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THERMODYNAMICS OF THE CRYSTAL IN PSEUDOHARMONIC APPROXIMATION

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1. Introduction

Recently Götze and Michel proposed a phenomenological quasiparticle picture of the crystal [1] . Generalizing a concept used by Landau in the theory of Fermi liquids the internal energy of the crystal is assumed to be given as a functional of deformation parameters $u_{\alpha\beta}$ and number of excitations $n(\vec{p}j)$ with quasimomentum $\vec{p}$ and polarization branch j . The dependence on $u_{\alpha\beta}$ refleots the static energy of the crystal - the "background" state. At the temperature $T \neq 0$ quasiparticles are excited above this "background".

Usually only small perturbations of the equilibrium state are studied. Therefore we do not need complete knowledge of the functional

$$E = E\{ u_{\alpha\beta}, n(\vec{p},j) \}.$$

Only first and second derivatives of E are quantities of interest. All the important parameters of the phonon gas and some thermodynamic functions describing the state of the "background" are to be defined in terms of the first and second derivatives of E .

Usually it is a formidable task to compute these derivatives microscopically, without using the methods of thermodynamics, and simple models are invited. For these reasons anharmonic crystal in pseudoharmonic approximation is frequently used. The crystal in this approximation is equivalent to a gas of noninteracting harmonic oscillators with temperature dependent frequencies (see for example Werthamer [2]).

Some of a quasiparticle parameters in pseudoharmonic approximation were considered by Götze and Michel [3,4] and some of a thermodynamic quantities by Werthamer [2]. The second order derivatives of the internal energy E or free energy F with respect to strain $u_{\alpha\beta}$ give the second order elastic constants, adiabatic $S^{(ad)}_{\alpha\beta,\gamma\delta}$ or isothermal $S^{(is)}_{\alpha\beta,\gamma\delta}$ respectively.

As it has been pointed firstly by Cowley [5] the hydrodynamic limit of phonon Green function mass operator $\Pi_{kj}(\omega)$ gives isothermal elastic constants $S^{(is)}_{\alpha\beta,\gamma\delta}$ and its collisionless limit gives $S^{(ad)}_{\alpha\beta,\gamma\delta}$ the adiabatic one. For the difference of elastic constants macrosoopic thermodynamics gives [6,7]

$$S^{(ad)}_{\alpha\beta,\gamma\delta} - S^{(is)}_{\alpha\beta,\gamma\delta} = \frac{T}{C_V} \tau_{\alpha\beta} \tau_{\gamma\delta} , \qquad (I)$$

(C_V being the heat capacity at constant strain, $\tau_{\alpha\beta}$ tension tensor). It is possible to calculate the mass operator of phonon Green function $\Pi_{kj}(\omega)$ accounting for all two-phonon prooesses [4,8,9,1o] and relate its hydrodynamic limit to isothermal elastic constants derived from pseudoharmonic free energy [4,8,1o].

If we compute the thermodynamic functions appearing on the right-hand side of Eq.(1) we may prove this relation, as it was done by Wehner and Klein for harmonic lattice with three-phonon interactions [7] .

In this work we will derive some quasiparticle parameters from pseudoharmonic internal energy and some thermodynamic functions from pseudoharmonic free energy considering after Choquard [11] and Klein et al. [12] , the set of correlation functions of the displacements of atoms to be intermediate variables describing fluctuational state of the crystal. In such a way we are in a position to relate considered quasiparticle parameters and thermodynamic functions to quantities describing two-phonon processes as the phonon bubble Γ^{0} or four phonon renormalized vertex.

In section 2 we give some definitions and notations and derive the quasiparticle parameters. In Section 3 we compute some thermodynamic functions and consider equation (I).

Section 2.

Let us consider, for simplicity, a Bravais lattice and denote the average of the instanteous position operator of ℓ-th atom $\vec{R}_{\ell}$ $(\ell=1,\dots,N)$ by $\vec{X}_{\ell}$

$$X_l \equiv \langle R_l \rangle = \mathrm{Tr}\left(R_l \, \frac{e^{-\frac{H}{\Theta}}}{\mathrm{Tr}\exp[-H/\Theta]} \right),$$

H being the Hamiltonian of the lattice

$$H = \sum_{l=1}^{N} \frac{P_l^2}{2M} + U(R_1, \dots, R_N),$$

with M the mass of the atoms, $\vec{P}_l$ -momentum operator, U -potential energy of the crystal. The displacement operator $\vec{u}_l$ of l-th atom is given as

$$\vec{u}_l = \vec{R}_l - \vec{X}_l \, .$$

In pseudoharmonic approximation the frequencies ω_Q and polarization vectors $\vec{e}(Q)$ (we use the abbreviation $Q = (\vec{q}, j)$ here and in the following) are solutions of an eigenvalue equation

$$\omega_Q^2 \, e_\alpha(Q) = \frac{1}{MN} \sum_{l,l'} \sum_{\beta} e_\beta(Q) \, e^{-i\vec{q}(\vec{X}_l - \vec{X}_{l'})} \tilde{\Phi}^{\alpha\beta}_{ll'} \, . \quad (1)$$

