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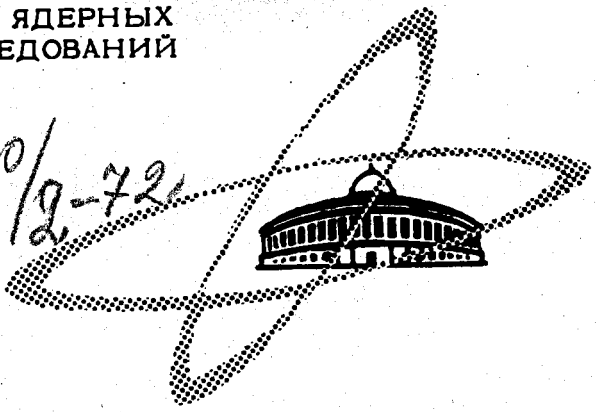

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SELF-CONSISTENT THEORY OF SECOND ORDER ELASTIC CONSTANTS FOR NONIONIC ANHARMONIC CRYSTALS

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Introduction.

Calculation of elastic constants can be made by two methods: the methods of homogeneous deformation [1] and the method of long waves [2]. Using these methods elastic constants for dielectric crystals were caloulated in the harmonic approximation and the results obtained from both methods were consistent [1].

Götze [3] and Götze and Michel [4] extended both these methods and calculated elastio oonstants for arbitrary dielectrio crystal lattices by taking into account the entire anharmonicity of the crystal.

Although results of [3] and [4] are exact of importance is the application of an approximate method which enables us to make numerical computations for strong anharmonic crystals saving at the same time the main exact relations such as elastic sum rules [3], [4]. For quantum crystals or strongly anharmonic crystals of rare gases the role of such an approximate method plays the method of average phonon fields (pseudoharmonic approximation) [5].

For primitive lattices of rare gases Klein et al. [6] calculated self-consistent isothermal elastic constants by expansion of the pseudoharmonic free energy of the crystal into a power series in deformation

parameters $u_{\alpha\beta}$ and made also some numeriolal computations.

In the present paper results of Klein et al. [6] are extended to the nonprimitive nonionic crystal lattices. Derivation of elastio constants [6] is modified in such a way that it is possible to compare the obtained results with those from the method of long waves. This comparison shows that for the results to be consistent it is necessary to take into accoount the vertex corrections [5,7] . The obtained relation between the seoond derivative of a free energy and the mass operator of the displaoement Green funotion makes it possible to eliminate the surfaoe effeots and therefore, to extend the method of a homogeneous deformation to a pseudoharmonio approximation. Comparison of the result of both methods leads to an exaot relation - the sum rule whioh is a partioular case of the general elastio sum rule [3,4,8,9] .

The most convenient method for our purposes is that of two-time Green funotion [7,1o,11] . This method enables us to calculate from the same point of view both the free energy and self-energy of displacement Green function.

In Sect.2. we shall give definitions and some results of [7,1o,11] necessary for our purposes. Section 3 will be devoted to the method of a homogeneous deformation and to the study of a symmetry properties of elastio constants. In Seot.4 the method of long waves will be used and

the comparison will be made between the results obtained from both methods.

1. Notation and Definitions.

We shall consider quantum crystals or crystals of rare gases at sufficiently high temperatures, where the harmonic approximation does not work. Sizable fluctuation of the nuclei around their lattice sites are allowed for by assuming their equilibrium positions rather than nuclei themselves to be arranged in a regular array. Thus at given temperature T $(\text{or } \Theta = k_\beta T)$, we identify the equilibrium value of position operator $\vec{R}(\ell, \varkappa) \equiv \vec{R}_L$ with the lattice site $\vec{X}_\ell + \vec{X}_\varkappa \equiv \vec{X}_L$ of $\varkappa$-th nucleus in the ℓ-th unit cell. That is

$$\vec{X}_L = \vec{X}_\ell + \vec{X}_\varkappa = Tr\left\{\vec{R}_L \frac{e^{-\frac{H}{\Theta}}}{Tr\, exp\left[-\frac{H}{\Theta}\right]}\right\} \equiv \langle \vec{R}_L \rangle, \qquad (1.1)$$

where the index L denotes the pair of indices $L \equiv (\ell, \varkappa)$ and $\varkappa = 1, \dots, s$; $\ell = 1, \dots, N$. We calculate the average value (1.1) with Hamiltonian of equilibrium crystal in the presence of external surface forces $\vec{F}_L$

$$H = \sum_L \frac{P_L^2}{2M_\varkappa} + U(\dots \vec{R}_L \dots) - \sum_L \vec{F}_L \vec{u}_L \qquad (1.2)$$

$$\vec{F}_L = 0 \qquad \text{for all the } L \text{ in the interior of the crystal.} \qquad (1.3)$$

Expanding the potential energy of the crystal $U(\dots \vec{R}_L \dots)$ into a series in the thermal displacements $\vec{u}_L = \vec{R}_L - \vec{X}_L$ leads the Hamiltonian (1.2) to the form [11]

$$H(\lambda) = H_0 + H_1(\lambda), \qquad (1.4)$$

where

$$H_0 = \sum_L \frac{P_L^2}{2M_\varkappa} + \frac{1}{2}\sum_{1,2} \Phi^0_{12} u_1 u_2 - \sum_1 F_1 u_1, \qquad (1.4a)$$

$$H_1(\lambda) = \sum_{n=1}^{\infty} \frac{\lambda^n}{n!} \sum_{1\ldots n} \Phi_{1\ldots n} u_1 \ldots u_n - \frac{\lambda^2}{2} \sum_{1,2} \Phi^0_{12} u_1 u_2, \qquad (1.4b)$$

where $1 \equiv (\alpha, \varkappa, \ell)$; $\alpha = x, y, z$; H_0 is a trial harmonic Hamiltonian, and its matrix of force constants $\Phi^{0\,\alpha\beta}_{\ell\ell'}$ will be defined further. The trial phonon frequencies ω_{kj} and vectors of polarization $e_\alpha(k, j; \varkappa)$ are determined from the eigenvalue equation

$$\omega^2_{kj} e_\alpha(\vec{k}j;\varkappa) = \sum_{\beta,\varkappa'} e_\beta(\vec{k}j;\varkappa) \frac{1}{\sqrt{M_\varkappa M_{\varkappa'}}} \sum_{\ell'} \Phi^{0\,\alpha\beta}_{\ell\ell'} e^{-i\vec{k}(\vec{X}_\ell - \vec{X}_{\ell'})} \qquad (1.5)$$

where $\vec{k}$ is the quasimomentum vector, j – the index of branch and polarization $j = 1, \ldots, 3s$. The Hamiltonian contains all vertices of anharmonic interaction

$$\Phi_{1\ldots n} = \Phi^{\alpha_1 \ldots \alpha_n}_{L_1 \ldots L_n} = \nabla^{\alpha_1}_{L_1} \ldots \nabla^{\alpha_n}_{L_n} U_0(\ldots \vec{X}_L \ldots). \qquad (1.6)$$

