PHASE TRANSITION IN A PHONON GAS WITH PAIR CORRELATIONS

Yu.M. Poluektov

National Science Center “Kharkov Institute of Physics and Technology”, 61108 Kharkov, Ukraine

The phase transition to the state of a phonon gas with pairwise correlations of interacting phonons with opposite momenta is studied. A method for describing such phonon systems within the framework of the self-consistent field model is developed and their thermodynamic characteristics are calculated. It is shown that a phonon gas with pair correlations can exist in a state of unstable thermodynamic equilibrium. The possibility of experimental observation of a solid in such a phase is discussed.

Key words: phonon, phase transition, phonon-phonon interaction, Debye model, entropy, heat capacity

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I. INTRODUCTION

A quantum mechanical description of a system of interacting bosons by the second quantization method was first realized by Bogolyubov [1]. He established the important role of correlations of particles with opposite momenta. Accounting for such pair correlations in Fermi systems later became the basis for constructing the theory of superconductivity [2, 3]. The role of pair correlations in Bose systems was studied in works [4–9]. Of undoubted interest is the theoretical study of the role of similar correlations in a system of massless particles (phonons). This problem is also relevant in connection with experimental studies of the properties of quantum crystals [10].

The purpose of this work is a theoretical study of the possibility of a phase transition of a gas of phonons in a solid into a state with correlations of pairs of phonons with opposite momenta. A general method for describing such states within the framework of the self-consistent field model is developed. It is shown that in the case of the existence of attraction between phonons, at a certain critical temperature there becomes possible a second-order phase transition to a state with correlations of phonon pairs, in which the symmetry with respect to the phase transformation is broken. The thermodynamic functions characterizing such a state are calculated: entropy, pressure, energy, heat capacities, thermodynamic coefficients. It is shown that, in contrast to the standard theory of second-order phase transitions, the transition of a phonon gas to the asymmetric state is accompanied not by a decrease, but by an increase in the free energy. As a consequence, the state with pair correlations of phonons is a state of unstable thermodynamic equilibrium. The possibility of experimental detection of such a state is discussed.

II. HAMILTONIAN OF INTERACTING PHONONS

We choose the Hamiltonian that takes into account the interaction of phonons with opposite momenta in the form analogous to the Bardeen-Cooper-Schrieffer (BCS) Hamiltonian in the theory of superconductivity [2]

$$H = \frac{1}{2} \sum_k \hbar \omega_k (a_k^+ a_k + a_{-k}^+ a_{-k}) + \sum_{k,k'} U_{kk'} a_k^+ a_{-k}^+ a_{-k'} a_{k'},$$

where \( \omega_k = \omega_{-k} \equiv \omega_k = ck \), and the operators \( a_k^+, a_k \) are subject to the usual commutation conditions for Bose particles. For simplicity, we will use the scalar model, disregarding the polarization of phonons, and assume that the phonon velocity \( c \) is independent of temperature. Accounting for polarization presents no fundamental difficulties. The difference from the BCS theory is that the Hamiltonian (1) describes a system of Bose particles, the number of which is not fixed and is determined by temperature. We will study the phonon gas in the model of a self-consistent field. The technique for studying systems of interacting phonons in this approach with the fulfillment of all thermodynamic relations was developed in works [11, 12]. To formulate the model of a self-consistent field, we break the total Hamiltonian (1) into the sum of two terms

$$H = H_S + H_C,$$

*Electronic address: yuripoluektov@kipt.kharkov.ua (y.poluekt52@gmail.com)
where
\[ H_S = \frac{1}{2} \sum_k \left[ \hbar \omega_k \left( a_k^+ a_k + a_{-k}^+ a_{-k} \right) + \Delta_k a_k^+ a_{-k}^+ + \Delta_k^* a_{-k} a_k \right] + E_0, \]  
\[ H_C = \frac{1}{2} \sum_{k,k'} U_{kk'} a_k^+ a_{-k} a_{-k'} a_{k'} - \frac{1}{2} \sum_k \left[ \Delta_k a_k^+ a_{-k} + \Delta_k^* a_{-k} a_k \right] - E_0. \]  

Let us note that, along with the phase-invariant operators \( a_k^+ a_k, a_{-k} a_{-k}^+ \), the Hamiltonian (3) also contains operators \( a_k^+ a_{-k}^+, a_{-k} a_k \), leading to a violation of the symmetry of the state with respect to the phase transformation \( a_k \to e^{i\theta} a_k \), \( a_{-k}^+ \to e^{-i\theta} a_{-k}^+ \), where \( \theta \) is a real number. Within the framework of the self-consistent field approximation, we will describe the phonon system with the help of the approximating Hamiltonian \( H_S \), which includes so far unknown parameters \( \Delta_k = \Delta_k^* \) and \( E_0 \) which will be determined later. The effects associated with the existence of the correlation Hamiltonian (4) can be taken into account using the perturbation theory [13, 14], but we restrict ourselves to the main approximation. The operators will be averaged using the statistical operator
\[ \rho = \exp \beta (F - H_S), \]  
where \( \beta = 1/T \) is the inverse temperature and \( F \) is the normalization constant, the meaning of which will be clarified below. The average of an arbitrary operator is \( \langle A \rangle = \text{Sp} \rho A \), where the trace is taken over all possible states in the self-consistent field approximation.

The Hamiltonian (3) is quadratic in the phonon creation and annihilation operators and, as a consequence, can be reduced to a diagonal form using the canonical Bogolyubov transformation [1]
\[ a_k = u_k \gamma_k + v_k^* \gamma_{-k}^+, \quad a_k^+ = u_k^* \gamma_k^+ + v_k \gamma_{-k}, \]  
while the condition
\[ |u_k|^2 - |v_k|^2 = 1 \]  
ensures the fulfillment of the correct commutation relationships for new operators \( \gamma_k^+, \gamma_k \). In order for off-diagonal terms to drop out in the Hamiltonian \( H_S \), it is necessary the fulfillment of the condition
\[ 2\hbar \omega_k u_k v_k + \Delta_k^2 u_k^2 + \Delta_k v_k^2 = 0. \]  
This leads to the system of linear homogeneous equations
\[ (\hbar \omega_k - \varepsilon_k) v_k + \Delta_k^* u_k = 0, \]  
\[ \Delta_k v_k + (\hbar \omega_k + \varepsilon_k) u_k = 0, \]  
and therefore
\[ \varepsilon_k = \sqrt{ (\hbar \omega_k)^2 - |\Delta_k|^2 }. \]  
(10)
Taking into account condition (7), we find
\[ |u_k|^2 = \frac{1}{2} \left( \frac{\hbar \omega_k}{\varepsilon_k} + 1 \right), \quad |v_k|^2 = \frac{1}{2} \left( \frac{\hbar \omega_k}{\varepsilon_k} - 1 \right), \]  
(11)
\[ u_k v_k^* = - \frac{\Delta_k}{2\varepsilon_k}. \]
As a result, the Hamiltonian (3) takes the form of the Hamiltonian of free phonons with energy \( \varepsilon_k \) (10):
\[ H_S = \sum_k \varepsilon_k \gamma_k^+ \gamma_k + \frac{1}{2} \sum_k \varepsilon_k + E_0. \]  
Here, the second term describes zero oscillations, and the quantity \( E_0 \) characterizes the shift in the energy of the ground state upon transition to a description in terms of new operators. The phonons described by the operators
$a_k, a_k^\dagger$ will be called “bare” phonons. The phonons described by the operators $\gamma_k, \gamma_k^\dagger$ will be called “dressed” phonons. The distribution function of the “dressed” phonons has the form of the Planck function