The vectors of polarization form the complete and orthonormal set. $\tilde{\Phi}^{\alpha\beta}_{ll'}$ is the second order renormalized vertex which we obtain by differentiation of the pseudoharmonic potential energy $\tilde{U}(X_1, \dots, X_N)$. Generally n-th order renormalized vertex is defined as

$$\tilde{\Phi}^{\alpha_1 \ldots \alpha_n}_{\ell_1 \ldots \ell_n} = \nabla^{\alpha_1}_{\ell_1} \ldots \nabla^{\alpha_n}_{\ell_n} \tilde{U}(\ldots \vec{X}_\ell \ldots), \tag{2}$$

where

$$\tilde{U}(\ldots \vec{X}_\ell \ldots) = \exp\left[\frac{1}{2}\sum_{1,2} \langle u_1 u_2 \rangle \nabla_1 \nabla_2\right] U_0(\ldots \vec{X}_\ell \ldots), \tag{3}$$

with U_0 being the static potential energy of the crystal. It is easy to compute the free energy and internal energy in the pseudoharmonic approximation (see for example [13])

$$F = \tilde{U} - \frac{1}{4}\sum_K \omega_k (2n_k + 1) + \Theta \sum_K \ln\left[2 sh \frac{\omega_k}{2\Theta}\right], \tag{4}$$

$$E = \tilde{U} + \frac{1}{4}\sum \omega_k (2n_k + 1), \tag{5}$$

with n_k the average number of phonons with quasimomentum $\vec{k}$ and polarization j

$$n_k = \left(\exp\left[\frac{\omega_k}{2\Theta}\right] - 1\right)^{-1}, \qquad \Theta = \frac{1}{\beta} = kT.$$

As we mentioned in the introduction these expressions correspond to the assembly of free oscillators, entropy of which is equal to

$$S = k \sum_K \left\{ (n_k + 1) \ln(n_k + 1) - n_k \ln n_k \right\}, \tag{6}$$

and the difference of E (5) and F (4) has to fulfill the thermodynamic identity

$$E = F + TS. \tag{7}$$

If we neglect the polarization mixing in pseudoharmonic approximation the correlation function $\langle u_l^{\gamma} u_{l'}^{\gamma'} \rangle$ is given by

$$\langle u_l^{\gamma} u_{l'}^{\gamma'} \rangle = \sum_K \frac{e_\gamma(K)\, e_{\gamma'}(K)}{2MN\omega_K} (2n_K + 1)\, e^{ik(X_l - X_{l'})}. \tag{8}$$

Let us denote the expression corresponding to free phonon bubble by $F^{\circ}(K_1, K_2; \omega)$

$$F^{\circ}(K_1, K_2, \omega) = \frac{2(\omega_{K_1} + \omega_{K_2})(n_{K_1} + n_{K_2} + 1)}{\omega^2 - (\omega_{K_1} + \omega_{K_2})^2} - \frac{2(\omega_{K_1} - \omega_{K_2})(n_{K_1} - n_{K_2})}{\omega^2 - (\omega_{K_1} - \omega_{K_2})^2}. \tag{9}$$

If $|\vec{k}_1| \to |\vec{k}_2|$ and $\omega \to 0$ for $j_1 = j_2$ F° behaves singularily as noted by Cowley [5], Götze [14] and Gotze and Michel [15]. Let us put $\vec{k}_1 = \vec{k} + \vec{q}$, $\vec{k}_2 = -\vec{k}$. For small $\vec{q}$, ω we have $(K = (\vec{k}, j))$

$$F^{\circ}(\vec{k}+\vec{q}, -\vec{k}, j, \omega) = -\frac{2n_K + 1}{\omega_K} - 2\frac{(\vec{v}\vec{q})^2}{\omega^2 - (\vec{v}\vec{q})^2} \frac{dn_K}{d\omega_K}. \tag{10}$$

The hydrodynamic limit of F° is defined as

$$\lim_{q \to 0} \left\{ \lim_{\omega \to 0} F^{\circ}(k+q, -k, j; \omega) \right\} = -\frac{2n_K + 1}{\omega_K} + 2\frac{dn_K}{d\omega_K} \equiv F^{(is)}(K), \tag{11}$$

and collisionless limit

$$\lim_{\omega\to 0}\left\{\lim_{q\to 0} F^{\circ}(\vec{k}+\vec{q},-\vec{k},j;\omega)\right\} = -\frac{2n_k+1}{\omega_k} \equiv F^{(ad)}(k). \tag{12}$$

The pseudoharmonic free energy is stationary with respect to change of the correlation function

$$\frac{\delta F}{\delta\langle u_l^{\gamma} u_{l'}^{\gamma'}\rangle} = 0. \tag{13}$$