As we need for our purposes the free energy in the lowest approximation we choose the matrix of force constants Φ^0_{12} in pseudoharmonic approximation

$$\Phi^{0\alpha\beta}_{ss'} = \nabla^{\alpha}_{s}\nabla^{\beta}_{s'}\widetilde{U}(\dots\vec{X}_{L}\dots) = \nabla^{\alpha}_{s}\nabla^{\beta}_{s'}\exp\left\{\frac{1}{2}\sum_{1,2}\langle u_1u_2\rangle\nabla_1\nabla_2\right\}U_0 , \quad (1.7)$$

where $U_0(\dots\vec{X}_{L}\dots)$ is the potential energy of a static lattice.

With this trial Hamiltonian we obtain with the help of one of the methods - Chequards's methods [12], variational method [5] or method of two-time Green funotions [11], the free energy in pseudoharmonio approximation.

$$F = U_0 + \sum_{kj}\ln\left(2\sh\frac{\omega_{kj}}{2\Theta}\right) + \left\{\exp\left[\frac{1}{2}\sum_{1,2}\langle u_1u_2\rangle\nabla_1\nabla_2\right]-1\right\}U_0 - \frac{1}{2}\sum_{1,2}\widetilde{\Phi}_{12}\langle u_1u_2\rangle_0 \quad (1.8)$$

Index 0 in $\langle u_1u_2\rangle$ denotes that we calculate the oorrelation function with Hamiltonian H_0. Let us consider the retarded Green funotions of displaoements $G^{(r)}_{ii'}(t-t')$

$$G^{(r)}_{ii'}(t-t') \equiv \ll u_i(t);\, u_{i'}(t')\gg = -i\Theta(t-t')\langle[u_i(t),u_{i'}(t')]\rangle = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}\ll u_i,u_{i'}\gg_{\omega}, \quad (1.9)$$

where $\langle\dots\rangle = \mathrm{Tr}\left(\dots\frac{e^{-H/\Theta}}{\mathrm{Tr}\left[\exp(-H/\Theta)\right]}\right)$, $u_i(t) = e^{iHt}u_i e^{-iHt}$.

We shall calculate this funotion in higher approximation. We put in Hamiltonian (1.4) $\lambda = 1$. In the equation of motion for $\ll u_i(t);\, u_{i'}(t')\gg$ there appear higher order Green funotions $\ll u_1(t)\dots u_n(t);\, u_{i'}(t')\gg$. Making the decoupling of this higher order Green funotions as proposed in [10] and keeping in the right-hand side of the equation of motion the first term only we obtain

$$\sum_j \left(M_i\omega^2\delta_{ij} - \tilde{\Phi}_{ij}\right)\langle\langle u_j; u_{i'}\rangle\rangle_\omega = \delta_{ii'} + \frac{1}{2}\sum_{1,2}\tilde{\Phi}_{i12}\langle\langle u_1u_2; u_{i'}\rangle\rangle_\omega \qquad (1.10)$$

The funotion $\langle\langle u_1u_2; u_{i'}\rangle\rangle$ is connected with $\langle\langle u_1P_2; u_{i'}\rangle\rangle$, $\langle\langle P_1\mu_2; u_{i'}\rangle\rangle$

$$\omega\langle\langle u_1u_2; u_{i'}\rangle\rangle_\omega = \frac{i}{M_1}\langle\langle P_1u_2; u_{i'}\rangle\rangle_\omega + \frac{i}{M_2}\langle\langle u_1P_2; u_{i'}\rangle\rangle_\omega . \qquad (1.11)$$

In order to calculate the Green function $\langle\langle u_1u_2; u_i\rangle\rangle_\omega$ we must consider the equation of motion for this two funotions

$$\omega\langle\langle P_1u_2, u_{i'}\rangle\rangle_\omega = \frac{i}{M_2}\langle\langle P_1P_2; u_{i'}\rangle\rangle_\omega - \frac{i}{2}\sum_{1',2',3'}\langle u_2u_{3'}\rangle_0\langle\langle u_{1'}u_{2'}; u_{i'}\rangle\rangle_\omega + \qquad (1.12)$$

$$- i\sum_{2',3'}\tilde{\Phi}_{12'3'}\langle u_2u_{2'}\rangle_0\langle\langle u_{1'}; u_{i'}\rangle\rangle_\omega - i\sum_{1'}\tilde{\Phi}_{11'}\langle\langle u_{1'}u_{2'}; u_{i'}\rangle\rangle_\omega .$$

where we keep only the first three terms of the sum in the right-hand side of (1.12)+, and use the condition of crystal equilibrium in pseudoharmonic approximation

$$\nabla_1\tilde{U}(\ldots\chi_L\ldots) = \tilde{\Phi}_1 = F_1 . \qquad (1.13)$$

This condition is easily obtained from the average of the equation of motion for momentum operator $\vec{P}_L(t)$.

+This method of claculation of Green funotion was proposed by N.M.Plakida

In derivation of (1.1o) and (1.12) we calculate all correlation funotions, with Hamiltonian H_0 .

$\widetilde{\Phi}_{1\ldots n}$ is the renormalized vertex

$$\widetilde{\Phi}_{1\ldots n} = \nabla_1 \ldots \nabla_n \widetilde{U}(\ldots \vec{x}_L \ldots) .$$

Equation for $\langle\langle u_1 P_2 ; u_i \rangle\rangle_\omega^{(r)}$ oan be obtained from (1.12) by ohanging the indioes $1 \rightleftarrows 2$.