$$f_k \equiv \langle \gamma_k^\dagger \gamma_k \rangle = \frac{1}{e^{\beta \varepsilon_k} - 1},$$

(13)

and their anomalous averages are equal to zero: $\langle \gamma_k^+ \gamma_k^- \rangle = \langle \gamma_k^- \gamma_k^+ \rangle = 0$. The total number of the “dressed” phonons is

$$N_{ph} = \sum_k \frac{1}{e^{\beta \varepsilon_k} - 1}.$$  

(14)

The pair averages for the “bare” phonons are given by the relations:

$$\langle a_k^+ a_k^- \rangle = \frac{\Delta_k}{2 \varepsilon_k} (1 + 2 f_k), \quad \langle a_k^- a_k^+ \rangle = -\frac{\Delta_k}{2 \varepsilon_k} (1 + 2 f_k),$$

$$\langle a_k^+ a_k^0 \rangle = \frac{\hbar \omega_k}{2 \varepsilon_k} (1 + 2 f_k) - \frac{1}{2}.$$  

(15)

The total number of the “bare” phonons is determined by the formula

$$N_{ph}^{(0)} = \sum_k \langle a_k^+ a_k^0 \rangle = \frac{1}{2} \sum_k \left[ \frac{\hbar \omega_k}{\varepsilon_k} (1 + 2 f_k) - 1 \right].$$  

(16)

At $T \to 0$, the total number of the “dressed” phonons $N_{ph}$ tends to zero, while the total number of the “bare” phonons $N_{ph}^{(0)}$ remains finite. The temperature dependences of the phonon numbers are shown in Fig. 4.

As we can see, along with the phase-invariant “normal” average $\langle a_k^+ a_k^0 \rangle$, there are also phase-noninvariant “anomalous” averages $\langle a_k^+ a_k^- \rangle, \langle a_k^- a_k^+ \rangle$, which under phase transformations of operators are transformed as follows: $\langle a_k^- a_k^0 \rangle \to e^{2i\theta} \langle a_k^- a_k^0 \rangle, \langle a_k^+ a_k^0 \rangle \to e^{-2i\theta} \langle a_k^+ a_k^0 \rangle$. With this in mind, it is obvious that the operator of the observed energy quantity (3) does not depend on the choice of phase and on the whole remains invariant with respect to phase transformations. The next task is to study the state of the phonon gas, in which the “anomalous” averages that violate the phase symmetry are nonzero.

### III. PARAMETERS OF THE SELF-CONSISTENT HAMILTONIAN

Let us move on to finding the parameters $\Delta_k$ and $E_0$, which enter into the approximating Hamiltonian (3). The normalization condition of the statistical operator $S_p \rho = 1$ determines the normalization constant

$$F = -T \ln S_p e^{-\beta H_S}.$$  

(17)

Taking into account the definition of entropy $S = -S_p \ln \rho$, we find

$$F = \langle H_S \rangle - TS,$$  

(18)

whence it follows that the quantity $F$ has the meaning of free energy in the self-consistent field model. The parameter $E_0$ is determined from the requirement that the approximating Hamiltonian (3) be as close as possible to the initial Hamiltonian (1), which can be formulated as $\langle (H - H_S) \rangle = 0$ or $\langle H_C \rangle = 0$, which gives

$$E_0 = \sum_{k, k'} U_{kk'} \langle a_k^+ a_{-k}^0 a_{-k'} a_{k'}^0 \rangle - \frac{1}{2} \sum_k \left[ \Delta_k \langle a_k^+ a_{-k}^+ \rangle + \Delta_k^* \langle a_k^- a_{-k}^+ \rangle \right].$$  

(19)

The average of four operators is expressed in terms of the products of the averages of pairs of operators

$$\langle a_k^+ a_{-k}^0 a_{-k'} a_{k'}^0 \rangle = \langle a_k^+ a_{-k}^0 \rangle \langle a_{-k} a_{k'} \rangle + \langle a_k^- a_{-k}^0 \rangle \langle a_{-k} a_{k'}^0 \rangle + \langle a_k^0 a_{k'} \rangle \langle a_{-k'} a_{-k} \rangle.$$  

(20)

Since we are interested in the effects associated with the existence of anomalous averages in the chosen model, we will take into account in expansion (20) the contribution of only the first term. Then, taking into account (15), we obtain

$$E_0 = \frac{1}{4} \sum_{k, k'} U_{kk'} \frac{\Delta_k \Delta_{k'} e^{\varepsilon_k e_{k'}}}{\varepsilon_{k'} e_k} (1 + 2 f_k) (1 + 2 f_{k'}) + \frac{1}{2} \sum_k \frac{\Delta_k^2}{\varepsilon_k} (1 + 2 f_k).$$  

