21

KFKI-1981-43

T. SIKLÓS

THE THERMODYNAMIC GREEN'S FUNCTION METHOD IN THE SELF-CONSISTENT PHONON THEORY OF ANHARMONIC CRYSTALS

Hungarian Academy of Sciences

**CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS**

BUDAPEST

KFKI-1981-43

THE THERMODYNAMIC GREEN'S FUNCTION METHOD IN THE SELF-CONSISTENT PHONON THEORY OF ANHARMONIC CRYSTALS

T. Siklós

Central Research Institute for Physics
H-1525 Budapest 114, P.O.B. 49, Hungary

To be published in
Acta Universitatis Lodziensis

HU ISSN 0368 5330
ISBN 963 371 825 2

ABSTRACT

A self-consistent phonon theory of lattice dynamics based on the thermodynamic double-time Green's function method is reviewed. The theory is applied for the investigation of the simplest model, the anharmonic linear chain with nearest neighbour central force interaction.

АННОТАЦИЯ

Теория самосогласованного фононного поля сформулирована на основе метода двухвременных термодинамических функций Грина. Теория применена для рассмотрения простейшей модели - ангармонической линейной цепочки с центральным парным взаимодействием ближайших соседей.

KIVONAT

A self-consistent fonon-tér elméletet a kétidős termodinamikai Green-függvények módszerének a felhasználásával foglaljuk össze. Az elméletet ezután a legegyszerübb model, az anharmonikus lineáris lánc tárgyalására alkalmazzuk, a közvetlenül szomszédos atomok párkölcsönhatását feltételezve.

1. INTRODUCTION

The theory of lattice dynamics founded on the classical works by Debye, Born and Kármán in its most simple approximation /in the harmonic approximation/ is considered to be a well established theory capable to describe many of the physical properties of the crystals in terms of independent normal modes--phonons. For more precise description the anharmonicity of lattice vibrations or the interaction between the phonons should be taken into account and usually the ordinary perturbation theory, considering the cubic and quartic interaction is quite appropriate for this purpose /see e.g. [1], [2], [3], [4]/.

The investigations of the past years showed, however, that this approach cannot be applied in certain cases: near the phase transition points, e.g. melting point; for the quantum crystals with large zero-point energy; for the light impurities with small binding energy etc., when the anharmonic effects are not small /see, e.g. [5]/.

Thus some modification of the well established Born-Kármán theory of lattice dynamics is needed in considering the highly anharmonic crystals: the quantum crystals and the crystals at high temperatures, $T > (0,3-0,5)\ T_m$, where T_m is the melting temperature. In order to obtain a theory which is convenient for these highly anharmonic crystals it is necessary to take into account all orders of the anharmonic interactions applying a self-consistent method. This very natural idea of introducing the self-consistent collective modes was already proposed by Born [6].

In recent years Born's idea was rediscovered and the self-consistent phonon theory (SCPT) of anharmonic crystals was elaborated simultaneously and independently by several authors by a variety of techniques. In one of these approaches the SCPT is based on the variational principle, the most elegant treatment of which is given by Werthamer [7]. A selective resummation of diagrammatic perturbation theory was used in another group of papers, the most detailed description of this approach being presented in Choquard's book [8]. The SCPT based on the thermodynamic double-time Green's function method was proposed independently in [9] , [10]. It was shown in [7], [11] that all of these three variants of the SCPT are equivalent.

Today the SCPT is considered to be a well established theory and it has been applied for the investigation of dynamical, thermodynamical and elastic properties of various crystals /see e.g. [5]/.

In the present paper the SCPT is formulated in general briefly using the thermodynamic double-time Green's function method [12]. In the next Section the Hamiltonian and the equilibrium conditions for an anharmonic crystal are discussed and the method of Green's functions is introduced. In Section 3 the SCPT is formulated in a rather simple but general way on the basis of the irreducible Green's function. In Section 4 the SCPT is applied for the investigation of the properties of an anharmonic linear chain in the first order of SCPT. Some conclusions are presented in the last Section.

2. DESCRIPTION OF ANHARMONIC CRYSTALS

2.1 The Hamiltonian

Let us consider a crystal in the adiabatic approximation [1] when it can be described by the Hamiltonian:

$$H = \sum_i \frac{\vec{p}_i^{\,2}}{2M_i} + U(\vec{R}_i) \qquad /2.1/$$

with the local potential energy $U(\vec{R}_i)$ depending only on the coordinates $\vec{R}_i = R_s^\alpha = R^\alpha\binom{\ell}{\kappa}$ of the atom of type $\kappa=1,2,\dots,r$ in the unit cell ℓ; $\alpha=(x,y,z)$; $\vec{p}_i = p_s^\alpha = -i\hbar\nabla_s^\alpha$ is the momentum operator and $M_i = M_\kappa$ is the mass of the κ-th type of atom. For the anharmonic crystal the equilibrium positions of atoms $\vec{x}_i = \langle\vec{R}_i\rangle = x^\alpha\binom{\ell}{\kappa}$ are temperature dependent and should be obtained from the equilibrium conditions. Let us apply an external static field with forces $\vec{F}_i$ acting on atoms at $\vec{R}_i$

$$H_1 = - \sum_i \vec{F}_i \vec{R}_i = - \sum_{s\alpha} F_s^\alpha R_s^\alpha . \qquad /2.2/$$

From the equation of motion for the momentum operator in the Heisenberg representation

$$\vec{p}_i(t) = e^{i\mathcal{H}t} \vec{p}_i e^{-i\mathcal{H}t}, \quad \mathcal{H} = H + H_1, \qquad /2.3/$$

one gets the equilibrium conditions in the form

$$\frac{d}{dt} < \vec{p}_i(t) > = < [\mathcal{H}, i\vec{p}_i] > = \vec{F}_i - < \frac{\partial U}{\partial \vec{R}_i} > = 0. \qquad /2.4/$$

From thermodynamical considerations and Eq. /2.4/ follows an equation for the stress tensor

$$\sigma_{\alpha\beta} = \frac{1}{V} \sum_s x_s^\alpha F_s^\beta = \frac{1}{V} \sum_s x_s^\alpha < \nabla_s^\beta U(\vec{R}_i) > \qquad /2.5/$$

or for the pressure

$$P = - \frac{1}{3} \sum_\alpha \sigma_{\alpha\alpha} = - \frac{1}{3V} \sum_{\alpha s} x_s^\alpha < \nabla_s^\alpha U(\vec{R}_i) >, \qquad /2.6/$$

where V is the volume of the crystal of N unit cells. The statistical average in Eqs. /2.4/-/2.6/ is taken over the canonical ensemble:

$$< A > = Sp\{e^{-\beta\mathcal{H}}A\}/Sp\{e^{-\beta\mathcal{H}}\}; \qquad \beta = \frac{1}{kT} . \qquad /2.7/$$

The lattice parameters can be obtained also directly from the partition function:

$$\vec{x}_i = < \vec{R}_i > = \frac{1}{\beta}\frac{\partial}{\partial\vec{F}_i}\ln Sp\{e^{-\beta\mathcal{H}}\}. \qquad /2.8/$$

Now introducing the dynamical displacements of the atoms $\vec{u}_i=\vec{R}_i-\vec{x}_i=u^{\alpha}\binom{\ell}{\kappa}$, the Hamiltonian /2.1/ can be written as

$$H = \sum_i \frac{\vec{p}_i^{\,2}}{2M_i} + U_o(\vec{x}_i) + \sum_{n=1}^{\infty}\frac{1}{n!}\sum_{1\ldots n}\Phi_{1\ldots n}\,\vec{u}_1\ldots\vec{u}_n, \qquad /2.9/$$

where the coefficients of the Taylor expansion

$$\Phi_{1\ldots n} = \nabla_1\ldots\nabla_n\,U_o(\vec{x}_i) \equiv \Phi^{\alpha_1\ldots\alpha_n}_{\ell_1\kappa_1\ldots\ell_n\kappa_n} \qquad /2.9a/$$

are symmetric functions of the index (1...n) and satisfy several conditions which follow from the invariance of the lattice under translations and rotations [1].

2.2 The Green's functions

Various dynamical and thermodynamical properties of the anharmonic crystal can be discussed in terms of the Green's function /GF/. Following [9],[10], [12] let us consider the thermodynamic GF [13]:

$$G_{ii'}(t-t')=\langle\langle\vec{u}_i(t);\ \vec{u}_{i'}(t')\rangle\rangle=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,e^{-i\omega(t-t')}\langle\langle\vec{u}_i/\vec{u}_{i'}\rangle\rangle_\omega \qquad /2.10/$$

in usual notations [14]. The spectral representation for it has the form

$$G_{ij}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega'}{\omega-\omega'}\,(e^{\beta\omega'}-1)J_{ij}(\omega'), \qquad /2.11/$$

where the Fourier transform $J_{ij}(\omega)$ for the correlation function

$$\langle\vec{u}_i(t)\ \vec{u}_j\rangle=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,e^{i\omega t}\,J_{ij}(\omega) \qquad /2.12/$$

is real and has the properties

$$\begin{aligned}J_{ij}(\omega)&=J_{ji}(\omega)=e^{-\beta\omega}J_{ij}(-\omega)=\\&=(e^{\beta\omega}-1)^{-1}\,[-2\mathrm{Im}G_{ij}(\omega+i\varepsilon)], \qquad /2.13/\\&\qquad(\varepsilon\to 0^{+})\end{aligned}$$

since the displacement operators $\vec{u}_i$ are hermitian. The GF /2.11/ obeys the sum rules [14]:

$$\int_{-\infty}^{\infty}\omega d\omega[-\frac{1}{\pi}\ \mathrm{Im}\ G_{ij}(\omega+i\varepsilon)]=\frac{1}{M_i}\ \delta_{ij}, \qquad /2.14/$$

$$\int_{-\infty}^{\infty}\omega^3 d\omega[-\frac{1}{\pi}\ \mathrm{Im}\ G_{ij}(\omega+i\varepsilon)]=\frac{1}{M_iM_j}\langle\nabla_i\nabla_jU(\vec{R}_i)\rangle. \qquad /2.15/$$

In the discussion of the anharmonic properties of the lattice an (n,n')-point GF of the type $\langle\langle A_n(t);\ A_{n'}(t')\rangle\rangle$, where

$A_n(t) = \{\vec{u}_1(t)\dots\vec{u}_n(t) - \langle\vec{u}_1\dots\vec{u}_n\rangle\}$ and
$A_{n}'(t') = \{\vec{u}_{1'}(t')\dots\vec{u}_{n'}(t') - \langle\vec{u}_{1'}\dots\vec{u}_{n'}\rangle\}$ will appear for which the representations similar to Eqs. /2.11/ - /2.13/ hold.