Let us consider the first derivative of F with respect to temperature T at constant $u_{\alpha\beta}$

$$\left(\frac{\partial F}{\partial T}\right)_{u_{\alpha\beta}} = \left(\frac{\partial F}{\partial T}\right)_{u_{\alpha\beta},\langle uu\rangle} + \sum_{\substack{\gamma\gamma'\\ ll'}} \frac{\partial F}{\partial\langle u_l^{\gamma} u_{l'}^{\gamma'}\rangle}\left(\frac{\partial\langle u_l^{\gamma} u_{l'}^{\gamma'}\rangle}{\partial T}\right)_{u_{\alpha\beta}}$$

But the first two terms of F depend on T only implicitely via $\langle u_l^{\gamma} u_{l'}^{\gamma'}\rangle$ and due to the stationarity of F we obtain

$$\left(\frac{\partial F}{\partial T}\right)_{u_{\alpha\beta}} = \left(\frac{\partial F}{\partial T}\right)_{u_{\alpha\beta},\langle uu\rangle} = -S. \tag{14}$$

Differentiating the identity (7) with respect to T at constant strain $u_{\alpha\beta}$ and making use of Eq. (14) we obtain thermodynamic identity

$$T\left(\frac{\partial S}{\partial T}\right)_{u_{\alpha\beta}} = \left(\frac{\partial E}{\partial T}\right)_{u_{\alpha\beta}} = C_V, \tag{14a}$$

C_V is the heat capacity at constant strain. This identity will be proved further.

The first derivative of F with respect to strain parameter $u_{\alpha\beta}$ at constant T gives the stress tensor $\sigma_{\alpha\beta}$

$$V\sigma_{\alpha\beta} = \left(\frac{\partial F}{\partial u_{\alpha\beta}}\right)_T = \left(\frac{\partial F}{\partial u_{\alpha\beta}}\right)_{T,\langle uu\rangle} + \sum_{\substack{\gamma\gamma'\\ ll'}} \frac{\partial F}{\partial\langle u_l^\gamma u_{l'}^{\gamma'}\rangle}\left(\frac{\partial\langle u_l^\gamma u_{l'}^{\gamma'}\rangle}{\partial u_{\alpha\beta}}\right)_T ,$$

where V is the volume of the crystal.

From stationarity equation (13) the second term disappears and we obtain

$$V\sigma_{\alpha\beta} = \sum_u X_u^\beta \, \tilde{\varphi}_u^\alpha , \qquad (15)$$

where $\tilde{\varphi}_u^\alpha$ is first order renormalized vertex.

In view of rotational invariance of the potential energy $\sigma_{\alpha\beta}$ is symmetric [16]

$$\sigma_{\alpha\beta} = \sigma_{\beta\alpha} .$$

Let us consider the derivatives of the internal energy E.

The first derivative of E with respect to number of quasiparticles $n(K)$ gives the first quasiparticle parameter-energy of quasiparticles $\omega(K)$

$$\left(\frac{\partial E}{\partial n_K}\right)_{u_{\alpha\beta}} = \left(\frac{\partial E}{\partial n_K}\right)_{u_{\alpha\beta},\langle uu\rangle} + \sum_{\substack{\gamma\gamma'\\ ll'}} \frac{\partial E}{\partial\langle u_l^\gamma u_{l'}^{\gamma'}\rangle}\left(\frac{\partial\langle u_l^\gamma u_{l'}^{\gamma'}\rangle}{\partial n_K}\right)_{u_{\alpha\beta}} .$$

With the help of Eq. (5) using the definition of second order vertex (2) and frequencies ω_Q (1) we obtain. [1,3,4]

$$\left(\frac{\partial E}{\partial n_K}\right)_{u_{\alpha\beta}} = \omega(K). \tag{16}$$

Next we are going to perform the calculation of the second derivative of the internal energy with respect to n_p defining the quasiparticle interaction $f(P,P')$

$$f(P,P') \equiv \left(\frac{\partial^2 E}{\partial n_P \partial n_{P'}}\right)_{u_{\alpha\beta}} = \frac{1}{2\omega_P}\left(\frac{\partial \omega_P^2}{\partial n_{P'}}\right)_{u_{\alpha\beta}} . \tag{17}$$

Using the definition of ω_Q (1) and the second order vertex (2) we put Eq. (1.7) in the form

$$f(P,P') = \frac{1}{2}\sum_{\substack{\gamma\gamma'\rho\rho' \\ \ell\ell' r r'}} \frac{e_P^{\gamma} e_P^{\gamma'}}{2MN\omega_P}\, e^{i\vec{P}(\vec{X}_\ell-\vec{X}_{\ell'})}\, \tilde{\Phi}^{\gamma\gamma'\rho\rho'}_{\ell\ell' r r'} \left(\frac{\partial\langle u_r^{\rho} u_{r'}^{\rho'}\rangle}{\partial n_{P'}}\right)_{u_{\alpha\beta}} . \tag{18}$$