(21)
Taking into account the form of the Hamiltonian (12), we find the formula for the free energy
\[ F = E_0 + \frac{1}{2} \sum_k \varepsilon_k - T \ln \text{Sp} e^{-\beta \sum_k \varepsilon_k} \gamma_k. \] (22)
Here, the last term describes the free energy of an ideal gas of “dressed” phonons:
\[ F_0 = -T \ln \text{Sp} e^{-\beta \sum_k \varepsilon_k} \gamma_k = T \sum_k \ln \left(1 - e^{-\beta \varepsilon_k}\right). \] (23)
Comparing formulas (12), (13), (18) and taking into account the definition of entropy, we find for entropy a natural expression in terms of the distribution function of “dressed” phonons:
\[ S = \sum_k \left[(1 + f_k) \ln (1 + f_k) - f_k \ln f_k\right]. \] (24)
Since in the limit \( T \to 0 \), the distribution function (13) tends to zero, then the entropy, as required, also tends to zero.
Since the dispersion law for “bare” phonons \( \omega_k = ck \) is linear in the wave number \( k \), then it is natural to assume, and this is justified by the result, that the same dependence is also preserved for the parameter \( \Delta_k \), so we set
\[ \Delta_k = \sigma \hbar c k = \sigma \hbar \omega_k, \] (25)
where \( \sigma \) has the meaning of the order parameter in the asymmetric state, which does not depend on the wave number of the photon. Then it turns out that the energy of the “dressed” photon (10)
\[ \varepsilon_k = \xi \cdot \hbar \omega_k = \hbar \omega_k \sqrt{1 - |\sigma|^2}, \quad \xi \equiv \sqrt{1 - |\sigma|^2} \] (26)
decreases with increasing \( |\sigma| \). In this case, formulas (11) will take the form
\[ |u_k|^2 = |u|^2 = \frac{1}{2} \left(\frac{1}{\xi} + 1\right), \quad |v_k|^2 = |v|^2 = \frac{1}{2} \left(\frac{1}{\xi} - 1\right), \quad u_k v_k^* = -\frac{\sigma}{2 \xi}. \] (27)
We will describe the interaction between phonons with the help of one constant \( g_0 \), assuming
\[ U_{kk'} = \frac{g_0}{V}, \] (28)
where \( V \) is the volume. We will not specify the nature of the interaction between phonons, assuming that the effective interaction between them can be caused by nonlinear effects. Then the energy of the ground state (21)
\[ E_0 = \frac{g_0}{4V} \frac{|\sigma|^2}{\xi^2} \left(\sum_k (1 + 2f_k)\right)^2 + \frac{\hbar c |\sigma|^2}{2 \xi} \sum_k k(1 + 2f_k), \] (29)
and free energy (22) can be written in the form
\[ F = \frac{g_0}{4V} \frac{|\sigma|^2}{\xi^2} I_2^2 + \frac{\hbar c |\sigma|^2}{2 \xi} I_3 + \frac{\hbar c}{2 \xi} I_1 - T \cdot I_4. \] (30)
Here \( T \) is temperature, and
\[ I_0 \equiv \sum_k 1, \quad I_1 \equiv \sum_k k, \quad I_2 \equiv \sum_k (1 + 2f_k), \quad I_3 \equiv \sum_k k(1 + 2f_k), \quad I_4 \equiv \sum_k \ln(1 + f_k). \] (31)
These quantities can be calculated using the transition in (31) from summation to integration. Integration is carried out from zero to the Debye wave number \( k_D \), which is determined by the density of number of particles in a solid
\[ n \equiv \frac{N}{V} = \frac{k_D^3}{6\pi^2}. \] (32)
The calculation results are expressed in terms of the Debye functions

\[ D_n(x) = \frac{n}{x^n} \int_0^x \frac{z^n dz}{e^z - 1}, \quad (n \geq 1), \]  

and related to them functions

\[ \Phi_n(x) = 1 + \frac{2(1+n)}{n} D_n(x). \]  

Some properties of these functions are given in Appendix A. The calculation gives:

\[ I_0 = \frac{V k_D^3}{6\pi^2} \equiv N, \quad I_1 = \frac{3}{4} N k_D, \quad I_2 = N \Phi_2 \left( \frac{\xi}{\tau} \right), \quad I_3 = \frac{3}{4} N k_D \Phi_3 \left( \frac{\xi}{\tau} \right), \]

\[ I_4 = \frac{N}{3} \left[ D_3 \left( \frac{\xi}{\tau} \right) - 3 \ln \left( 1 - e^{-\xi/\tau} \right) \right]. \]  

Here, the reduced dimensionless temperature is defined

\[ \tau \equiv \frac{T}{\Theta_D}, \]  

where \( \Theta_D \equiv \hbar c k_D \) is Debye energy or Debye temperature in energy units. In what follows, we will also use the notation \( \tau \equiv 1/\tau \) for the reciprocal reduced temperature. Taking into account relations (34), (35), the free energy for the state with pair correlations takes the form

\[ \frac{F}{\Theta_D N} \equiv f(\xi, \tau) = \frac{\xi}{2} + \frac{3}{16} g(\xi^2 - 1) \Phi_2(\xi \tau) + \frac{3}{8} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau) + \tau \ln \left( 1 - e^{-\xi/\tau} \right), \]  

where the notation for the dimensionless interaction constant of phonons is used

\[ g = \frac{4 g_0 n}{3 \Theta_D}. \]  

Thermodynamic potentials, which, along with equilibrium values, additionally include arbitrary parameters, in our case it is \( \sigma \text{ or } \xi \equiv \sqrt{1 - |\sigma|^2} \), are potentials with incomplete thermodynamic equilibrium. The equilibrium value of the parameter is found from the condition of the extremum of such a thermodynamic potential

\[ \frac{\partial F}{\partial |\sigma|} = -\frac{\partial F}{\partial |\xi|} = 0. \]  

This equation has two solutions. The first solution \( \sigma = 0 \) corresponds to the normal phase, for which the Debye theory is valid and the free energy is given by

\[ \frac{F_D}{\Theta_D N} \equiv f_D(\tau) = \frac{1}{2} - \frac{1}{8} \Phi_3(\tau) + \tau \ln \left( 1 - e^{-\tau} \right). \]  

We will also refer to this normal state as the Debye phase. The second solution, where \( \partial F/\partial \xi = 0 \) and \( \sigma \neq 0 \), corresponds to the phase with broken phase symmetry, in which the correlations of phonons with opposite momenta are nonzero. The condition \( \partial F/\partial \xi = \partial f/\partial \xi = 0 \) leads to the equation

\[ \frac{3}{4} g \left[ (\xi^2 - 1) \text{cth} \frac{\xi}{2\tau} - \left( \frac{4}{3} \xi^2 - 1 \right) \Phi_2(\xi \tau) \right] \Phi_2(\xi \tau) + \xi \left[ (\xi^2 - 1) \text{cth} \frac{\xi}{2\tau} - \left( \frac{5}{4} \xi^2 - 1 \right) \Phi_3(\xi \tau) \right] = 0. \]  

This equation together with formula (37) in parametric form determines the temperature dependence of the equilibrium free energy in the asymmetric phase. The order parameter can vary within limits \( \xi_0 \leq \xi \leq 1 \). Equation (41) has a solution only for a negative interaction constant \( g = -|g| \), such that \( |g| < 1 \). At zero temperature, as follows from (41), we have \( \xi_0 = |g| \). The transition from the asymmetric phase, where \( \sigma \neq 0 \), to the symmetric phase occurs when the order parameter vanishes, \( \sigma = 0 \) or \( \xi = 1 \). Thus, the phase transition temperature \( \tau_c = T_c/\Theta_D \) is determined by the equation

\[ |g| \Phi_2^2(\tau_c) - \Phi_3(\tau_c) = 0, \]  

(42)
where \( \tau_c = 1/\tau \). The dependence of the critical temperature \( \tau_c \) on the modulus of the interaction constant \( |g| \) is shown in Figure 1. The unusual character of this dependence is noteworthy. As we can see, the critical temperature increases with decreasing the modulus of the interaction constant, and when \( |g| = 1 \) the critical temperature turns to zero. It would seem that, by decreasing the interaction we can thereby increase the phase transition temperature, but, as will be shown below, with decreasing \( |g| \) the stability region of the asymmetric phase narrows. It should be emphasized that the states of free phonons and systems of phonons with pair correlations are qualitatively different due to their different symmetries. Since the dependence of thermodynamic quantities on the interaction constant in the asymmetric phase is non-analytical, it is impossible to pass to the limit \( |g| \to 0 \). Therefore, the asymmetric phase does not pass into the symmetric phase when the interaction is weakened. This situation is typical for all systems with broken phase symmetry [15].

