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The quantum field theory of crystalline solids with the renormalization

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Abstract

We consider a crystalline solid as a system of electrons and atomic nuclei interacting by the Coulomb interaction. The crystalline solid is regarded as a given ordered array of atoms, each one fixed to a lattice site and free to move about it with a small displacement in the harmonic approximation. The system is represented by the quantum field theory of interacting electron and vector fields which needs a renormalization. The renormalization provides phonon spectra in explicit forms. The phonon spectra determine exactly the effective interaction potential between electric charges which is a quasiperiodic function of coordinates and differs essentially from the Coulomb potential. Theoretical results are compared to experimental data of monatomic solids with the f.c.c. crystal structures.

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1. Introduction

The quantum field theory of crystalline solids, as presented in all text books on this subject, e.g. [1–3], is based on the following generally accepted paradigm. The large ionic masses and their locations in sites of a lattice entitle us to an important simplification in searching for a solution to this dynamical many-body problem. This simplification consists in three distinct consecutive steps. First, the small amplitudes of the ions motion allow us to consider ions as fixed at their lattice sites in calculating the electron wavefunction. Thus the energy of the electronic subsystem is parametrically dependent on the ion positions. Second, one assumes that it is a good approximation to consider the electronic system and the ionic system as two independent subsystems. This is the well-known Born–Oppenheimer approximation discussed

in all the textbooks. From this approximation one can calculate the interaction energy between ions. The interaction energy between ions is, of course, influenced by the given state of the electronic subsystem. The low frequencies of the ionic motions are then determined from the change of the interaction energy between ions in the harmonic approximation by assuming that the electrons have the wavefunction appropriate for the instantaneous ionic configuration. Third, the electron wavefunction is expressed in the Hartree–Fock approximation to get the effective Hamiltonian H for this many-body system in the form [4]

$$H = \sum_{\nu,\sigma} (\varepsilon_{\nu,\sigma} - \mu) a_{\nu,\sigma}^+ a_{\nu,\sigma} + \sum_{\mathbf{k},\lambda}' \hbar\omega_{\mathbf{k},\lambda} \left(b_{\mathbf{k},\lambda}^+ b_{\mathbf{k},\lambda} + \frac{1}{2} \right) + \gamma \int d^3\mathbf{x} \sum_{\sigma} \Psi_{\sigma}^+(\mathbf{x}) \Psi_{\sigma}(\mathbf{x}) \varphi(\mathbf{x}). \quad (1)$$

Here $\varepsilon_{\nu,\sigma}$ are eigenvalues associated with the single electron wavefunctions $f_{\nu,\sigma}(\mathbf{x})$ of the Hartree–Fock equation, σ denotes the spin of the electron, $a_{\nu,\sigma}^+$ and $a_{\nu,\sigma}$ are creation and annihilation electron field operators in the electron states (ν, σ) and μ is the chemical potential of the electrons.

The symbol $\omega_{\mathbf{k},\lambda}$ stands for the frequency spectrum of phonons with the wave numbers \mathbf{k} and the polarizations $\lambda = \pm 1$ for the transversal phonons and $\lambda = 0$ for the longitudinal phonons, $b_{\mathbf{k},\lambda}^+$ and $b_{\mathbf{k},\lambda}$ are the creation and annihilation operators of the phonons in the states (\mathbf{k}, λ) . The field operators $\Psi_{\sigma}^+(\mathbf{x})$, $\Psi_{\sigma}(\mathbf{x})$ and $\varphi(\mathbf{x})$ are defined by the formulae

$$\Psi_{\sigma}^+(\mathbf{x}) = \sum_{\nu} f_{\nu,\sigma}(\mathbf{x}) a_{\nu,\sigma}^+, \quad \Psi_{\sigma}(\mathbf{x}) = \sum_{\nu} f_{\nu,\sigma}(\mathbf{x}) a_{\nu,\sigma}, \quad (2)$$

$$\varphi(\mathbf{x}) = \sum_{\mathbf{k}} \left(\frac{\hbar\omega_{\mathbf{k},0}}{2V} \right)^{1/2} (b_{\mathbf{k},0} e^{i\mathbf{k}\cdot\mathbf{x}} + b_{\mathbf{k},0}^+ e^{-i\mathbf{k}\cdot\mathbf{x}})$$

and γ is the electron–phonon coupling constant.

The first two terms in the Hamiltonian (1) are considered as unperturbed Hamiltonian H_0 and effects of the third term in (1) are treated perturbatively.

All the parameters, as the electron energies $\varepsilon_{\nu,\sigma}$, single electron wavefunctions $f_{\nu,\sigma}(\mathbf{x})$, phonon spectra $\omega_{\mathbf{k},\lambda}$, densities of phonon states g_{ω} and the electron–phonon coupling constant γ , entering the Hamiltonian (1) are, in principle, calculable from the first principles of quantum mechanics, but not in practical calculations. To the best of our knowledge, there is not even one known example, where all these characteristic parameters have been calculated systematically for a given crystalline solid in the lines of the paradigm explained above and compared to existing experimental data. In practical calculations one takes these parameters on a quasi-phenomenological basis with additional simplifying assumptions. This treatment has been very successful in qualitative explanations of almost all phenomena in insulators, metals, semiconductors [5, 6] and low-temperature superconductivity [7]. This success with the phenomenological parameters $\varepsilon_{\nu,\sigma}$, $\omega_{\mathbf{k},\lambda}$ and γ in H without their mutual interrelations can be easily understood.

The reason for this is in the fact that the Hamiltonian (1), with suitably chosen parameters $\varepsilon_{\nu,\sigma}$, $f_{\nu,\sigma}(\mathbf{x})$ and $\omega_{\mathbf{k},\lambda}$, represents the most general form of H which can be derived for any crystalline solid in the harmonic approximation. No other form seems to be conceivable.

The aim of this paper is to derive the effective Hamiltonian of the type (1) for a genuine crystalline solid with one atom per a given primitive cell in the harmonic approximation without any other approximations. The derivation is made on the basis of the first principles of quantum field theory and statistical mechanics. In this approach the spectra of phonons $\omega_{\mathbf{k},\lambda}$ and the densities of phonon states g_{ω} are explicitly calculated. The phonon spectra $\omega_{\mathbf{k},\lambda}$

modify the Coulomb potential essentially and give rise to the effective potential $U(\mathbf{x} - \mathbf{x}')$ between charges in the exact, explicit and rather simple form. The explicitly known effective potential $U(\mathbf{x} - \mathbf{x}')$ permits one to make the Hartree–Fock approximation in calculating the single electron energies $\varepsilon_{v,\sigma}$ and eigenfunction $f_{v,\sigma}(\mathbf{x})$ from the Hartree–Fock equations. From this approach the chain of approximations discussed in the beginning of section 1 and leading to the effective Hamiltonian (1) will appear as a general frame or a manual how to calculate the parameters $\varepsilon_{v,\sigma}$, $f_{v,\sigma}(\mathbf{x})$, $\omega_{k,\lambda}$ and γ approximatively and implicitly within the framework of quantum mechanics, despite the fact that they can be calculated exactly and explicitly within the framework of quantum field theory and statistical mechanics.

For the sake of simplicity, we apply the mentioned method to crystalline solids with the f.c.c. crystal lattice in which the velocity of sound waves is isotropic. The crystal lattice of aluminum meets this conditions [2]. We compare the theoretical results with existing experimental data for almost all metals which have the f.c.c. lattice.

2. *Ab initio* form of the Hamiltonian of a crystalline solid

We start by considering a system of N atomic nuclei with the charge Ze , mass M and of n electrons interacting by the Coulomb interaction in the same way as quantum chemists treat many atomic molecules [8]. The quantum-mechanical Hamiltonian of this system has the form

$$\mathbf{H} = - \sum_{j=1}^n \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{x}_j^2} - \sum_{\alpha=1}^N \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \mathbf{X}_\alpha^2} + \frac{1}{2} \int \frac{d^3\mathbf{x} d^3\mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \tilde{\rho}(\mathbf{x})\tilde{\rho}(\mathbf{x}'), \quad (3)$$

where

$$\tilde{\rho}(\mathbf{x}) = -e \sum_{j=1}^n \delta(\mathbf{x} - \mathbf{x}_j) + Ze \sum_{\alpha=1}^N \delta(\mathbf{x} - \mathbf{X}_\alpha) \quad (4)$$

is the operator of the charge density. This quantum-mechanical system has the finite number of degrees of freedom $f = 3n + 3N$. The crystalline solid may be viewed as an ordered array of atoms, each one fixed to a lattice site \mathbf{R}_α and free to move about the lattice site with a small displacement \mathbf{u}_α , i.e.,

$$\mathbf{X}_\alpha = \mathbf{R}_\alpha + \mathbf{u}_\alpha, \quad (5)$$

where \mathbf{R}_α is a lattice vector of a given crystal lattice with one atom per its primitive cell. Next, we make the harmonic approximation to the Hamiltonian (3). The harmonic approximation is the only approximation we are going to make in this paper.

In the harmonic approximation the charge density operator (4) gets the form

$$\tilde{\rho}(\mathbf{x}) = \rho(\mathbf{x}) - Ze \sum_{\alpha=1}^N \mathbf{u}_\alpha \cdot \nabla \delta(\mathbf{x} - \mathbf{R}_\alpha), \quad (6)$$

where

$$\rho(\mathbf{x}) = -e \sum_{j=1}^n \delta(\mathbf{x} - \mathbf{x}_j) + Ze \sum_{\alpha=1}^N \delta(\mathbf{x} - \mathbf{R}_\alpha) \quad (7)$$

is the charge density of the electrons and atomic nuclei localized at the lattice sides \mathbf{R}_α . In the harmonic approximation the Hamiltonian (3) consists of three terms,

$$\mathbf{H} = \mathbf{H}_{0,e} + \mathbf{H}_{0,i} + \mathbf{H}_I, \quad (8)$$

where

$$\mathbf{H}_{0,e} = - \sum_{j=1}^n \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{x}_j^2} + \frac{1}{2} \int \frac{d^3 \mathbf{x} d^3 \mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}) \rho(\mathbf{x}'), \quad (9)$$

$$\begin{aligned} \mathbf{H}_{0,i} = & - \sum_{\alpha=1}^N \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \mathbf{u}_\alpha^2} + \frac{(Ze)^2}{2} \sum'_{\alpha \neq \beta} \int \frac{d^3 \mathbf{x} d^3 \mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \\ & \times [(\mathbf{u}_\alpha \cdot \nabla) \delta(\mathbf{x} - \mathbf{R}_\alpha)] [(\mathbf{u}_\beta \cdot \nabla') \delta(\mathbf{x}' - \mathbf{R}_\beta)], \end{aligned} \quad (10)$$

$$\mathbf{H}_I = -Ze \int \frac{d^3 \mathbf{x} d^3 \mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}') \sum_{\alpha=1}^N (\mathbf{u}_\alpha \cdot \nabla) \delta(\mathbf{x} - \mathbf{R}_\alpha). \quad (11)$$

One may say that $\mathbf{H}_{0,e}$ is the Hamiltonian of the electronic subsystem in the Born–Oppenheimer approximation, $\mathbf{H}_{0,i}$ represents the Hamiltonian of the ionic subsystem and \mathbf{H}_I is the interaction Hamiltonian.

In what follows, we describe the crystalline solid governed by the Hamiltonian (8)–(11) by methods of the second quantization, i.e., by the quantum field theory.

In order to do it we use the δ -function representation

$$\delta(\mathbf{x} - \mathbf{R}_\alpha) = \frac{1}{V} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{x} - \mathbf{R}_\alpha)}$$

to define the field $\pi(\mathbf{x})$ of the ion momenta by the formula

$$\pi(\mathbf{x}) = -i\hbar \sqrt{\frac{V}{MN}} \sum_{\alpha=1}^N \delta(\mathbf{x} - \mathbf{R}_\alpha) \frac{\partial}{\partial \mathbf{u}_\alpha} \quad (12)$$

and the field $\mathbf{u}(\mathbf{x})$ of the displacements by the relation

$$\mathbf{u}(\mathbf{x}) = \sqrt{\frac{MV}{N}} \sum_{\alpha=1}^N \mathbf{u}_\alpha \delta(\mathbf{x} - \mathbf{R}_\alpha), \quad (13)$$

where V is the volume of the crystal and \mathbf{k} are wave vectors in the space of the inverse lattice. The field operators $\pi(\mathbf{x})$ and $\mathbf{u}(\mathbf{x})$ satisfy the canonical commutation relations

$$[\pi_{j'}(\mathbf{x}'), \mathbf{u}_j(\mathbf{x})] = -i\hbar \delta_{jj'} \delta(\mathbf{x} - \mathbf{x}')$$

which follow directly from definitions (12) and (13).

The electron field operators $\Psi_\sigma^+(\mathbf{x})$ and $\Psi_\sigma(\mathbf{x})$ satisfy the canonical anticommutation relations

$$\{\Psi_\sigma^+(\mathbf{x}'), \Psi_\sigma(\mathbf{x})\} = \delta_{\sigma\sigma'} \delta(\mathbf{x} - \mathbf{x}'),$$

where $\sigma = +, -$ denotes the spin of the electron.