For the derivative of correlation function with respect to $n_{P'}$ following Choquard [11] and Klein et al. [12] we obtain an integral equation

$$\left(\frac{\partial\langle u_r^{\rho} u_{r'}^{\rho'}\rangle}{\partial n_{P'}}\right)_{u_{\alpha\beta}} = \frac{e_{P'}^{\rho} e_{P'}^{\rho'}}{MN\omega_{P'}}\, e^{i\vec{P}'(\vec{X}_r-\vec{X}_{r'})} + \sum_{\substack{\nu\nu'\mu\mu' \\ nn' mm'}} L^{(ad)\,\rho\rho'\nu\nu'}_{rr'nn'}\, \tilde{\Phi}^{\nu\nu'\mu\mu'}_{nn'mm'} \left(\frac{\partial\langle u_m^{\mu} u_{m'}^{\mu'}\rangle}{\partial n_{P'}}\right)_{u_{\alpha\beta}}, \tag{19}$$

where

$$L^{(aa)\,\rho\rho'\nu\nu'}_{\quad rr'nn'} = \sum_{Q} \frac{e_{\rho}(Q)e_{\rho'}(Q)\,e_{\nu}(Q)\,e_{\nu'}(Q)}{\omega_Q^2\,(2MN)^2}\, e^{i\vec{q}(\vec{X}_r-\vec{X}_{r'})-i\vec{q}(\vec{X}_n-\vec{X}_{n'})}\,\frac{F^{ad}(Q)}{2}\,. \tag{20}$$

Putting the solution of the integral equation (19) into expression (18) we get

$$f(\ell,\ell') = \sum_{\substack{\gamma\gamma'\rho\rho'\nu\nu' \\ \ell\ell' rr' nn'}} \frac{e_{\gamma}(\ell)e_{\gamma'}(\ell)\,e_{\rho}(\ell')e_{\rho'}(\ell')}{(2MN)^2\,\omega_{\ell}\,\omega_{\ell'}}\, e^{i\vec{p}(\vec{X}_{\ell}-\vec{X}_{\ell'})+i\vec{p}'(\vec{X}_r-\vec{X}_{r'})}\, \tilde{\Phi}^{\gamma\gamma'\nu\nu'}_{\ell\ell' nn'} \left[(1-\tilde{C}^{(ad)})^{-1}\right]^{\nu\nu'\rho\rho'}_{nn'rr'} \tag{21}$$

where

$$\left[\tilde{C}^{(ad)}\right]^{\nu\nu'\rho\rho'}_{nn'rr'} \equiv \sum_{\substack{\mu\mu' \\ mm'}} L^{(aa)\,\nu\nu'\mu\mu'}_{\quad nn'mm'}\, \tilde{\Phi}^{\mu\mu'\rho\rho'}_{mm'rr'}\,.$$

Following [10] we put (21) in the form in which only phonon quantities appear. Expanding $(1-\tilde{C}^{aa})^{-1}$ into a series and using the definition of the phonon vertices

$$V_n(K_1,\dots,K_n) = \left(\frac{1}{2MN}\right)^{\frac{n}{2}} \sum_{\substack{\alpha_1,\dots,\alpha_n \\ \ell_1,\dots,\ell_n}} \frac{e_{\alpha_1}(K_1)\dots e_{\alpha_n}(K_n)}{(\omega_{K_1}\dots\omega_{K_n})^{1/2}}\, e^{i\vec{k}_1\vec{X}_{\ell_1}+\dots+i\vec{k}_n\vec{X}_{\ell_n}}\, \tilde{\Phi}^{\alpha_1\dots\alpha_n}_{\ell_1\dots\ell_n} \tag{22}$$

we obtain

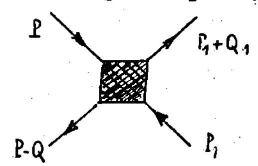
$$f(P,P_1) = \sum_{K} \widetilde{V}(P,-P;K,-K)\left[(1-C^{(ad)})^{-1}\right]_{K,-K;P_1,-P_1} . \qquad (23)$$

$C^{(ad)}$ is the collisionless limit of the irregular part of $\left[C(\omega)\right]_{K_1K_2;K_1'K_2'}$ [9,10]

$$\left[C(\omega)\right]_{K_1K_2;K_1'K_2'} = \frac{1}{2}\overset{\circ}{F}(K_1K_2;\omega)\,\widetilde{V}_4(-K_1,-K_2;K_1',K_2') , \qquad (24)$$

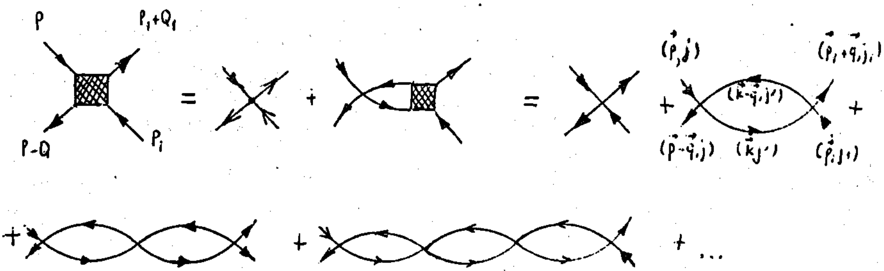
$$\left[C^{(ad)}\right]_{K,-K;P_1,-P_1} = \lim_{\omega\to 0}\left\{\lim_{q\to 0} \frac{1}{2}\overset{\circ}{F}(\vec{k}+\vec{q},-\vec{k},j,\omega)\,\widetilde{V}_4(-\vec{k}-\vec{q},j,\vec{k}j;\vec{p}_1+\vec{q},j_1,-\vec{p}_1j_1)\right\}.$$

