can be produced that include a large number of filaments. This case is considered in chapter IV, §1.

In the present section we consider the case of *strong elastic coupling*

$$\alpha/\lambda \gg 1$$

which corresponds to system with fully isotropic elastic properties at an anisotropic electronic spectrum. In this case the *self-trapping of an electron* on one chain is accompanied by deformation of a large number of surrounding chains. As a result, the deformation of the gap $\delta_1(x)$ turns out to be small, $|\delta_1(x)| \ll \Delta_0$, the electron level $E_0 = \Delta_0 - \epsilon_1$ is shallow, $\epsilon_1 \ll \Delta_0$, and the longitudinal size λ_1 of the deformation $\delta_1(x)$ and of the localization of the electron is large: $\lambda_1 \gg \xi_0$. However, if the *self-trapping* involves several (N) electrons located on nearest chains, the state becomes deeper

$$l_n \sim N^{-1} l_1; \qquad \epsilon_n \sim N^2 \epsilon_1; \qquad |\delta(x)| \sim N^2 \epsilon_1$$

For real parameters we have even at $N = 3$–4

$$\epsilon_n \sim |\delta(x)| \sim \Delta_0 ; \qquad l_0 \sim \xi_0$$

and at larger N the multielectron self-trapped state should break up into two *domain walls*. The walls bound a three dimensional region in the shape of a disk, inside of which the sign of $\Delta(x)$ is opposite the sign in the surrounding volume.

Let the system in the metallic phase be characterized by an electron Fermi velocity v_F, by an electron-phonon interaction constant $\lambda = g^2/\pi\hbar v_F$, and by a phonon spectrum near the planes $\pm 2p_F$:

$$\bar{\omega}^2(2p_F + q_{\parallel}, q_{\perp}) \approx \bar{\omega}^2 + \Omega^2(q_{\perp}) \tag{3}$$

where $\mathbf{q}_{\perp} = (q_1, q_2)$, $|q_j| \leqslant \pi/aj$ $(j = 1,2)$ is the wave vector in a plane perpendicular to the conducting chains. The quantity

$$\alpha = \left[\max \Omega^2(q_{\perp}) - \min \Omega^2(q_{\perp})\right]/\bar{\omega}^2; \qquad \alpha \lesssim 1$$

characterizes the anisotropy of the phonon spectrum. We shall define $\bar{\omega}$ hereafter in such a way that

$$\min \Omega^2(q_{\perp}) = \Omega^2(q_0) = 0$$

In the dielectric phase, the spectrum of the electrons (e) or holes (h), without allowance for *self-trapping*, takes the form

$$\epsilon(k) = \sqrt{(k\hbar v_F)^2 + \Delta_0^2} \approx \Delta_0^2 + \hbar^2 k^2/2m^*; \quad m^* = \Delta_0/v_F^2 \quad k \ll \xi_0^{-1}$$

The spectrum of the *amplitude phonons* is of the form

$$\omega_0^2(\mathbf{q}_{\perp}) = \omega_0^2 + \Omega^2(\mathbf{q}_{\perp}); \qquad \omega_0^2 = 2\lambda\bar{\omega}^2 \tag{4}$$

The role of the anisotropy parameter is now played by the ratio $b = \alpha/\lambda$, which can be large: $b > 1$ at $\alpha < \lambda \leqslant 1$, i.e., *the Kohn anomaly* enhances effectively the *elastic coupling between the chains.*

In the adiabatic approximation the lattice deformation in the presence of N electrons or holes above the gap is described by a

Lagrangian that generalizes the Lagrangian (II.1.7–10) for one chain:

$$\mathcal{L} = \int dx \left\{ \frac{1}{2}\delta \hat{D}^{-1}\delta - \sum_{i=1}^{N} \sum_{n} \psi_{in}^{*}(x)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \delta_n(x) - \epsilon_i \right]\psi_{in}(x) \right\} \tag{5}$$

$$\psi_{in}(x) = \psi_i(x, \mathbf{R}_n); \qquad \delta_n(x) = \delta(x, \mathbf{R}_n)$$

where n is the index of the chain R_n, i—index of the electronic state,

$$D^{-1} = \frac{2}{\pi v_F \hbar}\left[\omega^2 - \omega_0^2 - \Omega^2(\mathbf{q}_1)\right]/\omega_0^2$$

is the reciprocal Green function of the phonons, $\psi_{in}(x)$ are the wave functions of the electrons localized on the chains n_i, and ϵ_i are their energies reckoned from the edge of the spectrum ϵ_0. If transitions of electrons between chains can be neglected, $t_\perp = 0$, then for each i, n we have

$$\int dx\, \psi_{in}^{*}(x)\psi_{in}(x) = 1$$

The stationary state of the system is obtained as an extremal of the functional (5). We get

$$D_{nm}^{-1}\delta_m + \rho_n = 0, \qquad \rho_n(x) = \sum_{i=1}^{N} \psi_{in}^{*}(x)\psi_{in}(x) \tag{6}$$

$$\left[-\frac{\hbar^2}{2m^*}\frac{\partial^2}{\partial x^2} + \delta_n \right]\psi_{in} = \epsilon_i \psi_{in} \tag{7}$$

For the *polaron* at rest we have from (6)

$$\delta_n(x) = -\frac{\pi \hbar v_F}{2}\int \frac{d^2 q_\perp S_\perp e^{i(\mathbf{q}_\perp - \mathbf{q}_0)(\mathbf{R}_n - \mathbf{R}_m)}\rho_m(x)}{(2\pi)^2\left(1 + \Omega^2(\mathbf{q}_\perp)/\omega_0^2\right)} \tag{8}$$

where $S_\perp = a_1 a_2$ and a_1 and a_2 are the transverse dimensions of the unit cell. Since $b \gg 1$, an important role in the integral (8) is played by values of $\mathbf{q}_\perp$ that are close to the minimum of $\Omega^2(\mathbf{q}_\perp)$ at $\mathbf{q}_\perp = \mathbf{q}_\perp^{(0)}$, where we can write

$$\frac{\Omega^2(\mathbf{q}_\perp)}{\omega_0^2} = \left(b_1\kappa_1^2 + b_2\kappa_2^2\right); \quad \kappa_j = \pi^{-d} a_j\left(q_j - q_j^{(0)}\right), \quad |\kappa_j| \ll 1\, j = 1;2.$$

We assume that the electrons are localized on one ($n = 0$, $R_0 = 0$) or on several nearest chains, so that $N^2 \ll b$. It follows then from (8) that $\delta_n(x)$ depends only on the total linear density of the electrons $\rho(x) = \sum_n \rho_n(x)$

$$\delta_n(x) = -\rho(x)\frac{\pi\hbar v_F}{2}\int \frac{d\kappa\, e^{i\kappa \mathbf{R}_n}}{1 + b_1\kappa_1^2 + b_2\kappa_2^2} = -\hbar v_F \rho(x) A_n$$

$$\kappa = (\kappa_1, \kappa_2) \tag{9}$$

We see also that in the electron-localization region δ_n depends little on the number of the chain, $\delta_n(x) \approx \delta_0(x)$.

If we neglect the *transfer of the electrons between the chains*, we have

$$\psi_i(x, R_n) = \psi_i(x)\delta_{n,i}$$

and, in addition, in the ground state all the wave functions are the same

$$i = 0, \qquad \epsilon_i = -\epsilon_0 = -\epsilon_0(N); \qquad \rho(x) = N\rho_0(x) = N\psi_0^*\psi_0$$

Substituting (9) in (7) we obtain

$$\left(-\frac{\partial^2}{\partial x^2} - \frac{NA_0}{\xi_0}\psi_0^2 + \frac{\epsilon_0}{\xi_0^2\Delta_0}\right)\psi_0 = 0 \tag{10}$$

According to (9), $A_0 \ll 1$ since $b \gg 1$: $A_0 \approx \pi^2 b^{-1}\ln(b^{-1})$ at $d = 2$ and $A_0 \approx \pi^2/2\sqrt{b}$ at $d = 1$. Equation (10), in contrast to the case of weakly bound chains ($b \ll 1$) considered in chapter II, §1, contains a small parameter NA_0, which defines the *self-trapped state* as a *shallow* *polaron*:

$$\psi_0(x) = \frac{1}{\sqrt{2\xi_N}\,\mathrm{ch}\,\frac{x}{\xi_N}}\,; \qquad \left(\frac{\xi_0}{\xi_N}\right)^2 = 2\,\frac{\epsilon_0}{\Delta_0} = \frac{A_0^2 N^2}{4} \tag{11}$$

The *total energy of the polaron* at rest is

$$\begin{aligned} E_p(N) &= -N\epsilon_0 + \sum_{n,m} \int \frac{1}{2}\,\delta_n(x) D_{nm}^{-1}\Big|_{\omega=0}\,\delta_m(x)\,dx \\ &\approx -N\epsilon_0 + \frac{N^2 A_0 \hbar v_F}{2} \int \rho_0^2(x)\,dx \\ &= -\frac{1}{24}\,N^3 A_0^2 \Delta_0 = -\frac{N}{3}\,\epsilon_0 \end{aligned} \tag{12}$$

i.e., the *self-trapping energy per electron*, E_1, is equal to

$$E_1 = \frac{1}{N}\,|E_p(N)| = \frac{N^2}{24}\,A_0^2 \Delta_0 = \frac{\epsilon_0}{3} \tag{13}$$

Assume that the *polaron mass* m_p is large compared with the free-electron mass, $m_p \gg m^*$. Then the *kinetic energy* $E_{\mathrm{kin}} = m_p v^2/2$ *of a polaron* moving with velocity $v \ll v_F$ can be calculated with account taken of only the kinetic energy of the lattice. As a result of (5) we have

$$E_{\mathrm{kin}} = \sum_n \frac{1}{\pi \hbar v_F \omega_0^2} \int \left(\frac{\partial \delta_n(x,t)}{\partial t}\right)^2 dx \approx \frac{m_p v^2}{2}$$

Substituting in this formula the relation $\delta(x,t) = \delta(x - vt)$ obtained from (9) and (11), we find the polaron mass

$$m_p = \frac{m^*}{30}\,N^5 A_0^5\,\frac{\Delta_0^2}{\hbar^2 \omega_0^2}\,; \qquad m^* = \frac{\Delta_0}{v_F^2} \tag{14}$$

The initial premises of the theory are the conditions that the *polaron* *effect* be weak

$$\epsilon_0 \ll \Delta_0 ; \qquad \xi \gg \xi_0 \tag{15}$$

and the adiabaticity condition

$$\epsilon_0 \gg \hbar\omega_0 \tag{16}$$

It follows from their compatibility that

$$\frac{\hbar\omega_0}{\Delta_0} \ll \left(\frac{A_0 N}{2}\right)^2 \ll 1 \tag{17}$$

Hence

$$\left(\frac{\Delta_0}{\hbar\omega_0}\right)^2 \gg \frac{m_p}{m^*} \gg \left(\frac{\hbar\omega_0}{\Delta}\right)^{1/2} NA_0 \tag{18}$$

We note that in contrast to the *theory of a one-dimensional tight-binding large-radius polaron* [45, 46], the adiabaticity condition does not lead automatically to a large *polaron mass*. If m_p calculated from Eq. (14) does not satisfy the inequality $m_p/m^* \gg 1$, then we must assume that $m_p \approx m^*$.