The quantum field operators are used to express the total charge density operator $\tilde{\rho}(\mathbf{x})$ in the form

$$\tilde{\rho}(\mathbf{x}) = \rho(\mathbf{x}) - \frac{\omega_p}{\sqrt{4\pi}} \nabla \cdot \mathbf{u}(\mathbf{x})$$

with

$$\rho(\mathbf{x}) = -e \sum_{\sigma} \Psi_\sigma^+(\mathbf{x}) \Psi_\sigma(\mathbf{x}) + Ze \sum_{\alpha=1}^N \delta(\mathbf{x} - \mathbf{R}_\alpha) \quad (14)$$

as the operator of the charge density of the electrons and localized ions, where ω_p is the plasma frequency of the atomic nuclei defined by

$$\omega_p^2 = \frac{4\pi(Ze)^2}{M} \frac{N}{V}. \quad (15)$$

The grand-canonical Hamiltonian of the system under consideration is again the sum of three terms

$$\mathbf{H} = \mathbf{H}_{0,e} + \mathbf{H}_{0,i} + \mathbf{H}_I, \quad (16)$$

where

$$\mathbf{H}_{0,e} = \sum_{\sigma} \int d^3\mathbf{x} \Psi_{\sigma}^{\dagger}(\mathbf{x}) \left[-\frac{\hbar^2}{2m} \Delta - \mu \right] \Psi_{\sigma}(\mathbf{x}) + \frac{1}{2} \int \frac{d^3\mathbf{x} d^3\mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} : \rho(\mathbf{x}) \rho(\mathbf{x}') : \quad (17)$$

$$\mathbf{H}_{0,i} = \frac{1}{2} \int d^3\mathbf{x} \pi^2(\mathbf{x}) + \frac{1}{2} \frac{\omega_p^2}{4\pi} \int \frac{d^3\mathbf{x} d^3\mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} (\nabla \cdot \mathbf{u}(\mathbf{x})) (\nabla' \cdot \mathbf{u}(\mathbf{x}')), \quad (18)$$

$$\mathbf{H}_I = -\frac{\omega_p}{\sqrt{4\pi}} \int \frac{d^3\mathbf{x} d^3\mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}') \nabla \cdot \mathbf{u}(\mathbf{x}). \quad (19)$$

In relation (17), μ is the chemical potential of the electrons and the symbol $: \rho(\mathbf{x}) \rho(\mathbf{x}') :$ stands for the normal product ordering of the electron field operators entering the product $\rho(\mathbf{x}) \rho(\mathbf{x}')$.

The Hamiltonian (16)–(19) represents the quantum field theory describing the interacting system of the electron fields $\Psi_{\sigma}^{\dagger}(\mathbf{x})$, $\Psi_{\sigma}(\mathbf{x})$ with the real vector field $\mathbf{u}(\mathbf{x})$, i.e., a system with infinitely many degrees of freedom in contradistinction to the quantum-mechanical Hamiltonian (8)–(11) which governs the system with the finite number of degrees of freedom. In order to respect the finite number of degrees freedom in the quantum field theory one introduces the chemical potential μ of the electrons in (17) and the ‘phonon’ representation for the fields $\pi(\mathbf{x})$ and $\mathbf{u}(\mathbf{x})$. For this reason we make the expansion of $\pi(\mathbf{x})$ and $\mathbf{u}(\mathbf{x})$ into the polarized plane waves,

$$\pi(\mathbf{x}) = \sum'_{\mathbf{k},\lambda} \left(\frac{\hbar\omega_{\mathbf{k}}}{2V} \right)^{1/2} [\varepsilon_{\mathbf{k},\lambda} \mathbf{b}_{\mathbf{k},\lambda} e^{i\mathbf{k}\cdot\mathbf{x}} + \varepsilon_{\mathbf{k},\lambda}^* \mathbf{b}_{\mathbf{k},\lambda}^{\dagger} e^{-i\mathbf{k}\cdot\mathbf{x}}] \quad (20)$$

$$\mathbf{u}(\mathbf{x}) = i \sum'_{\mathbf{k},\lambda} \left(\frac{\hbar}{2\omega_{\mathbf{k}}V} \right)^{1/2} [\varepsilon_{\mathbf{k},\lambda} \mathbf{b}_{\mathbf{k},\lambda} e^{i\mathbf{k}\cdot\mathbf{x}} - \varepsilon_{\mathbf{k},\lambda}^* \mathbf{b}_{\mathbf{k},\lambda}^{\dagger} e^{-i\mathbf{k}\cdot\mathbf{x}}], \quad (21)$$

where

$$\hbar\omega_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2M} \quad (22)$$

is the kinetic energy of the atomic nucleus with the momentum $\hbar\mathbf{k}$ and $\lambda = \pm 1, 0$ denotes the three different polarizations of the plane waves. The complex polarization vectors $\varepsilon_{\mathbf{k},\lambda}$ and $\varepsilon_{\mathbf{k},\lambda}^*$ satisfy the conditions

$$\varepsilon_{\mathbf{k},\lambda}^* \cdot \varepsilon_{\mathbf{k},\lambda'} = \delta_{\lambda\lambda'}, \quad (23a)$$

$$\sum_{\lambda} \varepsilon_{\mathbf{k},\lambda}^{*j} \varepsilon_{\mathbf{k},\lambda}^l = \delta^{jl}, \quad (23b)$$

$$\varepsilon_{-\mathbf{k},\lambda}^* = \varepsilon_{\mathbf{k},\lambda} \quad (23c)$$

of the orthogonality, completeness and the reality of the fields $\pi(\mathbf{x})$ and $\mathbf{u}(\mathbf{x})$ respectively. If we identify

$$\varepsilon_{\mathbf{k},0} \equiv i \frac{\mathbf{k}}{|\mathbf{k}|}$$

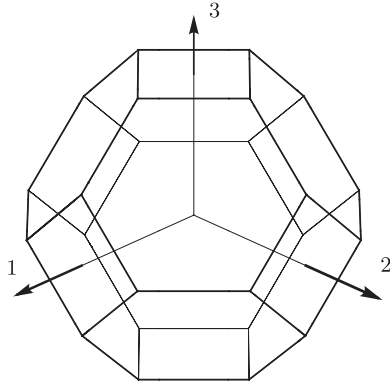


Figure 1. The first Brillouin zone of f.c.c. lattice in k -space.

then $\lambda = 0$ corresponds to the longitudinal plane waves and $\lambda = \pm 1$ corresponds to two transversal plane waves. The operators $b_{\mathbf{k},\lambda}^+$ and $b_{\mathbf{k},\lambda}$ are the creation and annihilation operators of the phonons in the states (\mathbf{k}, λ) . These operators satisfy the canonical commutation relations

$$[b_{\mathbf{k},\lambda}, b_{\mathbf{k}',\lambda'}^+] = \delta_{\lambda,\lambda'} \delta_{\mathbf{k},\mathbf{k}'}. \quad (24)$$

In order to respect the finite number of degrees of freedom $3N$ of the atomic nuclei one requires the number of the phonon states (\mathbf{k}, λ) to be equal to $3N$, i.e.

$$3N = \sum_{\lambda=0,\pm 1} \sum'_{\mathbf{k}} 1 = 3 \sum'_{\mathbf{k}} 1 = \frac{3V}{(2\pi)^3} \int d^3 \mathbf{k}. \quad (25)$$

Thus the wave vectors \mathbf{k} of phonons are restricted to the Brillouin zone of the inverse crystal lattice. As an example, in figure 1, we have depicted the Brillouin zone corresponding to the f.c.c. crystal lattice. We denote the domain of the \mathbf{k} -space corresponding to the Brillouin zone by \mathcal{B} . Thus the sums over \mathbf{k} (20) and (21) are restricted to $\mathbf{k} \in \mathcal{B}$ what is indicated by the prime at the summation symbols in (20) and (21).

Next we insert formulae (20) and (21) into (16)–(19) to get the Hamiltonian respecting the finite number of degrees of freedom of the system under consideration in the form

$$H = H_{0,e} + H_{0,ph} + H_{c,ph}, \quad (26)$$

where

$$H_{0,e} = \sum_{\sigma} \int d^3 \mathbf{x} \Psi_{\sigma}^{\dagger}(\mathbf{x}) \left[-\frac{\hbar^2}{2m} \Delta - \mu \right] \Psi_{\sigma}(\mathbf{x}) + \frac{1}{2} \int \frac{d^3 \mathbf{x} d^3 \mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} : \rho(\mathbf{x}) \rho(\mathbf{x}') :, \quad (27)$$

$$\begin{aligned} H_{0,ph} = H_{0,i} &= \sum'_{\mathbf{k}} \sum_{\lambda=\pm 1} \frac{\hbar \omega_{\mathbf{k}}}{4} (b_{\mathbf{k},\lambda}^+ b_{\mathbf{k},\lambda} + b_{\mathbf{k},\lambda} b_{\mathbf{k},\lambda}^+ + b_{-\mathbf{k},\lambda}^+ b_{-\mathbf{k},\lambda} + b_{-\mathbf{k},\lambda} b_{-\mathbf{k},\lambda}^+) \\ &+ \frac{\hbar}{4} \sum'_{\mathbf{k}} \left\{ \left(\omega_{\mathbf{k}} + \frac{\omega_p^2}{\omega_{\mathbf{k}}} \right) (b_{\mathbf{k},0}^+ b_{\mathbf{k},0} + b_{\mathbf{k},0} b_{\mathbf{k},0}^+) \right. \\ &\left. + \left(\omega_{\mathbf{k}} - \frac{\omega_p^2}{\omega_{\mathbf{k}}} \right) (b_{-\mathbf{k},0}^+ b_{\mathbf{k},0}^+ + b_{-\mathbf{k},0} b_{\mathbf{k},0}) \right\}, \quad (28) \end{aligned}$$

$$H_{c,ph} = H_I = \frac{i\omega_p}{\sqrt{4\pi}} \int \frac{d^3x d^3x'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}') \sum_k \left(\frac{\hbar}{2\omega_k V} \right)^{1/2} |\mathbf{k}| (b_{\mathbf{k},0} e^{i\mathbf{k}\cdot\mathbf{x}} - b_{\mathbf{k},0}^+ e^{-i\mathbf{k}\cdot\mathbf{x}}) \tag{29}$$

describes the interaction of the phonons with the electrons and localized atomic nuclei.

Despite the fact that the Hamiltonian (26)–(29) respects the finite number of degrees of freedom of the system under consideration, it generates qualitatively new phenomena in the thermodynamic limit $V \rightarrow \infty, N \rightarrow \infty$ and $\frac{N}{V} = \text{constant}$ which one does not encounter in quantum mechanics. In the thermodynamic limit, the number of the creation and annihilation operators $b_{\mathbf{k},\lambda}^+$ and $b_{\mathbf{k},\lambda}$ resp. becomes infinite. In this case the canonical commutation relations (24) have infinitely many unitary inequivalent representations as was first pointed by von Neumann [9] and later by Haag [10]. The existence of the infinitely many unitarily inequivalent representations for $b_{\mathbf{k},\lambda}^+$ and $b_{\mathbf{k},\lambda}$ in the thermodynamic limit implies the existence of infinitely many macrostates of the system governed by the Hamiltonian (26)–(29) as will be explained below.

All thermodynamical properties of the system governed by the Hamiltonian H are given by the grand canonical partition function

$$\mathcal{Z} = \text{Tr} e^{-\beta H}, \tag{30}$$

grand-canonical potential Ω ,

$$\Omega = -k_B T \ln \mathcal{Z} \tag{31}$$

and by the statistical averages of physical observables $F(\Psi^+, \Psi, \mathbf{b}^+, \mathbf{b})$ as defined by the formula

$$\langle F \rangle = \frac{1}{\mathcal{Z}} \text{Tr}\{F(\Psi^+, \Psi, \mathbf{b}^+, \mathbf{b}) e^{-\beta H}\}, \tag{32}$$

where $\beta = (k_B T)^{-1}$ is proportional to the inverse temperature T and k_B is the Boltzmann constant.

Intuitively speaking one may regard the Hamiltonian H as an infinite matrix which is distinct for each particular unitarily inequivalent representation of the operators $b_{\mathbf{k},\lambda}^+$ and $b_{\mathbf{k},\lambda}$. Thus the physical quantities (30)–(32) which specify the macrostate of the system are distinct for each particular unitarily inequivalent representation of the field operators $b_{\mathbf{k},\lambda}^+$ and $b_{\mathbf{k},\lambda}$. In this sense the distinct unitarily inequivalent representations of the field operators are very important, because they are connected with the appearance of distinct macrostates—phases of the physical system [11, 12]. The macrostate of the phonon subsystem corresponding to its thermodynamic equilibrium must be selected out of infinitely many macrostates by applying the second law of thermodynamics. Namely, one calculates the statistical weight W as the number of the microstates generating the given macrostate determined by relations (30)–(32). To each macrostate one may find the Boltzmann entropy S_B as defined by

$$S_B = k_B \ln W. \tag{33}$$

The Boltzmann entropy can be defined for every macrostate, even for those which are far away from the thermodynamic equilibrium. Thus, the single unitarily inequivalent representation of the field operators $b_{\mathbf{k},\lambda}^+$ and $b_{\mathbf{k},\lambda}$ corresponding to the thermodynamic equilibrium of the phonon subsystem is determined by selecting that one which gives the maximal value for the Boltzmann entropy (33).