It is possible to give Eq.(23) a diagramatic representation

$f(P,P_1) =$ 

, $Q = (\vec{q},j)$, $Q_1 = (\vec{q},j_1)$

where the effective two-phonon interaction vertex is a solution of equation



The result (23) differs from that obtained by Götze and Michel [3,4] by regular part of F° which we drop as we have neglected the polarization mixing. The regular part of $F^{\circ}(K_1, K_2; \omega)$ $(j_1 \neq j_2)$ is practically independent of $\vec{q}$ and ω [7] . The generalization of the Eq.(23) was recently given by Werthamer [17] .

Now we consider the Grüneisen constant $\gamma_{\alpha\beta}(K)$ which defines a change of energy of the quasiparticle with deformation $u_{\alpha\beta}$ at constant temperature

$$\gamma_{\alpha\beta}(K) = -\frac{1}{\omega_K}\left(\frac{\partial \omega_K}{\partial u_{\alpha\beta}}\right)_T . \tag{25}$$

We are concerned with

$$\frac{1}{\omega_K}\left(\frac{\partial \omega_K}{\partial u_{\alpha\beta}}\right)_T = \frac{1}{2}\left(\frac{\partial \omega_K^2}{\partial u_{\alpha\beta}}\right)_T = \sum_{\substack{\gamma\gamma' \\ \ell\ell'}} \frac{e_\gamma(K) e_{\gamma'}(K)}{2MN} e^{iK(X_\ell - X_{\ell'})} \times$$

$$\times\left\{\left(\frac{\partial \tilde{\Phi}^{\gamma\gamma'}_{\ell\ell'}}{\partial u_{\alpha\beta}}\right)_{T,\langle uu\rangle} + \sum_{\substack{\rho\rho' \\ rr'}} \frac{\partial \tilde{\Phi}^{\gamma\gamma'}_{\ell\ell'}}{\partial \langle u^\rho_r u^{\rho'}_{r'}\rangle}\left(\frac{\partial \langle u^\rho_r u^{\rho'}_{r'}\rangle}{\partial u_{\alpha\beta}}\right)_T\right\}.$$

Instead of deriving the integral equation for derivative of the correlation function with respect to $u_{\alpha\beta}$ at constant T we use Eq.(8) . In such a way we obtain an integral equation for $\left(\frac{\partial \omega_K}{\partial u_{\alpha\beta}}\right)_T$. The solution of this equation is equal to

$$\left(\frac{\partial \omega_K}{\partial u_{\alpha\beta}}\right)_T = \sum_P \left[(1 - C^{(s)})^{-1}\right]_{K-K, P-P} \sum_{\substack{\gamma\gamma' \\ \ell\ell', v}} \frac{e_\gamma(P) e_{\gamma'}(P)}{2MN\omega_P} e^{i\vec{p}(\vec{X}_\ell - \vec{X}_{\ell'})} X^\beta_v \tilde{\Phi}^{\alpha\gamma\gamma'}_{v\ell\ell'} \,. \tag{26}$$

where $\left[C^{(is)}\right]_{K,-K;P,-P}$ is the hydrodynamic limit of

$$\left[C^{(is)}\right]_{K,-K;P',-P'} = \lim_{q\to 0}\left\{\lim_{\omega\to 0}\frac{1}{2}\overset{\circ}{F}(\vec{k}+\vec{q}j,-\vec{k}j;\omega)\,\widetilde{V}_4(-\vec{k}-\vec{q}j,\vec{k}j;\vec{p}'+\vec{q}j',-\vec{p}'j')\right\}.$$

Making use of Eq.(26) finally we obtain the Grüneisen constant in the form

$$\gamma_{\alpha\beta}(K) = -\sum_{P}\left[(1-C^{(is)})^{-1}\right]_{K,-K;P,-P}\sum_{\substack{\gamma\gamma'\\ \ell\ell'\upsilon}}\frac{e_{\gamma}(\ell)e_{\gamma'}(\ell)}{2MN\omega_k\omega_p}\,e^{ip(X_l-X_{l'})}X_{\upsilon}^{\beta}\,\widetilde{\Phi}^{\alpha\gamma\gamma'}_{\upsilon\ell\ell'}. \tag{27}$$

The coordinate representation of this equation was obtained by Klein et al [18] (see also Choquard [11], Horner [19], Götze and Michel [3,4]).