Besides the adiabaticity condition (16), for a *polaron* to exist it is necessary to satisfy the condition that the *transverse dispersion of the electrons* $t_\perp^*$ be bounded:

$$t_\perp^* \ll \epsilon_0(N) \tag{19}$$

For a *system of weakly bound chains* $\epsilon_0 \sim \Delta_0$, so that condition (19) is satisfied by virtue of the existence of *Peierls instability* in the given substance. Thus, violation of condition (17) or (19) leads to a destruction of the *polaron effect* and restores the simple picture of electron and hole excitations. It can apparently be assumed that in substances with *strong elastic coupling the polaron effects* for one electron are insignificant.

We consider now states with $N > 1$. Here the adiabaticity condition (16) and the requirement that the electron be one-dimensional (1) become less stringent with increasing N. It is necessary here, now, however, to take into account the *Coulomb repulsion effect*. The corresponding energy is estimated at

$$U(N) \sim \frac{N(N-1)}{2} \frac{e^2}{\epsilon \xi_N} \approx \frac{N^2(N-1)}{2} U_1 \tag{20}$$

where

$$\epsilon \gtrsim \frac{\hbar^2 \omega_p^2}{6\Delta_0^2} \approx \frac{4}{3} \frac{e^2}{v_F \hbar} \frac{\xi_0^2}{S_\perp}$$

is the *dielectric constant* (see (II.1.6)), and

$$U_1 \approx \frac{e^2}{\epsilon \xi_1}; \qquad \frac{U_1}{E_p(1)} \approx \frac{S_\perp \xi_1}{\xi_0^3}; \tag{21}$$

The *total energy of an N-electron polaron*, with allowance for the Coulomb forces, can be estimated at

$$E_p(N) = -N^3 E_1 + \frac{N^2(N-1)}{2} U_1 \tag{22}$$

It follows from (21) that the energy defect $\delta E_1(N)$ per particle, due to *coalescence of N one-electron polarons*, is equal to

$$\delta E_1(N) = \frac{1}{N} E_p(N) - E_p(1) = -N(N-1)\left(E_1 - \frac{U_1}{2}\right)$$

We conclude that the *coalescence* takes place only if $E_1 > v_1/2$, i.e., as a result of (21), if

$$\frac{\xi_1}{\xi_0} < \frac{C\xi_0^2}{S_\perp}; \qquad C \sim 1 \tag{23}$$

Using (11) we can write down the inequalities (23) in the form: $b < b_1$ at $d = 1$ and $b > b_2$ at $d = 2$, where

$$b_1 \sim \left(\frac{\xi_0^2}{S_\perp}\right)^2; \qquad b_2 \sim \frac{\xi_0^2}{S_\perp} \tag{24}$$

When the condition (24) is violated, there will exist in the system only the *one-electron elementary excitations* discussed above.

A more typical situation is one in which the chains are sufficiently closely packed, so that the condition (24) is satisfied. We see that the rapid growth of the binding energy $\delta E(N)$ is restricted by the number $N < N_m$ such that

$$\xi(N_m) \lesssim \xi_0 ; \qquad \epsilon_0(N_m) \approx \Delta_0 \tag{25}$$

Bearing in mind the fact that for all the known compounds $\Delta_0/\epsilon_F > 10^{-2}$, i.e., $b < 1/\lambda < 5$, we find from (25), taking (11) into account, that the *weak-coupling theory* can be used for *N-particle polarons* only at $N = 1$, 2 and 3, i.e., $N_m = 3$–4. We conclude that the *self-trapping* becomes deep already in the case when the electrons are on the nearest chains.

At $N \gg N_m$ in the internal chains, bounded by a transition layer of width $\sim N_m$, the changes of the gap parameter $\Delta_N(x)$ depend weakly on the number N. In this limit, the stationary states will be the same as for isolated chains. Since now the *Coulomb interaction* over a length ξ_0 is small compared with Δ_0 in terms of the parameter $S_\perp/\xi_0^2 \ll 1$, we must consider a distribution such that there are two excess electrons for each chain. In a system with $\rho = 1$ (*model B*) there are produced in this case repelling *domain walls* (see Chapter II, §§3, 4), which are contracted in the considered system by edge effects. A disk-shaped region is produced, inside of which the sign of the dimerization parameter is opposite that in the surrounding volume. The statistics of such objects is considered in chapter VI.

§2 Spontaneous Development of Superstructures and Metallization in a Peierls System with a Three-Dimensional Electron Spectrum

In chapter III we considered one-dimensional models that describe substances with *weak interaction between the chains*. *Periodic superstructures* were produced in this case as a result of the change in the electron density in the chain. In the present section we consider the *Peierls model* for substances in which a *strong elastic interaction* takes place *between the chains*, and the electron spectrum is three-dimensional enough for the width $t_\perp$ of the *transverse dispersion* of the electron spectrum to be comparable with the gap 2Δ.

It is precisely such substances that were investigated most intensively in recent years in connection with the success in stabilization of the metallic state. Examples were indicated in chapter I, §1. We assume that with increasing $t_\perp$, say as a result of external pressure, a phase transition can take place with formation of a periodic superstructure. The resultant deformation is similar to that investigated in §1, but with a half-filled central band. Such a transition should manifest itself experimentally in a metallization of the system, especially in a steep increase of the transverse conductivity. The mechanism of this transition was indicated by Brazovskii, Gor'kov, and Schrieffer [74]. More detailed calculations were given by Brazovskii, Gor'kov, and Lebed' [75], whose paper we follow for the most part hereafter.

The phenomenon considered should be quite general for systems with a three-dimensional electron spectrum, regardless of the degree of three-dimensionality of the phonons. However, methodological restrictions make it possible so far to construct a theory for systems in which a *strong elastic coupling exists between the chains*. Under this condition we can regard the *domain walls* as flat and use the result of the one-dimensional model investigated in §1.

The energy scales of Δ and $t_\perp$ are comparable but are small compared with the total width of the electron band. Therefore the Fermi surface in the metallic phase should take the form of two open sheets corresponding to the spectrum

$$\epsilon(p_{\|}, p_\perp) = \epsilon(\pm p_F + k, p_\perp) \approx \pm v_F \hbar k + t_\pm(\mathbf{p}_\perp) \tag{1}$$

The parameters of the interaction of the electrons with the lattice deformations $g(\mathbf{k}_\perp)$, $\max g(\mathbf{k}_\perp) = g(\mathbf{k}_\perp^{(0)}) = g$, now depend also on the transverse momentum $\mathbf{k}_\perp$. We assume that in the *Peierls state* the lattice deformation $\zeta(\mathbf{r})$ is characterized by a very simple star of vectors $(\pm\mathbf{k}_1, \pm\pi/a)$

$$\zeta(\mathbf{r}) \sim \sin(\pi x/a)\left[\Delta_{\mathbf{k}_\perp}(x)\exp(i\mathbf{k}_\perp \mathbf{r}_\perp) + c.c.\right]$$

i.e., the lattice deformation is of the form

$$\zeta(r) \sim \sin(\pi x/a)\left[\Delta_{\mathbf{k}_\perp}(x)\exp(i\mathbf{k}_\perp \mathbf{r}_\perp) + c.c.\right] \tag{2}$$

where $\Delta_{\mathbf{k}_\perp}(x)$ are slow functions of the coordinate x. The functional of the system energy (per chain) (at zero temperature) can then be written in the form

$$W = \int \frac{d\mathbf{p}_\perp}{\Omega} \sum_{E(\mathbf{p}_\perp)<\mu} E(\mathbf{p}_\perp) + \int dx \frac{|\Delta_{\mathbf{k}_\perp}(x)|^2}{g^2}$$

$$+ \int dx\, |\Delta_{\mathbf{k}_\perp}(x)|^2 \left(-\frac{1}{g^2} + \frac{1}{g^2_{\mathbf{k}_\perp}} \right); \qquad \Omega = \frac{(2\pi)^2}{S_\perp} \tag{3}$$

where $E(\mathbf{p}_\perp)$ are the energy levels and depend on the transverse momentum $\mathbf{p}_\perp$ in the field $\zeta(\mathbf{r})$, $g_{\mathbf{k}_\perp}$ is the electron-phonon interaction constant, with g the maximum value of the function $g_{\mathbf{k}_\perp}$.

The dispersion $\delta g^2_{\mathbf{k}_\perp}$ includes, generally speaking, the *dispersions of the phonon frequency* as well as of the interactions themselves. The assumption that a *strong structural coupling* is present means that $\delta g^2_{\mathbf{k}_\perp} \sim g^2$.

As usually, due to the cancellation of the logarithmic contributions the first two terms in (3), taken together, are of the order of Δ^2, whereas the order of the last term is

$$\Delta^2 \delta g^2_{\mathbf{k}_\perp}/g^4 \sim \Delta^2/g^2 \gg \Delta^2/\hbar v_F$$

Consequently, $\mathbf{k}_\perp$ is determined primarily from the condition that $g(\mathbf{k}_\perp)$ be a maximum, and can be regarded as a fixed specified: $\mathbf{k}_\perp = \mathbf{k}^{(0)}$, $g(\mathbf{k}_\perp) = g$. Without limiting the generality we can assume that $\mathbf{k}_\perp = 0$. The function $\psi_{\mathbf{p}_\perp^\pm}(x)$ satisfies the equations

$$\begin{gathered} \left[-i\hbar \frac{d}{dx} + t_+(\mathbf{p}_\perp) - E(\mathbf{p}_\perp) \right] \psi_{\mathbf{p}_\perp^+}(x) + i\Delta(x) \psi_{\mathbf{p}_\perp^-}(x) = 0 \\ \left[-i\hbar \frac{d}{dx} - t_-(\mathbf{p}_\perp) - E(\mathbf{p}_\perp) \right] \psi_{\mathbf{p}_\perp^-}(x) - i\Delta(x) \psi_{\mathbf{p}_\perp^+}(x) = 0 \end{gathered} \tag{4}$$

We make in (4) the following change of variables

$$\psi_{\mathbf{p}_\perp^\pm}(x) = \psi_\pm(x) \exp\left[-i\tilde{t}(\mathbf{p}_\perp) x \right]$$

$$2\tilde{t}(\mathbf{p}_\perp) = t_+(\mathbf{p}_\perp) - t_-(\mathbf{p}_\perp)$$

The functional (3) then takes the form

$$\frac{W}{L} = \frac{\langle\Delta^2\rangle}{g^2} + \frac{1}{L}\int\frac{d\mathbf{p}_\perp}{\Omega}\int_{E<\alpha(\mathbf{p}_\perp)}\frac{dN}{dE}\left[E + t(\mathbf{p}_\perp)\right]dE$$

$$\alpha(\mathbf{p}_\perp) = \mu - t(\mathbf{p}_\perp) \tag{5}$$

Here L is the length of the system, dN/dE is the density of states, E is the eigenvalue of the Hamiltonian $\hat{H}$,

$$\hat{H} = i\begin{bmatrix} -\hbar\dfrac{d}{dx} & \Delta(x) \\ -\Delta(x) & \hbar\dfrac{d}{dx}\end{bmatrix}; \qquad \hat{H}\psi = E\psi; \qquad \psi = (\psi_+, \psi_-) \tag{6}$$

The functional (5), (6) is similar to that already used before (chapter III, §1) for the one-dimensional *Peierls model.* As follows from the results of chapter IV, functionals of this type have extrema in the class of the so-called finite-band potentials $\Delta(x)$. We consider the simplest case of potentials with two forbidden bands. It corresponds to deformation of a lattice $\Delta(x)$ of the type of a single-periodic superstructure (III.1.6a), and the Hamiltonian (6) has the spectrum shown in Fig. 7. We also have the relations (III.1.7) between the parameters k, Δ_k, r and E_+, E_- as well as a formula (III, 1.8) for the density of states for Hamiltonian (6).