![Figure 1: Dependence of the critical temperature \( \tau_c = T_c/\Theta_D \) on the interaction constant \( |g| \).](image1)

Formulas (37) and (41) make it possible to construct the temperature dependence of the equilibrium free energy, which is shown in Fig. 2. This figure also shows the temperature dependence (40) of the free energy of the Debye phase.

![Figure 2: The free energies in the asymmetric (1) and symmetric (2) states at \( |g| = 0.6 \).](image2)

For the asymmetric phase to be thermodynamically stable, the extremum of the free energy must be a minimum. In present case, this condition is not satisfied at all temperatures, since \( \partial^2 f/\partial \xi^2 < 0 \) and the free energy of the asymmetric phase is always greater than the free energy of the symmetric phase. Thus, the state with pair correlations of phonons is a state with unstable thermodynamic equilibrium. The possibility of experimental observation of such a state will be discussed below.
IV. THERMODYNAMIC QUANTITIES

Although the equilibrium state of phonons with pair correlations corresponds not to the minimum, but to the maximum of the free energy, and therefore is a state with an unstable equilibrium, nevertheless, let us analyze the thermodynamic properties of such a state. Having expressions (37), (40) for the equilibrium free energy, we can calculate all thermodynamic quantities in the asymmetric phase. We first write down the free energy differential

\[ dF = \left( \frac{\partial F}{\partial \xi} \right)_{T,V} d\xi + \left( \frac{\partial F}{\partial T} \right)_{V,\xi} dT + \left( \frac{\partial F}{\partial V} \right)_{T,\xi} dV. \]  

(43)

When condition (41) is satisfied, the first term in (43) is equal to zero. Taking into account the general thermodynamic identities \( dF = -SdT - p dV \) and \( E = F + TS \), we find that the entropy, pressure and energy in the self-consistent field model are determined by the usual formulas

\[ S = -\left( \frac{\partial F}{\partial T} \right)_{V,\xi}, \quad p = -\left( \frac{\partial F}{\partial V} \right)_{T,\xi}, \quad E = F - T \left( \frac{\partial F}{\partial T} \right)_{V,\xi}. \]  

(44)

It should be emphasized that, due to (39), here it is not necessary to differentiate with respect to the parameter \( \xi \). Since we assumed that the speed of “bare” phonons does not depend on temperature, then in this approximation the Debye energy is a function of only density or, at a constant number of particles in a solid \( V, \Theta \), expressed in terms of the function \( f(\xi, \tau) \) and its derivatives. Let us introduce the definitions of the following functions of variables \( \xi, \tau \):

\[ \psi(\xi, \tau) \equiv \frac{\partial f}{\partial \xi} = \frac{1}{2} \coth \left( \frac{\xi}{2\tau} \right) - \frac{3g}{8} \xi^{-3} \Phi_2(\xi \tau) + \frac{3g}{8} (\xi^{-2} - 1) \Phi_2(\xi \tau) \frac{1}{\tau} \Phi_2(\xi \tau) - \frac{3}{8} \left( \xi^{-2} + \frac{4}{3} \xi \right) \Phi_3(\xi \tau) + \frac{3}{8} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau) - \frac{1}{\tau} \Phi_3(\xi \tau) \].

(46)

\[ s(\xi, \tau) \equiv -\frac{\partial f}{\partial \tau} = \frac{3g}{8} \frac{\xi}{\tau^2} (\xi^{-2} - 1) \Phi_2(\xi \tau) \Phi_2(\xi \tau) + \frac{3}{8} \frac{\xi}{\tau^2} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau) - \frac{1}{\tau} \left( 1 - e^{-\xi \tau} \right) \frac{1}{\tau} \coth \left( \frac{\xi}{2\tau} \right) + \frac{3g}{16} (\xi^{-2} - 1) \Phi_2(\xi \tau) \left[ 6 \coth \left( \frac{\xi}{2\tau} \right) - 5 \Phi_2(\xi \tau) \right] - \frac{9g}{8} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau). \]

(47)

Taking into account the condition \( \psi(\xi, \tau) = 0 \) equivalent to (41), the corresponding equilibrium functions \( s(\tau) \) and \( \varphi(\tau) \) can be calculated, which always take positive values. The equilibrium values of entropy, pressure and energy are expressed through these functions:

\[ \frac{S}{N} = s(\tau), \quad p = \Gamma n \Theta D \varphi(\tau), \quad E = N \Theta D \varphi(\tau). \]

(49)

From (49), in particular, it follows that pressure and energy are related as

\[ p = \Gamma \frac{E}{V}. \]  

(50)
At $\Gamma = 1/3$, this formula coincides with the equation of state for a photon gas [17, 18]. The temperature dependences of entropy, pressure and energy are shown in Fig. 3.

The numbers of “dressed” $N_{ph}$ and “bare” $N_{ph}^{(0)}$ phonons, according to (14) and (16), are expressed by the formulas

$$N_{ph} = \frac{3}{2}N\frac{\tau}{\xi}D_2\left(\frac{\xi}{\tau}\right), \quad N_{ph}^{(0)} = \frac{N}{2}\left(\frac{1}{\xi} - 1\right) + \frac{3}{2}N\frac{\tau}{\xi^2}D_2\left(\frac{\xi}{\tau}\right). \quad (51)$$

The temperature dependences of the number of phonons are shown in Fig. 4. As was noted, the number of “dressed” phonons, which determine the temperature dependences of thermodynamic quantities, also tends to zero as the temperature approaches zero (curve 1 in Fig. 4). In this case, the number of “bare” phonons, which do not contribute to entropy, remains finite and even increases (curve 2 in Fig. 4).