Using periodio boundary oonditions we go to the expansion of $\vec{u}_L$ and $\vec{P}_L$ in plane waves. The polarization veotors $\vec{e}(kj,\varkappa)$ form an orthonormal and oomplete set and we ohoose $\vec{e}_\alpha(kj;\varkappa) = \vec{e}^{\,*}(-kj;\varkappa)$. Differentiating Eqs. for $\langle\langle u_1(t) P_2(t); u_{i'}(t') \rangle\rangle^{(r)}$ and $\langle\langle P_1(t) u_2(t); u_{i'}(t') \rangle\rangle^{(r)}$ once more with respeot to t and expanding u_L, P_L in the plane waves we obtain a system of equations whioh allows us to find $\langle\langle A_{K_1} A_{K_2} ; A_Q \rangle\rangle_\omega$, where $A_Q = A_{-Q}^+ = a_Q + a_{-Q}^+$, $Q=(\vec{q},j)$, $-Q=(-\vec{q},j)$. Putting this expression into equation for $\langle\langle A_{qj}, A_{q'j'}^+ \rangle\rangle_\omega^{(r)}$ whioh oan be obtained from (1.1o) negleoting a polarization mixing $(j = j')$ we obtain

$$\langle\langle A_Q, A_Q^+ \rangle\rangle_\omega = \frac{2\omega_Q}{\omega^2 - (\omega_Q^2 + 2\omega_Q \Pi_Q(\omega))} . \qquad (1.14)$$

The funotion $\langle\langle A_Q, A_Q^+ \rangle\rangle_\omega$ is an analytic continuation of retarded Green funotion into the oomplex plane of ω . The mass operator of Green funotion $\langle\langle A_Q ; A_Q^+ \rangle\rangle_\omega$ $\Pi_Q(\omega)$ is equal to [4,7].

$$\Pi_Q(\omega) = \frac{1}{2}\sum_{K_1K_2K_1'K_2'} \widetilde{V}(-Q,K_1,K_2)\Big[\big(1-C(\omega)\big)^{-1}\Big]_{K_1,K_2;K_1',K_2'} F^{0}(K_1',K_2';\omega)\widetilde{V}_3(Q,-K_1',-K_2'), \quad (1.15)$$

where $\widetilde{V}(K_1,\dots,K_n)$ is the phonon vertex

$$\widetilde{V}(K_1,\dots,K_n) = (2N)^{-\frac{n}{2}} \sum_{\substack{\alpha_1,\dots,\alpha_n \\ L_1,\dots,L_n}} \frac{e_{\alpha_1}(K_1,\varkappa_1)\dots e_{\alpha_n}(K_n,\varkappa_n)}{\big(M_{\varkappa_1}\omega_{K_1}\dots M_{\varkappa_n}\omega_{K_n}\big)^{1/2}} e^{i\vec{K}_1\vec{X}_{L_1}+\dots+i\vec{K}_n\vec{L}_n} \widetilde{\Phi}^{\alpha_1\dots\alpha_n}_{L_1\dots L_n} \quad (1.16)$$

$F^{0}(K_1,K_2;\omega)$ is a phonon bubble

$$F^{0}(K_1,K_2;\omega) = \frac{2(\omega_{K_1}+\omega_{K_2})(n_{K_1}+n_{K_2}+1)}{\omega^2-(\omega_{K_1}+\omega_{K_2})^2} - \frac{2(\omega_{K_1}-\omega_{K_2})(n_{K_1}-n_{K_2})}{\omega^2-(\omega_{K_1}-\omega_{K_2})^2}, \quad (1.17)$$

$$n_{K_1} = n(\omega_{K_1}) = \Big(e^{\frac{\omega_{K_1}}{\Theta}}-1\Big)^{-1},$$

$$\big[C(\omega)\big]_{K_1K_2;K_3K_4} = F^{0}(K_1,K_2;\omega)\widetilde{V}_4(-K_1,-K_2,K_3,K_4).$$

In the calculation of the mass operator we take into acoount all two-phonon processes. As we shall see further this renormalization of three phonon vertices is necessary to obtain a correspondence between results of the method of homogeneous deformation and the method of long waves. The real part of the mass operator $\Pi_Q(\omega+i\varepsilon)$ gives renormalized phonon frequency

$$\widetilde{\omega}_Q^2(\omega) = \omega_Q^2 + 2\omega_Q \operatorname{Re}\Pi_Q(\omega+i\varepsilon), \quad (1.18)$$

and its imaginary part gives the life-time of phonons.

2. Method of the Homogeneous Deformation. Symmetries of Elastic Constants.

We shall discuss the case of finite stresses in the initial equilibrium state, which are produced by forces $\vec{F}_s$ applied to surface atoms. The homogeneous elastic deformation of a crystal is caused by additional applied small surface forces $\vec{f}_s$. In this case both the free energy and potential energy of a crystal depend also on a deformation $u_{\alpha\beta}$ (primitive lattices) and also on relative displacements of sublattices $\vec{u}_\kappa$ (nonprimitive lattices).

To obtain total derivatives (space) we shall assume according to Choquard [12] and Klein et al. [6] the set of correlation functions $\langle u_i u_j \rangle_0$ to be intermediate variables describing fluctuational state of a crystal and then we shall use the chain rule of differentiation. As we are interested in crystals we assume that an influence of external forces leads to a change in coordinates of atoms but the fluctuational state of the system does not change. This means that the derivative $\left(\frac{\partial \tilde{U}}{\partial X_s^\alpha}\right)_T$ in (1.13) denotes the derivative at constant T and $\langle u_s^\gamma u_{s'}^{\gamma'} \rangle_0$

$$\tilde{\Phi}_s^\alpha = \left(\frac{\partial \tilde{U}(\ldots \vec{X}_L \ldots)}{\partial X_s^\alpha}\right)_{T,\langle uu \rangle} = F_s^\alpha \,, \qquad (1.13a)$$

Pseudoharmonic free energy (1.8) is stationary with respect to variation of $\langle u_s^\alpha u_{s'}^{\alpha'} \rangle_0$.

Following Choquard [12] and Klein et al. [6] we obtain the second derivative of free energy with respect to spacelike varibles (i.e. it does not depend on temperature) ε_1, ε_2 in terms of isofluctional derivatives only

$$\left(\frac{\partial^2 F}{\partial\varepsilon_1\partial\varepsilon_2}\right)_T = \left(\frac{\partial^2 \tilde{U}}{\partial\varepsilon_1\partial\varepsilon_2}\right)_{T_i<\omega_i>} + \sum_{\substack{\nu\mu \\ s\,M}}\left(\frac{\partial\tilde{\Phi}^{\nu\mu}_{sS'}}{\partial\varepsilon_1}\right)_{T_i<\omega_i>} L^{\nu\nu\,\rho\rho'}_{ss'LL'}\left[(1-\tilde{C})^{-1}\right]^{\rho'\mu'}_{LL'MM'}\left(\frac{\partial\tilde{\Phi}^{\mu\mu'}_{MM'}}{\partial\varepsilon_2}\right)_{T_i<\omega_i>}, \quad (2.1)$$

where

$$L^{\nu\nu\,\rho\rho'}_{ss'LL'} = \left(\frac{1}{2N}\right)^2\sum_{K}\frac{e_\nu(k,\varkappa)e^*_{\nu'}(k,\varkappa')e_\rho(K\varkappa_1)e_{\rho'}(k,\varkappa_1')}{(M_\varkappa M_{\varkappa'}M_{\varkappa_1}M_{\varkappa_1'})^{1/2}}\,e^{ik(X_s-X_{s'})+ik(X_L-X_{L'})}\frac{F^{is}(k)}{2\omega_K^2}, \quad (2.2)$$

$$(1-\tilde{C}^{is})^{\rho\rho'\mu\mu'}_{RR'MM'} = \left\{\delta_{\rho\mu}\delta_{\rho'\mu'}\delta_{RM}\delta_{R'M'} - \sum_{\substack{\lambda,\lambda' \\ L,L'}}\tilde{\Phi}^{\rho\rho'\lambda\lambda'}_{RR'LL'}L^{\lambda\lambda'\mu\mu'}_{LL'MM'}\right\}, \quad (2.3)$$