In contrast to the one-dimensional model, each eigenvalue corresponds here to a band $E(p_\perp) = E + t(p_\perp)$, see Fig. 13a.

Just as in the one dimensional case of §1, the following *self-consistency condition* holds:

$$\frac{1}{g^2} + \int\frac{d\mathbf{p}_\perp}{\Omega}\int_{E<\alpha(\mathbf{p}_\perp)}\frac{E\,\mathrm{sign}\left(E^2 - E_-^2\right)dE}{\pi\sqrt{\left(E^2 - E_-^2\right)\left(E^2 - E_+^2\right)}} = 0 \tag{7}$$

It differs in the fact that the integration region is bounded by the condition $E(\mathbf{p}_\perp) < \mu$, i.e., $E < \alpha(\mathbf{p}_\perp)$.

The system energy (5), under the condition (7) is equal, in analogy with (III.1.22), to

$$W = \frac{1}{2\pi\hbar v_F}\left[-E_+^2 - E_-^2 + 4E_+^2\frac{E(r)}{K(r)}\right] + 2n\int_{t(\mathbf{p}_\perp)<\mu}\frac{d\mathbf{p}_\perp}{\Omega}\,t(\mathbf{p}_\perp)$$

$$-\frac{1}{\pi\hbar v_F}\int_{|\alpha|<E_-}\frac{d\mathbf{p}_\perp}{\Omega}\sqrt{(E_-^2-\alpha)(E_+^2-\alpha)}$$

$$+\int_{|\alpha|<E_-}\frac{d\mathbf{p}_\perp}{\Omega}\,t(\mathbf{p}_\perp)\Phi(\mathbf{p}_\perp)\,\mathrm{sign}\,d \tag{8}$$

where

$$\Phi(\mathbf{p}_\perp) = \frac{1}{L}\int_{\alpha^2}^{E_-^2}\frac{dN}{dE^2}\,dE^2 = \frac{2}{\pi\hbar v_F}\left\{E_+\frac{E(r)-K(r)}{K(r)}F(\varphi,r')\right.$$

$$\left. + E_+E(\varphi,r') - |\alpha|\sqrt{\frac{E_-^2-\alpha}{E_+^2-\alpha}}\right\}; \tag{9}$$

$$\varphi = \arcsin\left[\frac{E_+}{E_-}\sqrt{\frac{E_-^2-\alpha}{E_+^2-\alpha}}\right]$$

$F(\varphi, r')$ and $E(\varphi, r')$ are *elliptic integrals.*

In the problem of chapter III, §1, the inhomogeneous states were due to a change in the electron density. The chemical potential μ was always in the forbidden band. The two free parameters E_+ and E_- were determined in terms of the specified electron density n and from the self-consistency condition.

Now we are considering the problem where the chemical potential is not known beforehand so that three parameters, μ, E_+, and E_- are to be determined. Two relations between them can be obtained from the *self-consistency condition* (7) and from the condition for the *conservation of the total number of particles*. The last free parameter is determined by minimizing the energy (8).

The condition for the conservation of the number of particles can obviously be written in the form

$$\int \frac{d\mathbf{p}_\perp}{\Omega} \int_{E<\alpha} \frac{dN}{dE}\, dE = \text{const}$$

Recognizing that the two states in the central bands are combinations of one state from the conduction band and one state from the "valence" band of the dielectric phase, we obtain

$$n\left(1 - 2\int_{\alpha>0} \frac{d\mathbf{p}_\perp}{\Omega}\right) = -\int_{|\alpha|<E_-} \frac{d\mathbf{p}_\perp}{\Omega}\,\varphi(\mathbf{p}_\perp)\operatorname{sign}\alpha \qquad (10)$$

Equation (10) has a simple meaning—the central band should on the average be half-filled. This condition is a consequence of the conservation of the *total number of states* and the total number of particles.

We now use the general relations obtained above to study the behavior of the system near the instability point of a homogeneous *Peierls state*, when the lattice deformation has the character of well separated *domain walls* produced against the background of a *Peierls structure*. To this end it is necessary to investigate equations (7)–(10) at small values of n, i.e., as $E_- \to 0$. We consider first the *particle-number conservation condition* (10). For any function $t(\mathbf{p}_\perp)$, the chemical potential μ_0 (as $E_- \to 0$) is determined from the condition that the contour l on which $t(\mathbf{p}_\perp) = \mu_0$ divides the cross section of the Brillouin zone into two parts of equal area.

It follows from (10) that at $E_- \neq 0$ we have

$$\mu = \mu_0 + O\left(E_-^2/E_+^2\right)$$

We note that for a sufficiently symmetrical form of $t(\mathbf{p}_\perp)$ we have $\mu \equiv \mu_0$, whereas for arbitrary $t(\mathbf{p}_\perp)$ we can assume that $\mu \approx \mu_0 = \text{const}$ only at the required accuracy $\sim O(E_-^2/E_+^2)$.

We consider now the *self-consistency condition* (7). It can be written in the form

$$\ln \frac{\Delta_0^2}{E_+^2 - E_-^2} = 2\int_{|\alpha|<E_-} \frac{d\mathbf{p}_\perp}{\Omega} \ln \frac{\sqrt{E_+^2 - \alpha^2} + \sqrt{E_-^2 - \alpha^2}}{\sqrt{E_+^2 - E_-^2}} \qquad (11)$$

where $\Delta_0 \sim \mathscr{D} \exp(-\pi\hbar v_F/g^2)$ is the gap in the homogeneous *Peierls dielectric*.

At $E_- \to 0$ we obtain from (11)

$$\Delta_0^2 = E_+^2 - E_-^2 + 2\Delta_0 \int_{|\alpha| < E_-} \frac{d\mathbf{p}_\perp}{\Omega} \sqrt{E_-^2 - \alpha^2} \tag{12}$$

where the integral term is of the order of E_-. The expression (8) for the energy can be written at small E_-, with allowance for (12), in the form

$$W = -\frac{\Delta_0^2}{2\pi\hbar v_F} + nA + nE_-^2 B \tag{13}$$

where

$$A = \frac{2\Delta_0}{\pi} + 2\int_{t(\mathbf{p}_\perp) < \mu_0} t(\mathbf{p}_\perp) \frac{d\mathbf{p}_\perp}{\Omega} \tag{14}$$

$$B = \frac{1}{2\pi\Delta_0} - \frac{1}{2\Omega} \oint_l \frac{dl}{\beta(l)}\,; \qquad \beta(l) = \left| \frac{dt(\mathbf{p}_\perp)}{d\mathbf{p}_\perp} \right|_{t(\mathbf{p}_\perp) = \mu_0} \tag{15}$$

Here $\beta(l)$ is the transverse component of the electron velocity on the contour l.

The quantity A is the energy required for the production of one *domain wall*. At $t(\mathbf{p}_\perp) \equiv 0$ it goes over into the *soliton energy* $E_s = 2\Delta_0/\pi$ for the one-dimensional *Peierls model*, chapter II, §3. We see that the *electron transfers between the chains* decreases the value of A and at a suitable form of the functions $t(\mathbf{p}_\perp)$ the quantity A can reverse sign. The condition $A = 0$ is the limit of the absolute instability of the one-dimensional *Peierls state*.

The quantity B characterizes the *interaction energy of the domain walls*. Just as in the one-dimensional model, this energy decreases exponentially with increasing distance between walls. However, whereas in the one-dimensional case we always have $B > 0$, now, as can be seen from (15), it is possible in principle to choose the function $t(\mathbf{p}_\perp)$ such that $B < 0$. At $B > 0$ the instability of the inhomogeneous state revolves as a second-order phase transition (with respect to pressure), while at $B < 0$ the phase transition takes place jumpwise at a certain $A > 0$. There is no unique connection between the definitions of A and B.

The periodic state considered by us is the alternative of the flow-order of particles from the valence band to the conduction band of a *Peierls dielectric*, which leads to formation of *electron-hole pockets* (*the "Lifshitz transition of order* 2.5"), Fig. 13b.

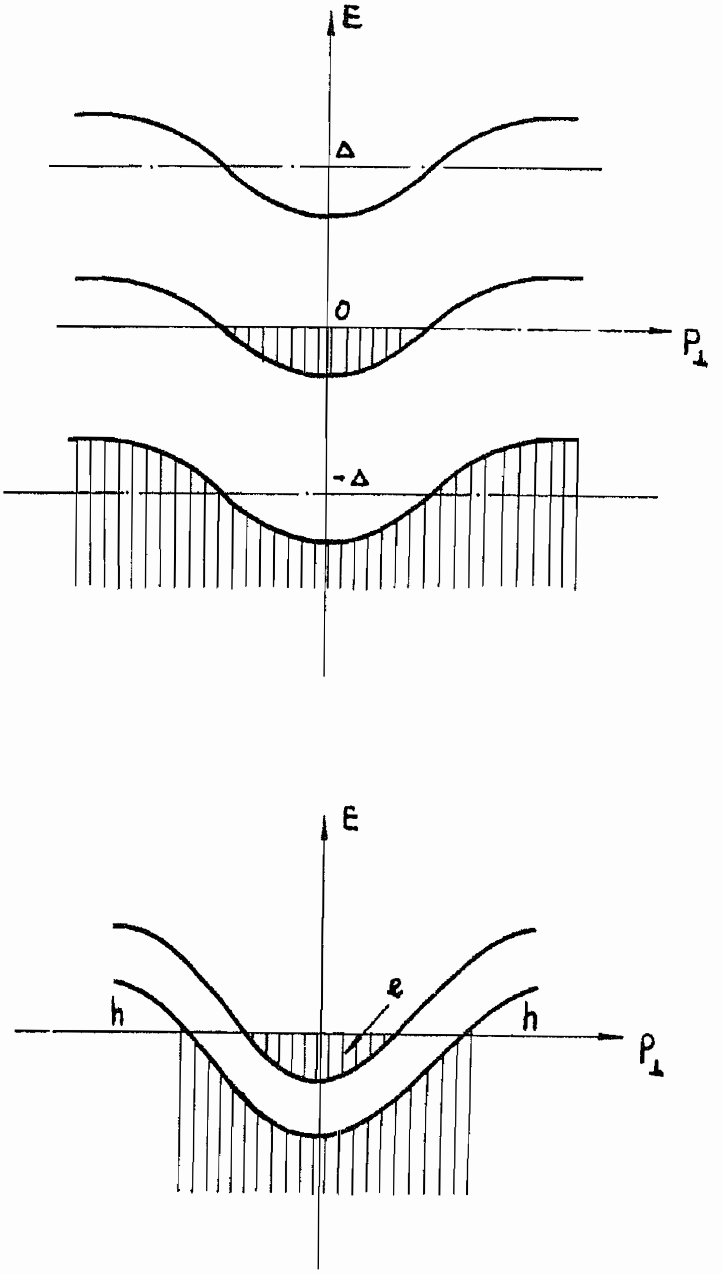

Figure 13

The latter, obviously, sets in when

$$\max_{\mathbf{p}_\perp} t(\mathbf{p}_\perp) - \min_{\mathbf{p}_\perp} t(\mathbf{p}_\perp) = 2\Delta_0 \tag{16}$$

This condition, in turn, is independent of the inequalities imposed on A and B. Consequently, for different functions $t(\mathbf{p}_\perp)$ there can take place arbitrary three different ways of transition from the dielectric *Peierls state* to the three-dimensional (anisotropic) metallic state.