In the translationally invariant lattice the GF /2.10/ depends only on the difference of the coordinates and the Fourier transformation for it can be written in the form:

$$\langle\langle u_s^\alpha | u_{s'}^\beta \rangle\rangle_\omega = \frac{1}{N} \sum_{\vec{q}jj'} \frac{e^{*\alpha}_{\vec{q}j}(\kappa)\, e^{\beta}_{\vec{q}j'}(\kappa')}{\sqrt{M_\kappa M_{\kappa'}}}\, e^{-i\vec{q}(\vec{x}_s-\vec{x}_{s'})}\, G_{jj'}(\vec{q},\omega). \qquad /2.16/$$

Here for each wave vector $\vec{q} = \{\vec{q}_1,\dots,\vec{q}_N\}$ the set of polarization vectors $\vec{e}_{\vec{q}j}(\kappa)$; $j = \{1\dots 3r\}$ satisfying the orthonormality and closure conditions:

$$\sum_{\kappa,\alpha} e^{*\alpha}_{\vec{q}j}(\kappa)\, e^{\alpha}_{\vec{q}j'}(\kappa) = \delta_{jj'}$$
$$\sum_{j} e^{*\alpha}_{\vec{q}j}(\kappa)\, e^{\beta}_{\vec{q}j}(\kappa') = \delta_{\alpha\beta}\, \delta_{\kappa\kappa'} \qquad /2.17/$$

are introduced.

The physical meaning of the retarded GF /2.16/ follows from linear response theory [14]: the energy of phonon-like excitations at given $(\vec{q},j)$ measured by inelastic neutron scattering, are defined by the imaginary part of the GF:

$$g_{j=j'}(\vec{q},\omega) = -\frac{1}{\pi}\, \mathrm{Im}\, G_{j=j'}(\vec{q},\omega+i\varepsilon). \qquad /2.18/$$

The position and the width of the maximum of /2.18/ give the energy and the inverse life-time of the excitations respectively. The long-wavelength $(\vec{q}\to 0)$ limit of the static $(\omega=0)$ self-energy of the GF defines the isothermal elastic constants [15].

Therefore the dynamical properties of the lattice are well defined by the GF /2.16/ and a direct comparison between theory and experiment is possible.

2.3 The free energy and the internal energy of the anharmonic crystal

To discuss the thermodynamical properties of the anharmonic crystal its free energy should be calculated. The most elegant way for doing this is to integrate the GF over the formal coupling constant λ [16]. For the anharmonic lattice Hamiltonian, Eq. /2.9/ λ can be introduced in the form:

$$H(\lambda) = H_o + H_1(\lambda), \qquad /2.19/$$

$$H_o = \sum_i \frac{\vec{p}_i^{\,2}}{2M_i} + U_o(\vec{x}_i) + \frac{1}{2}\sum_{ij} \Phi^o_{ij}\vec{u}_i\vec{u}_j , \qquad /2.19a/$$

$$H_1(\lambda) = \sum_{n=1}^{\infty} \frac{\lambda^n}{n!} \sum_{1\ldots n} \Phi_{1\ldots n}\vec{u}_1\ldots\vec{u}_n - \frac{\lambda^2}{2}\sum_{ij} \Phi^o_{ij}\vec{u}_i\vec{u}_j . \qquad /2.19b/$$

Then for the free energy

$$F(\lambda) = -\frac{1}{\beta}\,\ln \mathrm{Sp}\{e^{-\beta H(\lambda)}\} = -\frac{1}{\beta}\,\ln Z(\lambda) \qquad /2.20/$$

one obtains the equation

$$\frac{\partial F(\lambda)}{\partial\lambda} = \frac{1}{Z(\lambda)}\mathrm{Sp}\,\{e^{-\beta H(\lambda)}\,\frac{\partial H_1(\lambda)}{\partial\lambda}\} \equiv \left< \frac{\partial H_1(\lambda)}{\partial\lambda} \right>_\lambda . \qquad /2.21/$$

To express F in terms of GF, Eq. /2.10/, consider an equation of motion for the GF with the Hamiltonian /2.19/

$$\sum_j \{M_i \omega^2 \delta_{ij} - \Phi^o_{ij}\} G_{ji'}(\omega) = \delta_{ii'} +$$

$$+ \sum_{n=2}^{\infty} \frac{\lambda^n}{(n-1)!} \sum_{2\ldots n} \Phi_{i2\ldots n} \langle\langle \vec{u}_2 \ldots \vec{u}_n | \vec{u}_{i'} \rangle\rangle_\omega - \lambda^2 \sum_j \Phi^o_{ij} G_{ji'}(\omega) \equiv$$

$$\equiv \delta_{ii'} + \sum_j \Pi_{ij}(\lambda,\omega)\, G_{ji'}(\omega). \qquad /2.22/$$

After integrating the imaginary part of it using Eqs. /2.12/ and /2.13/ one gets the right hand side of /2.21/ and the free energy in the form

$$F - F_o(\lambda=o) = \int_o^1 d\lambda \, \langle \frac{\partial H_1}{\partial \lambda} \rangle_\lambda =$$

$$= \int_o^1 \frac{d\lambda}{\lambda} \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega}{e^{\beta\omega}-1} \sum_{ij} (M_i \omega^2 \delta_{ij} - \Phi^o_{ij}) [-2 \mathrm{Im}\, G_{ij}(\omega + i\varepsilon)] = \qquad /2.23/$$

$$= \int_o^1 \frac{d\lambda}{\lambda} \frac{i}{2\pi} \int_C \frac{dz}{e^{\beta z}-1} \sum_{ij} \Pi_{ij}(\lambda z)\, G_{ij}(z),$$

where in the last line the integration over the complex variable z is performed along the contour C of two straight lines: $(-\infty+i\varepsilon) \to (\infty+i\varepsilon)$ and $(\infty-i\varepsilon) \to (-\infty-i\varepsilon)$. Deforming the contour C to circle the imaginary axes of z one obtains, by counting the residues from the poles of $(e^{\beta z}-1)^{-1}$ at $z_n = (2\pi i n/\beta)$, the same result as in [17] based on the imaginary time GF [16].

The internal energy of the anharmonic crystal apart from being calculated thermodynamically from the free energy /2.23/ can be obtained in a more direct way by writing it in the form

$$E = \langle H \rangle = \langle T \rangle + \langle U(\vec{x}_i + \vec{u}_i) \rangle \,, \qquad /2.24/$$

where the average kinetic energy is easily expressed in terms of GF with the help of Eqs. /2.12/, /2.13/ as:

$$\langle T \rangle = \sum_i \frac{1}{2M_i} \langle \vec{p}_i^{\,2} \rangle =$$

$$= \int_0^\infty \omega^2 d\omega \coth \frac{\beta\omega}{2} \sum_i \frac{M_i}{2} \left[-\frac{1}{\pi} \mathrm{Im}\, G_{ii}(\omega + i\varepsilon) \right]. \qquad /2.25/$$

The average potential energy can be written in the form of a cumulant expansion:

$$\langle U(\vec{x}_i + \vec{u}_i) \rangle = \langle \exp\{ \sum \vec{u}_i \vec{\nabla}_i \} \rangle \, U_o(\vec{x}_i) =$$

$$= \exp \left\{ \sum_{n=2}^{\infty} \frac{1}{n!} \sum_{1 \ldots n} \langle \vec{u}_1 \ldots \vec{u}_n \rangle^c \nabla_1 \ldots \nabla_n \right\} U_o(\vec{x}_i), \qquad /2.26/$$

where the cumulants $\langle \vec{u}_1 \ldots \vec{u}_n \rangle^c$ can also be defined from the GF as it will be shown in the next Section. Then from a given approximation for the self-energy $\Pi_{ij}(\omega)$ and GF in /2.23/, /2.25/ and /2.26/ one obtains a corresponding approximate value for the thermodynamical functions.

Therefore the dynamical as well as the thermodynamical properties of anharmonic crystals can be investigated by means of GF. This procedure greatly simplifies the calculation and allows one to perform them in a unified self-consistent manner.