In order to calculate the heat capacities and thermodynamic coefficients, one should find the entropy and pressure differentials. Here it is necessary to take into account that, due to condition $d\psi(\xi,\tau) = 0$, the differentials of $\xi$ and $\tau$ are related as follows

$$d\xi = -\frac{(\partial \psi / \partial \tau)_\xi}{(\partial \psi / \partial \xi)_\tau} d\tau, \quad (52)$$
\[
\frac{d\tau}{\Theta_D} = dT + \Gamma \frac{T}{\Theta_D} dV.
\] (53)

As a result, we get:

\[
\frac{dS}{N} = \tau \Omega \left( \frac{dT}{T} + \Gamma \frac{dV}{V} \right),
\] (54)

\[
dp = \Gamma n \Omega T \frac{dT}{\Theta_D} + \Gamma (1 + \Gamma) n \Theta_D \varphi \left[ \frac{\Gamma}{(1 + \Gamma)} \frac{\Omega \tau^2}{\varphi} - 1 \right] dV.
\] (55)

Here the quantity

\[
\Omega = \Omega(\xi, \tau) \equiv \left( \frac{\partial^2 f}{\partial \xi \partial \tau} \right)^2 - \left( \frac{\partial^2 f}{\partial \xi^2} \right) \left( \frac{\partial^2 f}{\partial \tau^2} \right) \left( \frac{\partial^2 f}{\partial \xi^2} \right)
\] (56)

is expressed in terms of the second derivatives of the function \( f(\xi, \tau) \) \( \text{[37]} \), the explicit form of which is given in Appendix B. Taking into account the condition \( \psi(\xi, \tau) = 0 \), the equilibrium function \( \Omega(\tau) \) is calculated, through which are expressed the heat capacities and thermodynamic coefficients.

**Heat capacities.** Assuming in formulas \( \text{[54]}, \text{[55]} \) first \( dV = 0 \), and then \( dp = 0 \), we obtain expressions for the isochoric and isobaric heat capacities:

\[
C_V = T \left( \frac{\partial S}{\partial T} \right)_V = \frac{NT\Omega}{\Theta_D},
\] (57)

\[
C_p = T \left( \frac{\partial S}{\partial T} \right)_p = \frac{NT\Omega}{\Theta_D Z}.
\] (58)

In \( \text{[55]} \), it is the notation \( Z \equiv 1 - \frac{\Gamma \tau^2}{(1 + \Gamma)} \frac{\varphi}{\varphi} \).

**Thermodynamic coefficients.** Similarly, using formulas \( \text{[54]}, \text{[55]} \), formulas can be obtained for the isobaric volume expansion coefficient \( \alpha_p \), isochoric pressure coefficient \( \beta_V \) and isothermal compressibility coefficient \( \gamma_T \):

\[
\beta_V = \frac{1}{p} \left( \frac{\partial p}{\partial T} \right)_V = \frac{T}{\Theta_D^2} \varphi,
\] (59)

\[
\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{T\Omega}{\Theta_D^2 (1 + \Gamma) \varphi Z},
\] (60)

\[
\gamma_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = \frac{1}{\Gamma (1 + \Gamma) n \Theta_D \varphi Z}.
\] (61)

The remaining thermodynamic coefficients, which can be constructed from the quantities \( T, S, p \) and \( V \), are expressed in terms of the coefficients and heat capacities given here \( \text{[18]} \). The difference in heat capacities, as required, is expressed through the given above thermodynamic coefficients \( \text{[17, 18]} \):

\[
C_p - C_V = \frac{VT}{\gamma_T} \alpha_p^2 = N \frac{\Gamma}{(1 + \Gamma)} \frac{T^3 \Omega^2}{\Theta_D \varphi Z} \equiv \frac{NT\Omega (1 - Z)}{\Theta_D Z}.
\] (62)

Similar formulas for thermodynamic quantities of the normal state according to the Debye theory are given for reference in Appendix C.
V. A JUMP OF HEAT CAPACITY

Above the phase transition temperature \( \tau > \tau_c \), in the self-consistent field model under consideration the phonon system is described by the Debye model with the free energy \( f_D(\tau) \) \(^{40}\). The transition to the phase-asymmetric state with pair correlations is accompanied by an appearance of an order parameter \( \sigma \). This occurs at the temperature \( \tau_c = T_c/\Theta_D \) determined by formula \( 42 \). Let us consider the behavior of the heat capacity near the transition temperature, assuming \( |\sigma| \ll 1 \) and \( \xi \approx 1 - \frac{1}{2}|\sigma|^2 - \frac{1}{8}|\sigma|^4 \). Then the expansion of the free energy in the state with broken symmetry at \( \tau < \tau_c \) in powers of the order parameter takes the form

\[
\begin{align*}
  f(\tau) & \approx f_D(\tau) + \alpha_0(\tau_c) \frac{(\tau - \tau_c)}{\tau_c} |\sigma|^2 + C(\tau_c) |\sigma|^4, \\
  \alpha_0(\tau_c) & = \frac{3}{8} \left[ 3g\Phi_2(\tau_c) \coth \left( \frac{1}{2\tau_c} \right) + \Phi_3(\tau_c) + 2\coth \left( \frac{1}{2\tau_c} \right) \right], \\
  C(\tau_c) & = \frac{9}{16} \left[ g\Phi_2(\tau_c) + 1 \right] \coth \left( \frac{1}{2\tau_c} \right) + \frac{3}{64} \Phi_3(\tau_c).
\end{align*}
\]

Here, just like before, \( \tau_c = 1/\tau_c \). From condition \( \frac{\partial f}{\partial |\sigma|} = 0 \) there follows the expression for the equilibrium value of the order parameter

\[
|\sigma|^2 = \frac{\alpha_0(\tau_c) (\tau - \tau_c)}{2C(\tau_c) \tau_c}. \tag{66}
\]

A substitution of \((66)\) into \((63)\) gives the expression for the equilibrium free energy

\[
\begin{align*}
  f(\tau) & \approx f_D(\tau) - \frac{\alpha_0^2 (\tau - \tau_c)^2}{4C \tau_c^2}. \\
  \Delta C_V & = C_V(\tau_c + 0) - C_V(\tau_c - 0) = N\Theta_D \frac{\alpha_0^2}{2CT_c}. \tag{68}
\end{align*}
\]

Jumps of other quantities can be found using well-known formulas \([17,18]\). The change in the heat capacity with temperature in the asymmetric phase and the temperature dependence of the Debye heat capacity are shown in Fig. 5.

Figure 5: The isochoric heat capacity in the asymmetric phase (1) and the Debye heat capacity (2) at \( |g| = 0.7 \).
In the conventional theory of second-order phase transitions \cite{17}, the heat capacity increases by a jump upon transition from the symmetric to the asymmetric phase. In this case, due to the fact that \( C(\tau_c) < 0 \), the heat capacity jump is negative. Thus, upon transition from the normal Debye phase to the phase where there exists a correlation of phonons with opposite momenta, the heat capacity decreases by a jump.