$F^{is}(K)$ is hydrodynamic (isothermal) limit of $F^0(K,\omega)$

$$F^{is}(K) = \lim_{|\vec{q}|\to 0}\lim_{\omega\to 0}F^0(k+q,j;-k,j;\omega) = \frac{\partial(2n_k+1)}{\partial\omega_k} - \frac{(1+2n_k)}{\omega_k}. \quad (2.4)$$

The applied procedure of evaluation of derivatives of the free energy is similar to the differentiation of quasiharmonic free energy where ω_{kj} are function of the volume. After differentiation of quasiharmonic free energy with respeot to volume the terms with

three-phonons and four-phonon vertices appear (see for example [1]).

In the theory of elasticity ε's are considered as homogeneous strain parameter $u_{\alpha\beta}$ $\left(\frac{\partial}{\partial u_{\alpha\beta}} = \sum_{\nu} X_{\nu}^{\beta} \frac{\partial}{\partial X_{\nu}^{\alpha}}\right)$ and relative displacement parameter $u_{\varkappa}^{\varkappa}$ $\left(\frac{\partial}{\partial u_{\varkappa}^{\varkappa}} = \sum_{u} \frac{\partial}{\partial X_{u}^{\varkappa}}\right)$. We expand free energy density $\frac{F}{V}$ in the strain parameters $u_{\alpha\beta}$ and relative displacement parameters $u_{\varkappa}^{\varkappa}$

$$\frac{F}{V} = \frac{F_0}{V} + \sum_{\alpha,\beta} S_{\alpha\beta} u_{\alpha\beta} + \frac{1}{2}\sum_{\alpha\beta,\gamma\delta} \hat{S}_{\alpha\beta,\gamma\delta} u_{\alpha\beta} u_{\gamma\delta} - \frac{1}{2}\sum_{\substack{\alpha\beta \\ \varkappa\varkappa'}} \hat{C}^{\alpha\beta}_{\varkappa\varkappa'} u_{\varkappa}^{\varkappa} u_{\varkappa'}^{\beta} - \sum_{\substack{\alpha\gamma\varepsilon \\ \varkappa}} \hat{C}^{\varkappa}_{\alpha,\gamma\delta} u_{\varkappa}^{\alpha} u_{\varkappa}^{\varepsilon} \quad (2.5)$$

The first derivatives of the density of free energy

$$S_{\alpha\beta} = \frac{1}{V}\left(\frac{\partial F}{\partial u_{\alpha\beta}}\right)_T \quad , \quad u_{\alpha\beta} = u_{\varkappa}^{\alpha} = 0 \qquad (2.6)$$

are the stresses in the initial state. The coefficients in terms of second order in (2.5) are defined as

$$\hat{S}_{\alpha\beta,\gamma\delta} \equiv \frac{1}{V}\left(\frac{\partial^2 F}{\partial u_{\alpha\beta}\partial u_{\gamma\delta}}\right)_T = \frac{1}{V}\sum_{\upsilon,\nu} X_{\upsilon}^{\beta}\left\{\tilde{\Phi}^{\alpha\gamma}_{\upsilon\nu} + \tilde{M}^{is\,\alpha\gamma}_{\upsilon\nu}\right\} X_{\nu}^{\delta} \qquad (2.7a)$$

$$\hat{C}^{\alpha\beta}_{\varkappa\varkappa'} = C^{\beta\alpha}_{\varkappa'\varkappa} \equiv -\frac{1}{V}\left(\frac{\partial^2 F}{\partial u_{\varkappa}^{\alpha}\partial u_{\varkappa'}^{\beta}}\right)_T = -\frac{1}{V}\sum_{u,\upsilon}\left\{\tilde{\Phi}^{\alpha\beta}_{\substack{\varkappa\varkappa' \\ u\upsilon}} + \tilde{M}^{is\,\alpha\beta}_{\substack{\varkappa\varkappa' \\ u\upsilon}}\right\}, \qquad (2.7b)$$

$$\hat{C}^{\varkappa}_{\alpha,\gamma\delta} \equiv -\frac{1}{V}\left(\frac{\partial^2 F}{\partial u_{\varkappa}^{\varkappa}\partial u_{\gamma\delta}}\right)_T = -\frac{1}{V}\sum_{u,\nu}\left\{\tilde{\Phi}^{\varkappa\gamma}_{\substack{\varkappa \\ u\nu}} + \tilde{M}^{is\,\varkappa\gamma}_{\substack{\varkappa \\ u\nu}}\right\} X_{\nu}^{\delta}. \qquad (2.7c)$$

$\widetilde{M}^{is\,\alpha\beta}_{uv}$ is equal to

$$\widetilde{M}^{is\,\alpha\gamma}_{uv} = \sum_{\substack{\nu\nu'\beta\beta'\mu\mu' \\ ss'RR'MM'}} \widetilde{\Phi}^{\alpha\nu\nu'}_{uss'} L^{\nu\nu'\beta\beta'}_{ss'RR'} \left[(1-\widetilde{C}^{is})^{-1}\right]^{\beta\beta'\mu\mu'}_{RR'MM'} \widetilde{\Phi}^{\gamma\mu\mu'}_{vMM'} . \qquad (2.8)$$

Matrices $\hat{S}_{\alpha\beta,\gamma\delta}$, $\hat{C}^{\alpha\beta}_{\varkappa\varkappa'}$, $\hat{C}^{\varkappa}_{\alpha,\gamma\delta}$ are generalizations of harmonic matrices of Leibfried and Ludwig [1]. In Sect.3 we shall show that $M^{is\,\alpha\beta}_{uv}$ is a function of $\vec{X}_u - \vec{X}_v$. This allows us to eliminate surface effects as it was done by Leibfried and Ludwig [1]. In such an elimination we use the condition of translation invariance of the potential energy (see Ludwig [1])

$$\sum_s \widetilde{\Phi}^{\alpha\beta\ldots}_{sR\ldots} = 0 . \qquad (2.9a)$$

In the third term of (2.5) elimination of surface effects is not possible, but in physically interesting formulas occur only combination $\frac{1}{2}(S_{\alpha\beta,\gamma\delta} + S_{\alpha\delta,\gamma\beta})$ which permits such an elimination.