We consider by way of example the *model of two-dimensional strong coupling* $t(\mathbf{p}_\perp) = t\cos(ap)$. This model is strongly degenerate. Indeed, *electron-hole pockets* are produced at $t = \Delta_0$. At the same point, according to (14) and (15), A and B vanish simultaneously. Thus, the points of all the phase transitions coincide.

As can be seen from these results, with increasing overlap of the chains the *formation of metallic sections of the Fermi surface* becomes possible via two mechanisms. In the first case, when the condition (16) is satisfied, the pockets are produced in the vicinity of $E = \pm\Delta_0$, Fig. 13b. In the other case, at $A = 0$, they are produced in the vicinity of $E = 0$, Fig. 13a.

One cannot exclude the possibility that more complicated lattice deformations lead to the appearance of new small forbidden bands on these Fermi surfaces. In the first case of (16) this can be regarded as an effect [60] of three-dimensional electron-hole pairing, while in the second case this would correspond to a deformation of the type III, §4, which produces an additional forbidden band near $E = 0$.

The rigorous results of chapter IV show that the results are stable, at least for a steplike Fermi surface corresponding to the *two-chain problem*.

We note in conclusion that the results of the present section can be applied equally to materials with $\rho = 1$ and to ones with *incommensurate superstructures*, such as $NbSe_3$. A common feature is that for both *Peierls models* (B and A) corresponding to these systems (I, §2) there exist stable *solitons with half-filled central level* (II, §§2, 3).

In light of the theory expounded above, it makes sense to review the experimental data on materials that preserve the residual metallization after structural phase transitions, such as $(TSeT)_2Cl$, $NbSe_3$, and $(SN)_x$. These data have so far been interpreted on the basis of the picture of *electron-hole pockets*. The most intriguing are the properties of the compounds $NbSe_3$ and TaS_3. The structure of these materials is such that there exists both a small chemical shift $\delta\epsilon_F = h$ between the two slightly nonequivalent sets of chains, as well as a substantial dispersion $t(p_\perp)$ on account of *electron transfer between chains*. It is therefore natural to expect the complete theory for these compounds to unify the models considered in chapter IV and in the present section. In this case we obtain an explanation for the coexistence of two *superstructures* with wave vectors $Q_\pm = (\pi/2a)(1 \pm \alpha)$, $\alpha \ll 1$ at $\rho = 1/4$. For $NbSe_3$, the phenomena described above, determined by the function $t(p_\perp)$, should predominate. For monoclinic TaS_3, which goes over after the formation of the two *superstructures* into the dielectric phase, the mechanisms of chapter IV, determined by the value of h, should predominate. The experimental relation $Q_+ + Q_- = \pi/2a$, corresponds to Eq. (IV.2.39). We conclude that in MX_3 compounds there can exist *periodic domain structures* made up of the *amplitude solitons* investigated in chapter II §2, for *model A*.

VI Solitons in a System of Weakly Coupled Chains

We investigate in this chapter the influence of *weak interaction between chains* (3d coupling) on the state and *statistics of the amplitude solitons* in *models A* and *B*, on the basis of publications [47, 53]. The weak 3d coupling does not influence substantially the process of *electron self-trapping* or the structure of the *soliton core* ($|x| \sim \xi_0$), but its role turns out to be fundamental at large distances x, especially below the *three-dimensional ordering temperature* $T < T_c$, $T_c \ll \Delta_0$. Since each soliton couples different states of the system, the *correlation between the chains* is violated in its vicinity. As a result, the system loses an energy

$$U \sim \mathscr{F}|x|; \quad \mathscr{F} \sim (\alpha/g^2)\Delta_0^2; \quad \mathscr{F} \sim t_\perp^2/v_F\hbar; \quad \alpha \ll g^2/v_F\hbar, \quad t_\perp \ll \Delta_0$$

(in the notation of chapter V), which increases in proportion to the distance x from the soliton, in analogy with the confinement in *models*

C in AC (I, §2; II, §4). A similar role is played by *commensurability effects* of odd order (I, §2).

In the case of *model A* considered in §1, the correlation can be restored by changes in the phase of the order parameter $\Delta(x)$, localized in the tails of a soliton of length $l \sim \hbar v_F / T_c \gg \xi_0$. In the case of *model B*, which is considered in §2, it is impossible to restore the correlation for one *soliton*. As a result, the solitons are coupled into pairs at $T < T_c$, and aggregation of pairs between the chains takes place at $T < T_0 \ll T_c$. For a three-dimensional system the temperature T_0 is a phase-transition point below which *plane domain walls* appear in the system and pass through the entire cross section. For a layered system a gradual increase of the transverse dimension of the paired walls takes place at $T < T_0$. A distinguishing feature of the *Peierls model* manifests itself in the fact that the solitons have quantum eigenvalues (s, e_s) that make it possible to monitor their concentration.

§1 Solitons in the Quasi-One-Dimensional Peierls–Fröhlich Model with Continuous Degeneracy of the Ground State

We consider the quasi-one-dimensional Peierls–Fröhlich model (model A), which is characterized by an equilibrium gap Δ_0 and by a low three-dimensional ordering temperature $T_c \ll \Delta_0$. The *soliton binding energy* is

$$\delta E_s = \Delta_0 - E_s = \Delta_0(1 - 2/\pi) \approx 0.36\Delta_0$$

i.e., $\delta E_s \gg T_c$, so that its formation (self-trapping of the electron) takes place mainly independently of the surrounding chains. As a result, however, the sign of the parameter $\Delta(x)$ is reversed on the central chain on going through the region of the *soliton* with center at the point x_0. Inasmuch as in the ordered phase the chains should be correlated, the change of the sign of $\Delta(x)$ far from the soliton becomes equalized, and this should be reflected in the soliton properties. The perturbations of the surrounding chains should decrease rapidly with increasing n, so that to describe the effect it suffices to take into account the chain with $n = 0$, which carries a soliton, and its Z nearest neighbors. Since the equalization will take place at a distance $l \sim \hbar v_F / T_c \gg \xi_0$, we can use a quasiclassical description [30] in terms of the phase φ_n on the chains, assuming that $|\Delta_n(x)| \equiv \Delta_0$. The presence of the soliton is taken into account here by the discontinuity of the phase $\varphi_0(x)$

$$\varphi_0(x_0 + 0) - \varphi_0(x_0 - 0) = \pi \tag{1}$$

at continuous phases $\varphi_n(x)$, $n \neq 0$.

The described model is characterized by an energy functional

$$\mathscr{H}\{\varphi\} = \sum_n \int \frac{dx}{4\pi\hbar v_F}\left[(\varphi_n')^2 - \frac{1}{(z+1)e^2}\cos(\varphi_n - \varphi_0)\right] \qquad l \sim \hbar v_F / T_c \tag{2}$$

where $T_c \ll \Delta_0$ is the three-dimensional ordering temperature.

The equilibrium state of the system is described by the extremals of the functional (2) with the supplementary condition (1). We define $\varphi_n(x) = \varphi_0(x) + \psi(x)$ at $n \neq 0$. The functions φ_0 and ψ satisfy the equations

$$\begin{aligned} &(z+1)\varphi_0'' + z\psi'' = 0 \\ &(z+1)\psi'' + (z+1)\varphi_0'' - e^{-2}\sin\psi = 0 \end{aligned} \tag{3}$$

with the boundary conditions*

$$\psi(x), \psi'(x), \varphi_0'(x) \to 0 \qquad \text{at} \quad x \to \pm\infty \tag{4a}$$

$$\varphi_0(x) = -\psi(x) = \frac{\pi}{2}\,\mathrm{sgn}(x - x_0) \qquad \text{at} \quad x \to x_0 \tag{4b}$$

---

*The condition (4b) presupposes, in addition to (1), that the extremal (2), which is antisymmetric with respect to x_0, has been chosen. It will be shown below that this choice corresponds to an absolute minimum of $\mathscr{H}$ (see (12a)).

From (3) and (4) we obtain the following solutions:

$$\psi(x) = -4\,\mathrm{arctg}\left\{\exp\frac{l_0 - |x - x_0|}{l}\right\}\mathrm{sgn}(x - x_0)$$

$$\varphi_0(x) = \frac{1}{z+1}\left\{\frac{\pi}{2}\,\mathrm{sgn}\,x - z\psi(x)\right\}; \tag{5}$$

$$\varphi_n(x) = \frac{1}{z+1}\left[\frac{\pi}{2}\,\mathrm{sgn}\,x + \psi(x)\right]$$

where $l_0 = l\ln[\mathrm{tg}(\pi/8)]$.

Plots of $\varphi_0(x)$ and $\varphi_n(x)$ are shown in Fig. 14a.

3 Although the core of the soliton is not charged, in the region of phase relaxation $\xi_0 \ll |x - x_0| \lesssim l$ there appear charges q_n with density $\rho_n(x) = e_n\varphi_n'(x)/\pi$. From (4a, b) we have

$$q_0 = 2\frac{e}{\pi}\left[\varphi_0(\infty) - \varphi_0(0)\right] = -\frac{ez}{z+1}$$

$$q_n = \frac{en}{\pi}\left[\varphi_n(+\infty) - \varphi_n(-\infty)\right] = \frac{e_n}{z+1}$$

We note that the sign of q_0 is opposite to the sign of the charge $e_0 = \pm e$ of the initial carriers. The total charge of the system q depends on the signs of the charges of the carriers e_n:

a) all of the chains have the same charges

$$e_n = e_0, \qquad q = q_0 + zq_n = 0$$

in accordance with the results of chapter II, §2;

b) the surrounding chains have charges opposite to that of the central chain

$$e_n = -e_0; \qquad q = q_0 - zq_n = -\frac{2z}{z+1}e_0$$

As $z \to \infty$ we have $q \to -2e$, the charge is doubled.