\section*{VI. REGION OF LOW TEMPERATURES}

Let us consider the thermodynamic quantities in the asymmetric phase at low temperatures \( T \ll \Theta_D \). It follows from formula (41) that at \( T = 0 \) the parameter \( \xi \) takes the finite value \( \xi_0 = |g| \). Therefore, at \( \tau \ll 1 \) we have \( \xi \tau \gg 1 \).

The temperature dependence of \( \xi \) at \( \tau \ll 1 \), up to exponentially small terms, has the form

\[ \xi = \xi_0 (1 + a_3 \tau^3 - a_4 \tau^4), \]

where

\[ a_3 = \frac{12 \zeta(3)}{\xi_0} \left( \frac{5}{\xi_0^2} - 3 \right), \quad a_4 = \frac{8 \pi^4}{15 \xi_0^4} \left( \frac{5}{\xi_0^2} - 4 \right), \]

and \( \zeta(3) = 1.202 \). The temperature dependence of the free energy in the low-temperature limit is given by the formula

\[ f(\tau) = f_0 - b_3 \tau^3 + b_4 \tau^4, \]

where

\[ f_0 = \frac{3}{16} \left( \xi_0 + \frac{1}{\xi_0} \right), \quad b_3 = \frac{9 \zeta(3)}{2} \frac{1}{\xi_0^2} \left( \frac{1}{\xi_0^2} - 1 \right), \quad b_4 = \frac{\pi^4}{5 \xi_0^4} \left( \frac{1}{\xi_0^2} - \frac{4}{3} \right). \]

As we can see, in contrast to the corresponding dependence in the Debye theory

\[ f_D(\tau) = \frac{3}{8} \frac{\pi^4}{15} \tau^4, \]

in the case under consideration there is the main contribution to the free energy of the cubic term with respect to temperature, and the term of the fourth degree enters with the opposite sign. It follows from (71) that at \( \tau \ll b_3/b_4 \) both entropy and heat capacity tend to zero at \( T \to 0 \) according to a quadratic law with a cubic correction:

\[ \frac{S}{N} \approx 3b_3 \tau^2 - 4b_4 \tau^3, \quad \frac{C_V}{N} \approx 6b_3 \tau^2 - 12b_4 \tau^3. \]

The decrease of these quantities in the low-temperature region is slower than their cubic dependence according to the Debye theory. The pressure and energy in this region are determined by the formula

\[ \frac{p}{\Gamma n \Theta_D} = \frac{E}{N \Theta_D} = f_0 + 2b_3 \tau^3 - 3b_4 \tau^4. \]

The first term on the right side of (75) describes the contribution to the pressure and energy of zero-point lattice vibrations.

\section*{VII. REGION OF EXISTENCE OF THE ASYMMETRIC PHASE}

The state of phonons with pair correlations considered in the article can exist in a state of unstable thermodynamic equilibrium only in those regions of temperatures and densities where the known thermodynamic inequalities are satisfied \cite{17}

\[ C_V > 0, \quad (\partial p/\partial V)_T < 0. \]

The satisfiability of inequalities (76) in the asymmetric phase depends on the value of the interaction constant \(|g|\), so that they are satisfied under the condition

\[ 0 < \Omega < \frac{\left( 1 + \Gamma \right) \varphi}{\Gamma \tau^2}. \]
Condition (77) also ensures the fulfillment of the inequality \( C_p - C_V > 0 \), since in this case \( 0 < Z < 1 \). If inequalities (76) are violated, then the system cannot exist even in a metastable state.

Figure 6 shows the change in the isochoric heat capacity with temperature for various values of the interaction constant. There are two characteristic values \( |g|_e = 0.66 \) and \( |g|_n = 0.425 \), at which the behavior of the heat capacity changes qualitatively. In the interval \( |g|_n < |g| < |g|_e \), the heat capacity increases monotonically with increasing temperature (curve 1 in Fig. 6). At \( |g| = |g|_e \), an inflection point appears on the temperature dependence of the heat capacity at \( \tau_e/\tau_c = 0.235 \) (curve 2, Fig. 6). In the range of values \( |g|_n < |g| < |g|_e \), the heat capacity remains positive, so that the stability conditions (76) are still satisfied, but it has a minimum (curve 3, Fig. 6). At \( |g| = |g|_n \) and temperature \( \tau_n/\tau_c = 0.151 \), the heat capacity turns to zero, and therefore the system loses stability (curve 4, Fig. 6). In the range of values \( 0 < |g| < |g|_n \), a temperature region arises where conditions (76) are not satisfied (curve 5, Fig. 6). As the interaction constant decreases, this region of instability expands.

As noted above, the transition temperature increases as the magnitude of the interaction decreases (Fig. 1), but, as we see, there narrows the temperature range where the metastable existence of a new phase is possible. Thus, the transition temperature is not likely to be high in reality.

**VIII. DISCUSSION, CONCLUSIONS**

It is shown in the paper that a gas of phonons, between which there is an attraction, can be in the unstable equilibrium state with broken phase symmetry in which there exist pair correlations between phonons with opposite momenta. The transition to such a state from the normal state, which is described by the Debye theory, can occur at a certain critical temperature as a result of the second-order phase transition. The critical temperature is determined by the value of the interaction constant, and it turns out that the critical temperature increases with the weakening of the interaction (Fig. 1). However, with a decrease in the modulus of the interaction constant and an increase in the critical temperature, there expands the temperature range in which the thermodynamic stability of the asymmetric phase is completely lost. In contrast to conventional equilibrium phase transitions, in this case it turns out that the free energy of the asymmetric state is higher than the energy of the normal state. This leads to the fact that such a state turns out to be metastable, and upon transition from the normal state to the asymmetric phase the heat capacity decreases by a jump.

Qualitatively, the situation considered in the paper can be explained by a simple example of a physical pendulum, which can be in two extreme states. In the lower position its energy is minimal and this state is stable. In the upper position the energy of the pendulum is maximum, its position is unstable and it can be withdrawn from it at the slightest fluctuation. If, however, the friction in the suspension of the pendulum is large, then it can remain in the upper metastable state for quite a long time.

Similarly, if the relaxation time of a state of a solid with pairwise phonon correlations turns out to be long, then such a state may be accessible for observation. The question of how the system can be transferred to the considered unstable state requires a separate study. There are considerations that this can be done with the help of external high-frequency forces. It is also possible that the new phase can be identified by its influence on the propagation and transmission of sound.
absorption of sound \cite{19}. The considered phase may turn out to be more stable under inhomogeneous conditions, for example, near boundaries. Theoretically, such states can also be studied within the framework of the generalized Debye model \cite{20}.