The purpose of this section was mainly to introduce the notations and to give theoretical arguments that characteristics of crystalline solids like phonon spectra, densities of phonon states and their relations with the effective interaction potential between electrons cannot, probably, be completely determined without statistical mechanics.

3. The renormalization, phonon spectra and the effective interaction potential between electric charges

In this section, we calculate the partition function

$$\mathcal{Z} = \text{Tr} e^{-\beta H} \quad (34)$$

with the Hamiltonian (26)–(29). The most effective way how to do it explicitly is to use the functional integral methods [13–15]. According to the general rules one replaces quantum field operators by anticommuting or commuting variables,

$$\Psi_\sigma(\mathbf{x}) \rightarrow \Psi_\sigma(\mathbf{x}, \tau), \quad \Psi_\sigma^+(\mathbf{x}) \rightarrow \Psi_\sigma^*(\mathbf{x}, \tau), \quad (35a)$$

$$\mathbf{b}_{k,\lambda} \rightarrow b_{k,\lambda}^*(\tau), \quad \mathbf{b}_{k,\lambda} \rightarrow b_{k,\lambda}(\tau), \quad (35b)$$

which are enumerated by the additional continuous parameter τ .

The Grassmann variables $\Psi_\sigma(\mathbf{x}, \tau)$ and $\Psi_\sigma^*(\mathbf{x}, \tau)$ satisfy the antiperiodic conditions

$$\Psi_\sigma(\mathbf{x}, \tau + 1) = -\Psi_\sigma(\mathbf{x}, \tau), \quad \Psi_\sigma^*(\mathbf{x}, \tau + 1) = -\Psi_\sigma^*(\mathbf{x}, \tau)$$

and the commuting variables $b_{k,\lambda}(\tau)$ and $b_{k,\lambda}^*(\tau)$ satisfy the periodic conditions

$$b_{k,\lambda}(\tau + 1) = b_{k,\lambda}(\tau), \quad b_{k,\lambda}^*(\tau + 1) = b_{k,\lambda}^*(\tau).$$

Operators like the Hamiltonians (26)–(29) are expressed in the normal forms and then the creation and annihilation operators are replaced by the anticommuting or commuting variables according to the relations (35). Thus one gets the normal symbols of the Hamiltonian (26)–(29) as functions of the anticommuting $\Psi_\sigma(\mathbf{x}, \tau)$, $\Psi_\sigma^*(\mathbf{x}, \tau)$ and commuting $b_{k,\lambda}(\tau)$, $b_{k,\lambda}^*(\tau)$ variables. Next, one defines the action functional $\mathcal{S}(\Psi^*, \Psi; b^*, b)$,

$$\begin{aligned} \mathcal{S}(\Psi^*, \Psi; b^*, b) = & \int_0^1 d\tau \left\{ \sum_\sigma \int d^3\mathbf{x} \Psi_\sigma^*(\mathbf{x}, \tau) \frac{\partial}{\partial \tau} \Psi_\sigma(\mathbf{x}, \tau) \right. \\ & \left. + \sum'_{k,\lambda} b_{k,\lambda}^*(\tau) \frac{\partial}{\partial \tau} b_{k,\lambda}(\tau) + \beta H(\Psi^*, \Psi; b^*, b) \right\}, \end{aligned} \quad (36)$$

where $H(\Psi^*, \Psi; b^*, b)$ is the normal symbol of the Hamiltonian (26)–(29). The explicit form of $\mathcal{S}(\Psi^*, \Psi; b^*, b)$ corresponding to the Hamiltonian (26)–(29) is given by the formula

$$\begin{aligned} \mathcal{S}(\Psi^*, \Psi; b^*, b) = & \int_0^1 d\tau \left\{ \sum_\sigma \int d^3\mathbf{x} \Psi_\sigma^*(\mathbf{x}, \tau) \left[\frac{\partial}{\partial \tau} - \beta \left(\frac{\hbar^2}{2m} \Delta + \mu \right) \right] \Psi_\sigma(\mathbf{x}, \tau) \right. \\ & + \frac{\beta}{2} \int \frac{d^3\mathbf{x} d^3\mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}, \tau) \rho(\mathbf{x}', \tau) \left. \right\} + \frac{\beta \hbar}{4} \sum'_k \left(3\omega_k + \frac{\omega_p^2}{\omega_k} \right) \\ & + \int_0^1 d\tau \sum'_{k,\lambda} b_{k,\lambda}^*(\tau) \frac{\partial}{\partial \tau} b_{k,\lambda}(\tau) + \frac{\beta \hbar}{4} \int_0^1 d\tau \sum_{\lambda=\pm 1} \sum'_k \omega_k \\ & \times [2b_{k,\lambda}^*(\tau) b_{k,\lambda}(\tau) + b_{-k,\lambda}^*(\tau) b_{k,\lambda}^*(\tau) + b_{-k,\lambda}(\tau) b_{k,\lambda}(\tau)] \\ & + \frac{\beta \hbar}{4} \int_0^1 d\tau \sum'_k \left\{ 2 \left(\omega_k + \frac{\omega_p^2}{\omega_k} \right) b_{k,0}^*(\tau) b_{k,0}(\tau) \right. \\ & + \left. \left(\omega_k - \frac{\omega_p^2}{\omega_k} \right) (b_{-k,0}^*(\tau) b_{k,0}^*(\tau) + b_{-k,0}(\tau) b_{k,0}(\tau)) \right\} \\ & + i \frac{\beta \omega_p}{\sqrt{4\pi}} \int_0^1 d\tau \int \frac{d^3\mathbf{x} d^3\mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}', \tau) \sum'_k \left(\frac{\hbar}{2\omega_k V} \right)^{1/2} \\ & \times |\mathbf{k}| (b_{k,0}(\tau) e^{i\mathbf{k}\cdot\mathbf{x}} - b_{k,0}^*(\tau) e^{-i\mathbf{k}\cdot\mathbf{x}}). \end{aligned} \quad (37)$$

With this notation the partition function (34) is given by the functional integral

$$\mathcal{Z} = \int \mathcal{D}(\Psi^*, \Psi; b^*, b) e^{-\mathcal{S}(\Psi^*, \Psi; b^*, b)} \tag{38}$$

where $\mathcal{D}(\Psi^*, \Psi; b^*, b)$ denotes the measure of the functional integration.

The functional integral (38) with the action functional (37) is divergent, i.e., it is not integrable. For its meaningful integration one has to adopt a renormalization procedure known in quantum field theories [16, 17]. In order to get the finite result for the partition function (38) we start by exploiting the following identity:

$$\begin{aligned} \mathcal{Z} &= \int \mathcal{D}(\Psi^*, \Psi; b^*, b) e^{-\mathcal{S}(\Psi^*, \Psi; b^*, b) - \Phi(b^*, b) + \Phi(b^*, b)} \\ &= \langle e^{\Phi(b^*, b)} \rangle \int \mathcal{D}(\Psi^*, \Psi; b^*, b) e^{-\mathcal{S}(\Psi^*, \Psi; b^*, b) - \Phi(b^*, b)} \\ &= \mathcal{Z}_r \langle e^{\Phi(b^*, b)} \rangle, \end{aligned}$$

where $\Phi(b^*, b)$ is a suitably chosen functional of the phonon fields $b_{k,\lambda}^*(\tau)$ and $b_{k,\lambda}(\tau)$ for which the functional integrals

$$\mathcal{Z}_r = \int \mathcal{D}(\Psi^*, \Psi; b^*, b) e^{-\tilde{\mathcal{S}}(\Psi^*, \Psi; b^*, b)}, \tag{39}$$

$$\langle e^{\Phi(b^*, b)} \rangle = \frac{1}{\mathcal{Z}_r} \int \mathcal{D}(\Psi^*, \Psi; b^*, b) e^{-\tilde{\mathcal{S}}(\Psi^*, \Psi; b^*, b) + \Phi(b^*, b)} \tag{40}$$

corresponding to the action functional

$$\tilde{\mathcal{S}}(\Psi^*, \Psi; b^*, b) = \mathcal{S}(\Psi^*, \Psi; b^*, b) + \Phi(b^*, b) \tag{41}$$

are integrable with finite results. The functional $\Phi(b^*, b)$ plays a role of counterterms in a renormalization procedure in quantum field theories as in [16, 17]. In the next step we require the functional $\Phi(b^*, b)$ to satisfy the following relations:

$$\langle e^{\Phi(b^*, b)} \rangle = \langle e^{(1-\Lambda^2)\Phi(b^*, b)} \rangle = 1 \tag{42}$$

exactly for any value of the parameter Λ^2 for which the mean value $\langle e^{(1-\Lambda^2)\Phi(b^*, b)} \rangle$ is integrable. If relations (42) are exactly satisfied then the partition function \mathcal{Z}_r given by formula (39) corresponding to the action (41) is a finite number and is equal to the partition function \mathcal{Z} given by relation (38) which was originally infinite. This may seem to be a paradox one meets in all quantum field theories which need renormalizations, where one generates finite results out of infinite ones. That is why the mathematicians Kobzarev and Manin [18] have expressed the following statement about (38)–(41): ‘From a mathematicians’s viewpoint almost every such computation is, in fact, a half baked and ad hoc definition but a readiness to work heuristically with such *a priori* undefined expressions as (38) is a must in this domain’.

The selection of the functional $\Phi(b^*, b)$ is not unique, thus the different functional $\Phi(b^*, b)$ correspond to different renormalization schemes which can be associated with different unitarily inequivalent representations of the field operators $b_{k,\lambda}^+$ and $b_{k,\lambda}$ [9, 10, 19].

There is, of course, a temptation to believe that relations (42) cannot be satisfied exactly except for $\Phi(b^*, b)$ equal identically to zero. We show explicitly that the special choice for $\Phi(b^*, b)$ corresponds to macrostates of crystalline solids quite correctly. For this reason we

consider the functional $\Phi(b^*, b)$ in the form

$$\Phi(b^*, b) = \frac{\beta}{2} \left\{ y^2 \frac{\omega_p^2}{k_0^2} \int d^3 \mathbf{x} (\nabla \times \mathbf{u})^2 - \frac{z^2}{k_0^4} \int d^3 \mathbf{x} [[\nabla(\nabla \cdot \boldsymbol{\pi})]^2 + \omega_p^2 [\nabla(\nabla \cdot \mathbf{u})]^2] \right\} \\ - \frac{\beta}{2} \xi^2 \left\{ \int d^3 \mathbf{x} [\boldsymbol{\pi}(\mathbf{x})]^2 + \frac{\omega_p^2}{4\pi} \int \frac{d^3 \mathbf{x} d^3 \mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} [\nabla \cdot \mathbf{u}(\mathbf{x})][\nabla' \cdot \mathbf{u}(\mathbf{x}')] \right\}, \quad (43)$$

where k_0 is the maximal value of $|\mathbf{k}|$ for $\mathbf{k} \in \mathcal{B}$ and the free parameters y, z and ξ are to be determined from relations (42). The functional $\Phi(b^*, b)$ is used in (41) to get the action $\tilde{\mathcal{S}}(\Psi^*, \Psi; b^*, b)$ in the form

$$\tilde{\mathcal{S}}(\Psi^*, \Psi; b^*, b) = \int_0^1 d\tau \left\{ \int d^3 \mathbf{x} \sum_{\sigma} \Psi_{\sigma}^*(\mathbf{x}, \tau) \left[\frac{\partial}{\partial \tau} - \beta \left(\frac{\hbar^2}{2m} \Delta + \mu \right) \right] \Psi_{\sigma}(\mathbf{x}, \tau) \right. \\ + \frac{\beta}{2} \int \frac{d^3 \mathbf{x} d^3 \mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}, \tau) \rho(\mathbf{x}', \tau) \left. \right\} + \frac{\beta \hbar}{4} \sum_{\mathbf{k}} \left\{ (1 - \xi^2) \left(3\omega_{\mathbf{k}} + \frac{\omega_p^2}{\omega_{\mathbf{k}}} \right) \right. \\ + 2y^2 \frac{\omega_p^2}{\omega_0} - \frac{z^2}{\omega_0^2} (\omega_{\mathbf{k}}^3 + \omega_p^2 \omega_{\mathbf{k}}) \left. \right\} + \int_0^1 d\tau \sum_{\lambda} \sum'_{\mathbf{k}} b_{\mathbf{k},\lambda}^*(\tau) \frac{\partial}{\partial \tau} b_{\mathbf{k},\lambda}(\tau) \\ + \frac{\beta \hbar}{4} \int_0^1 d\tau \sum_{\lambda=\pm 1} \sum'_{\mathbf{k}} \left\{ 2 \left[(1 - \xi^2) \omega_{\mathbf{k}} + y^2 \frac{\omega_p^2}{\omega_0} \right] b_{\mathbf{k},\lambda}^*(\tau) b_{\mathbf{k},\lambda}(\tau) \right. \\ + \left. \left[(1 - \xi^2) \omega_{\mathbf{k}} - y^2 \frac{\omega_p^2}{\omega_0} \right] [b_{\mathbf{k},\lambda}(\tau) b_{-\mathbf{k},\lambda}(\tau) + b_{\mathbf{k},\lambda}^*(\tau) b_{-\mathbf{k},\lambda}^*(\tau)] \right\} \\ + \frac{\beta \hbar}{4} \int_0^1 d\tau \sum'_{\mathbf{k}} \left\{ 2 \left[(1 - \xi^2) \left(\omega_{\mathbf{k}} + \frac{\omega_p^2}{\omega_{\mathbf{k}}} \right) - \frac{z^2}{\omega_0^2} (\omega_{\mathbf{k}}^3 + \omega_p^2 \omega_{\mathbf{k}}) \right] b_{\mathbf{k},0}^*(\tau) b_{\mathbf{k},0}(\tau) \right. \\ + \left. \left[(1 - \xi^2) \left(\omega_{\mathbf{k}} - \frac{\omega_p^2}{\omega_{\mathbf{k}}} \right) - \frac{z^2}{\omega_0^2} (\omega_{\mathbf{k}}^3 - \omega_p^2 \omega_{\mathbf{k}}) \right] \right. \\ \times [b_{\mathbf{k},0}(\tau) b_{-\mathbf{k},0}(\tau) + b_{\mathbf{k},0}^*(\tau) b_{-\mathbf{k},0}^*(\tau)] + i \frac{\beta \omega_p}{\sqrt{4\pi}} \int_0^1 d\tau \int \frac{d^3 \mathbf{x} d^3 \mathbf{x}'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}', \tau) \\ \left. \times \sum'_{\mathbf{k}} \left(\frac{\hbar}{2\omega_{\mathbf{k}} V} \right)^{1/2} |\mathbf{k}| \left[b_{\mathbf{k},0}(\tau) e^{i\mathbf{k} \cdot \mathbf{x}} - b_{\mathbf{k},0}^*(\tau) e^{-i\mathbf{k} \cdot \mathbf{x}} \right] \right\}, \quad (44)$$