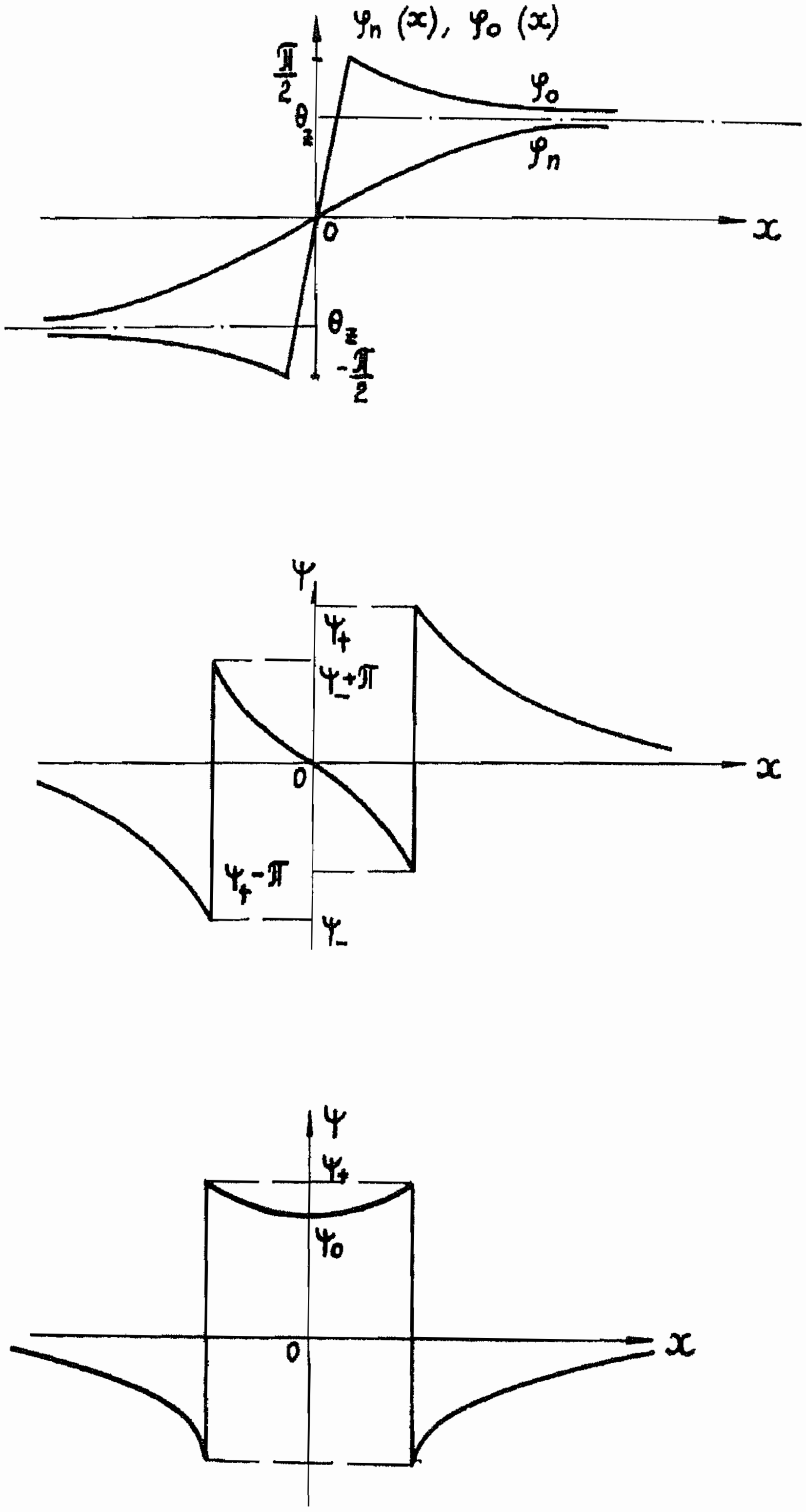
$\varphi_n(x)$, $\varphi_o(x)$
$\frac{\pi}{2}$
θ_z
φ_o
φ_n
0
x
θ_z
$-\frac{\pi}{2}$
ψ
ψ_+
$\psi_- + \pi$
0
x
$\psi_+ - \pi$
ψ_-
ψ
ψ_+
ψ_0
0
x

Figure 14

c) The charges of the chains alternate

$$\sum_{n\neq 0} e_n = 0; \qquad q = q_0 = -\frac{z}{z+1}e$$

as $z \to \infty$ we have $q \to -e$, and the system has a single charge. The case (a) corresponds to *systems with total charge transfer*, such as TaS_3 or *KCP*, while case (c) corresponds to *systems with partial transfer*, such as *TTF-TCNQ*. Thus, in KCP the *solitons* remain uncharged, and in TTF-TCNQ they have a charge $\sim -e$ localized in the region $l \sim \hbar v_F / T_c$.

4 The presence of a connection between the chains leads also to the most substantial interaction between the solitons. As indicated in the footnote above, the change of $\Delta(x)$ for a single soliton proceeds along a definite diameter perpendicular to the ordering direction $\Delta(+\infty) = \Delta(-\infty)$. We can therefore speak of solitons having two signs respectively, $\psi(x) \approx \pm(\pi/2)\mathrm{sgn}(x - x_i)$ at $x \to x_i$ (see (4b) and (12a)).

We consider two solitons of the same sign, located at the points $\pm d/2$. The boundary condition (4b) is generalized in accordance with Fig. 14b:

$$\begin{aligned} \psi\left(-\frac{d}{2}-0\right) &= \pi + \psi\left(-\frac{d}{2}+0\right) = \psi_- \\ \psi\left(\frac{d}{2}+0\right) &= -\pi + \psi\left(-\frac{d}{2}-0\right) = \psi_+ \end{aligned} \tag{6}$$

The solutions of Eqs. (3) outside the discontinuity points $x = \pm d/2$ are characterized by a first integral H or k

$$\frac{1}{2} l^2 \psi'^2 - (1 - \cos\psi) = H; \qquad H = \frac{2(1-k^2)}{k^2} \tag{7}$$

It follows from (4a) that at $|x| > d/2$ we have $H = 0$ and $k = 1$. At $|x| < d/2$, according to the least-action principle for the functional (2) the quantity $H = H(d)$ is proportional to the force $\mathscr{F}$ of the *interaction between the solitons*:

$$\mathscr{F} = -\frac{\partial \mathscr{H}}{\partial d} = \frac{z}{z+1}\,\frac{\hbar v_F H}{2\pi^2 l} \tag{8}$$

The quantity (2) on the extremal (7) is equal to

$$\frac{2\pi}{v_p} l^2 \frac{z+1}{z} \mathscr{H} = \int_{\psi_-}^{\psi_+} \sqrt{2H + 4\sin^2\frac{\psi}{2}}\; d\psi + \int_{\psi_+ - \pi}^{\psi_- + \pi} 2\left|\sin\frac{\psi}{2}\right| d\psi - Hd \tag{9}$$

Varying (9) with respect to ψ_+ and ψ_- at a specified H, we find that the solution is antisymmetric and

$$\cos\frac{\psi_\pm}{2} = \frac{1}{\sqrt{2}\,k}; \qquad \psi_+ = -\psi_-; \qquad \frac{1}{\sqrt{2}} \leqslant k \leqslant 1 \tag{10}$$

The solution (7) can be written in the form

$$\cos\frac{\psi}{2} = sn\left(K(k) - \frac{x}{kl}\,; k\right) \tag{11}$$

where $K(k)$ is a *complete elliptic integral* of the first kind. The value of k is determined according to (6) from the equation

$$sn\left(K(k) - \frac{d}{2kl}\,, k\right) = \frac{1}{\sqrt{2}\,k} \tag{12}$$

at

$$d \gg l, \qquad k \to 1, \qquad \psi_\pm \to \pi/2 \tag{12a}$$

$$H = \left[32/\left(\sqrt{2}+1\right)^2\right] e^{-d}$$

We have found, in particular, that for a *single soliton* the *phase relaxation* proceeds antisymmetrically (see the footnote on p. 240).

At $d \ll l$ we have $k \to 1/\sqrt{2}$, $\psi_\pm \to 0$, and $H \to 0$, i.e., the repulsion force is finite.

We consider now the case of *solitons* of opposite sign. In place of

(6) we have, in accordance with Fig. 14c,

$$\begin{aligned} \psi\left(-\frac{d}{2}+0\right) &= \psi\left(\frac{d}{2}-0\right) = \psi_+ \\ \psi\left(-\frac{d}{2}-0\right) &= \psi\left(\frac{d}{2}+0\right) = \pi - \psi_+ \end{aligned} \tag{13}$$

Since $\psi'(0) = 0$ and $\psi(0) \neq 0$, we now have in (7) $H < 0$, i.e., attraction takes place. In place of (8) we have

$$\frac{2\pi}{v_F} l^2 \frac{z+1}{z} \mathcal{H} = 2\int_{\psi_0}^{\psi} \sqrt{2\mathcal{H} + 4\sin\frac{2\psi}{2}}\; d\psi + 4\int_{\psi_+ - \pi}^{0} \sin^2\psi\, d\psi - Hd \tag{14}$$

Varying (14) with respect to ψ_0 and ψ_+ we obtain

$$\cos\psi_+ = -\sin^2\frac{\psi_0}{2}\,; \qquad H = -2\sin^2\frac{\psi_0}{2} \tag{15}$$

The solution of (7) is now

$$\cos\frac{\psi}{2} = \cos\frac{\psi_0}{2}\, sn\left[K\left(\cos\frac{\psi_0}{2}\right) - \frac{x}{l}\,, \cos\frac{\psi_0}{2}\right] \tag{16}$$

According to (14)–(16), the value of ψ_0 is determined from the equation

$$sn\left[K\left(\cos\frac{\psi_0}{2} - \frac{d}{2l}\right), \cos\frac{\psi_0}{2}\right] = \frac{1}{\sqrt{2}} \tag{17}$$

The solution (17) has a continuous singularity at the point $d/l = \pi/2$. At $d \gg l$ we have $\psi_0 \to 0$, $\psi_+ \to \pi/2$, and

$$H \approx -\left[32/(\sqrt{2}+1)^2\right] e^{-d}$$

At $d \lesssim \pi l/2$ we have $\psi_0 \equiv \psi_+ \equiv \pi$ and $H = 2$. In this region we have a finite attraction force (8) independent of the distance at $H = 2$.

Calculation of the energy $\mathscr{H}$ and of the interaction force $\mathscr{F} = -\partial \mathscr{H}/\partial d$ shows that solitons having opposite signs on the same filament and equal signs on neighboring filaments are attracted: $\mathscr{F}_{\uparrow\downarrow} > 0$, while solitons having equal signs at one filament and opposite signs at neighboring filaments are repelled, $\mathscr{F}_{\uparrow\uparrow}, \mathscr{F}_{\downarrow\downarrow} < 0$. According to (8), (12), and (17) we have

$$\begin{aligned} d \lesssim l \qquad & |\mathscr{F}| \sim \hbar_V / l^2 \sim T_c^2 / v_F \hbar \\ d \gtrsim l \qquad & |\mathscr{F}| \sim (\hbar v_F / l^2) \exp\{-2d/l\} \end{aligned} \tag{18}$$

At a finite temperature $T \ll T_c$ the attracting *solitons* are located in the region $d \lesssim l/T$, where the thermal length l_T was determined from the relation $\mathscr{F} l_T \sim T$ under the condition that $l_T \ll l$. We obtain

$$l_T \sim \hbar v_F T / T_c^2; \qquad l_T / l \sim T / T_c \ll 1$$

At $T < T_c^2/\Delta_0 \ll T_c$ we have $l_T \sim \xi_0$. In this case solitons bound on one filament should annihilate.