Let us consider a change of the phonon energy under external influence leading to the deformation $u_{\alpha\beta}$

$$\delta\omega(K) = -\sum_{\alpha\beta}\gamma_{\alpha\beta}(K)u_{\alpha\beta}\,. \tag{28}$$

But from the method of long waves $u_{\alpha\beta}$ is equal to (see for example [20])

$$u_{\alpha\beta} = iq_{\beta}u^{\alpha}_{\eta}\,, \tag{29}$$

where

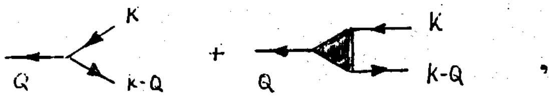
$$u^{\alpha}_{\eta} = \frac{e_{\alpha}(q\eta)}{\sqrt{M}}\,,$$

$\eta = 1,2,3$ is polarization index of the accoustic mode

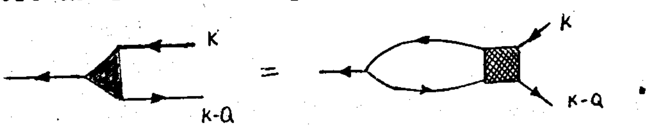
Substituting (27) and (29) into Eq. (28) we get $(Q=(\vec{q},\eta))$

$$\delta\omega_K = \lim_{q\to 0}\Big\{\lim_{\omega\to 0}\sum_{P_1,P_2}\Big[(1-C(\omega))^{-1}\Big]_{K,-K+Q;\,P_1,P_2}\frac{(2\omega_Q N)^{1/2}}{\omega_K}\tilde{V}_3(P_1,P_2,-Q)\Big\}. \quad (30)$$

It means that a change of the phonon energy ω_K can be represented by the following diagrams



where the renormalized phonon vertex is equal to



The equation (30) is similar to that obtained by Wehner and Klein [7] who consider the harmonic approximation and three-phonon interactions only.

Section 3

In this section we consider the elastic constants and all thermodynamic quantities needed to obtain the correct thermodynamical result for the difference of adiabatic and isothermal elastic constants $S^{ad} - S^{is}$.

Let us begin with deriving the heat capacity at constant strain $u_{\alpha\beta}$ .From definition

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_{u_{\alpha\beta}} .$$

Differentiating the entropy S (6) with respeot to temperature T we obtain

$$T\left(\frac{\partial S}{\partial T}\right)_{u_{\alpha\beta}} = \sum_K \omega_K \frac{dn_K}{dT} - T\sum_{\substack{\gamma,\gamma',K\\ \ell,\ell'}} \left(\frac{dn_K}{dT}\right)\frac{\partial \omega_K}{\partial\langle u_\ell^\gamma u_{\ell'}^{\gamma'}\rangle}\left(\frac{\partial\langle u_\ell^\gamma u_{\ell'}^{\gamma'}\rangle}{\partial T}\right)_{u_{\alpha\beta}} . \quad (31)$$

For the derivative of the oorrelation function with respect to T we obtain an integral equation, solution of which is equal to

$$\left(\frac{\partial\langle u_\ell^\gamma u_{\ell'}^{\gamma'}\rangle}{\partial T}\right)_{u_{\alpha\beta}} = \sum_{\substack{\mu\mu'\\ mm'\rho}} \left[\left(1-\widetilde{C}^{(is)}\right)^{-1}\right]^{\gamma\gamma'\mu\mu'}_{\ell\ell' mm'} \frac{e_\mu(\rho)e_{\mu'}(\rho)}{MN\omega_\rho} e^{i\vec{p}(\vec{X}_m-\vec{X}_{m'})}\frac{dn_\rho}{dT} , \quad (32)$$

where $\left(\widetilde{C}^{(is)}\right)^{\gamma\gamma'\mu\mu'}_{\ell\ell' mm'}$ can be obtained from $\left(\widetilde{C}^{(ad)}\right)^{\gamma\gamma'\mu\mu'}_{\ell\ell' mm'}$ changing in $L^{(ad)}$ (20) $F^{(ad)}$ to $F^{(is)}$ (11).

Similarly as in the derivation of the formula (23) for $f(\rho,\rho')$, we expand $(1-\widetilde{C}^{(is)})^{-1}$ in the series and use the definition of phonon vertioes (22). In suoh a way we get

$$\left(\frac{\partial\langle u_\ell^\gamma u_{\ell'}^{\gamma'}\rangle}{\partial T}\right)_{u_{\alpha\beta}} = \sum_{\rho,\rho'} \frac{e_\gamma(\rho)e_{\gamma'}(\rho)}{MN\omega_\rho} e^{i\vec{p}(\vec{X}_\ell-\vec{X}_{\ell'})}\left[\left(1-C^{(is)}\right)^{-1}\right]_{\rho,-\rho;\rho',-\rho'}\frac{dn_{\rho'}}{dT} .$$

Inserting this into Eq.(31) we have

$$C_v = \sum_K \omega_K \frac{dn_K}{dT} - T\sum_{K,\rho,\rho'} \frac{dn_K}{dT}\widetilde{V}_4(K,-K;\rho,-\rho)\left[\left(1-C^{(is)}\right)^{-1}\right]_{\rho,-\rho;\rho',-\rho'}\frac{dn_{\rho'}}{dT} . \quad (33)$$

The heat capacity in this form was firstly obtained by Werthamer [2] . It may be proved that the derivative of the internal energy with respect to temperature gives the same result conforming (14a) .