where $\omega_0 = \frac{\hbar k_0^2}{2M}$. As one can see, the phonon part of the action $\tilde{\mathcal{S}}(\Psi^*, \Psi; b^*, b)$ is very ugly and untransparent. In order to simplify its notation we make substitutions for the integration variables $b_{\mathbf{k},\lambda}(\tau)$ and $b_{\mathbf{k},\lambda}^*(\tau)$ in the functional integral (39). These substitutions are the Bogoliubov–Valatin transformations [20, 21]

$$b_{\mathbf{k},\lambda}(\tau) = \cosh v_{\mathbf{k},\lambda} c_{\mathbf{k},\lambda}(\tau) + \sinh v_{\mathbf{k},\lambda} c_{-\mathbf{k},\lambda}^*(\tau), \quad (45a)$$

$$b_{\mathbf{k},\lambda}^*(\tau) = \cosh v_{\mathbf{k},\lambda} c_{\mathbf{k},\lambda}^*(\tau) + \sinh v_{\mathbf{k},\lambda} c_{-\mathbf{k},\lambda}(\tau), \quad (45b)$$

where $v_{\mathbf{k},\lambda}$ are parameters of the transformations to the new integration variables $c_{\mathbf{k},\lambda}(\tau)$ and $c_{\mathbf{k},\lambda}^*(\tau)$. We choose these parameters as given by the relations

$$\cosh^2 v_{\mathbf{k},\pm 1} = \frac{1}{2} \left\{ \frac{1}{2\omega_{\mathbf{k},\pm 1}} \left[(1 - \xi^2) \omega_{\mathbf{k}} + y^2 \frac{\omega_p^2}{\omega_0} \right] + 1 \right\},$$

$$\cosh^2 v_{k,0} = \frac{1}{2} \left\{ \frac{1}{2\omega_{k,0}} \left[(1 - \xi^2) \left(\omega_k + \frac{\omega_p^2}{\omega_k} \right) - \frac{z^2}{\omega_0^2} (\omega_k^3 + \omega_p^2 \omega_k) \right] + 1 \right\}$$

where

$$\omega_{k,\pm 1} = \sqrt{1 - \xi^2} \omega_p y \frac{k}{k_0} \tag{46}$$

and

$$\omega_{k,0} = \omega_p \left[1 - \xi^2 - z^2 \left(\frac{k}{k_0} \right)^4 \right]. \tag{47}$$

By the substitutions (45) the action functional $\tilde{\mathcal{S}}(\Psi^*, \Psi; c^*, c)$ gets the simple form

$$\begin{aligned} \tilde{\mathcal{S}}(\Psi^*, \Psi; c^*, c) = & \int_0^1 d\tau \left\{ \int d^3x \sum_{\sigma} \Psi_{\sigma}^*(\mathbf{x}, \tau) \left[\frac{\partial}{\partial \tau} - \beta \left(\frac{\hbar^2}{2m} \Delta + \mu \right) \right] \Psi_{\sigma}(\mathbf{x}, \tau) \right. \\ & \left. + \frac{\beta}{2} \int \frac{d^3x d^3x'}{|\mathbf{x} - \mathbf{x}'|} \rho(\mathbf{x}, \tau) \rho(\mathbf{x}', \tau) \right\} + \frac{\beta \hbar}{2} \sum_{\lambda=\pm 1,0} \sum'_{\mathbf{k}} \omega_{k,\lambda} \\ & + \int_0^1 d\tau \sum_{\lambda=\pm 1,0} \sum'_{\mathbf{k}} c_{k,\lambda}^*(\tau) \left[\frac{\partial}{\partial \tau} + \beta \hbar \omega_{k,\lambda} \right] c_{k,\lambda}(\tau) \\ & + i\beta \omega_p \sqrt{4\pi} \sum'_{\mathbf{k}} \left(\frac{\hbar}{2\omega_{\mathbf{k}} V} \right)^{1/2} \frac{e^{-v_{k,0}}}{|\mathbf{k}|} [\rho_{-\mathbf{k}}(\tau) c_{\mathbf{k},0}(\tau) - \rho_{\mathbf{k}}(\tau) c_{\mathbf{k},0}^*(\tau)], \end{aligned} \tag{48}$$

where

$$\rho_{\mathbf{k}}(\tau) = \int d^3x e^{-i\mathbf{k}\cdot\mathbf{x}} \left[Z e \sum_{\alpha} \delta(\mathbf{x} - \mathbf{R}_{\alpha}) - e \sum_{\sigma} \Psi_{\sigma}^*(\mathbf{x}, \tau) \Psi_{\sigma}(\mathbf{x}, \tau) \right]$$

is the Fourier transform of the normal symbol $\rho(\mathbf{x}, \tau)$ of the charge density operator (14).

As one sees, the action functional (48) is a bilinear functional of the integration variables $c_{k,\lambda}^*(\tau)$ and $c_{k,\lambda}(\tau)$. The functional integral

$$\mathcal{Z}_{\tau} = \int \mathcal{D}(\Psi^*, \Psi; c^*, c) e^{-\tilde{\mathcal{S}}(\Psi^*, \Psi; c^*, c)} \tag{49}$$

is a Gaussian integral with respect to the variables $c_{k,\lambda}^*(\tau)$ and $c_{k,\lambda}(\tau)$ and therefore can be exactly and explicitly integrated with the result

$$\mathcal{Z}_{\tau} = \mathcal{Z}_{0,\text{ph}} \int \mathcal{D}(\Psi^*, \Psi) e^{\mathcal{S}_c(\Psi^*, \Psi)} \equiv \mathcal{Z}_{0,\text{ph}} \mathcal{Z}_c. \tag{50}$$

Here $\mathcal{Z}_{0,\text{ph}}$ is the partition function of the phonons,

$$\mathcal{Z}_{0,\text{ph}} = \prod_{\lambda=\pm 1,0} \prod'_{\mathbf{k}} \left[2 \sinh \left(\frac{1}{2} \beta \hbar \omega_{k,\lambda} \right) \right]^{-1}, \tag{51}$$

where $\omega_{k,\lambda}$ are the spectra of the transversal $\lambda = \pm 1$ and longitudinal $\lambda = 0$ phonons which are given by formulae (46) and (47), respectively. \mathcal{Z}_c is the partition function corresponding to the electrons and the localized atomic nuclei expressed by the functional integral

$$\mathcal{Z}_c = \int \mathcal{D}(\Psi^*, \Psi) e^{-\mathcal{S}_c(\Psi^*, \Psi)} \tag{52}$$

over anticommuting variables $\Psi_\sigma^*(\mathbf{x}, \tau)$ and $\Psi_\sigma(\mathbf{x}, \tau)$. The effective action functional $\mathcal{L}_c(\Psi^*, \Psi)$ entering (52) is expressed by the exact formula

$$\begin{aligned} \mathcal{L}_c(\Psi^*, \Psi) = & \int_0^1 d\tau \sum_\sigma \int d^3\mathbf{x} \Psi_\sigma^*(\mathbf{x}, \tau) \left[\frac{\partial}{\partial \tau} - \beta \left(\frac{\hbar^2}{2m} \Delta + \mu \right) \right] \Psi_\sigma(\mathbf{x}, \tau) \\ & + \frac{\beta}{2} \int_0^1 d\tau \int_0^1 d\tau' \int d^3\mathbf{x} d^3\mathbf{x}' U(\mathbf{x} - \mathbf{x}'; \tau - \tau') \rho(\mathbf{x}, \tau) \rho(\mathbf{x}', \tau'), \end{aligned} \quad (53)$$

where $U(\mathbf{x} - \mathbf{x}', \tau - \tau')$ is the effective interaction potential between electrons and localized atomic nuclei. It is expressed by its Fourier transform $\mathbf{u}_k(\tau - \tau')$ as given by

$$U(\mathbf{x} - \mathbf{x}', \tau - \tau') = \frac{1}{V} \sum_{\mathbf{k}} u_{\mathbf{k}}(\tau - \tau') e^{i\mathbf{k} \cdot (\mathbf{x} - \mathbf{x}')}, \quad (54)$$

where

$$u_{\mathbf{k}}(\tau - \tau') = \frac{4\pi}{\mathbf{k}^2} \left[\delta(\tau - \tau') - \frac{\omega_p}{\omega_{\mathbf{k},0}} G_{\mathbf{k}}(\tau - \tau') \right]. \quad (55)$$

The symbol $G_{\mathbf{k}}(\tau - \tau')$ stands for the temperature Green's function of the longitudinal phonons as defined by the relations

$$G_{\mathbf{k}}(\tau - \tau') = \beta \hbar \omega_p \left(\frac{\partial}{\partial \tau} + \beta \hbar \omega_{\mathbf{k},0} \right)^{-1} \delta(\tau - \tau') \quad \text{if } \mathbf{k} \in \mathcal{B} \quad (56a)$$

and

$$G_{\mathbf{k}}(\tau - \tau') = 0 \quad \text{if } \mathbf{k} \notin \mathcal{B}. \quad (56b)$$

The $\delta(\tau - \tau')$ -function in (56a) has the spectral representation

$$\delta(\tau - \tau') = \sum_{\nu=-\infty}^{\infty} e^{-i2\pi\nu(\tau-\tau')},$$

where ν are integers. In this representation the temperature Green's function (56a) has the explicit form

$$G_{\mathbf{k}}(\tau - \tau') = \beta \hbar \omega_p \sum_{\nu=-\infty}^{+\infty} \frac{e^{-i2\pi\nu(\tau-\tau')}}{-i2\pi\nu + \beta \hbar \omega_{\mathbf{k},0}} \quad \text{if } \mathbf{k} \in \mathcal{B}. \quad (57)$$

The partition function \mathcal{Z}_r of the crystalline solid under consideration as given by (50) shows that the subsystems of the phonons and electrons are exactly statistically independent. The longitudinal phonons, however, modify the original Coulomb interaction between charges very significantly and lead to the effective potential $U(\mathbf{x} - \mathbf{x}'; \tau - \tau')$ as is given by formulae (54)–(57). Note that if $\Phi(b^*, b)$ were zero then $\mathcal{Z}_{0,\text{ph}}$ would become infinite, i.e., the functional integral (38) would not be integrable.

The partition function (50) is dependent on the ordinary thermodynamical variables like the temperature T , volume V and the chemical potential μ of the electrons. In addition to the variables T, V, μ it depends also on the parameters y, z and ξ entering the phonon spectra (46), (47) and the effective potential $U(\mathbf{x} - \mathbf{x}'; \tau - \tau')$. Thus

$$\mathcal{Z}_r = \mathcal{Z}_r(y, z, \xi), \quad (58)$$

where we have suppressed the dependence of \mathcal{Z}_r on the variables T, V, μ . In the same way, the grand canonical potential

$$\Omega = -k_B T \ln \mathcal{Z}_r = \Omega(y, z, \xi) \quad (59)$$

is also dependent on these free parameters. These parameters must be chosen in such a way as to satisfy relations (42). We calculate exactly the statistical average value $\langle e^{(1-\Lambda^2)\Psi(b^*,b)} \rangle$ with the result

$$\langle e^{(1-\Lambda^2)\Psi(b^*,b)} \rangle = \frac{\mathcal{Z}_r(\Lambda y, \Lambda z, \Lambda \xi)}{\mathcal{Z}_r(y, z, \xi)} = 1. \tag{60}$$

The last equations implies the relations

$$\mathcal{Z}_r(\Lambda y, \Lambda z, \Lambda \xi) = \mathcal{Z}_r(y, z, \xi), \tag{61a}$$

$$\Omega(\Lambda y, \Lambda z, \Lambda \xi) = \Omega(y, z, \xi) \tag{61b}$$

telling us that both $\mathcal{Z}(y, z, \xi)$ and $\Omega(y, z, \xi)$ are homogeneous functions of the zero order of the variables z , y and ξ . Thus the grand canonical potential Ω must satisfy the Euler equation

$$y \frac{\partial \Omega}{\partial y} + z \frac{\partial \Omega}{\partial z} + \xi \frac{\partial \Omega}{\partial \xi} = 0 \tag{62}$$

which is, in fact, the renormalization group equation in the Lie form [17] for the chosen renormalization scheme with the counterterms represented by the functional $\Phi(b^*, b)$. The renormalization group equation (62) tells us that only two out of three parameters y, z, ξ entering the counterterms (43) are independent parameters. Thus we get the quantum field theory of crystalline solids with two free parameters. However, the second law of thermodynamics, represented by the maximum of the Boltzmann entropy of the phonons, determines together with the renormalization group equation (62) the free parameters y, z, ξ uniquely as certain numbers.