The *quantum oscillations of a pair of solitons* at distances $\xi_0 < |x| < l$ can be described by the Hamiltonian

$$\hat{\mathscr{H}} = -\frac{\hbar^2}{2M_s} \frac{\partial^2}{\partial x^2} + \frac{\hbar v_F}{l^2} |x| \tag{19}$$

where M_s is determined by Eq. (II.2.28). From (19) we can estimate the amplitude of the zero-point oscillations $l_0 = \langle |x| \rangle$

$$\frac{l_0}{l} \sim \left(\frac{u}{v_F} \right)^{2/3} \left(\frac{T_c}{\Delta} \right)^{1/3} \sim \frac{(\hbar^2 \omega_0^2 T_c)^{1/3}}{\Delta} \tag{20}$$

At the typical parameters $u/v_F \sim T_c/\Delta \sim 10^{-1}$ we have $l_0/l \sim 10^{-1}$. The foregoing estimates are valid if $l_0 \gg \xi_0$. Actually, however,

$$\frac{l_0}{\xi_0} \sim \left(\frac{u}{v_F} \frac{\Delta_0}{T_c} \right)^{2/3} \sim 1 \sim \left(\frac{\hbar \omega_0}{T_c} \right)^{2/3} \sim 1$$

5 From the foregoing estimates it follows that at $T \ll T_c$ the thermal motion should cause the solitons on the same chain to be attracted and annihilated, and those on neighboring chains to form classical bound states at $l_T > l_0$ or quantum bound states at $l_T < l_0$. The soliton linear concentration $\overline{\overline{C}}$ is equal to (under the condition $\overline{\overline{C}}l \ll 1$)

$$C = \left(\frac{M_s T}{2\pi} \right)^{1/2} \exp(-E_s/T), \qquad T \ll \hbar\omega_0$$

Actually,

$$Cl \sim 10^2 (T/E_s)^{1/2} \exp(-E_s/T)$$

whence at $T < T_c \sim \hbar\omega_0$ we have $Cl \ll 1$.

We find that at $T < T_c$ individual *solitons* and bound complexes are on the average far from one another and do not interact in practice. On account of the rare collisions, solitons of the same sign can become bound in this case on a large number of neighboring filaments so that planes with simultaneous reversal of the sign of all $\Delta_n(x)$ are produced. These effects are investigated in detail in §2.

The interaction of a *charge-density wave* with the main structure in the case of *odd-order commensurability* leads qualitatively to the same effects as the chain interaction described above. The distribution of the phase on the *tails of the amplitude soliton* is shown in Fig. 5a. The *soliton charge* as indicated in chapter II, §2, is equal to $\pm e/3$.

Commensurability effects manifest themselves if the pinning energy $\sim T_p^2/\Delta_0$ exceeds the energy $\sim T_c^2/\Delta_0$ of the *interaction between the chains*. In real systems this is possible apparently only in *systems with threefold commensurability*, if the following condition is satisfied

$$\frac{T_c}{\Delta_0} \ll \frac{T_p}{\Delta_0} \sim \left(\frac{\Delta_0}{D} \right)^{1/2}$$

The *combined dielectrics* described by the *AC model* are a special case. The phase equalization takes place here in analogy with the interaction, considered above, between chains. *The soliton charge* is $\pm 2e$.

§2 Statistics of Kink Ensemble in a System of Weakly Bound Chains

In this section we consider the static properties of a gas of *amplitude solitons* for *models A* and *B* when the average distance between *solitons* is much larger than the microscopic width ξ_0 of the soliton, but smaller (for the model A) than the *equalization length l* (§1).

2.1 Equivalent Ising Model

The system considered can be described by an order parameter $\eta_\alpha(x)$, where α is the index of the chain and x is the coordinate along the chain. We normalize $\eta_\alpha(x)$ in such a way that $\eta_\alpha(x) \approx \pm 1$ in the regions between solitons far from their cores, and takes the form $\eta_\alpha(x) = \pm f(x - x_0)$; $f(\pm\infty) = \pm 1$ in the vicinity of a soliton with center at the point x_0. The function $f(x)$ describes the shape of the soliton and takes for the *Peierls model* the form

$$f(x) = \mathrm{th}(x/\xi_0); \qquad \xi_0 \sim aD/\Delta_0 \tag{1}$$

For *polyacetylene* [37] we have $\xi_0 \approx 7a_0$, where a_0 is the distance between the atoms. We introduce the local *linear soliton concentration* $C_\alpha(x)$, which must satisfy for the considered dilute system the condition

$$\xi_0 C_\alpha(x) \ll 1 \tag{2}$$

The average concentration $\overline{C}$ can be fixed by the composition of the material. For example, in *polyacetylene* $\overline{C}$ is equal to the concentration of the electrons injected as a result of doping. The concentration of the *spin solitons* (II, §2) can be fixed in principle by the magnetization of the system, or produced by optical pumping. We shall assume that the *energy E_s of the soliton*, for an isolated chain, is high enough to be able to neglect the thermal activation of the solitons:

$$E_s \gg T, \qquad C_T \gg \overline{C}$$

As is usual in statistical mechanics, it is simpler to investigate the properties of a system in a grand canonical ensemble at a given chemical potential μ of the solitons. The value of μ is fixed, e.g., in the case of a *system of two chains* in one cell or at a given magnetic field (chapter IV).

The functional of the configuration energy for an arbitrary inhomogeneous disposition of the solitons can be written under condition (2) in the form

$$\mathscr{H} - \mu N_s = \int_0^L dx \left\{ - \sum_{\langle \alpha, \beta \rangle} V \eta_\alpha(x) \eta_\beta(x) + \sum_\alpha (E_s - \mu) C_\alpha(x) \right\}$$

$$N_s = \bar{C} L; \qquad V > 0 \tag{3}$$

where $\langle \alpha, \beta \rangle$ are the nearest interacting chains and V is the energy difference (per unit length of one chain) between the fully ordered ($T = 0$, $\bar{C} = 0$) and disordered state of the chains. For sufficiently simple lattices the signs of $\eta_\alpha(x)$ can be redefined in a way to make $V > 0$.

We introduce now a new length scale a, such that $a > \xi_0 > a_0$, and coarse-grain the chain, considering only points $x = x_n = na$. The function $\eta_\alpha(x_n)$ can be regarded here as an *Ising spin* $S_{n,\alpha}$ defined at the site (n, α). We introduce analogously in place of the *soliton concentration* $C_\alpha(x)$ the dimensionless density $\rho_{n,\alpha}$:

$$\rho_{n,\alpha} = C_\alpha(x_n) a; \qquad S_{n,\alpha} = \eta_\alpha(x_n); \qquad x_n = na \tag{4}$$

A procedurally important circumstance is that the density $\rho_{n,\alpha}$ can be expressed in terms of $S_{n,\alpha}$:

$$\rho_{n,\alpha} = \left(\frac{S_{n+1,\alpha} - S_{n,\alpha}}{2} \right)^2 = \frac{1}{2} (1 - S_{n,\alpha} S_{n+1,\alpha}) \tag{5}$$

In (5) it is assumed that the sites $\{n\}$ of the possible locations of the *solitons* are placed between the sites n and $n + 1$ of the spin chain S_n. Using (4) and (5) we can now write down the functional (3) in the form of a Hamiltonian for the *Ising model*

$$H = -J_\perp \sum_{n, \langle \alpha, \beta \rangle} S_{n,\beta} - J_\parallel \sum_{n,\alpha} (S_{n,\alpha} S_{n+1,\alpha} - 1) \tag{6}$$

where

$$J_{\perp} = aV; \qquad J_{\|} = \frac{1}{2}(E_s - \mu) \tag{7}$$

For a system with a given concentration $\nu = \bar{\rho}_{n,\alpha} = \overline{C}_{\alpha}$ the quantity $J_{\|}$ is determined from the *self-consistency condition*

$$\frac{1}{2}\left[1 - \langle S_{n,\alpha} S_{n+1,\alpha} \rangle_H\right] = \nu = \overline{C}a \tag{7a}$$

where

$$\langle A \rangle = \frac{\underset{S_{n,\alpha}}{\mathrm{sp}}\, A \exp\{-\beta H\}}{\underset{S_{n,\alpha}}{\mathrm{sp}} \exp\{-\beta H\}}$$

From (3) and (6) we see that the Gibbs energy $\Omega(\mu, T)$ for a *grand canonical ensemble of solitons* is expressed in terms of the free energy of the *Ising model* (6), F_s. For the energy per lattice site (i.e., per length a of the unit cell) we have

$$\begin{gathered} \Omega(\mu, T) = F(K_{\|}, K_{\perp}) + TK_{\|} \\ K_{\|} = \beta J_{\|}; \qquad K_{\perp} = \beta J_{\perp} \end{gathered} \tag{8}$$

The *soliton density* ν is determined from the relation

$$\nu = -\frac{\partial \Omega}{\partial \mu} = \frac{1}{2} + \frac{1}{2T}\frac{\partial F}{\partial K_{\|}} \tag{9}$$

which is equivalent to the condition (7a).

The parameters $J_{\perp}$ and ν for the Hamiltonian (6) and for the *self-consistency condition* (7a) or (9) are still not connected with the physical parameters V and $\overline{C}$, inasmuch as the unit length a has not been determined for the coarse-grain density (4). We shall show that a should coincide with the equilibrium distance l_0 determined from the condition that equilibrium exists between the repulsion of the *soliton cores* and their attraction on account of the *interaction between chains*, as investigated in §1. At distances $l \gg \xi_0$ the energy of a pair of solitons on one chain has a typical form

$$U(l) = 2ZVl + U_{\text{rep}}(l); \qquad U_{\text{rep}} \sim E_s e^{-l/\xi_0} \tag{10}$$

where Z is the number of nearest neighbors. The equilibrium position l_0 is determined from the condition

$$\left.\frac{dU}{dl}\right|_{l=l_0} = 0; \qquad l_0 \approx \xi_0 \ln \frac{E_s}{zV\xi_0}; \qquad l_0 > \xi_0 \tag{11}$$

It is important that, as a result of (10) and (11), the equilibrium per energy is equal to

$$U(l_0) = 2ZVl(1 + \xi_0/l_0) \approx 2ZVl_0 (12)$$

i.e., it is determined mainly by the contribution of the energy (10). At large distances $l \gg l_0$ the *interaction at the solitons* is determined already exclusively by the first part of the energy (10). On the other hand, in the *Ising model* (6) two *solitons* at sites n_1 and n_2 on a chain confine a segment of length $n = n_2 - n_1$ with reversed spin. The minimum distance corresponds to $n = 1$. The energy of such a configuration is

$$U(n) = 2ZJ_{\perp} n \tag{13}$$

To reconcile the models (3) and (6) it is necessary that (13) coincide with (10) at $l = na$, and (12) coincide with (13) at $n = 1$. We obtain

$$a = l_0, \qquad J_{\perp} = Vl_0, \qquad \nu = \bar{C} l_0 \tag{14}$$

§3 Exact Results for a Linear System of Chains

For a *linear system with nearest-chain interaction* ($\beta = \alpha + 1$) we can use the exact results for the two-dimensional Ising model. All the necessary data for the anisotropic case ($K_{\parallel} \neq K_{\perp}$) are contained, e.g., in review [77].