Another interesting quantity is the tension tensor $\tau_{\alpha\beta}$

$$\tau_{\alpha\beta} = -\left(\frac{\partial \sigma_{\alpha\beta}}{\partial T}\right)_{u_{\alpha\beta}} = \frac{1}{V}\frac{\partial^2 F}{\partial u_{\alpha\beta}\partial T} = \frac{1}{V}\left(\frac{\partial S}{\partial u_{\alpha\beta}}\right)_T .$$

Using the definition of the entropy we obtain

$$\tau_{\alpha\beta} = \frac{1}{V}\sum_K \omega_K \frac{dn_K}{dT}\left[-\frac{1}{\omega_K}\left(\frac{\partial \omega_K}{\partial u_{\alpha\beta}}\right)_T\right] = \frac{1}{V}\sum_K \omega_K \frac{dn_K}{dT}\gamma_{\alpha\beta}(K).$$

The term in the brackets is the familiar Grüneisen constant $\gamma_{\alpha\beta}(K)$. Using the representation for $\gamma_{\alpha\beta}(K)$ which corresponds to Eq. (27), we obtain the following alternative form

$$\tau_{\alpha\beta} = -\frac{1}{V}\sum_{K,P}\frac{dn_K}{dT}\left[(1-C^{(is)})^{-1}\right]_{K,-K;P,-P}\sum_{\substack{\gamma\gamma'\\ \ell\ell' v}}\frac{e_\gamma(P)e_{\gamma'}(P)}{2MN\omega_P}e^{i\vec{p}(\vec{X}_\ell-\vec{X}_{\ell'})}X_v^\beta\tilde{\Phi}_{v\ell\ell'}^{\alpha\gamma\gamma'} \quad (34)$$

This result can be obtained from differentiation of $\sigma_{\alpha\beta}$ with respect to T . The elastic constants can be obtained from the mass operator $\Pi_Q(\omega)$ of the phonon Green function $\langle\langle A_Q, A_Q^+\rangle\rangle_\omega$ where operators A_Q are obtained from expansion of the displacement

operators u_ℓ in plane waves

$$u_\ell^\alpha = \sum_Q \frac{e_\alpha(Q)}{(2MN\omega_Q)^{1/2}} e^{i\vec{q}\vec{X}_\ell} A_Q ,$$

$$A_{-Q} = A_Q^+ , \quad -Q = (-\vec{q}, j) .$$

The mass operator $\Pi_Q(\omega)$ is equal to [9]

$$\Pi_Q(\omega) = \frac{1}{2}\sum_{\substack{K_1K_2\\ K_1'K_2'}}\tilde{V}_3(-Q,K_1,K_2)\left[(1-C(\omega))^{-1}\right]_{K_1K_2;K_1'K_2'}F^c(K_1',K_2';\omega)\tilde{V}_3(Q,-K_1',-K_2') .$$

Using the method of long waves [2o] we find from collisionless and hydrodynamic limit the adiabatic and isothermal elastic constants [1o]

$$S_{\alpha\beta,\gamma\delta}^{\binom{ad}{is}} = \frac{1}{V}\sum_{u,v}X_u^\beta\left(\tilde{\Phi}_{uv}^{\alpha\gamma} + M_{uv}^{\binom{ad}{is}\alpha\gamma}\right)X_v^\delta , \quad (35)$$

where

$$M_{uv}^{\binom{ad}{is}\alpha\gamma} = \left(\frac{1}{2MN}\right)^2\sum_{\substack{\nu\nu'\mu\mu'\\ nn'mm'}}\tilde{\Phi}_{unn'}^{\alpha\nu\nu'}\tilde{\Phi}_{vmm'}^{\gamma\mu\mu'}\frac{e_\nu(k)e_{\nu'}(k)e_\mu(k')e_{\mu'}(k')}{\omega_k\omega_{k'}}\times$$

$$\times e^{i\vec{k}(\vec{X}_n-\vec{X}_{n'})+i\vec{k}'(\vec{X}_m-\vec{X}_{m'})}\left[(1-C^{\binom{ad}{is}})^{-1}\right]_{K,-K;K',-K'}\frac{F^{\binom{ad}{is}}(k')}{2} . \quad (36)$$

Now we are in position to calculate the difference of the elastic constants

$$S^{(ad)}_{\alpha\beta,\gamma\delta} - S^{(is)}_{\alpha\beta,\gamma\delta} = \frac{1}{V}\sum_{u,v} X^{\beta}_{u}\left(M^{(ad)\alpha\gamma}_{uv} - M^{(is)\alpha\gamma}_{u,v}\right)X^{\delta}_{v} \,. \tag{37}$$