3. SELF-CONSISTENT PHONON THEORY

3.1 Irreducible GF

Consider an equation of motion for the GF /2.10/ by differentiating it twice with respect to the time t and performing the necessary commutations. Then for the Fourier transform of the GF one gets

$$M_i \omega^2 G_{ii'}(\omega) = \delta_{ii'} + \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{1\ldots n} \Phi_{i1\ldots n} \langle\langle \vec{u}_1 \ldots \vec{u}_n | \vec{u}_{i'} \rangle\rangle_{\omega} \quad /3.1/$$

where the symmetry properties of /2.9a/ were taken into account. There is a large class of n-point /multi-phonon/ GF in /3.1/ that describes an uncorrelated propagation of phonons in an averaged phonon field. This class should be summed up not only for the simplification of further calculations but also for physical reasons: in highly anharmonic crystals atoms move not in a static field but rather in the dynamic potential of their vibrating neighbours and this renormalization should be taken into account from the beginning. Therefore we introduce the irreducible /or cumulant/ GF [18] that have no disconnected parts of average field renormalization

$$<<\vec{u}_1\ldots\vec{u}_n|\vec{u}_{i'}>>^{irr} = <<\vec{u}_1\ldots\vec{u}_n|\vec{u}_{i'}>> - \sum_{m=1}^{n-1} C_n^{n-m} <\vec{u}_{m+1}\ldots\vec{u}_n> <<\vec{u}_1\ldots\vec{u}_m|\vec{u}_{i'}>>^{irr} . \qquad /3.2/$$

Here the symmetry with respect to permutations of the commuting operators $\vec{u}_1\ldots\vec{u}_n$ has been taken into account and the corresponding coefficient $C_n^{n-m} = C_n^m = n!/m!(n-m)!$ was introduced. The GF /3.2/ can not be reduced to lower order ones by the usual decoupling procedure [14] and so it describes the correlations between n-particle vibrations. The definition /3.2/ can be rewritten in the form of the decomposition for the n-point GF as the sum of the irreducible ones:

$$<<\vec{u}_1\ldots\vec{u}_n|\vec{u}_{i'}>> = \sum_{m=1}^{n} C_n^m <\vec{u}_{m+1}\ldots\vec{u}_n><<\vec{u}_1\ldots\vec{u}_m|\vec{u}_{i'}>>^{irr} . \qquad /3.2a/$$

By using a spectral representation of the type given in Eqs. /2.12/, /2.13/ one gets from /3.2a/ the decomposition for the n-point correlation functions in terms of the irreducible /or cumulant/ ones:

$$<\vec{u}_1\ldots\vec{u}_n> = \sum_{m=1}^{n-1} C_{n-1}^m <\vec{u}_{m+2}\ldots\vec{u}_n> (<\vec{u}_1\ldots\vec{u}_{m+1}>^c) . \qquad /3.3/$$

In obtaining Eq. /3.3/ some obvious changes of indices have been performed in Eq. /3.2a/.

Substituting now /3.2a/ into the equation /3.1/ and performing the summation at first over n for each m-particle irreducible GF and then over all m, one obtains:

$$\sum_j (M_i \omega^2 \delta_{ij} - \tilde{\Phi}_{ij})\, G_{ji'}(\omega) = \delta_{ii'} + \sum_{n=2}^{\infty} \frac{1}{n!} \sum_{1\ldots n} \tilde{\Phi}_{i1\ldots n} \langle\langle \vec{u}_1 \ldots \vec{u}_n | \vec{u}_{i'} \rangle\rangle^{irr}, \qquad /3.4/$$

where the renormalized interaction has the form:

$$\tilde{\Phi}_{1\ldots n} = \sum_{n'=0}^{\infty} \frac{1}{n'!} \sum_{1'\ldots n'} \Phi_{1\ldots n, 1'\ldots n'} \langle \vec{u}_{1'} \ldots \vec{u}_{n'} \rangle = \langle \nabla_1 \ldots \nabla_n U(\vec{x}_i + \vec{u}_i) \rangle =$$

$$= \nabla_1 \ldots \nabla_n \exp\{ \sum_{n'=2}^{\infty} \frac{1}{n'!} \sum_{1'\ldots n'} \langle \vec{u}_{1'} \ldots \vec{u}_{n'} \rangle^c \nabla_{1'} \ldots \nabla_{n'} \} U_o(\vec{x}_i). \qquad /3.5/$$

The cumulant expansion in the last line /as well as in /2.26// follows from the equation [19]:

$$\frac{\partial}{\partial\lambda} \langle U(\lambda) \rangle = \frac{\partial}{\partial\lambda} \sum_{n=o}^{\infty} \frac{\lambda^n}{n!} \sum_{1\ldots n} \Phi_{1\ldots n} \langle \vec{u}_1 \ldots \vec{u}_n \rangle \qquad /3.6/$$

that can be easily solved in the form /2.26/ by introducing the expansion /3.3/ and performing the summation over n and m in the same manner as in /3.4/.

To obtain the equation of motion for the n-point irreducible GF in Eq. /3.4/ let us differentiate the operator $\vec{u}_{i'}(t')$ with respect to t'. Then taking into account the identity

$$\langle [\vec{u}_1 \ldots \vec{u}_n, i\vec{p}_{i'}] \rangle^{irr} = 0 \quad (n \geq 2)$$

that follows from the definition /3.2/, and introducing the same decomposition as in Eq. /3.2a/ for the operators $\{\vec{u}_1(t')\ldots\vec{u}_{n'}(t')\}$ on the right hand side of the (n,n')-point GF, one gets

$$\sum_{j'} \{M_{i'}\,\omega^2\,\delta_{i'j'} - \tilde{\Phi}_{i'j'}\} \;\langle\langle \vec{u}_1\ldots\vec{u}_n|\vec{u}_{j'}\rangle\rangle^{irr}_{\omega} = \qquad /3.7/$$

$$= \sum_{n'=2}^{\infty} \frac{1}{n'!} \sum_{1'\ldots n'} \tilde{\Phi}_{i'1'\ldots n'}\; G^{irr}_{1\ldots n,\,1'\ldots n'}(\omega),$$

where

$$G^{irr}_{1\ldots n,\,1'\ldots n'}(\omega) = \langle\langle \vec{u}_1\ldots\vec{u}_n|\vec{u}_{1'}\ldots\vec{u}_{n'}\rangle\rangle^{irr}_{\omega}$$

is the (n,n') -point GF irreducible both in the n-point and n'-point parts of it.

Now it is convenient to define the zero order GF by the equation

$$\sum_j (M_i\omega^2\delta_{ij} - \tilde{\Phi}_{ij})\; G^{o}_{ji'}(\omega) = \delta_{ii''} \qquad /3.8/$$

which describes the undamped vibrations /or one-phonon propagation/ in an average phonon field. Then solving the matrix equations /3.4/ and /3.7/ with the help of Eq. /3.8/ one gets for the GF:

$$G_{ii'}(\omega) = G^{o}_{ii'}(\omega) + \sum_{jj'} G^{o}_{ij}\; P_{jj'}(\omega)\; G^{o}_{j'i'}(\omega), \qquad /3.9/$$

where the scattering matrix is defined by

$$P_{jj'}(\omega)= \sum_{n,n'=2}^{\infty} \frac{1}{n!n'!} \sum_{\substack{1\ldots n\\ 1'\ldots n'}} \tilde{\Phi}_{j1\ldots n}\, G^{irr}_{1\ldots n,1'\ldots n'}(\omega)\tilde{\Phi}_{j'1'\ldots n'}, \qquad /3.10/$$

Then the one-phonon GF can be written in the form of the Dyson equation

$$G_{ii'}(\omega) = \{M_i\omega^2\delta_{ii'} - \tilde{\Phi}_{ii'} - \Pi_{ii'}(\omega)\}^{-1}, \qquad /3.11/$$

where the self-energy operator $\Pi_{ii'}(\omega)$ is given by the proper part (p) of the scattering matrix /3.10/: $\Pi_{ii'}(\omega)=P^{(p)}_{ii'}(\omega)$. According to Eqs. /3.9/ and /3.11/ $\Pi_{ii'}$ satisfies the equation:

$$P_{ii'}(\omega) = \Pi_{ii'}(\omega) + \sum_{jj'} \Pi_{ij}(\omega)\, G^{o}_{jj'}(\omega)\, P_{j'i'}(\omega). \qquad /3.12/$$

Hence, the self-energy operator $\Pi_{ii'}(\omega)$ has the same form as Eq. /3.10/ where the (n,n')-point GF is replaced by its proper part $K_{1\ldots n,\,1'\ldots n'}(\omega)=G^{(irr,p)}_{1\ldots n,\,1'\ldots n'}(\omega)$. $K(\omega)$ according to Eq. /3.12/ can not be cut into two pieces by cutting only one G^{o}-line; G^{o} is defined by Eq. /3.8/.

The n-point irreducible GF in /3.7/ can also be written in terms of $K_{1\ldots n,\,1'\ldots n'}(\omega)$ if one uses equations /3.8/ - /3.12/:

$$\langle\langle u_1\ldots u_n | u_{i'}\rangle\rangle^{irr}_{\omega} =$$

$$= \sum_{j'} G^{o}_{i'j'}(\omega) \sum_{n'=2}^{\infty} \frac{1}{n'!} \sum_{1'\ldots n'} \tilde{\Phi}_{j'1'\ldots n'}\, G^{irr}_{1\ldots n,1'\ldots n'}(\omega) = \qquad /3.13/$$

$$= \sum_{j'} G_{i'j'}(\omega) \sum_{n'=2}^{\infty} \frac{1}{n'!} \sum_{1'\ldots n'} \tilde{\Phi}_{j'1'\ldots n'}\, K_{1\ldots n,\,1'\ldots n'}(\omega).$$

Then from the spectral representation, Eqs. /2.11/ - /2.13/ for the cumulant part of the correlation functions one gets:

$$<\vec{u}_1 \ldots \vec{u}_n>^c =$$

$$= \int_{-\infty}^{\infty} \frac{d\omega}{e^{\beta\omega}-1} \left[-\frac{1}{\pi} \mathrm{Im} << \vec{u}_2 \ldots \vec{u}_n | \vec{u}_1 >>^{irr}_{\omega+i\varepsilon} \right] = \qquad /3.14/$$

$$= 2\mathrm{Im} \int_0^{\infty} dt \sum_{n'=3}^{\infty} \frac{1}{(n'-1)!} \sum_{1' \ldots n'} \tilde{\Phi}_{1' \ldots n'} <\vec{u}_1(t) \vec{u}_{1'}> <\vec{u}_2(t) \ldots \vec{u}_n(t) | u_{2'} \ldots u_{n'}>^{irr,p},$$

where a two-time proper irreducible correlation function, corresponding to $K_{2 \ldots n,\, 2' \ldots n'}(t)$, has been introduced.