The model (6) has a line of phase transitions determined by the equation

$$K = K(K_\perp, K_\parallel) = 1 \tag{15}$$

where

$$K = \operatorname{sh} K_\perp \operatorname{sh} K_\parallel \tag{16}$$

On this line the *soliton concentration* ν is equal to

$$\nu = \frac{1}{2} - \frac{1}{\pi} \operatorname{ch} K_\perp \operatorname{arctg} \frac{1}{\operatorname{sh} K_\perp} \tag{17}$$

Equation (17) defines the point $K_\perp(\nu)$ on the critical line (15). Since $J_\perp$, according to (14), is fixed, we obtain a unique connection between the critical temperature T_c and the soliton concentration ν:

$$T_c(\nu) = \frac{J_\perp}{2K_\perp(\nu)} \tag{18}$$

Equation (17) has a solution if

$$\nu < \nu_{\max} = \frac{1}{2} - \frac{1}{\pi} \approx 0.23$$

The numerical smallness of ν allows us to assume that this value lies within the region of applicability of the model (6), determined generally speaking by the condition $\nu \ll 1$. At $\nu \ll 1$ we obtain from (17) and (18)

$$T_c(\nu) \approx \frac{2}{\pi} \frac{J_\perp}{\nu}, \qquad \nu \ll 1 \tag{19}$$

Consequently, at least if the concentration is not too large ($\nu < \nu_{\max}$), the *soliton gas* undergoes a phase transition at a temperature T_c determined by Eqs. (17) and (18), or approximately by Eq. (19).

The value of the chemical potential μ on the critical line

$$\mu = \mu_c(\nu)$$

is determined from the conditions (15) and (16) with allowance for the definitions (7) and (8a). Near the critical line, the compressibility κ of the soliton gas has the same singularity as the specific heat in the *Ising model*

$$\kappa = \left(\frac{\partial \nu}{\partial \mu} \right)_T = \frac{1}{T^2} \frac{\partial^2 F}{\partial K_{\|}^2} \approx \frac{1}{T_c} \ln \tau \tag{20}$$

where

$$\tau \sim \frac{T - T_c}{T_c} \sim \frac{\mu - \mu_c}{\mu_c}$$

From the point of view of the structural properties of the system, it is obvious that at $T = T_c(\nu)$ a transition takes place into a three-dimensionally ordered phase with nonzero mean value of the order parameter

$$\langle \zeta_\alpha(x) \rangle \neq 0, \qquad T < T_c(\nu)$$

In the disordered phase, $T > T_c(\nu)$, Eq. (7a) is of the form

$$\nu = \frac{1}{2} - \frac{1}{\pi} \operatorname{ch} K_{\|} \operatorname{cth} K_{\|} \left[\Pi(\operatorname{sh}^2 K_{\|}, k) - \frac{K(k)}{\operatorname{ch}^2 K_{\|}} \right]$$

where $\Pi(m, k)$ and $K(k)$ are *complete elliptic integrals* of the third and first kind, and k is defined by formula (16) with $k < 1$.

At $T \gg T_c$ we have $K_\perp \ll 1$ and we obtain from (21) approximately

$$\nu \approx \frac{1}{1 + \exp K_{\|}} \approx \exp\{ \beta(\mu - E_s) \} \tag{22}$$

Consequently, in the high-temperature region the *ensemble of solitons* is thermodynamically equivalent to a gas of free heavy Fermi particles.

In a disordered phase, at $T < T_c(\nu)$, we have $k > 1$ and

$$\nu = \frac{1}{2} - \frac{1}{\pi} \operatorname{cth}^2 K_{\|} \operatorname{cth} K_\perp \left[\Pi(\operatorname{sh}^{-2} K_\perp ; k^{-1}) - \operatorname{ch}^{-2} K_{\|} K(k^{-1}) \right] \tag{23}$$

At $T < T_c(\nu)$ we can rewrite (23) approximately in the form

$$\nu = \frac{1}{D(T)\mathrm{sh}^2 K_{\|}}; \qquad D(T) = 2(e^{2k_{\perp}} - 1) \tag{24}$$

With the aid of (24) we easily obtain an approximate expression for the *free energy* F_s and for the *internal energy* U_s *of the solitons*

$$SF_s = F - \nu E_s = \nu(\mu - E_s) - \int_{-\infty}^{\mu} \nu \, d\mu$$

$$= -T\left[\frac{1}{D}\left(\sqrt{1+\nu D} - 1\right) + \nu \ln \frac{1+\sqrt{1+\nu D}}{\sqrt{\nu D}}\right] \tag{25}$$

$$\delta U_s = \frac{\partial}{\partial \beta}(\beta \delta F_s) \tag{25a}$$

In the investigation of formulas (24) and (25) we can distinguish between three different regions.

I $J_{\perp} \ll T \ll T_c \approx J_{\perp}/\nu$

In this region $K_{\perp} \ll 1$, $K_{\|} \gg 1$, and we obtain

$$\nu \approx 4\overline{N} \exp\{2(\mu - E_s)\} \tag{26}$$

$$\delta F_s \approx \frac{1}{2}\nu T\left[\ln \frac{\nu}{\overline{N}} - 1\right] \tag{27}$$

$$\delta U_s \approx \frac{1}{2}\nu \delta E_2; \qquad \delta E_2 = 4J_{\perp}\overline{N} \tag{28}$$

$$\overline{N} = \overline{N}(T) = \frac{T}{8J_{\perp}} \tag{29}$$

Formulas (26) and (27) show clearly that the *solitons* are bound into pairs with energy $2E_s$, with a chemical potential 2μ, and with a concentration $\nu/2$, and the interaction between the pairs is of little importance. Comparison of Eq. (28) for the internal pair energy E_2 with Eq. (13) at $Z = 2$ shows that the quantity $\overline{N}$ defined by formula (29) is the average thermal length of the pair. The factors $\overline{N}$ in (26) and (27) reflect the entropy of the internal thermal vibrations of the pair. In fact, using formula (10) for the energy of a pair with a given distance n, we can write for the concentration $\nu/2$ of the isolated pairs:

$$\frac{1}{2}\nu \approx \sum_n \exp\{\beta[2(\mu - E_s) - 4J_\perp n]\}$$

from which follows Eq. (26) at $\beta J_\perp \ll 1$.

II The intermediate region

$$J_\perp \gg T \gg T_0; \qquad T_0 = \frac{4J_\perp}{\ln(1/\nu)} \tag{30}$$

which can be determined at $\nu \ll 1$. In this region

$$k \ll 1; \qquad K_\perp \gg 1; \qquad K_\| \gg 1$$

and we obtain

$$\nu \approx 2\exp\{\beta[2(\mu - E_s) - 4J_\perp]\} \tag{31}$$

$$\delta f_s \approx \frac{\nu}{2}\{T[\ln(2\nu) - 1] + 4J_\perp\}; \qquad \delta U_s = 2\nu J_\perp \tag{32}$$

Equations (21) and (32) show that in the region (30) we have a *gas of soliton pairs* with a frozen-in internal degree of freedom, i.e., the pairs are separated by the minimum distance l_0 defined in (11).

III The low-temperature region

$$T \ll T_0 = 4J_\perp/|\ln\nu| \tag{33}$$

In this region $k \ll 1$, $K_\perp \ll 1$, $K_\| \ll 1$, and we obtain

$$\nu = \frac{2T^2}{(E_s - \mu)^2}\, e^{-4\beta J_\perp} \tag{34}$$

$$\delta f_s \approx -T\sqrt{\frac{\nu}{2}}\, e^{-4\beta J_\perp} \tag{35}$$

The thermodynamic relations (34) and (35) no longer correspond to the gas picture. The equation of state (34) shows that the activation energy vanishes and the effective chemical potential tends to zero

$$\mu^* = \mu - E_s \sim T/T_0(\nu) \ll 1$$

The relation $\delta f_s \sim \sqrt{\nu}$ given by (35) is typical of surface effects. These results show that the *solitons* become aggregated in the systems into large groups, so that a gain in the *binding energy* $J_\perp$ *of the chains* can be obtained. The structure of this aggregate can be investigated accurately by calculating the correlation function of the *soliton density*

$$F_{n\alpha} = \langle (\rho_{n\alpha} - \nu)(\rho_{00} - \nu) \rangle \tag{36}$$

According to the definition (5), the function (36) is a four-spin correlation function for the *Ising model* (6). Its calculation is greatly facilitated by the fact that in the fermion representation of the Transfer Matrix for the Ising model that is dual to (6) the soliton density $\rho_{n\alpha}$ coincides with the fermion-density operator

$$\rho_{n\alpha} = C_n^+ C_n$$

The calculations performed in [53] yield at $T \ll T_0$

$$F_{n\alpha} = \frac{1}{2} \nu e^{-\alpha / l_\perp} \left[\delta_{n,1} + \delta_{n,-1} \right] \tag{37}$$

$$l_\perp = \sqrt{\frac{\nu}{2}}\, e^{2\beta J_\perp}; \qquad l_\perp \gg 1 \tag{38}$$

Equations (37) and (38) show that the *solitons* gather into segments of the type of *double domain walls* with the nearest distance between them l_0. The average length $l_\perp$ of the segment directed perpendicular to the chains increases with decreasing temperature.

Bearing this picture in mind, we can easily obtain the thermodynamic relations (34) and (35) without resorting to the results of the exact solution. We consider an ensemble of transverse segments made up of *soliton pairs*. The segments can have arbitrary lengths l in the transverse direction (α) and characterized by a distribution over the lengths $f(l)$. The energy of a segment of length l is obviously equal to

$$E(l) = 2E_s l + 4J_\perp \tag{39}$$

and the chemical potential $\mu(l)$, by virtue of the thermodynamic equilibrium, is equal to

$$\mu(l) = l\mu(1) = 2\mu l \tag{40}$$

From (39) and (40) we obtain the distribution

$$n(l) = \exp\{\beta[2(\mu - E_s)l - 4J_\perp]\} \tag{41}$$

From (41) we obtain the total concentration of all the segments:

$$n = \sum_{l=1}^{\infty} n(l) = \frac{e^{-2\beta J_\perp}}{e^{2\beta(E_s - \mu)} - 1} \tag{42}$$

and the *concentration of the solitons*

$$\nu = \sum_{l=1}^{\infty} 2\ln(l) = \nu e^{2\beta J_\perp}(e^{2\beta(E_s - 2\mu)} - 1) \tag{43}$$

The average length of the segment is

$$l_\perp = \frac{\nu}{n} = \nu e^{2\beta J_\perp}(e^{2\beta(E_s - \mu)} - 1) \tag{44}$$

Formulas (42)–(44) agree fully with the results, presented above, of the exact investigation in both regions II and III, i.e., wherever $T \ll J_\perp$.