For this reason we study general properties of the phonon spectra $\omega_{k,\lambda}$ given by formulae (46) and (47). For the shorthand notation we introduce the following abbreviations:

$$\omega_m \equiv \omega_p(1 - \xi^2), \tag{63a}$$

$$\eta \equiv \frac{y}{\sqrt{1 - \xi^2}} > 0, \tag{63b}$$

$$\zeta \equiv \frac{z}{\sqrt{1 - \xi^2}} \leq 1, \tag{63c}$$

where ω_m is the maximal frequency of the phonon spectrum. With this notation we express the phonon spectra in the forms

$$\omega_{k,\pm 1} = \omega_m \eta \frac{k}{k_0} \equiv v_{tr} k \tag{64}$$

and

$$\omega_{k,0} = \omega_m \left[1 - \zeta^2 \left(\frac{k}{k_0} \right)^4 \right]. \tag{65}$$

Here $v_{tr} = \omega_m \eta / k_0$ is the velocity of the sound corresponding to the transversal waves which is isotropic in all directions. One would intuitively expect the form (64) for the spectrum of the transversal phonons. However, the form (65) for the spectrum of the longitudinal phonons is a novel one and completely unexpected on an intuitive ground.

From the known phonon spectra (64) and (65) we can calculate the density $g_{\omega,\lambda}$ of the phonon states from the formula

$$\begin{aligned} g_{\omega,\lambda} &= \sum'_k \delta(\omega - \omega_{k,\lambda}) = \frac{V}{(2\pi)^3} \int d^3 \mathbf{k} \delta(\omega - \omega_{k,\lambda}) \\ &= \frac{V}{(2\pi)^3} S(k) \left| \frac{dk}{d\omega_{k,\lambda}} \right|, \end{aligned} \tag{66}$$

where $S(k)$ denotes the size area of the sphere with the radius $k = k(\omega_\lambda)$ which is inside of a given Brillouin zone \mathcal{B} . Thus the form of $g_{\omega,\lambda}$ depends in details on a given crystal lattice. If one approximates the Brillouin zone \mathcal{B} by the ball of the radius k_D in the Debye approximation then he gets

$$g_{\omega,\pm 1} = \frac{V}{2\pi^2} \frac{k_D^3}{\omega_m} \frac{1}{\eta^3} x^2 \theta(\eta - x), \quad (67a)$$

$$g_{\omega,0} = \frac{V}{2\pi^2} \frac{k_D^3}{\omega_m} \frac{1}{4\xi^{3/2}} \frac{1}{(1-x)^{1/4}} \theta[x - (1 - \xi^2)]\theta(1 - x), \quad (67b)$$

$$x \equiv \frac{\omega}{\omega_m}.$$

In this approximation k_0 is approximated by the Debye wave number

$$k_D = \left(6\pi^2 \frac{N}{V}\right)^{1/3}. \quad (68)$$

We, however, emphasize that the Debye approximation (67) is not always admissible because it can lead to spurious results in some cases which will be seen below. That is why one has to consider the proper Brillouin zones.

Macrostates of the phonon subsystem are specified by given sets $\{n_{\omega,\lambda}\}$ of the phonon occupation numbers $n_{\omega,\lambda}$. To each macrostate of the phonons one calculates its statistical weight

$$W = \prod_{\omega,\lambda} \frac{(g_{\omega,\lambda} - 1 + n_{\omega,\lambda})!}{(g_{\omega,\lambda} - 1)!n_{\omega,\lambda}!} \quad (69)$$

and the corresponding Boltzmann entropy

$$S_B = k_B \ln W.$$

In formula (69) one considers a discretized spectrum ω_λ of the frequencies for each polarization λ and $g_{\omega,\lambda}$ denotes the number of the phonon states with the frequency ω and the polarization λ . For $g_{\omega,\lambda} \gg 1$ and for the macrostates $n_{\omega,\lambda} \gg 1$ the Boltzmann entropy S_B becomes maximal if the size \mathcal{D} of the domain of ω in which $g_{\omega,\lambda} > 0$ is maximal, i.e.

$$\mathcal{D} = \sum_{\lambda} \int d\omega \theta(g_{\omega,\lambda}) = \omega_m(2\eta + \xi^2) \quad (70)$$

must be maximal under the constrain given by the renormalization group equation (62). Thus, the maximum of the entropy of phonons and the renormalization group equation determine the numerical values of the parameters z , y and ξ uniquely. Note that the macrostate of phonons for $y = z = \xi = 0$, i.e., $\omega_{k,\pm 1} = 0$, $\omega_{k,0} = \omega_p$ has the Boltzmann entropy as minimal as possible and therefore this macrostate is highly improbable. From relations (63) and (70) one can intuitively expect the value $\zeta \approx 1$. The explicit calculation of the parameters η , ζ and ξ will be carried out for the f.c.c. lattice in the following section.

At the end of this section we study general properties of the effective interaction potential $U(\mathbf{x} - \mathbf{x}'; \tau - \tau')$ between charges as given by relations (54)–(57) in the limit $T \rightarrow 0$. In this limit the temperature Green's function $G_k(\tau - \tau')$ given by (56) and (57) reduces to the form

$$G_k(\tau - \tau') = \frac{\omega_p}{\omega_{k,0}} \delta(\tau - \tau'), \quad \mathbf{k} \in \mathcal{B},$$

$$G_k(\tau - \tau') = 0, \quad \mathbf{k} \notin \mathcal{B}.$$

The effective action functional $\mathcal{S}_c(\Psi^*, \Psi)$ given by (53) gets the form

$$\mathcal{S}_c(\Psi^*, \Psi) = \int_0^1 d\tau \left\{ \sum_{\sigma} \int d^3x \Psi_{\sigma}^*(x, \tau) \left[\frac{\partial}{\partial \tau} - \beta \left(\frac{\hbar^2}{2m} \Delta + \mu \right) \right] \Psi_{\sigma}(x, \tau) + \frac{\beta}{2} \int d^3x d^3x' U(x - x') \rho(x, \tau) \rho(x', \tau) \right\}. \quad (71)$$

Here $U(x - x')$ is the effective interaction potential between charges which is independent of the variable τ and is given by the relations

$$U(x - x') = \frac{1}{V} \sum_k u_k e^{ik \cdot (x - x')}, \quad (72)$$

$$u_k = \frac{4\pi}{k^2} \left(1 - \frac{\omega_p^2}{\omega_{k,0}^2} \right), \quad k \in \mathcal{B}, \quad (73a)$$

$$u_k = \frac{4\pi}{k^2}, \quad k \notin \mathcal{B}. \quad (73b)$$

The effective action (71) corresponds to the effective Hamiltonian $H_c(\Psi^+, \Psi)$ in the operator form

$$H_c(\Psi^+, \Psi) = \sum_{\sigma} \int d^3x \Psi_{\sigma}^+(x) \left[-\frac{\hbar^2}{2m} \Delta - \mu \right] \Psi_{\sigma}(x) + \frac{1}{2} \int d^3x d^3x' U(x - x') : \rho(x) \rho(x') : \quad (74)$$

where $\rho(x)$ is the charge density operator for the electrons and the localized atomic nuclei given by (14). Thus we have derived the exact form of the effective interaction potential $U(r)$ between electric charges due to phonons which is essentially different from the Coulomb potential $V(r) = 1/r$. For $k_0 r \ll 1$, $U(r) > 0$ and corresponds to a repulsive interaction between electrons. However for $k_0 r \gtrsim \pi$, if $\omega_p > \omega_{k,0}$, $U(r) < 0$ and behaves as a quasiscillating function of r with period $\lambda \approx 2\pi/k_0$ and giving rise to an attractive interaction between electrons.

As a concrete example we discuss properties of $U(r)$ explicitly for $\omega_{k,0}$ given by relation (65) with $\zeta = 1$. In this case, we get the result

$$U(r) = \frac{1}{r} - \frac{1}{(2\pi)^3} \frac{4\pi}{(1 - \xi^2)^2} \int_{(\mathcal{B})} \frac{d^3k}{k^2} \frac{e^{ik \cdot r}}{\left[1 - \left(\frac{k}{k_0} \right)^4 \right]^2} \quad (75)$$

which can be approximated by the formula

$$U(r) = \frac{1}{r} - \frac{1}{2\pi^2 r} \frac{k_0^2}{(1 - \xi^2)^2} \int_0^{k_0} \frac{dk}{k^2} \frac{s(k/k_0)}{\left[1 - \left(\frac{k}{k_0} \right)^4 \right]^2} \frac{\sin kr}{k}. \quad (76)$$

Here $k_0^2 s(k/k_0)$ is the size area of the sphere of the radius k which is inside of a given Brillouin zone \mathcal{B} . If the Brillouin zone \mathcal{B} is approximated by the ball of the radius k_0 in the Debye approximation then the integral (76) is divergent. Thus the Debye approximation for some cases can lead to spurious results. In the following section, we make the explicit calculation of $k_0^2 s(k/k_0)$ for the f.c.c. crystal lattice. However one can convince himself that for the simple cubic, f.c.c. and b.c.c. lattices the function

$$\frac{k_0^2 s(k/k_0)}{k^2} \frac{1}{\left[1 - \left(\frac{k}{k_0} \right)^4 \right]^2} \equiv \frac{s(w)}{w^2} \frac{1}{(1 - w^4)^2}, \quad w \equiv \frac{k}{k_0}$$

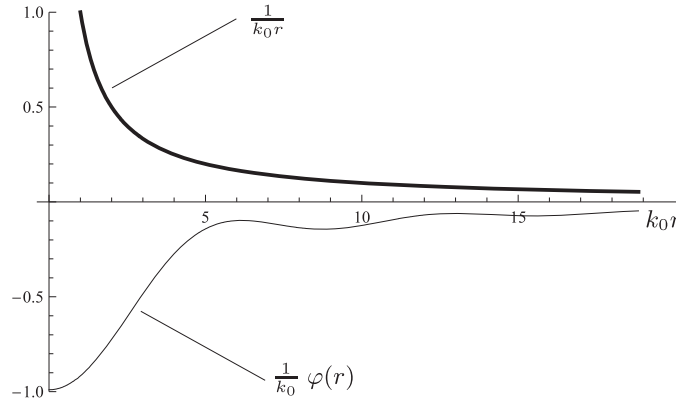


Figure 2. The plot of $1/(k_0 r)$ (thick solid line) and the plot of $\varphi(r)/k_0$ (thin solid line) as the functions of the variable $k_0 r$.

is a perfectly integrable function on the interval $w \in (0, 1)$ and permits $U(r)$ to be expressed by the formula

$$U(r) = \frac{1}{r} - \frac{1}{2\pi^2 r} \frac{1}{(1 - \xi^2)^2} \int_0^1 \frac{dw}{w^2} \frac{s(w)}{(1 - w^4)^2} \frac{\sin(wk_0 r)}{w}. \quad (77)$$

The last formula evidently shows that the function $rU(r)$ has minima at $k_0 r = (2\nu - 1)\pi$ and maxima at $k_0 r = 2\nu\pi$, where ν are positive integers. Thus the effective potential $U(r)$ is a quasiperiodic function of r with the period $\lambda \approx 2\pi/k_0$. The effective potential $U(r)$ has the following asymptotic behavior:

$$U(r) = \frac{1}{r} \{1 - ak_0 r + bk_0^3 r^3\}, \quad k_0 r \ll 1, \quad (78)$$

where a and b are constants calculable from (77), and

$$U(r) = \frac{1}{r} \left\{ 1 - \frac{1}{(1 - \xi^2)^2} \frac{2}{\pi} \text{Si}(k_0 r) \right\}, \quad k_0 r \gg 1. \quad (79)$$

Here $\text{Si}(x)$ denotes the ordinary sinus integral function

$$\text{Si}(x) = \int_0^x \frac{dw}{w} \sin w.$$

The effective potential $U(r)$ is the superposition of two terms

$$U(r) = \frac{1}{r} + \frac{1}{(1 - \xi^2)^2} \varphi(r), \quad (80)$$

where the potential

$$\varphi(r) = -\frac{1}{2\pi^2 r} \int_0^1 \frac{dw}{w^2} \frac{s(w)}{(1 - w^4)^2} \frac{\sin(wk_0 r)}{w} \quad (81)$$

represents the modification of the Coulomb potential $1/r$ due to the phonon interactions with electric charges. The plot of $\varphi(r)/k_0$ as the function of the variable $k_0 r$, for the f.c.c. lattice, is shown in figure 2 to be compared with the Coulomb potential $1/(k_0 r)$.