Thus the one-phonon GF Eq. /3.11/ as well as the cumulants /3.14/ in the renormalized interaction /3.5/ are written in terms of the (n,n')-point GF $K_{1..n,\, 1' \ldots n'}(\omega) = << \vec{u}_1 \ldots \vec{u}_n | \vec{u}_{1'} \ldots \vec{u}_{n'} >>^{irr,p}_{\omega}$. The equations obtained are exact but unclosed and therefore some approximations to the $K_{1 \ldots n,\, 1' \ldots n'}(\omega)$ should be considered in order to obtain a self-consistent system of equations.

3.2 First order or renormalized harmonic approximation

In the first order of the SCPT /SC1/ only the renormalization of phonons in the self-consistent field is taken into account. Thus the SC1 is obtained by neglecting all the terms which contribute to the damping /or correlations/ of phonons. In that case the self-energy operator $\Pi_{ii'}(\omega)$ in the GF /3.11/ and the cumulants /3.14/ for $n \geq 3$

should be put equal to zero. Therefore the SCl GF is equal to the zero order one /3.8/ with the renormalized pseudo-harmonic force-constant matrix

$$\tilde{\Phi}^{(1)}_{ij} = \nabla_i \nabla_j \exp\{\frac{1}{2} \sum_{1,2} \langle \vec{u}_1 \vec{u}_2 \rangle \nabla_1 \nabla_2 \} U_o(\vec{x}_i) \equiv \nabla_i \nabla_j \tilde{U}_1(\vec{x}_i) \ . \qquad /3.15/$$

The system of equations gets closed by the equation for the pair-correlation function in /3.15/. From the spectral representation Eqs. /2.12/, /2.13/ and /2.16/, one gets

$$\langle u^{\alpha}_{s} u^{\beta}_{s'} \rangle =$$

$$= \frac{1}{N} \sum_{\vec{q}j} \frac{e^{*\alpha}_{\vec{q}j}(\kappa)\, e^{\beta}_{\vec{q}j}(\kappa')}{\sqrt{M_{\kappa} M_{\kappa'}}} \frac{1}{2\omega_{qj}} \coth \frac{\beta\omega_{qj}}{2}\, e^{-i\vec{q}(\vec{x}_s - \vec{x}_{s'})} , \qquad /3.16/$$

where the frequencies ω_{qj} and the polarization vectors $\vec{e}_{qj}(\kappa)$ are defined by the equation

$$\omega^2_{qj}\, e^{\alpha}_{qj}(\kappa) = \sum_{\beta s'} e^{\beta}_{qj}(\kappa') \frac{1}{\sqrt{M_{\kappa} M_{\kappa'}}} \tilde{\Phi}^{(1)\alpha\beta}_{ss'}\, e^{-i\vec{q}(\vec{x}_s - \vec{x}_{s'})} . \qquad /3.17/$$

The free energy /2.23/ in SCl is obtained by using the mean-field self-energy operator /2.22/:

$$\Pi^{(1)}_{ij}(\lambda) = \lambda^2 \{ \tilde{\Phi}^{(1)}_{ij}(\lambda) - \Phi^{o}_{ij} \} =$$

$$= \lambda^2 \{ \nabla_i \nabla_j \exp(\frac{\lambda^2}{2} \sum_{1,2} \langle \vec{u}_1 \vec{u}_2 \rangle \nabla_1 \nabla_2) U_o(\vec{x}_i) - \Phi^{o}_{ij} \} . \qquad /3.18/$$

So one finds

$$F_1 = F_o + \int_o^1 \frac{d\lambda}{\lambda} \sum_{ij} \Pi_{ij}^{(1)}(\lambda) \langle \vec{u}_i\ \vec{u}_j \rangle_o =$$

$$= F_o + \tilde{U}_1(\vec{x}_i) - U_o(\vec{x}_i) - \frac{1}{2} \sum_{ij} \Phi_{ij}^o \langle \vec{u}_i\ \vec{u}_j \rangle_o . \qquad /3.19/$$

The trial force-constant matrix Φ_{ij}^o in /2.19/ has not been specified yet. From the self-consistency condition Φ_{ij}^o should be put equal to $\tilde{\Phi}_{ij}^{(1)}$ in /3.15/ since the latter one defines the spectrum of excitations in SC1 according to /3.17/. Then for the free energy one gets

$$F_1 = \tilde{U}_1(x_i) + \frac{1}{\beta} \sum_{\vec{q}j} \ell n\left(2 \sinh \frac{\beta\omega_{\vec{q}j}}{2}\right) - \frac{1}{4} \sum_{\vec{q}j} \omega_{\vec{q}j} \coth \frac{\beta\omega_{\vec{q}j}}{2}, \qquad /3.19a/$$

which coincides with that obtained from the variational approach:

$$\frac{\delta F_1}{\delta \Phi_{ij}^o} = 0, \qquad \Phi_{ij}^o = \tilde{\Phi}_{ij}^{(1)} .$$

For the internal energy /2.24/ one easily obtains from Eqs. /2.25/ and /2.26/ in the SC1

$$E_1 = \frac{1}{4} \sum_{\vec{q}j} \omega_{\vec{q}j} \coth \frac{\beta\omega_{\vec{q}j}}{2} + \tilde{U}_1(\vec{x}_i). \qquad /3.20/$$

Therefore in the SC1 approximation one treats the vibrations of an anharmonic crystal as a system of noninteracting pseudoharmonic phonons with the δ-function type behaviour for the phonon spectrum /2.18/. This approximation simplifies the calculations; but due to this approximation all the odd terms in the anharmonic interaction /2.9a/ are missing. One should not hope to obtain a quantitative description in SC1: even in the limit of weak anharmonicity the results do not coincide with those of the ordinary perturbation theory /see, e.g.[20]/.

3.3 Second order of SCPT

Since the self-energy operator $\Pi_{ii'}(\omega)$ in the GF /3.11/ on account of /3.10/ is proportional to the second order of the renormalized anharmonic interaction /3.5/ one should calculate the (n,n')-point GF in the lowest order. This is done by taking account only the uncorrelated propagation of $n=n'$ "dressed" phonons and results in the following approximation for the (n,n')-point two-time correlation function $(n \geq 2)$:

$$<\vec{u}_1(t)\ldots\vec{u}_n(t)|\vec{u}_{1'},\ldots\vec{u}_{n'}>^{irr,p} \approx n!\,\delta_{nn'}\prod_{i=1}^{n}<\vec{u}_i(t)\vec{u}_{i'}> . \qquad /3.21/$$

Now employing the spectral representation for the (n,n')-point GF one obtains for the self-energy operator in the second order of the SCPT /SC2/

$$\Pi^{(2)}_{ii'}(\omega) = \int_{-\infty}^{\infty}\frac{d\omega'}{\omega-\omega'}\,(e^{\beta\omega'}-1)\int_{-\infty}^{\infty}\frac{dt}{2\pi}\,e^{-i\omega' t}\times$$

$$\times\sum_{n=2}^{\infty}\frac{1}{n!}\Big(\sum_{jj'}<\vec{u}_j(t)\vec{u}_{j'}>\nabla_j\nabla_{j'}\Big)^n<\nabla_i U(\vec{x}_i+\vec{u}_i)><\nabla_{i'} U(\vec{x}_{i'}+\vec{u}_{i'})>, \qquad /3.22/$$

where $\nabla_j = \partial/\partial\vec{x}_j$ and $\nabla_{j'} = \partial/\partial\vec{x}_{j'}$ are acting on $U(\vec{x}_i)$ and $U(\vec{x}_{i'})$ respectively.

For the cumulants /3.14/ one gets in the same SC2 approximation /3.21/:

$$<\vec{u}_1 \ldots \vec{u}_n>^c \approx$$

$$\approx 2\,\mathrm{Im} \int_0^\infty dt \prod_{i=1}^{n} \{\sum_{i'} <\vec{u}_i(t)\vec{u}_{i'}>\nabla_{i'}\} <U(\vec{x}_{i'} + \vec{u}_{i'})>. \qquad /3.23/$$

The equation for the pair correlation function

$$<\vec{u}_i(t)\vec{u}_j> =$$

$$= \int_{-\infty}^{\infty} \frac{d\omega}{e^{\beta\omega}-1}\, e^{i\omega t}\left[-\frac{1}{\pi}\,\mathrm{Im}\{\omega^2 M_i \delta_{ij} - \tilde{\Phi}_{ij} - \Pi_{ij}^{(2)}(\omega+i\varepsilon)\}^{-1}\right] \qquad /3.24/$$

closes the system of self-consistent equations /3.5/, /3.22/-/3.24/. In the present form the SC2 system of equations can be applied for anharmonic crystals with strong repulsive interactions since only fully renormalized vertices $\tilde{\Phi}_{1\ldots n}$ /3.5/ appear in the equations /3.22/, /3.23/, as in the Horner theory [21]. But just due to the full renormalization of the vertices the system of equations is rather untractable. To solve it one should either introduce a trial short-range correlation function $\hat{g}_{sr}(x_i)$ in Eq. /3.5/:

$$<U(x_i+u_i)>=\exp\{\sum_{n=3}^{\infty}\frac{1}{n!}\sum_{1\ldots n}<\vec{u}_1\ldots\vec{u}_n>^c\nabla_1\ldots\nabla_n\}\tilde{U}_1(\vec{x}_i)\equiv\hat{g}_{sr}(\vec{x}_i)\breve{U}_1(\vec{x}_i), \qquad /3.25/$$

or, employing some cut-off procedure for the strong repulsive part of the interaction expand /3.25/ in powers of cumulants:

$$\langle U(\vec{x}_i + \vec{u}_i)\rangle \approx$$

$$\approx \{ 1 + \sum_{n=3}^{\infty} \frac{1}{n!} \sum_{1\ldots n} \langle \vec{u}_1 \ldots \vec{u}_n \rangle^c \nabla_1 \ldots \nabla_n + \ldots \} \tilde{U}_1(\vec{x}_i) = \qquad /3.26/$$

$$= \tilde{U}_1(\vec{x}_i) + \Delta\tilde{U}_2(\vec{x}_i) + \ldots$$

The renormalized potential energy in the pseudoharmonic approximation

$$\tilde{U}_1(x_i) = \exp \{\frac{1}{2} \sum_{ij} \langle \vec{u}_i \, \vec{u}_j \rangle \nabla_i \nabla_j \} U_o(\vec{x}_i) \qquad /3.26a/$$

is calculated by integration with a Gaussian function.