The free energy density still depends on relative displacements $u^{\alpha}_{\varkappa}$. This can be eliminated by using the equilibrium condition after the small forces $\vec{f}_s$ have been applied

$$F^{\alpha}_s + f^{\alpha}_s = \left(\frac{\partial \widetilde{U}(\ldots \vec{X}_L \ldots)}{\partial X^{\alpha}_s}\right)_{T,\langle uu\rangle} . \qquad (2.10)$$

Expanding $\widetilde{U}(\ldots \vec{X}_L \ldots)$ in $u_{\alpha\beta}$ and $u^{\alpha}_{\varkappa}$ and taking into account the equilibrium condition (1.13a) we obtain the

equation which gives the relation between these two parameters

$$\sum_{\beta,\varkappa'} \hat{C}^{\alpha\beta}_{\varkappa\varkappa'} u^{\beta}_{\varkappa'} = -\sum_{\gamma,\varepsilon} \hat{C}^{\varkappa}_{\alpha,\gamma\varepsilon} u_{\gamma\varepsilon} \,. \tag{2.11}$$

Here we have neglected f^{α}_{s} as it is sufficient to solve (2.11) in the interior of the crystal. Matrices $\hat{C}^{\alpha\beta}_{\varkappa\varkappa'}$ $\hat{C}^{\varkappa}_{\alpha,\gamma\varepsilon}$ have the same properties as harmonic ones defined by Liebfried and Ludwig [1] . Equation (2.11) differs from equation of Leibfried and Ludwig by definition of $C^{\alpha\beta}_{\varkappa\varkappa'}$, $C^{\varkappa}_{\alpha,\gamma\varepsilon}$ only, so we give here only final results

$$u^{\alpha}_{\varkappa} = -\sum_{\mu\rho\lambda\varkappa_1} R^{\alpha\mu}_{\varkappa\varkappa_1} \hat{C}^{\varkappa_1}_{\mu,\rho\lambda} u_{\rho\lambda} \,, \tag{2.12}$$

where the R is symmetric (in indices $\alpha\varkappa$ and $\mu\varkappa_1$) right-hand side reciprocal to $\hat{C}$ matrix

$$\sum_{\beta,\varkappa_1} \hat{C}^{\alpha\beta}_{\varkappa\varkappa_1} R^{\beta\delta}_{\varkappa_1\varkappa'} = \delta_{\alpha\delta}\,\delta_{\varkappa,\varkappa'} \,.$$

Now we insert (2.12) into the righ-hand side of (2.5) and finally we obtain

$$\frac{F}{V} = \frac{F_0}{V} + \sum_{\alpha\beta} S_{\alpha\beta} u_{\alpha\beta} + \frac{1}{2}\sum_{\alpha\beta\gamma\varepsilon} S_{\alpha\beta,\gamma\varepsilon} u_{\alpha\beta} u_{\gamma\varepsilon} \,, \tag{2.13}$$

where $S_{\alpha\beta,\gamma\delta}$ is the second order elastic constant equal to

$$S_{\alpha\beta,\gamma\varepsilon} = \left\{ \hat{S}_{\alpha\beta,\gamma\varepsilon} + \sum_{\substack{\varkappa,\varkappa_1\\ \lambda,\rho}} \hat{C}^{\varkappa}_{\lambda,\alpha\beta} R^{\lambda\rho}_{\varkappa\varkappa_1} \hat{C}^{\varkappa_1}_{\rho,\gamma\varepsilon} \right\}. \tag{2.14}$$

Let us consider the symmetry properties of $S_{\alpha\beta,\gamma\varepsilon}$.
As the matrix R is symmetric $S_{\alpha\beta,\gamma\delta}$ is symmetric too in the pair oi indioes

$$S_{\alpha\beta,\gamma\delta} = S_{\gamma\delta,\alpha\beta} . \tag{2.15a}$$

We derive symmetry properties of $S_{\alpha\beta,\gamma\varepsilon}$ connected with changes of $\alpha \leftrightarrow \beta$, $\gamma \leftrightarrow \delta$ with the help of the conditions of rotational invariance of the potential energy [1]

$$\sum_{U} \tilde{\Phi}^{\alpha}_{U} \chi^{\beta}_{U} = \sum_{U} \tilde{\Phi}^{\beta}_{U} \chi^{\alpha}_{U} , \tag{2.16a}$$

$$\sum_{M} \tilde{\Phi}^{\alpha\lambda}_{MN} \chi^{\beta}_{M} + \tilde{\Phi}^{\alpha}_{N} \delta_{\beta\lambda} = \sum_{M} \tilde{\Phi}^{\beta\lambda}_{MN} \chi^{\alpha}_{M} + \tilde{\Phi}^{\beta}_{N} \delta_{\alpha\lambda} , \tag{2.16b}$$

$$\sum_{U} \tilde{\Phi}^{\gamma\delta\alpha}_{SS'U} \chi^{\beta}_{U} + \tilde{\Phi}^{\alpha\delta}_{SS'} \delta_{\gamma\beta} + \tilde{\Phi}^{\alpha\gamma}_{SS'} \delta_{\beta\varepsilon} = \sum_{U} \tilde{\Phi}^{\gamma\delta\beta}_{SS'U} \chi^{\alpha}_{U} + \tilde{\Phi}^{\beta\delta}_{SS'} \delta_{\gamma} + \tilde{\Phi}^{\delta\varepsilon}_{SS'} \delta_{\delta\alpha} . \tag{2.16c}$$

Following Liebfried and Ludwig it is possible to show that a part of $S_{\alpha\beta,\gamma\varepsilon}$

$$\hat{S}^{(1)}_{\alpha\beta,\gamma\delta} \equiv \frac{1}{V} \sum_{U,V} \chi^{\beta}_{U} \tilde{\Phi}^{\alpha\rho}_{UV} \chi^{\delta}_{V}$$

has the symmetry properties of Born and Huang

$$\hat{S}^{(1)}_{\alpha\beta,\gamma\delta} + S_{\alpha\beta} \delta_{\delta\delta} = \hat{S}^{(1)}_{\alpha\beta,\delta\gamma} + S_{\beta\delta} \delta_{\alpha\gamma} , \tag{2.17a}$$

$$\hat{S}^{(1)}_{\alpha\beta,\gamma\varepsilon} + S_{\alpha\varepsilon}\delta_{\beta\delta} = \hat{S}^{(1)}_{\beta\alpha,\gamma\varepsilon} + S_{\beta\varepsilon}\delta_{\alpha\gamma}, \tag{2.17b}$$

$$\hat{S}^{(1)}_{\alpha\beta,\gamma\varepsilon} + S_{\gamma\varepsilon}\delta_{\alpha\beta} = \hat{S}^{(1)}_{\beta\alpha,\delta\gamma} + S_{\beta\varepsilon}\delta_{\alpha\gamma}. \tag{2.17c}$$