It should be noted that the effective potential (76) or (81) has formally the similar form as the interionic pseudopotential introduced by Cochran [22] as a useful device for calculations of elastic properties of simple metals [23].

After the demonstration of properties of the effective interaction potential $U(\mathbf{r})$ between electric charges on the explicit example we pass again to general considerations. By having derived the general relationships (72) between $U(\mathbf{r})$ and the spectrum $\omega_{\mathbf{k},0}$ of the longitudinal phonons one can reconstruct $U(\mathbf{r})$ from experimental data on a quasiphenomenological basis. The phonon spectrum $\omega_{\mathbf{k},0}$ can be easily extracted from experimentally observed densities of phonon states. The main features of the densities of phonon states almost of all metals [24, 25] are two peaks. The first peak is referred as to the transverse peak and the second peak as to the longitudinal peak. The transverse peak is situated approximately in the middle and the longitudinal peak is approximately at the end of the phonon spectrum. By extrapolating $\omega_{\mathbf{k},\lambda}$ from given experimental data one can construct the effective Hamiltonian in the form

$$H_{\text{eff}} = \sum_{\sigma} \int d^3x \Psi_{\sigma}^{+}(\mathbf{x}) \left[-\frac{\hbar^2}{2m} \Delta - \mu \right] \Psi_{\sigma}(\mathbf{x}) + \frac{1}{2} \int d^3x d^3x' U(\mathbf{x} - \mathbf{x}') : \rho(\mathbf{x}) \rho(\mathbf{x}') : + \sum'_{\mathbf{k},\lambda} \hbar \omega_{\mathbf{k},\lambda} \left(c_{\mathbf{k},\lambda}^{+} c_{\mathbf{k},\lambda} + \frac{1}{2} \right) \quad (82)$$

with the corresponding phonon spectra $\omega_{\mathbf{k},\lambda}$ and the quasiperiodic effective potential $U(\mathbf{r})$ between electric charges for each monatomic crystalline solid.

With the calculated $U(\mathbf{r})$ one can do the Hartree–Fock calculations to determine the energy band structure $\tilde{\epsilon}_{\nu,\sigma}(\mathbf{k})$ of single electron states $(\nu, \sigma, \mathbf{k})$ in the Hartree–Fock approximation. Here ν enumerates the energy bands, σ denotes the spin and \mathbf{k} is the wave number of the electron. $\tilde{\epsilon}_{\nu,\sigma}(\mathbf{k})$ is a quasiperiodic function of the variable \mathbf{k} with the period of the lattice vectors of the inverse lattice. By this process one can construct the effective Hamiltonian H_{eff} for each individual crystalline solid with one atom per the primitive cell in the form

$$H_{\text{eff}} = \sum'_{\nu,\sigma,\mathbf{k}} [\tilde{\epsilon}_{\nu,\sigma}(\mathbf{k}) - \mu] a_{\nu,\sigma,\mathbf{k}}^{+} a_{\nu,\sigma,\mathbf{k}} + \sum'_{\mathbf{k},\lambda} \hbar \omega_{\mathbf{k},\lambda} \left(c_{\mathbf{k},\lambda}^{+} c_{\mathbf{k},\lambda} + \frac{1}{2} \right). \quad (83)$$

Both forms (82) and (83) of H_{eff} show that the electron and phonon subsystems are formally statistically independent. However, the influence of the phonons on the electrons is completely incorporated in the energy spectrum $\tilde{\epsilon}_{\nu,\sigma}(\mathbf{k})$ of the single electron states. The energy spectrum $\tilde{\epsilon}_{\nu,\sigma}(\mathbf{k})$ is, of course, a nontrivial function of the parameters ξ and k_0 . It should be noted that in the Hartree–Fock approximation one ignores a possibility to have the crystalline solid in the superconducting state.

The effective Hamiltonian (83) is formally similar to the Hamiltonian (1) discussed in section 1. The difference between Hamiltonians (83) and (1) consists mainly in the different origins of the electron energy spectra $\tilde{\epsilon}_{\nu,\sigma}(\mathbf{k})$ and $\epsilon_{\nu,\sigma}$ entering the Hamiltonians (83) and (1), respectively.

The quantum field theory of crystalline solids presented in this section will be applied to the f.c.c. crystal lattice in the following section. The obtained theoretical results will be compared to the experimental data concerning mainly the aluminum, but also almost all metals having the f.c.c. crystal structure.

4. The applications to the f.c.c. crystal lattice

In this section we consider the phonon spectra (64) and (65), i.e.

$$\omega_{\mathbf{k},\pm 1} = \omega_m \eta \frac{k}{k_0}, \quad \omega_{\mathbf{k},0} = \omega_m \left[1 - \zeta^2 \left(\frac{k}{k_0} \right)^4 \right] \quad (84)$$

which resulted from the renormalization procedure adopted in the previous section. The phonon spectra (84) imply the isotropic sound velocity. There are two candidates which

approximately satisfy these properties, namely the aluminum and tungsten [2]. The aluminum has the f.c.c. lattice and tungsten has the b.c.c. lattice. The Brillouin zone \mathcal{B} of the f.c.c. lattice is depicted in figure 1. We choose the f.c.c. lattice, because for analytic calculations, whenever it is permitted, we can replace \mathcal{B} by the ball of the radius k_0 as a good approximation. That is why our theoretical results should be compared to the experimental data concerning mainly the aluminum.

We first analyze the consequences coming out from the renormalization group equation (62). The grand canonical potential $\Omega(y, z, \xi)$ of the crystalline solid is the sum

$$\Omega(y, z, \xi) = \Omega_c(z, \xi) + \mathcal{F}(y, z, \xi), \quad (85)$$

where $\Omega_c(z, \xi)$ is the grand canonical potential of the electrons and localized nuclei. $\mathcal{F}(y, z, \xi)$ is, in fact, the Helmholtz free energy of the phonons which is explicitly and exactly known in the form

$$\mathcal{F}(y, z, \xi) = k_B T \sum'_{k,\lambda} \ln \left[2 \sinh \frac{\beta \hbar \omega_{k,\lambda}}{2} \right]. \quad (86)$$

The explicit calculation of $\Omega_c(z, \xi)$ is, of course, a complicated problem, it cannot be solved exactly and we do not calculate it perturbatively in this paper. The renormalization group equation

$$y \frac{\partial \mathcal{F}}{\partial y} + z \frac{\partial \mathcal{F}}{\partial z} + \xi \frac{\partial \mathcal{F}}{\partial \xi} + z \frac{\partial \Omega_c}{\partial z} + \xi \frac{\partial \Omega_c}{\partial \xi} = 0 \quad (87)$$

provides us one solution for y and z even without the explicit knowledge of $\Omega_c(z, \xi)$. We satisfy (87) by requiring the validity of the following equations:

$$y \frac{\partial \mathcal{F}}{\partial y} + z \frac{\partial \mathcal{F}}{\partial z} = 0 \quad (88)$$

and

$$\xi \frac{\partial \mathcal{F}}{\partial \xi} + z \frac{\partial \Omega_c}{\partial z} + \xi \frac{\partial \Omega_c}{\partial \xi} = 0. \quad (89)$$

The solution to (88), which maximizes \mathcal{D} given by (70), determines the numerical values y and z . Then the solution to equation (89) determines ξ for given values of y and z obtained from equation (88).

By employing formula (86) in (88) we get the equation

$$\sum'_k \left\{ \omega_{k,\pm 1} \coth \left(\frac{1}{2} \beta \hbar \omega_{k,\pm 1} \right) - \omega_m \zeta^2 \left(\frac{k}{k_0} \right)^4 \coth \left(\frac{1}{2} \beta \hbar \omega_{k,0} \right) \right\} = 0. \quad (90)$$

We analyze its solution in analytic forms in the asymptotic regions $\beta \hbar \omega_m \gg 1$, and $\beta \hbar \omega_m \ll 1$, i.e., at low and high temperatures respectively, by replacing the Brillouin zone \mathcal{B} by the ball of the radius k_0 . For $\beta \hbar \omega_m \rightarrow \infty$ equation (90) gets the form

$$\frac{1}{4} \eta - \frac{1}{7} \zeta^2 = 0.$$

Its solution which maximizes \mathcal{D} given by (70) is

$$\zeta^2 = 1, \quad \eta = \frac{4}{7} \doteq 0.57143 \dots, \quad \beta \hbar \omega_m \gg 1 \quad (91)$$

For $\beta \hbar \omega_m \rightarrow 0$ equation (90) reduces to the form

$$\frac{2}{3} - \frac{1}{2\zeta^{3/2}} \left[\frac{1}{2} \ln \frac{1+\zeta}{1-\zeta} - \arctan \sqrt{\zeta} \right] + \frac{1}{3} \left(\frac{\hbar \omega_m}{k_B T} \right)^2 \left[\frac{1}{5} \eta^2 - \zeta^2 \left(\frac{1}{7} - \frac{\zeta^2}{11} \right) \right] = 0.$$

Its numerical solution is

$$\zeta \doteq 0.96708\dots \quad \eta \doteq 0.52005\dots, \quad \beta\hbar\omega_m \ll 1. \quad (92)$$

From the solutions (91) and (92) one sees that the parameters η and ζ are almost temperature independent in the whole temperature interval.

We next calculate the density of phonon states $g_{\omega,\lambda}$ according to formula (66). The size area $S(k)$ for the f.c.c. crystal lattice is given by the formulae

$$S(k) = 4\pi k^2, \quad k \in I_1 \quad (93a)$$

$$S(k) = -12\pi k^2 + 16\pi\sqrt{\frac{3}{5}} k_0 k, \quad k \in I_2 \quad (93b)$$

$$S(k) = -24\pi k^2 + \frac{8}{\sqrt{5}} \pi(3 + 2\sqrt{3})k_0 k \quad k \in I_3 \quad (93c)$$

$$S(k) = 24k \int_{z_-}^{z_+} dz \arcsin \left[\frac{(\sqrt{\frac{9}{5}} k_0 - z)^2}{k^2 - z^2} - 1 \right], \quad k \in I_4, \quad (93d)$$

where

$$I_1 = \langle 0, \sqrt{\frac{3}{5}} k_0 \rangle, \quad I_2 = \langle \sqrt{\frac{3}{5}} k_0, \frac{2}{\sqrt{5}} k_0 \rangle,$$

$$I_3 = \langle \frac{2}{\sqrt{5}} k_0, \frac{3}{\sqrt{10}} k_0 \rangle, \quad I_4 = \langle \frac{3}{\sqrt{10}} k_0, k_0 \rangle$$

and

$$z_+ = \sqrt{\frac{4}{5}} k_0, \quad z_- = \frac{3}{2\sqrt{5}} k_0 + \sqrt{\frac{1}{2} k^2 - \frac{9}{20} k_0^2}.$$

The integral in (93d) can be exactly calculated. However the exact result is given by a long formula. In order to save the space and for the practical calculations we use for it the Taylor series

$$S(k) = 10\sqrt{5}k_0 k \left\{ 3 \left[1 - \left(\frac{k}{k_0} \right)^2 \right]^2 + 20 \left[1 - \left(\frac{k}{k_0} \right)^2 \right]^3 \right\}, \quad k \in I_4 \quad (94)$$

restricted to the first two nonvanishing terms. The approximation (94) agrees with the exact result with the accuracy of the order 10^{-2} . Note that the size area $S(k)$ of the sphere with the radius k which is inside of the Brillouin zone \mathcal{B} of the f.c.c. lattice can be indeed expressed as $S(k) = k_0^2 s(k/k_0)$ and has the properties exploited in relations (76)–(79).