We shall not discuss the problem of hard core interaction here since an elegant presentation of it is given by Horner [21] and consider only the cumulant expansion in Eq. /3.26/ up to second order in $\Delta\tilde{U}_2(\vec{x}_i)$. In this approximation the renormalized vertices /3.15/·

$$\tilde{\Phi}^{(2)}_{1\ldots n} = \nabla_1 \ldots \nabla_n \{\tilde{U}_1(\vec{x}_i) + \Delta\tilde{U}_2(\vec{x}_i)\} \qquad /3.27/$$

can be calculated on account of Eqs. /3.23/, /3.26/ by iteration. In the classical limit of high temperatures, $\beta\omega_{max} \ll 1$, the integration over time in cumulants /3.23/ using the spectral representation can easily be done with the result

$$\langle \vec{u}_1 \ldots \vec{u}_n \rangle^c \approx -\beta \prod_{i=1}^{n} (\sum_{i'} \langle \vec{u}_i \vec{u}_{i'} \rangle \nabla_{i'}) \langle U(\vec{x}_i + \vec{u}_i) \rangle, \qquad /3.28/$$

and

$$\Delta\tilde{U}_2(\vec{x}_i) \approx -\beta \sum_{n=3}^{\infty} \frac{1}{n!} (\sum_{ii'} \langle \vec{u}_i \vec{u}_{i'} \rangle \nabla_i \nabla_{i'})^n \tilde{U}_1(\vec{x}_i). \qquad /3.29/$$

The thermodynamical properties in the SC2 approximation can be obtained from the internal energy /2.24/, where the average kinetic energy /2.25/ is calculated by using GF /3.11/ with the self-energy operator /3.22/ and the average potential energy /2.26/ is given by /3.26/. To calculate the second order correction to the free energy in /2.23/ one should introduce first the irreducible GF in /2.22/ as done in the Section 3.1. Then by integration over frequencies using Eq. /3.14/ one gets:

$$\Delta F_2 = \int_0^1 \frac{d\lambda}{\lambda}\{\lambda^2 \sum_{ij} \langle\vec{u}_i\vec{u}_j\rangle\, \nabla_i\nabla_j\, \Delta\tilde{U}_2(\lambda,\vec{x}_i) + \\ + \sum_{n=3}^{\infty} \frac{\lambda^n}{(n-1)!} \sum_{1\ldots n} \langle\vec{u}_1\ldots\vec{u}_n\rangle^c_\lambda \nabla_1\ldots\nabla_n\, \tilde{U}_1(\lambda,\vec{x}_i)\}$$

where the first term is due to the second order correction to the renormalized pseudoharmonic matrix $\hat{\Phi}^{(2)}_{ij}(\lambda)$ as in /3.27/. The λ-dependent function $\langle\vec{u}_1\ldots\vec{u}_n\rangle^c_\lambda$, $\Delta\tilde{U}_2(\lambda,\vec{x}_i)$ and $\tilde{U}_1(\lambda,\vec{x}_i)$ are given by /3.23/, /3.26/, and /3.26a/ respectively with every power of u_i multiplied by λ. After the integration over λ with $\langle\vec{u}_i\vec{u}_j\rangle$, $\langle\vec{u}_i(t)\vec{u}_j\rangle$ being independent of λ, one gets

$$\Delta F_2 = \mathrm{Im} \int_0^\infty dt \sum_{n=3}^{\infty} \frac{1}{n!}\Big(\sum_{ii'} \langle\vec{u}_i(t)\vec{u}_{i'}\rangle\nabla_i\nabla_{i'}\Big)^n \tilde{U}_1(\vec{x}_i)\, \tilde{U}_1(\vec{x}'_i) = \\ = \frac{1}{2}\sum_{n=3}^{\infty}\frac{1}{n!}\sum_{1\ldots n} \langle\vec{u}_1\ldots\vec{u}_n\rangle^c\, \nabla_1\ldots\nabla_n\tilde{U}_1(\vec{x}_i) = \frac{1}{2}\Delta\tilde{U}_2(\vec{x}_i)\ . \qquad /3.30/$$

In the calculation of the first two terms $F_o+\Delta F_1$ in the free energy expansion one should employ /3.19/ with the SC1 frequencies $\omega_{\vec{q}j}$ being replaced by the SC2 frequencies $\Omega_{\vec{q}j}$ defined as the maxima of the imaginary part of the GF in the SC2 approximation according to /2.18/.

The proposed cumulant expansions for the average potential energy /3.26/ and the free energy /3.30/ with the GF /3.11/ and equations /3.22/ - /3.24/ give the same results as other methods based on diagrammatic techniques or on the variational approach proposed by Werthamer [7] /see e.g. [5]/.

4. THE ANHARMONIC LINEAR CHAIN

In the present Section a simple model of the crystals, the anharmonic linear chain with nearest neighbour interaction will be investigated briefly in the first order of the SCPT [22], [23]. In this case we can obtain a simple explicit solution which helps to clarify some aspects of the SCPT.

4.1 The self-consistent system of equations

Let us consider an anharmonic linear chain of length L which consists of N+1 identical atoms with mass M. Taking into account only nearest neighbour interaction, the Hamiltonian in the adiabatic approximation [1] reads:

$$\mathcal{H} = H + H_1 = \sum_{n=o}^{N} \frac{\vec{p}_n^{\,2}}{2M} + \frac{1}{2} \sum_{n=1}^{N} \varphi(R_n - R_{n-1}) + H_1 \quad , \qquad /4.1/$$

where p_n and R_n are the momentum and position operators for the n-th atom. The interaction potential between the neighbouring atoms is denoted by $\varphi(R_n - R_{n-1})$. In the case of a one-dimensional chain the effect of the external forces can be described by the external tension P which acts on the ends of the chain:

$$H_1 = P\,(R_N - R_o) = P \sum_{n=1}^{N} (R_n - R_{n-1}) \; . \qquad /4.2/$$

It is convenient to introduce the equilibrium separation ℓ between the neighbouring atoms and the relative displacement operators by the following definition:

$$R_n - R_{n-1} = \langle R_n - R_{n-1} \rangle + u_n - u_{n-1} \equiv \ell + u_n - u_{n-1} \quad , \qquad /4.3/$$

where the statistical average $\langle \dots \rangle$ is calculated for the equilibrium state of the system described by the Hamiltonian /4.1/:

$$\langle \dots \rangle = \mathrm{Sp}\,\{ e^{-\mathcal{H}/\theta} \dots \} \,/\, \mathrm{Sp}\,\{ e^{-\mathcal{H}/\theta} \} \;\; (\theta = kT) \quad . \qquad /4.4/$$

The equilibrium separation ℓ in the one-dimensional case can be obtained from the equation

$$P = -\frac{1}{2} \left\langle \frac{\partial}{\partial R_n} \varphi(R_n - R_{n-1}) \right\rangle = -\frac{1}{2} \langle \varphi'(\ell) \rangle \quad , \qquad /4.5/$$

which shows that the average force acting on an arbitrary atom in the equilibrium position is equal to zero.

It is convenient to introduce explicitely the displacement operators in the Hamiltonian /4.1/ by the Fourier transformation:

$$\varphi(R) = \sum_q \varphi(q)\, e^{iqR} \; ; \quad \varphi(q) = \frac{1}{L} \int_{-L/2}^{+L/2} dR\, \varphi(R)\, e^{-iqR} \quad . \qquad /4.6/$$

In this representation the Hamiltonian of the linear chain

/4.1/ takes the form:

$$\mathcal{H} = \sum_n \frac{p_n^2}{2M} + \frac{1}{2} \sum_n \sum_q \varphi(q)\, e^{iq\ell}\, e^{iq(u_n - u_{n-1})} + H_1 \quad . \qquad /4.7/$$

For the calculation of the correlation function of nearest neighbours and the frequency of the lattice vibration we apply the method of thermodynamic double-time GF [13] . We use the following one-phonon GF:

$$G_{nn'}(t-t') = \langle\langle u_n(t) \; ; \quad u_{n'}(t') \rangle\rangle = - i\theta(t-t') \langle [\, u_n(t) \; ; \; u_{n'}(t')] \rangle \qquad /4.8/$$

in usual notations [14].