As we mentioned in the Introduction from purely thermodynamic arguments [6,7] it follows that the difference of elastic constants is equal to

$$S^{(ad)}_{\alpha\beta,\gamma\delta} - S^{(is)}_{\alpha\beta,\gamma\delta} = \frac{T}{C_v}\tau_{\alpha\beta}\tau_{\gamma\delta} \,. \tag{I}$$

But from Eqs.(36), (37) and (33), (34) it follows that (37) will be approximately equal to right-hand side of Eq. (I) only if we discard $C^{(is)}$ and $C^{(ad)}$ in all quantities appearing in Eq.(I). This approximation corresponds to the case of bare phonon bubble considering by Wehner and Klein [7] .

We shall show that $S^{(ad)}_{\alpha\beta,\gamma\delta}$ (36) can be obtained from internal energy by differentiation with respect to strain $u_{\alpha\beta}$ at constant numbers of occupation $n(k)$. It is easy to show that

$$\frac{1}{V}\left(\frac{\partial E}{\partial u_{\alpha\beta}}\right)_{n} = \frac{1}{V}\left(\frac{\partial \tilde{U}}{\partial u_{\alpha\beta}}\right)_{n,\langle uu\rangle} = \sigma_{\alpha\beta} \,.$$

Using this equation we obtain the second order derivative of internal energy

$$\left(\frac{\partial^2 E}{\partial u_{\alpha\beta}\partial u_{\gamma\delta}}\right)_{n} = \left(\frac{\partial^2 \tilde{U}}{\partial u_{\alpha\beta}\partial u_{\gamma\delta}}\right)_{n,\langle uu\rangle} + \frac{1}{2}\sum_{\gamma\gamma' \ell\ell'}\left(\frac{\partial\tilde{\phi}^{\gamma\gamma'}_{\ell\ell'}}{\partial u_{\alpha\beta}}\right)_{\langle uu\rangle}\left(\frac{\partial\langle u^{\gamma}_{i}u^{\gamma'}_{i'}\rangle}{\partial u_{\gamma\delta}}\right)_{n} \tag{38}$$

Similarly as in [10,12] the derivative of the correlation function is connected with the derivative of the second order vertex

$$\left(\frac{\partial\langle u^{\gamma}_{i}u^{\gamma'}_{i'}\rangle}{\partial u_{\gamma\delta}}\right)_{n} = 2\sum_{\rho\rho' rr'} L^{(ad)\nu\nu'\rho\rho'}_{nn'rr'}\left(\frac{\partial\tilde{\phi}^{\rho\rho'}_{rr'}}{\partial u_{\gamma\delta}}\right)_{n} \,. \tag{39}$$

This derivative is the solution of an integral equation

$$\left(\frac{\partial\tilde{\phi}^{\rho\rho'}_{rr'}}{\partial u_{\gamma\delta}}\right)_{n} = \sum_{\substack{\mu,\mu'\\ m,m'}}\left[(1-\tilde{C}^{(ad)})^{-1}\right]^{\rho\rho'\mu\mu'}_{rr'mm'}\left(\frac{\partial\tilde{\phi}^{\mu\mu'}_{mm'}}{\partial u_{\gamma\delta}}\right)_{n,\langle uu\rangle} \,. \tag{40}$$

Inserting (39), (40) into Eq. (38), expanding $\left[(1-\tilde{C}^{(ad)})^{-1}\right]$ into a series we recover the adiabatic elastic constants (36)

$$S^{(ad)}_{\alpha\beta,\gamma\delta} = \frac{1}{V}\left(\frac{\partial^2 E}{\partial u_{\gamma\delta}\partial u_{\alpha\beta}}\right)_{n} \,. \tag{41}$$

The constancy of numbers of occupation is equivalent to constancy of entropy S.

But the entropy will not change even if the numbers of occupation varies. Equation (41) means that in obtaining the collisionless limit of mass operator $\Pi_{Q}(\omega)$ we completly missed all dissipative processes connected with changes of n_k's . These processes are contained in collision integral of Boltzmann equation (see for example [7] and references given therein).

4. Conclusions.

In our work we show that approximated mass operator $\Pi_{Q}(\omega)$ with all two-phonon processes accounted is not sufficient to reproduce the correct thermodynamic result for the difference of elastic constants. This approximation gives only non-dissipative terms connected with the interactions of the phonons. As it was shown by Wehner and Klein [7] it is necessary to consider dissipative terms to obtain the difference $S^{(ad)}_{\alpha\beta\gamma\delta} - S^{(is)}_{\alpha\beta\gamma\delta}$ in agreement with classical thermodynamics. The dissipative terms are connected with three-phonon processes and have form of a collision integral in Boltzmann-like equation for three-phonon vertex [7] . Thus although four-phonon processes are important in obtaining correct numerical results for elastic constants [12] , they are insufficient to describe the transport processes in crystals (see also [8]).

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