In this paper, the problem was considered in the scalar approximation without taking into account phonon polarizations, under the assumption that the speed of all phonons is the same. However, already in an isotropic medium there are two elastic moduli and, consequently, two types of phonons—longitudinal and transverse. This circumstance must be taken into account in a more realistic model \cite{21}. In addition, nonlinear effects in the considered model were taken into account in a minimal way by introducing the interaction of phonons with opposite momenta into the Hamiltonian \cite{11}. In real crystals, a significant role can be played by nonlinear effects described by elastic moduli of the third and fourth order \cite{12,22}. Nonlinear effects in the considered model are two elastic moduli and, consequently, two types of phonons—longitudinal and transverse. This circumstance must be taken into account in a more realistic model \cite{21}. In addition, nonlinear effects in the considered model were taken into account in a minimal way by introducing the interaction of phonons with opposite momenta into the Hamiltonian \cite{11}. In real crystals, a significant role can be played by nonlinear effects described by elastic moduli of the third and fourth order \cite{12,22}. Nonlinear effects in the considered model were taken into account in a minimal way by introducing the interaction of phonons with opposite momenta into the Hamiltonian \cite{11}. In real crystals, a significant role can be played by nonlinear effects described by elastic moduli of the third and fourth order \cite{12,22}.

Thus, the model of a crystal with correlations of phonons with opposite momenta needs further development and generalization. Phase symmetry breaking in multiparticle systems is accompanied by the manifestation of superfluid properties \cite{24-27}. In the considered model, the phase transition is also accompanied by the breaking of the phase symmetry. In this connection, as well as in connection with experimental studies of quantum crystals \cite{10}, the question of the manifestation of superfluidity effects in phonon systems is of considerable interest.

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**Appendix A: Debye functions with integer index \(n \geq 1\) and related functions**

**Definitions:**

\[
D_n(x) = \frac{n}{x^n} \int_0^x \frac{z^n dz}{e^z - 1}, \quad (n \geq 1),
\]

\[
\Phi_n(x) = 1 + \frac{2(1 + n) D_n(x)}{n},
\]

Functions \(D_n(x)\) can be represented as

\[
D_n(x) = \frac{n}{x^n} \left[ n! \zeta(n + 1) - \sum_{m=0}^{\infty} \int_x^\infty e^{-(m+1)z} z^n dz \right],
\]

\(\zeta(n + 1)\) is the Riemann zeta function. The functions with \(n = 2, 3\) are used in this paper, so that

\[
\Phi_2(x) = 1 + 3 \frac{D_2(x)}{x}, \quad \Phi_3(x) = 1 + \frac{8 D_3(x)}{3 x}.
\]

**Large arguments \(x \gg 1\):** Up to exponentially small terms:

\[
D_n(x) \approx \frac{n \cdot n!}{x^n} \zeta(n + 1), \quad D_2(x) \approx \frac{4}{x^2} \zeta(3), \quad D_3(x) \approx \frac{\pi^4}{5 x^3},
\]

\[
\Phi_n(x) \approx 1 + \frac{2(1 + n) \cdot n!}{x^{n+1}} \zeta(n + 1), \quad \Phi_2(x) \approx 1 + \frac{12}{x^3} \zeta(3), \quad \Phi_3(x) \approx 1 + \frac{8 \pi^4}{15 x^4}.
\]

**Small arguments \(x \ll 1\):**

\[
D_n(x) \approx 1 - \frac{n}{2(n + 1)} x + \frac{n}{12(n + 2)} x^2, \quad D_2(x) \approx 1 - \frac{x}{3} + \frac{x^2}{24}, \quad D_3(x) \approx 1 - \frac{3}{8} x + \frac{x^2}{20},
\]

\[
\Phi_n(x) \approx \frac{2(n + 1)}{nx} + \frac{(n + 1)}{6(n + 2)} x, \quad \Phi_2(x) \approx \frac{3}{x} + \frac{x}{8}, \quad \Phi_3(x) \approx \frac{8}{3 x} + \frac{2}{15} x.
\]

**Derivatives** (used designations are \(dD_n(x)/dx \equiv \dot{D}_n(x)\), \(d^2D_n(x)/dx^2 \equiv \ddot{D}_n(x)\) and so on):

\[
\dot{D}_n(x) = \frac{n}{e^x - 1} - \frac{n}{x} D_n(x),
\]

\[
\dot{D}_2(x) = \frac{2}{e^x - 1} - \frac{2}{x} D_2(x), \quad \ddot{D}_3(x) = \frac{3}{e^x - 1} - \frac{3}{x} D_3(x).
\]
\[ \Phi_n(x) = \frac{2(n+1)}{x(e^x - 1)} + \frac{(n+1)}{x} \Phi_n(x) = \frac{(n+1)}{x} \left[ \text{cth} \frac{x}{2} - \Phi_n(x) \right], \]

\[ \Phi_2(x) = \frac{6}{x(e^x - 1)} + \frac{3}{x} \Phi_2(x) = \frac{3}{x} \left[ \text{cth} \frac{x}{2} - \Phi_2(x) \right], \]

\[ \Phi_3(x) = \frac{8}{x(e^x - 1)} + \frac{4}{x} \Phi_3(x) = \frac{4}{x} \left[ \text{cth} \frac{x}{2} - \Phi_3(x) \right]. \]

\[ \Phi_n(x) = -\frac{2(n+1)}{x(e^x - 1)} \left( 1 + \frac{(n+2)}{x} \right) - \frac{2(n+1)}{x(e^x - 1)^2} - \frac{(n+1)(n+2)}{x^2} + \frac{2(n+1)(n+2)}{x^2} \Phi_n(x), \]

\[ \Phi_2(x) = -\frac{6}{x(e^x - 1)} \left( 1 + \frac{4}{x} \right) - \frac{6}{x(e^x - 1)^2} - \frac{12}{x^2} + \frac{12}{x^2} \Phi_2(x), \]

\[ \Phi_3(x) = -\frac{8}{x(e^x - 1)} \left( 1 + \frac{5}{x} \right) - \frac{8}{x(e^x - 1)^2} - \frac{20}{x^2} + \frac{20}{x^2} \Phi_3(x). \]