To obtain the equation of motion for the GF /4.8/ we differentiate it twice with respect to time t and employ the equation of motion for the Heisenberg operators $u_n(t)$ and $p_n(t)$. In this manner we get:

$$M\, i^2 \frac{d^2}{dt^2} G_{nn'}(t-t') = \delta(t-t')\, \delta_{nn'} + $$
$$+ \frac{1}{2} \sum_q \varphi(q)\, e^{iq\ell}\, iq \langle\langle \{ e^{iq(u_n - u_{n-1})} - e^{iq(u_{n+1} - u_n)} \}; \quad u_{n'}(t') \rangle\rangle \quad . \qquad /4.9/$$

The multiphonon GF on the r.h.s. of Eq. /4.9/ describes an uncorrelated propagation of phonons in an averaged phonon field. We use the first order or renormalized harmonic approximation of the SCPT here, in which the processes connected with the damping of phonons are not considered, but the renormalization of the energy of phonons in the phonon self-consistent field is taken into account. In this approximation the multiphonon GF can be written in the form:

$$\ll e^{iq(u_n-u_{n-1})} ; u_{n'} \gg = \sum_{s=1}^{\infty} \frac{1}{s!} \ll \{ iq(u_n-u_{n-1})\}^s ; u_{n'} \gg \approx$$

$$\approx \sum_{s=1}^{\infty} \frac{1}{s!} < \{ i q(u_n-u_{n-1})\}^{s-1} > s \ll iq (u_n-u_{n-1}) ; u_{n'} \gg =$$

$$= < e^{iq(u_n-u_{n-1})} > iq \ll (u_n-u_{n-1}) ; u_{n'} \gg . \qquad /4.10/$$

For the calculation of the correlation function on the r.h.s. of Eq. /4.10/ we use the same approximation. We introduce the following function:

$$F(\lambda) = < e^{\lambda q(u_n-u_{n-1})} > ; \quad F(o) = 1 . \qquad /4.11/$$

Differentiating it on λ and using the similar approximations as in Eq. /4.10/ we get:

$$\frac{\partial F(\lambda)}{\partial \lambda} = < q(u_n-u_{n-1}) \; e^{\lambda q(u_n-u_{n-1})} > =$$

$$= < q(u_n-u_{n-1}) \sum_{s=1}^{\infty} \frac{(q\lambda)^s}{s!} (u_n-u_{n-1})^s > \approx$$

$$\approx \lambda \, q^2 < (u_n-u_{n-1})^2 > F(\lambda) . \qquad /4.12/$$

The integration of this equation over λ from $\lambda=o$ to $\lambda=i$ gives us:

$$< e^{iq(u_n-u_{n-1})} > = e^{-\frac{1}{2}q^2 <(u_n-u_{n-1})^2>} = e^{-\frac{1}{2}q^2\overline{u^2}} , \qquad /4.13/$$

where we take into account that the correlation function of nearest neighbour atoms does not depend on n:

$$\overline{u^2} = \langle (u_{n+1}-u_n)^2 \rangle = \langle (u_n-u_{n-1})^2 \rangle \ . \qquad /4.14/$$

Now we introduce the Fourier transform for the GF /4.8/:

$$G_{nn'}(t-t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, e^{-i\omega(t-t')} \, G_{nn'}(\omega) \qquad /4.15/$$

and take into account that it depends only on the difference of lattice sites (n-n'):

$$G_{nn'}(\omega) = \frac{1}{MN} \sum_k e^{ik\ell(n-n')} \, G_k(\omega) \ . \qquad /4.16/$$

Then Eq. /4.9/ takes the form:

$$\omega^2 \, G_k(\omega) = 1 +$$

$$+ \frac{1}{2M} \sum_q \varphi(q) \, e^{iq\ell} (iq)^2 \, e^{-\frac{1}{2}q^2\overline{u^2}} \, 2(1-\cos k\ell) \, G_k(\omega) \ , \qquad /4.17/$$

where Eqs. /4.10/, /4.13/ have been used. The solution of Eq. /4.17/ reads

$$G_k(\omega) = \frac{1}{\omega^2-\omega_k^2} \qquad /4.18/$$

as in the harmonic approximation except for the renormalization of the force constant:

$$\omega_k^2 = \frac{4f(\theta,\ell)}{M} \sin^2 \frac{k\ell}{2} = \frac{f(\theta,\ell)}{f} \, \omega_{ok}^2 \equiv \alpha^2 \, \omega_{ok}^2 \ , \qquad /4.19/$$

where ω_{ok} is the harmonic frequency of vibration and f stands for the harmonic force constant. The renormalized force constant $f(\theta,\ell)$ according to Eq. (13) can be written as:

$$f(\theta,\ell) = \frac{1}{2} \sum_{q} \varphi(q)\, e^{iq\ell} (iq)^2\, e^{-\frac{1}{2}q^2\overline{u^2}} = \frac{1}{2}\, \tilde{\varphi}''(\ell) \quad , \qquad /4.20/$$

where we introduced the self-consistent potential

$$< \varphi(R_n - R_{n-1}) > \approx \tilde{\varphi}(\ell) = \sum_{q} \varphi(q)\, e^{iq\ell}\, e^{-\frac{1}{2}q^2\overline{u^2}} =$$

$$= \sum_{s=0}^{\infty} \frac{1}{s!} \left(\frac{\overline{u^2}}{2} \right)^s \varphi^{(2s)}(\ell) \quad . \qquad /4.21/$$

In obtaining Eq. /4.21/ we decomposed the function $\exp(-\frac{1}{2}\, q^2\overline{u^2})$ into the series of $\overline{u^2}$ and integrated it over q. The self-consistent potential can also be written in the form

$$\tilde{\varphi}(\ell) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, e^{-x^2/2}\, \varphi(\ell + x\sqrt{\overline{u^2}}) \quad , \qquad /4.22/$$

where $x = R/\sqrt{\overline{u^2}}$. It is easy to see that in Eq. /4.22/ the renormalization of the potential due to the vibrations of the atoms is taken into account by averaging it over the small region $R \sim \sqrt{\overline{u^2}} \ll \ell$ with the Gaussian function $\exp(-x^2/2)$ which describes the effect of the phonon self-consistent field. Owing to this function only the shape of the potential $\varphi(R)$ at the bottom of the potential well is of importance.

The correlation function of nearest neighbours in Eqs. /4.21/, /4.22/ can be obtained from the spectral theorem [13] [14] for the GF:

$$< u_{n'} u_n > = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega}{e^{\omega/\theta} - 1} \{ -2 \operatorname{Im} G_{nn'}(\omega + i\delta) \} \quad . \qquad /4.23/$$

From Eq. /4.18/ we get:

$$\overline{u^2} = \langle (u_n - u_{n-1})^2 \rangle = \frac{1}{Nf} \sum_k \frac{\omega_{ok}^2}{2\omega_k} \coth \frac{\omega_k}{2\theta} =$$

$$= \frac{\omega_{ok}}{\pi f} \frac{1}{\alpha} \int_o^{\pi/2} d\varphi \sin\varphi \coth \frac{\alpha \sin\varphi}{2\tau} , \qquad /4.24/$$

where in the second line of Eq. /4.24/ we have replaced the sum over k by an integral over $\varphi = k\ell/2$. The maximum value of the vibrational frequency of the chain in the harmonic approximation is denoted by $\omega_{oL} = (4f/M)^{\frac{1}{2}}$ and $\tau = \theta/\omega_{oL}$ stands for the reduced temperature. In the high temperature $(\tau \gg 1)$ and low temperature $(\tau \ll 1)$ limit the integral in Eq. /4.24/ becomes

$$\frac{\pi f}{\omega_{oL}} \alpha^2 \overline{u^2} = \pi \tau \{ 1 + \frac{1}{24} (\frac{\alpha}{\tau})^2 \} + O(\tau^{-3}) \quad (\tau \gg 1) , \qquad /4.25/$$

$$\frac{\pi f}{\omega_{oL}} \alpha \overline{u^2} = 1 + \frac{\pi^2}{3} (\frac{\tau}{\alpha})^2 + O(\tau^4) \quad (\tau \ll 1) . \qquad /4.26/$$

In addition to the temperature τ the properties of the linear chain are determined also by the length of the chain $L = N\ell$ or by the external tension P . According to Eqs. /4.5/, /4.21/ these parameters satisfy the following equation:

$$P = - \frac{1}{2} \langle \varphi'(R_n - R_{n-1}) \rangle = - \frac{1}{2} \tilde{\varphi}'(\ell) . \qquad /4.27/$$

The internal energy is given in our approximation by the equation

$$\frac{1}{N} E_1 = \frac{1}{N} < H > = < \frac{p_n^2}{2M} > + \frac{1}{2} < \varphi(R_n - R_{n-1}) > =$$

$$= \frac{1}{2N} \sum_k \frac{\omega_k}{2} \coth(\omega_k/2\theta) + \frac{1}{2} \tilde{\varphi}(\ell) =$$

$$= \frac{1}{2} \{ \tilde{\varphi}(\ell) + f(\theta,\ell) \overline{u^2} \} . \qquad /4.28/$$

Then for the free energy of the anharmonic linear chain according to Eq. /3.19/ in our approximation one gets:

$$\frac{1}{N} F_1 = \frac{\theta}{N} \sum_k \ln \{ 2 \sinh(\omega_k/2\theta) \} + \frac{1}{2} \{ \tilde{\varphi}(\ell) - f(\theta,\ell) \overline{u^2} \} . \qquad /4.29/$$

In this way we have a closed system of self-consistent equations /4.19/, /4.20/, /4.21/ or /4.22/, /4.24/, /4.27/, /4.28/, /4.29/ which determine the dynamical, thermodynamical and elastic properties of the anharmonic linear chain in the renormalized harmonic approximation. This self-consistent system of equations is determined by the self-consistent potential /4.21/ or /4.22/, which can be obtained if the form of the interaction potential in the Hamiltonian /4.1/ is known.

4.2 The self-consistent system of equation for the Morse potential

Let us take the Morse potential as a model potential

$$\varphi(R) = D \{ [e^{-a(R-r_o)} - 1]^2 - 1 \} , \qquad /4.30/$$

where r_o is the average distance between the neighbouring atoms in the harmonic approximation: $\varphi'(r_o)=o$ and D is the depth of the potential: $\varphi(r_o) = -D$. The force constant in the harmonic approximation is given by $f = 1/2\ \varphi''(r_o) = D\,a^2$.

Applying the expansion of Eq. /4.21/ or taking the integral of Eq. /4.22/ we get the following expression for the self-consistent potential:

$$\tilde{\varphi}(x) = D\ \{\ e^{-2ar_o x}\ e^{2y} - 2\ e^{-ar_o x}\ e^{y/2}\ \}\ , \qquad /4.31/$$

where $y = a^2\,\overline{u^2} = (a\,r_o)^2\,(\overline{u^2}/r_o^2)$ and $x = (\ell/r_o) - 1$. In Fig. 1.