The densities of phonon states $g_{\omega,\lambda}$ for η and ζ given by relations (91) have the following expressions:

$$g_{\omega,\pm 1} = \frac{V}{2\pi^2} \frac{k_0^3}{\omega_m} \left\{ \frac{x^2}{\eta^3} \theta\left(\sqrt{\frac{3}{5}} \eta - x\right) + \left[4\sqrt{\frac{3}{5}} \frac{x}{\eta^2} - 3\frac{x^2}{\eta^3} \right] \theta\left(\frac{2}{\sqrt{5}} \eta - x\right) \theta\left(x - \sqrt{\frac{3}{5}} \eta\right) \right.$$

$$+ \left[\frac{2}{\sqrt{5}} (3 + 2\sqrt{3}) \frac{x}{\eta^2} - 6\frac{x^2}{\eta^3} \right] \theta\left(\frac{3}{\sqrt{10}} \eta - x\right) \theta\left(x - \frac{2}{\sqrt{5}} \eta\right)$$

$$\left. + \frac{5\sqrt{5}}{2\pi} \frac{x}{\eta^2} \left(1 - \frac{x^2}{\eta^2}\right)^2 \left[3 + 20\left(1 - \frac{x^2}{\eta^2}\right) \right] \theta(\eta - x) \theta\left(x - \frac{3}{\sqrt{10}} \eta\right) \right\}$$

$$\equiv \frac{V}{2\pi^2} \frac{k_0^3}{\omega_m} \frac{1}{2} g_{\text{tr}}(x), \quad (95a)$$

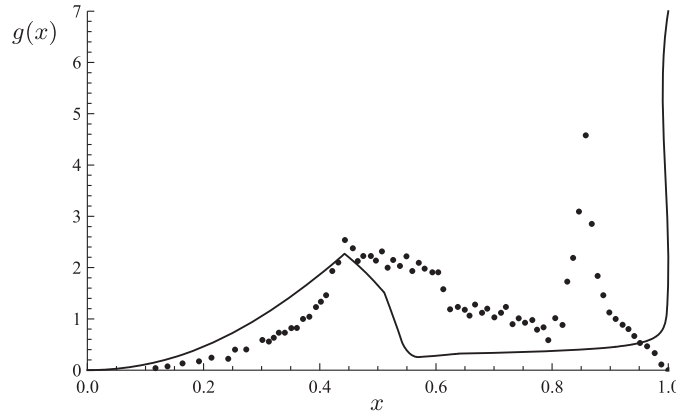


Figure 3. The plot of $g(x)$ (solid line) compared to the density of the phonon states of the aluminum which is reproduced from [1] (dots).

$$\begin{aligned}
 g_{\omega,0} = \frac{V}{2\pi^2} \frac{k_0^3}{\omega_m} & \left\{ \frac{5\sqrt{5}}{8\pi} \frac{(1 - \sqrt{1-x})^2}{\sqrt{1-x}} [3 + 20(1 - \sqrt{1-x})] \theta\left(1 - \left(\frac{9}{10}\right)^2 - x\right) \right. \\
 & + \left[\frac{1}{2\sqrt{5}} \frac{3 + 2\sqrt{3}}{\sqrt{1-x}} - \frac{3}{2} \frac{1}{(1-x)^{1/4}} \right] \theta\left(x - 1 + \left(\frac{9}{10}\right)^2\right) \theta\left(1 - \left(\frac{4}{5}\right)^2 - x\right) \\
 & + \left[\frac{\sqrt{3}}{5} \frac{1}{\sqrt{1-x}} - \frac{3}{4} \frac{1}{(1-x)^{1/4}} \right] \theta\left(x - 1 + \left(\frac{4}{5}\right)^2\right) \theta\left(1 - \left(\frac{3}{5}\right)^2 - x\right) \\
 & \left. + \frac{1}{4} \frac{1}{(1-x)^{1/4}} \theta\left(x - 1 + \left(\frac{3}{5}\right)^2\right) \theta(1-x) \right\} \equiv \frac{V}{2\pi^2} \frac{k_0^3}{\omega_m} g_1, \quad x = \frac{\omega}{\omega_m}.
 \end{aligned} \tag{95b}$$

The total density of the phonon states is the sum

$$g_{\omega} = 2g_{\omega,\pm 1} + g_{\omega,0} \equiv \frac{V}{2\pi^2} \frac{k_0^3}{\omega_m} [g_{tr}(x) + g_1(x)] \equiv \frac{V}{2\pi^2} \frac{k_0^3}{\omega_m} g(x), \quad x = \frac{\omega}{\omega_m}, \tag{96}$$

by which we have defined the dimensionless density $g(x)$ of the phonon states. The density $g(x)$ satisfies the relation

$$\int_0^1 g(x) dx = \frac{6\pi^2}{k_0^3} \frac{N}{V}. \tag{97}$$

The value of k_0 for the f.c.c. lattice is given by

$$k_0^3 = \pi^3 \frac{5\sqrt{5}}{4} \frac{N}{V} \tag{98}$$

and differs a little bit from the Debye wave number k_D . Their ratio is

$$\frac{k_0}{k_D} = \left(\frac{5\sqrt{5}}{24} \pi \right)^{1/3} \doteq 1.135.$$

The plot of $g(x)$ is shown in figure 3 and compared to the density of the phonon states of the aluminum which is reproduced from [1].

It is very important to note that the densities of the phonon states (95) for both $g_{\omega,\pm 1}$ and $g_{\omega,0}$ have the same threshold behaviors for $\omega \ll \omega_m$, i.e. for $x \ll 1$,

$$g_{\omega,\pm 1} = \frac{V}{2\pi^2} \frac{k_0^3}{\omega_m} \frac{x^2}{\eta^3}, \tag{99a}$$

$$g_{\omega,0} = \frac{V}{2\pi^2} \frac{k_0^3}{\omega_m} \frac{15\sqrt{5}}{32\pi} x^2, \quad x \ll 1. \tag{99b}$$

Thus, the density $g_{\omega,0}$ for $\omega \ll \omega_m$ imitates the situation as if the spectrum of the longitudinal phonons had the form

$$\omega_{k,0} = \omega_m \varkappa \frac{k}{k_0} \equiv v_1 k, \quad k \ll k_0 \tag{100}$$

where

$$\varkappa = \left(\frac{32\pi}{15\sqrt{5}} \right)^{1/3} \doteq 1.44.$$

The spectrum (100) corresponds to the velocity $v_1 = \omega_m \varkappa / k_0$ of the sound due to the longitudinal phonons. Thus we get the ratio v_1/v_{tr} , between the velocities of the longitudinal and transverse waves given by the universal number for the f.c.c. lattice

$$\frac{v_1}{v_{tr}} = \frac{7}{4} \left(\frac{32\pi}{15\sqrt{5}} \right)^{1/3} \doteq 2.52 \tag{101}$$

which is approximately satisfied for almost all metals [2].

The Debye density of phonon states and the Debye frequency ω_D are defined in all text books by the relations

$$g(\omega) = \frac{V}{2\pi^2} \left(\frac{2}{v_{tr}^3} + \frac{1}{v_l^3} \right) \omega^2 \theta(\omega_D - \omega) \equiv \frac{V}{2\pi^2} \frac{3}{v^3} \omega^2 \theta(\omega_D - \omega), \tag{102a}$$

$$\int_0^{\omega_D} g(\omega) d\omega = 3N \tag{102b}$$

irrespectively of genuine forms of densities of phonon states. The definition (102) and equations (84) and (100) give us the relation between ω_m and ω_D in the form

$$\frac{18\pi^2}{k_0^3} \frac{N}{V} = \left[2 \left(\frac{7}{4} \right)^3 + \frac{15\sqrt{5}}{32\pi} \right] \left(\frac{\omega_D}{\omega_m} \right)^3, \tag{103}$$

which has the solution

$$\frac{\omega_D}{\omega_m} \doteq 0.57028.$$

We next show the explicit form of relation (89) to convince ourselves that it can be satisfied. By employing formulae (72)–(73) and (84) and (89) for $\beta\hbar\omega_p \gg 1$ we derive the following equation:

$$-\frac{8\pi}{V} \sum'_k \frac{\omega_p^3}{k^2 \omega_{k,0}^3} \left[1 - \frac{\omega_{k,0}}{\omega_p} \right] \int d^3x e^{ik \cdot (x-x')} \langle : \rho(x) \rho(x') : \rangle - N\hbar\omega_p \xi^2 \left(\frac{3}{4} \eta + 1 \right) = 0, \tag{104}$$

where $\langle : \rho(x) \rho(x') : \rangle$ denotes the statistical average value of $: \rho(x) \rho(x') :$ with the Hamiltonian (74). For the electrically neutral crystalline solid

$$\begin{aligned} \langle : \rho(x) \rho(x') : \rangle &= e^2 \sum_{\sigma, \sigma'} \{ \langle \Psi_{\sigma}^+(x) \Psi_{\sigma'}^+(x') \rangle \langle \Psi_{\sigma'}(x') \Psi_{\sigma}(x) \rangle \\ &\quad - \langle \Psi_{\sigma}^+(x) \Psi_{\sigma'}(x') \rangle \langle \Psi_{\sigma'}^+(x') \Psi_{\sigma}(x) \rangle \}, \end{aligned}$$

where the statistical average values $\langle \Psi_{\sigma}^+(\mathbf{x})\Psi_{\sigma'}^+(\mathbf{x}') \rangle$ and $\langle \Psi_{\sigma}^+(\mathbf{x})\Psi_{\sigma'}(\mathbf{x}') \rangle$ are, of course, functions of ξ , ζ and k_0 and are unknown for us at present. In order to show at least that (104) can be satisfied we consider the system for $k_B T \ll \hbar\omega_p$, but above the critical temperature of the superconducting state. In this case $\langle \Psi_{\sigma}^+(\mathbf{x})\Psi_{\sigma'}^+(\mathbf{x}') \rangle = 0$. Now we can use the effective Hamiltonian (80) in the Hartree–Fock approximation (83) to get the relations

$$\begin{aligned} F(\mathbf{k}) &\equiv - \int d^3\mathbf{k} d^3\mathbf{k}' e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} \langle : \rho(\mathbf{x})\rho(\mathbf{x}') : \rangle \\ &= \sum_{\sigma,\sigma'} \int d^3\mathbf{x} d^3\mathbf{x}' e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} |\langle \Psi_{\sigma}^+(\mathbf{x})\Psi_{\sigma'}(\mathbf{x}') \rangle|^2 \\ &= \frac{e^2}{V} \sum_{v,v',\sigma} \sum_{q,q'} \langle \mathbf{a}_{v,\sigma,q}^+ \mathbf{a}_{v,\sigma,q} \rangle \langle \mathbf{a}_{v',\sigma,q'}^+ \mathbf{a}_{v',\sigma,q'} \rangle \\ &\quad \times \int d^3\mathbf{x} d^3\mathbf{x}' \varphi_{v,q}^*(\mathbf{x}) \varphi_{v,q}(\mathbf{x}') \varphi_{v',q'}^*(\mathbf{x}') \varphi_{v',q'}(\mathbf{x}) e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} \end{aligned} \quad (105)$$

where $\varphi_{v,q}(\mathbf{x})$ are the Hartree–Fock single electron wavefunction in the electron states (v, \mathbf{q}) . $F(\mathbf{k}) > 0$. Combining (105) and (104) we get the equation

$$\frac{4\pi}{V} \sum_k' \frac{\omega_p^3}{k^2 \omega_{k,0}^3} \left(1 - \frac{\omega_{k,0}}{\omega_p}\right) F(\mathbf{k}) - N\hbar\omega_p \xi^2 \left(\frac{3}{4}\eta + 1\right) = 0 \quad (106)$$

which is identically satisfied for $\zeta = 0$, $\xi = 0$ irrespectively of the function $F(\mathbf{k})$. It admits the solution in the vicinity of this point and one can believe that this solution can be extrapolated even to $\zeta = 1$ and to the corresponding $\xi \neq 0$. In what follows, we consider ξ as a free parameter which determines the maximal frequency ω_m of the phonon spectrum according to relation (63).

Now we calculate the thermodynamic functions of the phonon subsystem. The Helmholtz free energy (86) is expressed in the form

$$\mathcal{F}(T, V, N) = k_B T \frac{V}{2\pi^2} k_0^3 \int_0^1 dx g(x) \ln \left[2 \sinh \frac{\beta\hbar\omega_m x}{2} \right]. \quad (107)$$

Its volume dependence comes only from $\omega_m = (1 - \xi^2)\omega_p$. From (107) one derives the energy

$$\begin{aligned} E(T, V, N) &= \frac{\hbar\omega_m}{2} \frac{V k_0^3}{2\pi^2} \int_0^1 dx x g(x) \coth \left(\frac{1}{2} \beta\hbar\omega_m x \right) \\ &\equiv 3N\hbar\omega_m \varphi(\beta\hbar\omega_m), \end{aligned} \quad (108)$$

and the equation of state

$$P = - \left(\frac{\partial \mathcal{F}}{\partial V} \right)_{T,N} = \frac{1}{2} \frac{E}{V}. \quad (109)$$

It is important to note that exactly as in the approximative Debye theory all thermodynamic functions (107)–(109) involve only the one transcendental function

$$\varphi(\beta\hbar\omega_m) = \frac{1}{12\pi^2} \frac{V}{N} k_0^3 \int_0^1 dx g(x) \coth \left(\frac{1}{2} \beta\hbar\omega_m x \right) \quad (110)$$

of the single variable $\beta\hbar\omega_m$. The limiting values of $\varphi(\beta\hbar\omega_m)$ easily outline the limiting behavior of the energy (108) at low and high temperatures.

At low temperatures, $\beta\hbar\omega_m \gg 1$, the limiting behavior of $\varphi(\beta\hbar\omega_m)$ is entirely determined by the threshold behavior of $g(x)$ as given by relations (99). In this case the Debye frequency ω_D is defined from the elastic properties of the solid as is given by relation (103) and is

absolutely insensitive on details of the density $g(x)$ of the phonon states far above the threshold. By employing relations (99)–(110) we get the result

$$\varphi(\beta\hbar\omega_m) = \varphi_0 + \frac{\pi^4}{5} \left(\frac{\omega_m}{\omega_D}\right)^3 \left(\frac{k_B T}{\hbar\omega_m}\right)^4, \quad \beta\hbar\omega_m \gg 1, \quad (111)$$

where

$$\varphi_0 = \frac{\pi 5\sqrt{5}}{48} \int_0^1 dx x g(x) = \frac{1}{4}.$$

The energy of the phonons gets the form

$$E = \frac{3}{4} N\hbar\omega_m + \frac{3}{5} \pi^4 N k_B T \left(\frac{k_B T}{\hbar\omega_D}\right)^3$$

and gives the heat capacity

$$c_V = \frac{12\pi^4}{5} N k_B \left(\frac{k_B T}{\hbar\omega_D}\right)^3, \quad \beta\hbar\omega_D \gg 1, \quad (112)$$

which is the same result as in the approximative Debye theory.