Appendix B: The function \( f(\xi, \tau) \) and its derivatives:

\[ f(\xi, \tau) = \frac{\xi}{2} + \frac{3}{16} g(\xi^{-2} - 1) \Phi_2(\xi \tau) + \frac{3}{8} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau) + \tau \ln(1 - e^{-\xi \tau}), \]

\[ \frac{\partial f}{\partial \xi} \equiv \psi(\xi, \tau) = \frac{1}{2} \text{cth} \frac{\xi}{2\tau} - \frac{3g}{8\tau} \xi^{-3} \Phi_2(\xi \tau) + \frac{3g}{8\tau} (\xi^{-2} - 1) \Phi_2(\xi \tau) \Phi_2(\xi \tau) - \frac{3}{8} \left( \xi^{-2} + \frac{4}{3} \right) \Phi_3(\xi \tau) + \frac{3}{8\tau} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau), \]

\[ \frac{\partial f}{\partial \tau} \equiv -s(\xi, \tau) = -\frac{3g}{8\tau^2} (\xi^{-2} - 1) \Phi_2(\xi \tau) \Phi_2(\xi \tau) - \frac{3}{8\tau^2} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau) + \ln(1 - e^{-\xi \tau}) - \frac{\xi}{\tau e^{\xi \tau} - 1}, \]

\[ \varphi(\xi, \tau) \equiv f - \tau \frac{\partial f}{\partial \tau} = \frac{\xi}{2} \text{cth} \frac{\xi}{2\tau} + \frac{3g}{16} (\xi^{-2} - 1) \Phi_2(\xi \tau) \left( \Phi_2(\xi \tau) + \frac{2}{\tau} \Phi_2(\xi \tau) \right) + \frac{3}{8} \left( \xi^{-1} - \frac{4}{3} \xi \right) \left[ \Phi_3(\xi \tau) + \frac{\xi}{\tau} \Phi_3(\xi \tau) \right], \]

\[ \frac{\partial^2 f}{\partial \xi^2} = \frac{1}{4\tau} \left[ 1 - \text{cth}^2 \frac{\xi}{2\tau} \right] + \frac{3g}{8} \left[ \frac{3}{4} \xi \Phi_2(\xi \tau) - \frac{4}{3\tau} (\xi^{-2} - 1) \Phi_2(\xi \tau) + \frac{1}{\tau^2} (\xi^{-2} - 1) \Phi_2(\xi \tau) \Phi_2(\xi \tau) \right] + \frac{3}{4\xi^3} \Phi_3(\xi \tau) - \frac{3}{4\tau} \left( \xi^{-2} + \frac{4}{3} \right) \Phi_3(\xi \tau) + \frac{3}{8\tau^2} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau), \]

\[ \frac{\partial^2 f}{\partial \tau^2} = \frac{3g}{4\tau^3} (\xi^{-2} - 1) \Phi_2(\xi \tau) \Phi_2(\xi \tau) + \frac{3g}{8\tau^4} (\xi^{-2} - 1) \left( \Phi_2^2(\xi \tau) + \Phi_2(\xi \tau) \Phi_2(\xi \tau) \right) + \frac{3}{4\tau^3} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau) + \frac{3}{8\tau^4} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau) - \frac{\xi^2}{\tau^3} e^{\xi \tau}, \]

\[ \frac{\partial^2 f}{\partial \xi \partial \tau} = \frac{3g}{8\tau^3} (\xi^{-2} - 1) \Phi_2(\xi \tau) \Phi_2(\xi \tau) - \frac{3g}{8\tau^3} (\xi^{-2} - 1) \left[ \Phi_2^2(\xi \tau) + \Phi_2(\xi \tau) \Phi_2(\xi \tau) \right] + \frac{3}{8\tau^3} \left( \xi^{-1} - \frac{4}{3} \xi \right) \Phi_3(\xi \tau) + \frac{\xi}{\tau} e^{\xi \tau} - \frac{\xi^2}{\tau^3} (e^{\xi \tau} - 1). \]
Appendix C: Thermodynamic functions in the Debye free phonon model

The free energy:

\[
\frac{F_D}{\Theta_D N} \equiv f_D(\tau) = \frac{1}{2} - \frac{1}{8} \Phi_3(\tau) + \tau \ln(1 - e^{-\tau}),
\]

(C1)

the entropy

\[
\frac{S}{N} = -\frac{\partial f_D}{\tau} = \frac{4}{3} D_3(\tau) - \ln(1 - e^{-\tau}),
\]

(C2)

the pressure

\[
p = \Gamma n \Theta_D \left( f_D - \tau \frac{\partial f_D}{\tau} \right) = \frac{3}{8} \Gamma n \Theta_D \Phi_3(\tau),
\]

(C3)

the energy

\[
E_D = N \Theta_D \left( f_D - \tau \frac{\partial f_D}{\tau} \right) = \frac{3}{8} N \Theta_D \Phi_3(\tau) = \frac{pV}{\Gamma},
\]

(C4)

the phonon number

\[
N_{ph}^{(D)} = \frac{3}{2} N \tau D_2(\tau).
\]

(C5)

The entropy and pressure differentials:

\[
\frac{dS}{N} = \tau \Omega_0 \left( \frac{dT}{T} + \Gamma \frac{dV}{V} \right),
\]

(C6)

\[
\frac{dp}{\Omega_0} = \frac{\Gamma n \Theta_D \phi_0}{1 + \Gamma} \left[ \frac{\Gamma}{1 + \Gamma} \frac{\Omega_0 \tau^2}{\phi_0} - 1 \right] \frac{dV}{V},
\]

(C7)

where

\[
\Omega_0 = \frac{1}{\tau} \left[ 4 \tau D_3(\tau) - \frac{3}{e^\tau - 1} \right] = -\frac{3}{8} \Phi_3(\tau), \quad \phi_0 \equiv \frac{3}{8} \Phi_3(\tau).
\]

(C8)

The formulas for the heat capacities and thermodynamic coefficients coincide with formulas (56) – (61) for the asymmetric phase, if we make the following substitutions in them

\[
\Omega \rightarrow \Omega_0, \quad \phi \rightarrow \phi_0, \quad Z \rightarrow Z_0 = 1 - \frac{\Gamma}{1 + \Gamma} \frac{\Omega_0 \tau^2}{\phi_0},
\]

so that we obtain

\[
C_V = \frac{N T \Omega_0}{\Theta_D}, \quad C_p = \frac{N T \Omega_0}{\Theta_D} \left( 1 + \frac{\Gamma}{1 + \Gamma} \frac{\Omega_0 \tau^2}{\phi_0 Z_0} \right),
\]

\[
C_p - C_V = \frac{V T}{\gamma_T} \alpha_p^2 = N \frac{\Gamma}{1 + \Gamma} \frac{T^3 \Omega_0^3}{\Theta_D^3 \phi_0 Z_0},
\]

(C9)

and also

\[
\beta_V = \frac{T}{\Theta_D \phi_0}, \quad \alpha_p = \frac{T \Omega_0}{\Theta_D^2 (1 + \Gamma) \phi_0 Z_0}, \quad \gamma_T = \frac{1}{\Gamma (1 + \Gamma) n \Theta_D \phi_0 Z_0}.
\]

(C10)

The stability condition (77) for the Debye state is always satisfied.
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