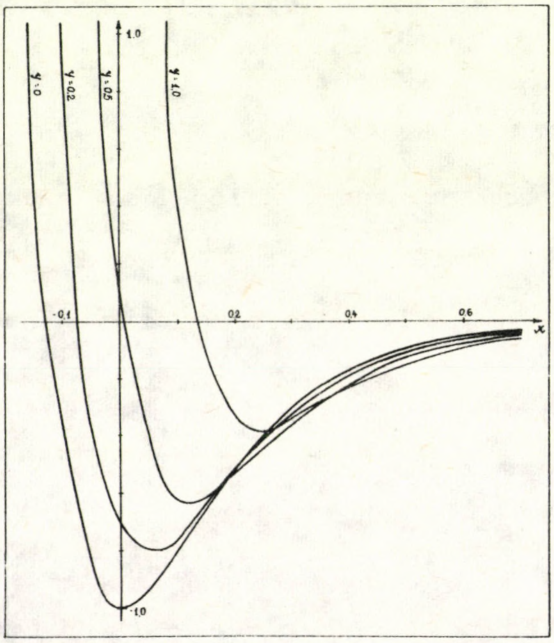

Fig. 1. The self-consistent potential $\tilde{\varphi}(x)/D$

the self-consistent potential $\tilde{\varphi}(x)/D$ is presented for some values of y . Since y depends on the temperature and, as we will see, in the quantum limit on the energy of zero-point vibrations, the larger values of y mean higher temperature or larger energies of the zero-point vibrations. The diagrams of the self-consistent potential in Fig. 1 show the thermal expansion of the crystals and the decrease of the binding energy of lattice atoms when the temperature or the energy of the zero-point vibrations increases. So for larger y values the self-consistent potential sufficiently differs from the interaction potential that means that the behaviour of the crystals differ sufficiently from that calculated in the harmonic approximation.

Eq. /4.5/ for the Morse potential reads:

$$P^* = 4 \{ e^{-2ar_o x} e^{2y} - e^{-ar_o x} e^{y/2} \} , \qquad /4.32/$$

where we introduced the reduced tension $P^* = (4/ar_o)\, P(r_o/D)$. We note, that the introduced reduced tension differs from that used in works [22], [23]. The renormalization factor of the frequency, according to Eqs. /4,19/, /4.20/, for the Morse potential takes the form:

$$\alpha^2(y) = \frac{1}{2} \{ P^* + e^{-y} [1 + \sqrt{1 + P^* e^{y}}] \} . \qquad /4.33/$$

Taking into account /4.31/ we can rewrite Eqs. /4.24/, /4.25/, /4.26/ as equations for y:

$$\lambda\, \alpha(y)\, y = \int_0^{\pi/2} d\varphi \sin\varphi \coth\left(\frac{\alpha \sin\varphi}{2\tau} \right) , \qquad /4.34/$$

$$\alpha^2(y)\; y = T^* \{ 1 + \frac{1}{24} \left(\frac{\pi\alpha}{\lambda T^*} \right)^2 \} \qquad \tau \gg 1 , \qquad /4.35/$$

$$\lambda\alpha(y)\; y = 1 + \frac{\pi^2}{3} \left(\frac{\tau}{\alpha} \right)^2 \qquad \tau \ll 1 . \qquad /4.36/$$

where $\lambda = (\pi D/\omega_{oL})$ is the dimensionless coupling constant and $T^* = \theta/D = \tau\pi/\lambda$ is the reduced temperature.

The expressions for the equilibrium separation of neighbouring atoms ℓ, the internal energy /4.28/ and the free energy /4.29/ in the case of Morse potential can be written as follows

$$\frac{\ell}{r_o} = 1 + \frac{3}{2ar_o}\, y - \frac{1}{ar_o}\, \ell n\, \frac{1}{2} \left\{ 1 + \sqrt{1 + P^* e^y} \right\} , \qquad /4.37/$$

$$\frac{1}{N} E_1 = \frac{D}{4} \left\{ \frac{3P^*}{2} + 2\,\alpha^2\, (y-1) \right\} , \qquad /4.38/$$

$$\frac{1}{N} F_1 = \frac{1}{N} F_o + \frac{D}{4} \left\{ \frac{3P^*}{2} - 2\alpha^2 (y+1) \right\} , \qquad /4.39/$$

where α^2 is given by Eq. /4.33/ and F_o stands for the harmonic free energy $F_o = \theta \sum\limits_k \ell n \{ 2 \sinh(\omega_k/2\theta) \}$.

The system of self-consistent equations /4.32/, /4.33/, /4.34/ determines the properties of the anharmonic linear chain, when λ, τ and P^* or ℓ are given, see Eqs. /4.37/-/4.39/.

Let us now consider the equation /4.34/ in the high temperature limit, Eq. /4.35/. Taking into account only the first term in the r.h.s. of Eq. /4.35/ and using /4.33/ the self-consistent equation can be written as follows

$$F(y) = 1 - \frac{y}{2T^*} \left\{ P^* + e^{-y} \left[1 + \sqrt{1 + P^* e^y} \right] \right\} = o . \qquad /4.40/$$

The dependence of the solution of Eq. /4.40/ on the reduced temperature T^* and reduced tension P^* is given in Fig. 2.

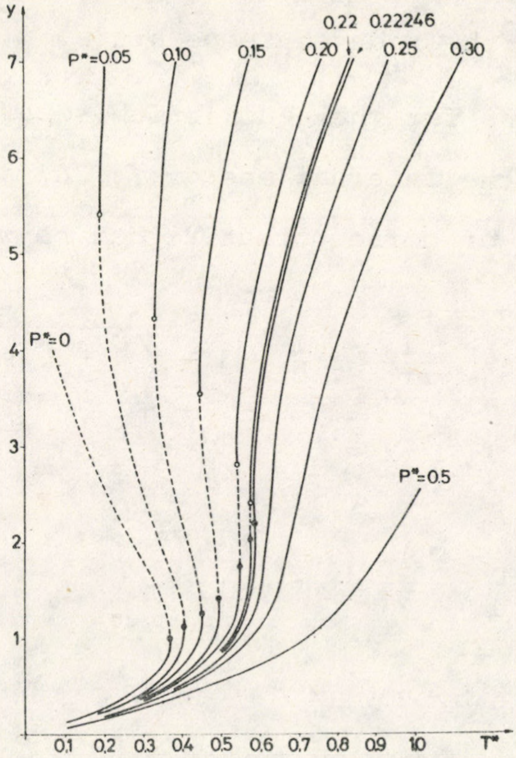

Fig. 2. The real solution of the self-consistent equation for $\tau \gg 1$

At sufficiently low temperature: $T^* < T_C^* = 0{,}578$, and pressure: $P^* < P_C^* = 0{,}222$ there are several real solutions for $y(T)$, the thermodynamically stable ones are shown by the full lines. The lowest line, $y_1(T) \leqslant 1$ corresponds to a crystalline state with small vibrational motions. In the limit of small anharmonicity /or lower temperature/, this solution gives the harmonic correlation function. But as $T^* \to T_s^*(P)$ /denoted by the full dots in Fig. 2./ $y_1(T)$ becomes unstable: $T_s^*(P)$ is the instability temperature. As can be seen from Fig. 2. and from the PV diagram corresponding to Eq. /4.32/ or /4.37/ (for $ar_o=6$), shown in Fig.3.

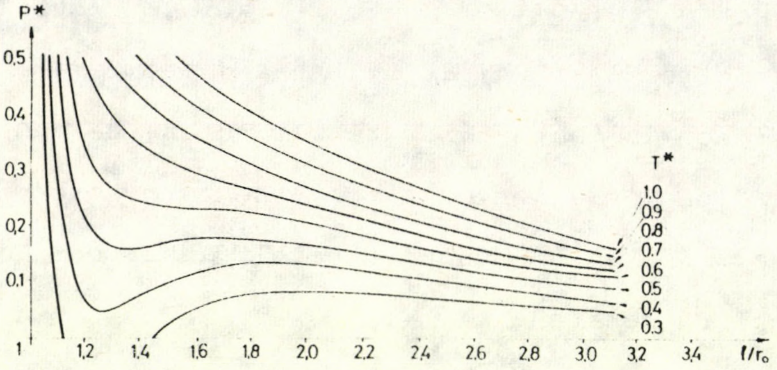

Fig. 3. The PV-diagram of the anharmonic linear chain for $\tau \gg 1$

at $T^* = T_s^*(P)$ there is a first order phase transition that drives the chain from the state with $y = y_1(T)$ to some other state with $y = y_2(T)$, shown by the upper full line in Fig. 2. The latter is also a "crystalline" state /due to the restrictions imposed by the theory/ but the vibrations of the atoms are rather large, $y_2(T)>1$ and are defined by the external pressure:in the limit $P\to o$ the solution $y_2(T)\to\infty$. At sufficiently high pressure $P^*>P_c^*$ or corresponding high temperature, $T^*>T_c^*$ this type of vibrational instability disappears. The two solutions at P_c^* coincide and there is only one stable solution for the correlation function y(T) for $P^*>P_c^*$. Physically it means that the external forces become more efficient than the interatomic ones and the former determine the lattice dynamics: they are strong enough to localize the atomic vibrations.