It can be seen from invariance condition (2.16a) that the stresses are symmetric

$$S_{\alpha\beta} = S_{\beta\alpha}. \tag{2.15b}$$

The full elastic constants $S_{\alpha\beta,\gamma\varepsilon}$ have to fulfil the Born-Huang symmetry relations (2.17). Neglecting a surface term from the invariance condition (2.16b) and stability condition (1.19a) we obtain for the interior of the crystal

$$\hat{C}^{\kappa}_{\alpha,\gamma\delta} = \hat{C}^{\kappa}_{\alpha,\delta\gamma}.$$

This means that the second part of $S_{\alpha\beta,\gamma\delta}$ does not change under $\alpha \leftrightarrow \beta$, $\gamma \leftrightarrow \delta$. Let us consider the last term of $S_{\alpha\beta,\gamma\varepsilon}$ -the second part of $\hat{S}_{\alpha\beta,\gamma\delta}$ connected with M^{is}. As it can be seen from (2.16c) after change $\alpha \leftrightarrow \beta$, $\gamma \leftrightarrow \delta$ four additional terms appear of a type $\tilde{\Phi}^{\alpha\delta}_{ss'} S_{\beta\gamma}$. But these additional terms canoel each other. This can be proved with the definition of frequencies ω_{α} (1.5) and the definition of $M^{is}_{uv}{}^{\alpha\beta}$. We have proved that $S_{\alpha\beta,\gamma\varepsilon}$ has a symmetry properties of Born and Huang (2.17).

In classical theory of elasticity the appropriate quantity to describe true strains is the tensor of finite strain $\eta_{\alpha\beta}$

$$\eta_{\alpha\beta} = \frac{1}{2}\left(u_{\alpha\beta} + u_{\beta\alpha} + \sum_{\gamma} u_{\gamma\alpha} u_{\gamma\beta}\right).$$

The coefficient of the second order term in expansion of the free energy in $\eta_{\alpha\beta}$ has the complete Voigt symmetry properties

$$C_{\alpha\beta,\gamma\delta} = C_{\beta\alpha,\gamma\delta} = C_{\alpha\beta,\delta\gamma} = C_{\beta\alpha,\delta\gamma}. \qquad (2.18)$$

$C_{\alpha\beta,\gamma\delta}$ is connected with $S_{\alpha\beta,\gamma\delta}$

$$C_{\alpha\beta,\gamma\delta} = S_{\alpha\beta,\gamma\delta} - S_{\beta\delta}\,\delta_{\alpha\gamma}. \qquad (2.19)$$

Relation (2.18), (2.19) are equivalent to Born-Huang relations for $S_{\alpha\beta,\gamma\delta}$.

The symmetrized quantity

$$\overline{S}_{\alpha\gamma,\beta\delta} = \frac{1}{2}\left(S_{\alpha\beta,\gamma\delta} + S_{\alpha\delta,\beta\gamma}\right)$$

appears in the equation of motion for displacement of phenomenological theory of elasticity (see for example [13]). The solution of this equation is a plane wave

$$u_{\alpha}(\vec{X},t) = u_{\eta}^{\alpha} e^{i\omega t - i\vec{q}\vec{X}}, \qquad \sum_{\alpha} u_{\eta}^{\alpha} u_{\eta'}^{\alpha} = \delta_{\eta,\eta'},$$

where η is a polarization index of an acoustic wave. With these displacements the equation of motion becomes

$$\omega_{q\eta}^{2} = \frac{V}{M_c N} \sum_{\alpha\beta\gamma\delta} u_{\eta}^{\alpha} q_{\beta}\, \overline{S}_{\alpha\gamma,\beta\delta}\, u_{\eta}^{\gamma} q_{\delta}, \qquad (2.20)$$

where M_c is the mass of unit cell $M_c = \sum_{\varkappa=1}^{s} M_{\varkappa}$.

We shall compare this expression with hydrodynamic limit of $\widetilde{\omega}_Q^2(\omega)$. Following Leibfried and Ludwig [1] it is possible to find $S_{\alpha\beta,\gamma\delta}$ in terms of measured quantity $\overline{S}_{\alpha\gamma,\beta\delta}$ and $S_{\alpha\beta}$, or lattice theoretical expressions: $S_{\alpha\beta}$, second term in the right hand side of (2.14) and symmetric part of $S_{\alpha\beta,\gamma\delta}$.

3. The Method of Long Waves.

Let us consider the hydrodynamic limit of $\widetilde{\omega}_Q^2(\omega)$

$$\lim_{|q|\to 0}\left\{\lim_{\omega\to 0}\widetilde{\omega}_Q^2(\omega)\right\}.$$

From (1.15) it can be seen that when $|\vec{q}|\to 0$, $\vec{k}_1\to -\vec{k}_2$, $\vec{k}_1'\to -\vec{k}_2'$. Let us write the mass operator in a more convenient form

$$\Pi_Q(\omega)=\frac{1}{2N}\sum_{U,V}M_{UV}^{\alpha\gamma}(\vec{q},\omega)\,e^{i\vec{q}(\vec{X}_U-\vec{X}_V)}\,\frac{e_\alpha^*(Q,\varkappa)\,e_\beta(Q,\varkappa')}{\omega_Q(M_\varkappa M_{\varkappa'})^{1/2}}\,, \tag{3.1}$$

where

$$M_{UV}^{\alpha\gamma}(\vec{q},\omega)=\frac{1}{4}\left(\frac{1}{2N}\right)^2\sum_{\substack{\nu\nu'\mu\mu'\\ ss'MM'}}\sum_{\substack{\vec{k}_1\vec{k}_2\vec{k}_1'\vec{k}_2'\\ j_1j_2j_1'j_2'}}\widetilde{\Phi}_{USS'}^{\alpha\nu\nu'}\,\widetilde{\Phi}_{VMM'}^{\gamma\mu\mu'}\,e^{i(\vec{k}_1+\vec{q})\vec{X}_S-i\vec{k}_1\vec{X}_{S'}}\times$$

$$\times\,e^{i(\vec{k}_2+\vec{q})\vec{X}_M-i\vec{k}_2\vec{X}_{M'}}\,\frac{e_\nu(\vec{k}_1+\vec{q},j_1,\varkappa_1)\,e_{\nu'}^*(k_1,j_1',\varkappa_1')\,e_\mu(\vec{k}_2+\vec{q},j_2,\varkappa_2)\,e_{\mu'}^*(\vec{k}_2,j_2',\varkappa_2')}{\left(\omega_{k_1+q,j_1}\,\omega_{k_1j_1'}\,\omega_{k_2+q,j_2}\,\omega_{k_2j_2'}\right)^{1/2}\left(M_{\varkappa_1}M_{\varkappa_1'}M_{\varkappa_2}M_{\varkappa_2'}\right)^{1/2}}\times \tag{3.2}$$

$$\times\,2F^{\circ}(k_1+q,j_2;-k_2j_2';\omega)\left[(1-C(\omega))^{-1}\right]_{k_1+q\,j_1,-k_1j_1';\;k_2+q,j_2,-k_2,j_2'}.$$