At high temperatures, $\beta\hbar\omega_D \ll 1$, the function (110) gets the form

$$\varphi(\beta\hbar\omega_m) = \frac{k_B T}{\hbar\omega_m} + \frac{1}{72\pi^2} \frac{V}{N} k_0^3 \frac{\hbar\omega_m}{k_B T} \int_0^1 dx x^2 g(x), \quad \beta\hbar\omega_D \ll 1. \quad (113)$$

This formula does not have the same standing as the low temperature one (111) because it is very sensitive on the details of the phonon density of states $g(x)$ in the whole spectrum interval $\omega \in (0, \omega_m)$. By employing (113) in (108) we express the energy of the phonons in the form

$$E = 3Nk_B T \left\{ 1 + \frac{\alpha^2}{20} \left(\frac{\hbar\omega_D}{k_B T}\right)^2 \right\}, \quad \beta\hbar\omega_m \ll 1, \quad (114)$$

where

$$\alpha^2 = \frac{5}{18\pi^2} \frac{V}{N} k_0^3 \left(\frac{\omega_m}{\omega_D}\right)^2 \int_0^1 dx x^2 g(x). \quad (115)$$

It is almost an unbelievable miracle that the numerical value of the constant α^2 is close to 1, namely $\alpha^2 = 1.5$ for the parameters ζ and η typical for $\beta\hbar\omega_m \gg 1$ and given by relation (91), and $\alpha^2 \doteq 1.4$ for these parameters typical for $\beta\hbar\omega_m \ll 1$ and given by relation (92). If the Brillouin zone \mathcal{B} of the f.c.c. lattice is approximated by the ball of the radius k_D then $\alpha^2 \doteq 1$. From (114) we get the heat capacity

$$c_V = 3Nk_B \left\{ 1 - \frac{\alpha^2}{20} \left(\frac{\hbar\omega_D}{k_B T}\right)^2 \right\}, \quad \beta\hbar\omega_D \ll 1 \quad (116)$$

which for $\alpha = 1$ is exactly the same as in the approximative Debye theory. From relations (112) and (116) we see that the Debye temperature $\theta = \hbar\omega_D/k_B$ is a slightly increasing function of the temperature T which is perfectly consistent with experimental observations [2].

Relation (115), by which we have defined the parameter α , relates the second moment of the density of the phonon states $g(x)$ to the numbers specifying its threshold behavior, namely,

$$g(x) = \frac{18\pi^2}{k_0^3} \frac{N}{V} \left(\frac{\omega_m}{\omega_D}\right)^3 x^2; \quad x \ll 1. \quad (117)$$

If the parameter α is close to 1 then the function

$$\mathcal{D}(\beta\hbar\omega_D) \equiv \frac{1}{3} \beta\hbar\omega_m \varphi(\beta\hbar\omega_m)$$

can be interpolated with a sufficient accuracy by the universal transcendental function

$$\mathcal{D}\left(\frac{\theta}{T}\right) = \frac{1}{2} \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} dx x^3 \coth \frac{x}{2} \quad (118)$$

which is identical with a function appearing in the approximative Debye theory. The function (118) should not be confused with the function

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3 dx}{e^x - 1} \quad (119)$$

which is called the Debye function. With the function $\mathcal{D}(\theta/T)$ we get the expression for the energy E of the phonon subsystem in the form

$$E = 9Nk_B T \mathcal{D}(\theta/T) \quad (120)$$

which gives the heat capacities of solids exactly the same as in the approximative Debye theory for all temperatures.

Now we turn to a general discussion. The Helmholtz free energy of a phonon subsystem has always the general form (107) with a certain density $g(x)$ of phonon states corresponding to a given monatomic solid. If the density $g(x)$ has the threshold behavior as given by (117) and the parameter α defined by relation (115) is closed to 1 then the energy of the phonon subsystem can be expressed with a sufficient accuracy by the universal function (120) exactly in the same way as in the approximative Debye theory. Thus from the microscopic theory we have found the reason for which the Debye theory of solid heat capacities is so remarkable that it yields heat capacities of monatomic solids by the simple universal function $\mathcal{D}(\theta/T)$ expressed by relation (118). The Debye theory of solid heat capacities is remarkably well verified for actual monatomic solids which have various densities of phonon states with the Debye temperatures θ varying widely and even for the temperatures in the broad temperature interval $T \in (0, 2\theta)$.

The presented application of the theory to the f.c.c. crystal lattice contains at present the only one undetermined parameter ξ or equivalently the value of the maximal frequency ω_m in the spectrum of the phonons. In what follows we fix ω_m from the elastic data, namely, from the velocity v_{tr} of the transversal sound waves $v_{tr} = \eta\omega_m/k_0 = 4\omega_m/(7k_0)$. Once this scale adjustment is made then we can calculate the rest of the parameters which are obtained from the elastic, spectroscopic and thermal measurements. We use the experimental values for v_{tr} from [2]. The experimental and theoretical values of the parameters ω_m , θ and v_l are collected in table 1. The agreement between the theoretical values and experimental data seems to be satisfactory despite the fact that the presented theory ignores the anisotropy in the velocities of the sound waves.

5. Discussion and conclusion

We have demonstrated the importance of the existence of unitarily inequivalent representations of the canonical commutation relations of field operators in the presented quantum field theory of crystalline solids. By the chosen renormalization procedure we have, in fact, selected one class out of infinitely many classes of unitarily inequivalent representations of the commutator ring of the phonon field operators. The unitarily inequivalent representations within the selected class are enumerated by the three parameters η , ζ and ξ which satisfy the renormalization group equation.

Any unitarily inequivalent representation from the selected class represents an exact solution to the many-body problem governed by the given Hamiltonian. The particular

Table 1. Values of maximal frequencies ω_m of phonons, Debye temperatures θ and velocities v_l of longitudinal waves.

Metal	k_0 (10^{10} m^{-1})	ω_p (10^{14} s^{-1})	v_{lr} (ms^{-1}) Exp. ^a	ω_m (10^{13} s^{-1})		θ (K)		v_l (ms^{-1})	
				Exp.	Theory	Exp. ^a	Theory	Exp. ^a	Theory
Al	1.734	8.093	3080	10.3 ^b 6.2 ^c	9.346	418	407	6260	7761
Ag	1,718	14.431	1590	3.2 ^d 3.5 ^e	4.780	225	208	3600	4006
Au	1.722	18.007	1200	3.0 ^d 3.2 ^e	3.616	165	158	3240	3024
Cu	1.940	13.917	2260	4.7 ^d 5.0 ^e	7.672	339	334	4700	5695
Fe	1.946	13.374	3230	7.6 ^f	11.002	467	479	5850	8139
Ni	1.993	14.544	2960	7.0 ^g	10.323	456	450	5630	7459
Pb	1.421	13.659	700	1.7 ^b	1.740	95	76	2160	1764
Pt	1.790	18.928	1670	4.5 ^h	5.231	229	227	3960	4208

The experimental data are taken from the following references: ^a [2]., ^b [24]., ^c [23]., ^d [26]., ^e [25]., ^f [27]., ^g [28]., ^h [29].

unitarily inequivalent representation, selected out of infinitely many of them within the given class, is that one which provides the maximal Boltzmann entropy of phonons. Then this representation determines the phonon spectra, the densities of phonon states and the effective interaction potential between electric charges by the explicit formulae.

Thus the presented quantum field theory of crystalline solids contains one crucial point concerning the selection of the counterterms in the renormalization procedure. For the renormalization of the quantum field theory of crystalline solids we do not have such general physical principle as e.g. the principle of the correspondence in the quantum electrodynamics [17, 18]. In the quantum electrodynamics, the principle of the correspondence dictates the form of counterterms in the renormalization in such a way that results of the quantum electrodynamics must reduce to the results of the classical electrodynamics at low frequencies of photons. The classical theory of crystalline solids based only on the Coulomb interaction between electric charges cannot exist and therefore the renormalization of the quantum field theory of crystalline solids lacks the principle of the correspondence. One may intuitively believe that the good guide for the selection of the renormalization can be the approximative Debye theory, because its remarkable agreement with experimental data cannot stand a theoretical tampering at low frequencies of phonons. Even if a selected renormalization respects properties of the approximative Debye theory and satisfies requirements of an extremely fine tuning for providing finite results of all physical quantities, its most general form is not uniquely specified from the very beginning. However, once concrete counterterms are chosen in explicit forms, as in section 3, then they give spectra of phonons and densities of phonon states explicitly as certain functions of the wave numbers. Our experience from the search of the renormalization presented in section 3 has convinced us that one can always construct such counterterms for the renormalization which can reproduce experimental data of phonon spectra and densities of phonon states with the accuracy within experimental errors for each individual monatomic solid. Such an individual renormalization of the quantum field theory for each distinct crystalline solid represents only a quasiphenomenological theory. From

this point of view the results of the quantum field theory presented in sections 3 and 4 should be regarded as results of the quasiphenomenological theory. Even if theoretical results of the quasiphenomenological theory agreed with experimental data exactly within experimental errors for each monatomic crystalline solid, such a theory could not satisfy us completely for the following reasons. The quasiphenomenological theory without a universal unifying principle for its renormalization would be only a useful device how to reproduce experimental data. It would not have a general approach to arbitrary monatomic solid and, of course, the elegance required by theoretical physics.

The quasiphenomenological theory presented in sections 3 and 4 owns three general properties which are present in every chosen renormalisation.

First, the subsystems of the electrons and phonons are formally statistically independent and governed by the Hamiltonian (82) with the phonon frequencies $\omega_{k,\lambda}$ which are to be determined later on.

Second, all influences of phonons on electric charges are exactly and completely incorporated into the effective interaction potential $U(\mathbf{r})$ between electric charges.

Third, the effective potential $U(\mathbf{r})$ is the explicitly known functional of the longitudinal phonon frequencies $\omega_{k,0}$ as given by relations (72) and (73).

These three general features are, indeed, the means for the formulation of the general quantum field theory of crystalline solids.

Counterterms $\phi(b^*, b)$ for the renormalization determining the phonon spectra $\omega_{k,\lambda}$ are not chosen explicitly as, e.g. by relation (43), but they are general bilinear functionals of the phonon fields. Then the counterterms give the phonon spectra

$$\omega_{k,\pm 1} = [(\omega_k + \alpha_{k,\pm 1})\beta_{k,\pm 1}]^{1/2}, \quad (121a)$$

$$\omega_{k,0} = \left[(\omega_k + \alpha_{k,0}) \left(\frac{\omega_p^2}{\omega_k} + \beta_{k,0} \right) \right]^{1/2} \quad (121b)$$

only in terms of general unspecified functions $\alpha_{k,\lambda}$ and $\beta_{k,\lambda}$. In this general renormalization the grand canonical potential Ω of a given crystalline solid becomes a functional of the parameters $\alpha_{k,\lambda}$ and $\beta_{k,\lambda}$ i.e.

$$\Omega = \Omega(T, V, \mu; \{\alpha_{k,\lambda}, \beta_{k,\lambda}\}),$$

which must satisfy the following renormalization group equation:

$$\sum'_{k,\lambda} \left(\alpha_{k,\lambda} \frac{\delta \Omega}{\delta \alpha_{k,\lambda}} + \beta_{k,\lambda} \frac{\delta \Omega}{\delta \beta_{k,\lambda}} \right) = 0. \quad (122)$$

Any solution to the renormalization group equation represents an exact solution of the quantum field theory governed by the Hamiltonian (82). Now we can formulate the universal principle for the determination of the phonon frequencies $\omega_{k,\lambda}$ or equivalently for the determination of the counterterms in the renormalization. The universal principle is the second law of thermodynamics which requires the grand-canonical potential Ω , at given values of the thermodynamical variables T, V and μ , to be minimal with respect to all free parameters on which it is dependent. These free parameters are functions $\alpha_{k,\lambda}$ and $\beta_{k,\lambda}$ of the wave numbers \mathbf{k} .

Thus we get the equation

$$(\delta \Omega)_{T,V,\mu} = 0 \quad (123)$$

which represents the condition for the minimum of Ω with respect to the parameters $\alpha_{k,\lambda}$ and $\beta_{k,\lambda}$ at the presence of the constraint (122). Equations (121)–(123) with the Hamiltonian (82) define the quantum field theory of crystalline solids with the renormalization.

From the process of the derivation of the last equations it is obvious why we cannot incorporate universal counterterms for the renormalization into the original action (37) for all crystalline solids as it is, e.g., in the case of the quantum electrodynamics. The main reasons are that the original action depends on the parameters like Ze and M which are different for different atoms and that solids can have different crystal structures which determine forms of grand canonical potentials as functionals of $\alpha_{k,\lambda}$ and $\beta_{k,\lambda}$. From this viewpoint the quantum field theory of crystalline solids with the renormalization is much more involved than the quantum electrodynamics.

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