3.1 *Peculiarities of Three-Dimensional System of Chains*

We consider now the general case, when the chains interact in both transverse directions. The properties considered above for a linear system of chains remain qualitatively in force in most high-temperature regions: $T > T_c$, $T_c > T > J_\perp$, and $J_\perp > T > T_0$. The *compressibility of the system* κ is connected as before with the *heat capacity* *of the Ising model* by Eq. (20). In the three-dimensional case the singularity takes the form

$$\frac{\partial \nu}{\partial \mu} \sim \tau^{-\alpha}; \qquad \alpha = 0; 1; 2$$

In the three-dimensional case, however, the region III, $T < T_0$ vanishes and the temperature T_0 becomes a point of a new phase transition, below which $J_{\|} = 0$. This conclusion follows rigorously from the inequality

$$\nu(\beta J_{\|};\, \beta J_{\perp}) \leqslant \nu(0;\, \beta J_{\perp}) = \tfrac{1}{2}(1 - m^2); \qquad m = m(\beta J_{\perp}) = \langle S_\alpha \rangle_{2d} \tag{45}$$

where $\langle \ldots \rangle_{2d}$ denotes the mean value for the *two-dimensional Ising model* defined by the Hamiltonian (6) at $J_{\|} = 0$ and $S_{n\alpha} = S_\alpha$. For example, for a rectangular lattice of chains, $J_{\perp} = (J_1, J_2)$, we have

$$J_{\|} \geqslant 0: \quad \nu \geqslant 2\exp\left[-4\beta(J_1 + J_2)\right]; \qquad T \geqslant T_0(\nu) = \frac{4(J_1 + J_2)}{\ln(2/\nu)} \tag{46}$$

At $T < T_0$, the conservation of a given ν is possible only at $J_{\|} = 0$, under the condition of formation of infinite *domain walls* that pass through the entire cross section. The *linear concentration* ν_0 *of the walls* can be obtained, just as the inequality (45), from Eq. (7a). In the course of averaging we must put $J_{\|} = 0$, but must take the correlation $S_{n,\alpha}S_{n+1,\alpha}$ into account if the planes (n, α) and $(n + 1, \alpha)$ are separated by a domain wall. We obtain

$$\begin{gathered} \nu = \frac{1}{2}\left[(1 - \nu_0)(1 - m^2) + \nu_0(1 + m^2)\right]; \\ \nu_0 = \frac{2\nu - 1 + m^2}{2m^2}; \qquad \text{for} \quad T \to 0 \quad \nu_0 \to \nu \end{gathered} \tag{47}$$

The difference from a linear system of chains is clearly seen when an attempt is made to use an approximate description of the type (39)–(44). Considering in three-dimensional space not segments but disks of diameter l, we obtain in place of (43)

$$\begin{gathered}\nu_{\text{exit}} \approx \sum_l A_l \exp\{-\beta J_{\parallel} A_l - \beta J_{\perp} B_l\} \\ l \gg 1; \qquad A_l \sim l^2; \qquad B_l \sim l\end{gathered} \tag{48}$$

The presence of the term $B_l \sim l$, which reflects the increasing length of the boundary of the *finite domain wall*, ensures, in contrast to (41) and (43), convergence of the sum in (48) even at $J_{\parallel} = 0$. Consequently, $J_{\parallel}(T) = 0$ at finite ν and $T = T_0(\nu)$. At $T < T_0$, formula (48) at $J_{\parallel} = 0$ must be understood as a distribution of excitations of finite size, whereas $\nu_0 = \nu - \nu_{\text{exit}}$ kinks are combined to form *infinite domain walls*, and formulas (48) is disregarded.

For an *ensemble of kinks*, the phenomenon considered is equivalent to condensation of an ideal Bose gas. It manifests itself in the structural properties of the system as a return to a three-dimensionally disordered phase at $T < T_c$. From the point of view of the *Ising model* it denotes a special phase transition with a lowering of the dimensionality of the system.

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Appendix

We consider the system defined by the Lagrangian (II.2.30) and by formulas (II.2.29, 29a, 30). We set up the equations of motion for the operators $\rho_n(x,t)$ and $j_n(x,t)$, using the commutation relations

$$\begin{gathered}[\rho_n(x), \eta_m(y)] = 0 \qquad [\rho_n(x), \eta_m^+(y)] = 0 \\ [\rho_n(x), j_m(y)] = 2\pi i \delta_{mn} \frac{\partial}{\partial x} \delta(x-y) \\ [j_n(x), \eta_m(y)] = 2\delta_{mn} \eta(x) \delta(x-y) \\ [j_n(x), \eta_m^+(y)] = -2\eta^+(x) \delta_{mn} \delta(x-y)\end{gathered} \tag{A.1}$$

These relations follow from the corresponding *boson representations* [65], which are valid for electrons in the vicinity of the Fermi level. They also call for refinement in the presence of an interaction of interatomic radius. These effects, however, as is customarily assumed, lead only to changes in the numerical coefficients in the equations that follow. What is important for us is the coefficient of $\partial\rho_n/\partial x$ in (A.3), and hereafter will be renormalized as the compressibility of the system. We obtain

$$\frac{\partial\rho_n}{\partial t}+\frac{\partial j_n}{\partial x}=-2\pi\sum_{m,i}\tilde{g}^{(i)}_{mn}\Phi_{im} \tag{A.2}$$

$$\frac{\partial j_n}{\partial t}+\frac{\partial\rho_n}{\partial x}=-2\pi\sum_{m,i}g^{(i)}_{mn}\frac{\partial\Phi_{im}}{\partial x}+\frac{2}{i}\sum_{\alpha}(\Delta_n\eta_n^{+}-\Delta_n^{+}\eta_n) \tag{A.3}$$

Varying (II.2.30) with respect to Φ_{in}, $B_{\alpha n}$, and $B_{\alpha n}^{+}$, we obtain

$$\begin{aligned}\Phi_{im}&=\sum_{l,n}D^{(i)}_{ml}\left[g^{(i)}_{ln}\rho_n+g^{(i)}_{ln}j_n\right]\\ B_{\alpha m}&=\sum_{l,n}D^{(\alpha)}_{ml}g^{(\alpha)}_{ln}\eta_n\end{aligned} \tag{A.4}$$

We substitute (A.4) in (A.3) and put $\tilde{g}^{(i)}=0$, corresponding to neglect of relativistic interactions. We obtain

$$\frac{\partial\rho_n}{\partial t}+\frac{\partial j_n}{\partial x}=0 \tag{A.5}$$

$$\frac{\partial j_n}{\partial t}+\frac{\partial}{\partial x}\sum_m\left[\delta_{mn}+2\pi\sum_{i,e}g^{(i)}_{nl}D^{(i)}_{lm}\right]\rho_m=\eta_n \tag{A.6}$$

where

$$\eta_n=\frac{2}{i}\sum_m(\eta_n^{+}R_{nm}\eta_m-\eta_m^{+}R^{*}_{nm}\eta_n) \tag{A.6a}$$

or

$$\eta_n=\frac{2}{i}\sum_m(\Delta_n^{+}R_{nm}^{-1}\Delta_n-\Delta_m^{+}R^{*-1}_{nm}\Delta_n)$$

and

$$R_{nm} = \sum_{k,l,m} g_{nl}^{(\alpha)} E_{lk}^{(\alpha)} g_{km}^{(\alpha)} \tag{A.7}$$

At small ω and k we write

$$R_{mn}^{-1}(k) = \frac{1}{g^2}\left[\left(1 + \frac{\bar{\varphi}}{\bar{\omega}}k - \frac{\omega^2}{\bar{\omega}^2}\right)\delta_{mn} + I_{mn}\right] \tag{A.8}$$

where

$$g^2 = \sum_{\alpha,m}\left(g_{mn}^{(\alpha)}\right)^2 \tag{A.8a}$$

If the coupling constants do not have dispersion, $g_{mn}^{(\alpha)} = g_\alpha \delta_{mn}$ then the quantities $\bar{s}/\bar{\omega}$, $\bar{\omega}^{-2}$, and I_{mn} in (A.8) are the corresponding quantities (II.2.30) averaged over α with a weight g_α^2/g^2. Substituting (A.8) in (A.5) we obtain

$$\frac{\partial}{\partial t}\left[j_n + \frac{2i}{g^2\bar{\omega}^2}\left(\Delta_n^+ \frac{\partial \Delta_n}{\partial t} - \frac{\partial \Delta_n}{\partial t}\Delta_n\right)\right]$$

$$+ \frac{\partial}{\partial x}\left\{\sum_m\left[\delta_{mn} + 2\pi\sum_{i,l}\left(g_{ml}^{(i)}\right)^2 D_{ln}^{(i)}\right]\rho_m + \frac{4\bar{\varphi}}{g^2\bar{\omega}}\Delta_n^+\Delta_n\right\}$$

$$= \frac{4i}{g^2\bar{\omega}^2}\sum_m{}' I_{mn}(\Delta_n^+\Delta_m - \Delta_m^+\Delta_n) \tag{A.9}$$

3 We introduce the charge density $\rho(x)$ and the current $J(x)$, both summed over the chains

$$\rho(x) = \sum_n{}' \rho_n(x); \qquad J(x) = \sum_n J_n(x) \tag{A.10}$$

If we sum (A.9) over n, then the right-hand side vanishes, and in the left-hand side we can write for the Fourier representation

$$2\pi \sum_{i,l,m,q} g_{ml}^{(i)} D_{lq}^{(i)} g_{qn}^{(i)} = \sum_{i \neq c}\frac{a_i k^2}{(\omega/\varphi_i)^2 - k^2} + \frac{4\pi e^2}{\epsilon_\infty S_\perp k^2} \tag{A.11}$$

where $a_i \sim 1$, $\Sigma a_i = a$ is the relative correction to the compressibility of the system, s_i are the velocities of sound, ϵ_∞ is the *dielectric constant of the core*, and $s_\perp$ is the area per filament. We obtain

$$\frac{\partial}{\partial t}\left[J + \frac{4i}{g^2\bar{\omega}^2}\sum_n(\dot{\Delta}_n\Delta_n^+ - \dot{\Delta}_n^+\Delta_n)\right]$$

$$+\frac{\partial}{\partial x}\left\{\left[1 - a + \sum_i \frac{a_i\omega^2}{\omega^2 - \varphi_i^2k^2} + \frac{\omega_p^2}{v_F^2k^2}\right]\rho(x)\right.$$

$$\left. + \frac{4}{g^2}\,\frac{\bar{\delta}}{\bar{\omega}}\sum_n \Delta_n^+\Delta_n\right\} = 0 \qquad \text{(A.12)}$$

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