We are interested in the behavior of Eq. (3.2) for small ω and $|\vec{q}|$. For all but one type of contributions to this equation $M^{\alpha\gamma}_{UV}(q,\omega)$ is continuous. The exception are those terms in Eq. (3.2) for which $j_1 = j_1'$, $j_2 = j_2'$ $F^0(k+q, j_1; -k, j_2; \omega)$ behaves singularly for small ω and $|\vec{q}|$, the hydrodynamic limit is different from the collisionless one

$$\lim_{|q|\to} \left\{ \lim_{\omega\to 0} F^0(k+q, j_1; -k, j_2; \omega) \right\} \neq \lim_{\omega\to 0} \left\{ \lim_{|q|\to 0} F^0(k+q, j_1; -kj_2; \omega) \right\}.$$

The singular behavior of $C(\omega)$ is due to the coupling with F^0. To obtain a connection with the theory of elasticity we consider only the part irregular in the limit of small ω and $|\vec{q}|$ of the real part of the mass operator $\mathrm{Re}\,\Pi_Q(\omega)$, i.e. we put $j_1 = j_1'$, $j_2 \neq j_2'$. It will be seen from further considerations that in the hydrodynamic limit and when we limit ourselves to terms of the order $|\vec{q}|^2$ we may neglect the dependence of irregular part of $M^{\alpha\gamma}_{UV}(q,\omega)$ on $|\vec{q}|$. Then we denote

$$M^{is\,\alpha\gamma}_{UV} = \left(\frac{1}{2N}\right)^2 \sum_{\substack{ss'MM' \\ \nu\nu'\mu\mu'}} \tilde{\Phi}^{\alpha\nu\nu'}_{Uss'} \tilde{\Phi}^{\gamma\mu\mu'}_{VMM'} \frac{e_\nu(K,\varkappa_1)\, e^*_{\nu'}(K,\varkappa_1')\, e_\mu(K',\varkappa_2)\, e^*_{\mu'}(K',\varkappa_2')}{\omega_K \omega_{K'} (M_{\varkappa_1} M_{\varkappa_2} M_{\varkappa_1'} M_{\varkappa_2'})^{1/2}}$$

$$e^{ik(X_s - X_{s'}) + ik'(X_M - X_{M'})} \left[(1 - C^{is})^{-1}\right]_{K,-K;K',-K'} \frac{F(K')}{2}, \qquad (3.3)$$

where C^{is} is the hydrodynamic limit of $[C(\omega)]_{k+q,j;-kj;k'+q,j';-k'j'}$ and it is equal to

$$C^{is}_{K_1,-K_1;K_2,-K_2} = \tilde{V}(-K_1, K_1; -K_2, K_2)\, \frac{1}{2} F(K_1),$$

Expanding in $\widetilde{M}^{\alpha\gamma}_{uv}\ (1-\widetilde{C})^{-1}$ in the series and using the definition of $\widetilde{V}_4$ (1.16) we prove that

$$\widetilde{M}^{is\,\alpha\gamma}_{uv} = M^{is\,\alpha\gamma}_{uv} .$$

From (3.1) it follows that $M^{is\,\alpha\gamma}_{uv}$ depends on the difference of coordinates $\vec{X}_u - \vec{X}_v$. This enables us to exclude surface effects from the combination $\overline{S}_{\alpha\gamma,\beta\delta}$.

The translated invariance condition (2.9a) leads to

$$\sum_u M^{\alpha\gamma}_{uv} = \sum_v M^{\alpha\delta}_{uv} = 0 . \qquad (2.9b)$$

Let us consider the long-wave limit of $\widetilde{\omega}^2_Q(0)$.
In this limit we put [2] ($|\vec{q}| \to \varepsilon|\vec{q}|$, ε is a formal parameter of expansion)

$$e_\beta(Q,\varkappa') = e^{(0)}_\beta(j,\varkappa') + i\varepsilon e^{(1)}_\beta(Q,\varkappa') + \tfrac{1}{2}\varepsilon^2 e^{(2)}_\beta(Q,\varkappa') + \ldots \qquad (3.4a)$$

and for $\widetilde{\omega}^2_Q(0) \equiv \widetilde{\omega}^2_Q$

$$\widetilde{\omega}^2_Q = \varepsilon^2 \left(\omega^{(1)}(Q)\right)^2 . \qquad (3.4b)$$

Putting (3.4a,b) into equation

$$\widetilde{\omega}^2_Q e^*_\alpha(Q,\varkappa) = \frac{1}{N}\sum_{u,v,\gamma} \frac{e_\gamma(Q,\varkappa')}{(M_\varkappa M_{\varkappa'})^{1/2}} e^{-i\vec{Q}(\vec{X}_u - \vec{X}_v)} \left\{\widetilde{\Phi}^{\alpha\gamma}_{uv} + M^{is\,\alpha\gamma}_{uv}\right\}, \qquad (3.5)$$

which can be obtained from the definition of renormalized frequencies $\widetilde{\omega}_Q(\omega)$ (1.18), equating to zero coefficients of terms of different order in ε we obtain the system of equations of the theory of perturbations. From conditions (29a,b) it follows that the equation of zero-order in ε

$$\sum_{\nu} (M_\varkappa M_{\varkappa'})^{-1/2} \left(\widetilde{\Phi}^{\alpha\gamma}_{\varkappa\nu} + M^{is}\, {}^{\alpha\gamma}_{\varkappa\nu} \right) e^{0}_{\gamma}(j,\varkappa') = 0 \qquad (3.6)$$

has a solution [2]

$$e^{(0)}_{\beta}(j,\varkappa') = \left(\frac{M_{\varkappa'}}{M_c}\right)^{\frac{1}{2}} u^{\beta}_{j}\, \delta_{j\eta} \qquad \eta = 1,2,3. \qquad (3.7)$$

where we introduce three polarization vectors describing in long waves limit accoustic oscillations

$$u^{\alpha}_{\eta} = \lim_{|\vec{q}|\to 0} \frac{e_{\alpha}(\vec{q}, j=\eta, \varkappa)}{(M_\varkappa)^{1/2}} (M_c)^{1/2} \qquad (3.8)$$

These vectors do not depend on $\varkappa$. From the condition of completeness of the set of vectors $e_\alpha(\vec{q},j,\varkappa)$

$$\sum_{\alpha=1}^{3} \sum_{\varkappa=1}^{S} e^{*}_{\alpha}(\vec{q},j,\varkappa)\, e_{\alpha}(\vec{q},j',\varkappa) = \delta_{jj'}$$

it follows that the set of vectors u_η $(\eta = 1,2,3)$ is the orthonormal one

$$\sum_{\alpha=1}^{3} u^{\alpha}_{\eta}\, u^{\alpha}_{\eta'} = \delta_{\eta\eta'}. \qquad (3.9)$$

The vectors u_η can be found from the equation of the second order, in ε. $e^{(1)}_\beta(Q,\varkappa')$ can be evaluated from the equation of the first order in ε

$$\sum_{\gamma,\varkappa'} \hat{C}^{\alpha\gamma}_{\varkappa\varkappa'} (M_\varkappa M_{\varkappa'})^{-\frac{1}{2}} e^{(1)}_\gamma(\vec{q},\eta,\varkappa') = -(M_c)^{-\frac{1}{2}} \sum_{\beta\gamma} \hat{C}^{\varkappa}_{\alpha,\beta\gamma} u^\beta_\eta q_\gamma . \quad (3.10)$$

This equation is identical to (2.11) and its solution is known as

$$e^{(1)}_\gamma(q,\eta,\varkappa') = -\left(\frac{M_{\varkappa'}}{M_c}\right)^{\frac{1}{2}} \sum_{\mu\lambda\varsigma\varkappa_1} R^{\gamma\mu}_{\varkappa'\varkappa_1} \hat{C}^{\varkappa_1}_{\mu,\lambda\varsigma} u^\varsigma_\eta q_\lambda \quad (3.11)$$

Let us consider the equation of the second order in ε

$$(\omega^{(1)}(\vec{q},\eta))^2 e^{(0)}_\alpha(\eta,\varkappa) = -\frac{1}{2N} \sum_{\gamma\beta\delta u,v} \frac{e^{(0)}_\beta(\eta,\varkappa')}{(M_\varkappa M_{\varkappa'})^{1/2}} \left\{ \tilde{\Phi}^{\alpha\gamma}_{uv} + M^{is\,\alpha\gamma}_{uv} \right\} \left(X^\beta_u - X^\beta_v\right) \times$$

$$\times \left(X^\delta_u - X^\delta_v\right) q_\beta q_\delta + \frac{1}{2N} \sum_{\gamma\beta uv} \frac{e^{(1)}_\gamma(\vec{q},\eta,\varkappa)}{(M_\varkappa M_{\varkappa'})^{1/2}} \left\{ \tilde{\Phi}^{\alpha\gamma}_{uv} + M^{is\,\alpha\gamma}_{uv} \right\} \times \quad (3.12)$$

$$\times \left(X^\beta_u - X^\beta_v\right) q_\beta + \frac{1}{2N} \sum_{\gamma uv} \frac{e^{(2)}_\gamma(\vec{q},\eta,\varkappa')}{(M_\varkappa M_{\varkappa'})^{1/2}} \left\{ \tilde{\Phi}^{\alpha\gamma}_{uv} + M^{is\,\alpha\gamma}_{uv} \right\} .$$

The system of homogeneous equations connected with (3.12) has a solution of the type (3.7). The system of non-homogeneous equations has a solution if and only if non-homogenity is orthogonal to the solutions of the homogeneous equations. This condition leads to the equation

$$\left(\omega^{(1)}(q,\eta)\right)^2 = \frac{V}{M_c N} \sum_{\alpha\beta\gamma\varepsilon} \bar{S}_{\alpha\gamma,\beta\delta}\, u^\alpha_\eta u^\gamma_\eta q_\beta q_\delta . \quad (3.13)$$

Equation (3.13) is identical with (2.20).

The result (3.13) can be used to derive a sum rule for the spectral function $\chi_Q(\omega)$ defined as follows

$$\langle [A_Q(t), A_Q^+(t')] \rangle = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \, \chi_Q(\omega) e^{-i\omega(t-t')} .$$

For $\langle\langle A_Q, A_Q^+ \rangle\rangle_\omega$ the usual spectral representation can be derived [14]

$$G_Q(\omega) = \langle\langle A_Q, A_Q^+ \rangle\rangle_\omega = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega' \, \frac{\chi_Q(\omega')}{\omega - \omega'} . \qquad (3.14)$$

Substituting (3.13) into the static limit of $G_Q^{-1}(\omega)$ we get the relation

$$\frac{1}{\rho} \sum_{\alpha\beta\gamma\delta} \bar{\Phi}_{\alpha\beta,\gamma\delta} u_\eta^\alpha u_\eta^\beta \lim_{q\to 0} \left\{ q_\gamma q_\delta \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega' \, \frac{\chi_{q\eta}(\omega')}{\omega'} \right\} = 1 \qquad (3.15)$$

ρ is the density of the orystal $\rho = \frac{M_c N}{V}$.

As we take only the diagonal part of the phonon Green function the sum rule [3,4] .

4. Conolusions.

We have presented the derivation of the elastic constants for strongly anharmonic crystals in the pseudo-harmonic approximation by the method of homogeneous deformation and the method of long waves. This gives a relation between the statio self-energy of Green function of displacements and second derivative of the free energy equivalent to sum rule. This connection enables us to exclude the surface effeots and to extend the Liebfried and Ludwig method to the pseudoharmonic approximation.

The elastic constants have the symmetry properties which lead to the rotational invariance of the free energy. Vertex corrections are valid as it follows from the comparison of results obtained from both methods.

The same results obtained from both the long waves and the homogeneous deformation methods in the pseudoharmonic approximation give us the very important information as it is usually much easier to calculate the mass operator than the free energy (e.g. for metals or some models of fluids). In addition, the mass operator enables us to find the adiabatic elastic constants and the life-time of phonons as well. This gives us the possibility of calculating the sound attenuation in the hydrodynamics and collisionless regimes which will be considered in the forthcoming papers.

Finally we mention some inconsistency in Klein et al. [6] and our calculations. As is seen from calculation of the mass operator $\Pi_Q(\omega)$ we do not take into account the corrections of the second order in the self-consistent determination of phonon vertices and frequencies [7] +. This may lead to some improvement of the numerical results of Klein et al. [6] .

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