At low temperatures ($\tau \ll 1$) the solution of the self-consistent equation /4.36/ for the correlation function $y(\lambda,T)$ leads to the same results [24] as in the high temperature limit. The only difference is that at low temperatures the amplitude of atomic vibrations is given mostly by the zero-point energy, proportional to λ^{-1} . As a result, a highly anharmonic chain with small coupling constant $\lambda<\lambda_c=1,207$ can be unstable even at T=OK, the critical value of the tension in this case is $P_c^*=0,037$. In Fig.4. the instability temperature τ_s is presented as a function of

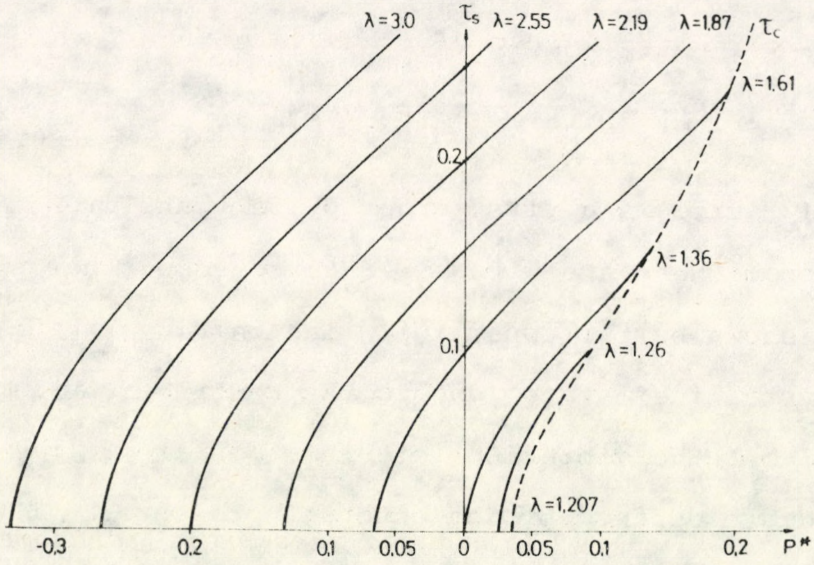

Fig. 4. The dependence of the instability temperature τ_s on the reduced tension P^* for some values of the dimensionless coupling constant λ in the low temperature limit $\tau \ll 1$

reduced tension P^* for some values of λ . The critical curve τ_c is denoted by the dotted line.

The self-consistent equation /4.34/ which is valid in the whole temperature region can be solved only numerically. In Fig. 5. the dependence of the instability temperature τ_s on the reduced tension P^* is shown for some values of λ . The critical curve τ_c is denoted by the dotted line. Using the solutions of

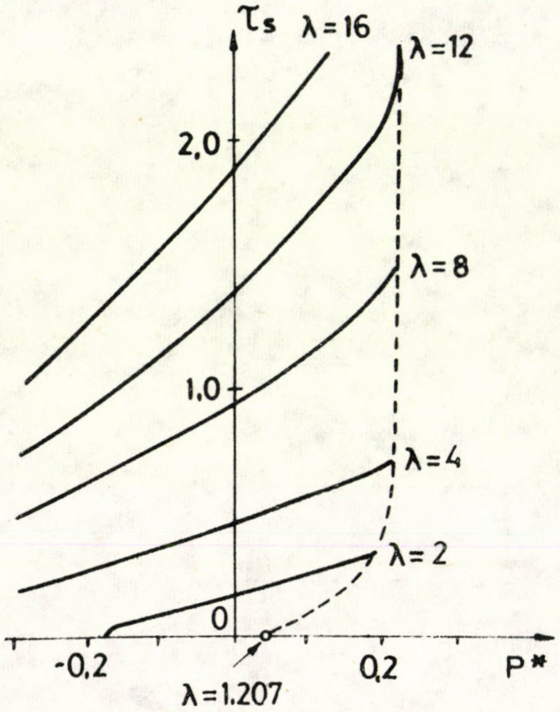

Fig. 5. The dependence of the instability temperature τ_s on the reduced tension P^* for some values of the dimensionless coupling constant λ .

Eq. /4.34/ and Eqs. /4.37/-/4.39/, we can calculate the "physical" properties of the anharmonic linear chain. But it is more interesting to elucidate better the physical meaning of the instability temperature T_s. It was shown, that at sufficiently high pressure $P^* > P_c^*$ the vibrational instability disappears. But the critical value of the tension is rather small even at high temperatures therefore it seems sufficient to investigate the small tension limit $P^* \ll 1$, when the results of the calculations can be presented in analytical form.

5. PROPERTIES OF THE ANHARMONIC LINEAR CHAIN IN THE CASE OF SMALL TENSION

If $P^* \ll 1$ the renormalization factor of the frequency, according to Eqs. /4.19/, /4.20/, /4.33/ takes the form

$$\alpha^2(y) = e^{-y} \{ 1 + \frac{3P^*}{4} e^y \} , \qquad /5.1/$$

and equations /4.35/, /4.36/ using /5.1/ can be rewritten as

$$\frac{D}{\theta} (y - \frac{D}{\theta} \eta) \{ 1 + \frac{3P^*}{4} e^y \} = e^y , \qquad (\tau \gg 1) \qquad /5.2/$$

$$\lambda^2 y^2 = e^y \{ 1 + \lambda^2 y^2 (2\gamma - \frac{3P^*}{4}) \} \qquad (\tau \ll 1) , \qquad /5.3/$$

where $\eta = (\omega_{oL}^2 / 24D^2) \ll 1$ and $\gamma = (\pi^2 \theta^2)/(3\omega_{oL}^2) \ll 1$.
The expressions for the equilibrium separation of neighbouring atoms /4.37/, the internal energy /4.38/ and free energy /4.39/ in the small tension limit can be written as follows ($ar_o = 6$):

$$\ell = r_o \{ 1 + \frac{1}{4} y - \frac{P^*}{24} e^y \} \quad , \qquad /5.4/$$

$$\frac{1}{N} E_1 = - \frac{D}{2} \{ e^{-y} (1-y) - y \frac{3P^*}{4} \} \quad , \qquad /5.5/$$

$$\frac{1}{N} F_1 = \frac{1}{N} F_o - \frac{D}{2} \{ e^{-y} (y+1) + \frac{3P^*}{4} y \} \quad . \qquad /5.6/$$

Let us investigate the high and low temperatures separately.

5.1 High temperature ($\tau \gg 1$) limit

Equation /5.2/ has a real solution only if $\theta \lesssim \theta_s$, where θ_s is the instability temperature. The solution $y_s = y(\theta_s)$ is obtained as the simultaneous solution of Eq. /5.2/ and its derivative. The calculation gives:

$$\theta_s \approx \frac{D}{e} \{ 1 + e [\frac{3P^*}{4} - \frac{1}{24} \frac{\omega_{oL}^2}{D^2}] \} \quad , \qquad /5.7/$$

$$y(\theta \lesssim \theta_s) \approx 1 + e \left(\frac{3P^*}{4} - \eta \right) - \sqrt{2(1-\theta/\theta_s)} \quad . \qquad /5.8/$$

The vibrational frequency ω_k at $\theta \lesssim \theta_s$ is given by

$$\omega_k^2 (\theta \lesssim \theta_s) \approx \frac{\omega_{ok}^2}{2} \{ 1 - e\eta + \sqrt{2(1-\theta/\theta_s)} + (1-\theta/\theta_s) \} \quad . \qquad /5.9/$$

It becomes complex if $\theta > \theta_s$, which shows the instability of the system. It means, that the state of the linear chain, which was stable at $\theta \lesssim \theta_s$ becomes unstable in the temperature region $\theta > \theta_s$.

The length of the chain, the internal energy and also the free energy, which can be obtained from Eqs. /5.4/, /5.5/, /5.6/

respectively remain finite at $\theta \to \theta_s$. But the coefficient of the linear thermal expansion

$$\alpha_T = \frac{k}{L}\frac{\partial L}{\partial \theta} \approx \frac{k}{\ell}\,\frac{3}{2aD}\,\frac{e}{\sqrt{2(1-\theta/\theta_s)}} \quad , \qquad /5.10/$$

and the specific heat at constant pressure

$$c_p = \frac{k}{N}\left[\frac{\partial}{\partial\theta}\left(E + \frac{DaP^*}{4}L\right)\right]_{P^*=\mathrm{const}} = k\left\{1 + \frac{0{,}3}{\sqrt{1-\theta/\theta_s}}\right\} \qquad /5.11/$$

tend to infinity if $\theta \to \theta_s$. It should be emphasized that the relative displacement of the atoms at the instability point is rather small:

$$\frac{\sqrt{\overline{u_s^2}}}{\ell_s} = \frac{\sqrt{y(\theta_s)}}{a\ell(\theta_s)} = \frac{1}{a\,r_o + \frac{3}{2}} \approx 0{,}13 \quad (ar_o=6) \ . \qquad /5.12/$$

In the range of temperatures where $\omega_{oL} \ll \theta \ll D$ the solution of Eq. /5.2/ has the following form:

$$y = \frac{\theta}{D}\left\{1 + \frac{\theta}{D} + \frac{1}{24}\,\frac{\omega_{oL}^2}{\theta^2}\left(1 + \frac{\theta}{D}\right) - \frac{3P^*}{4}\right\} \ . \qquad /5.13/$$

In this case the renormalized frequency ω_k , the equilibrium separation of the neighbouring atoms ℓ, the linear thermal expression α_T , the internal energy $(1/N)E$, and the specific heat at constant pressure c_p are given by the following formulae

$$\omega_k^2 = \omega_{ok}^2\left\{1 + \frac{3P^*}{4} - \frac{\theta}{D}\left[1 + \frac{1}{2}\,\frac{\theta}{D} + \frac{1}{24}\,\frac{\omega_{oL}^2}{\theta^2} - \frac{3P^*}{4}\right]\right\} , \qquad /5.14/$$

$$\ell = r_o\left\{1 - \frac{P^*}{24} + \frac{1}{4}\,\frac{\theta}{D}\left[1 + \frac{1}{24}\,\frac{\omega_{oL}^2}{\theta^2} + \frac{\theta}{D} - \frac{11}{12}\,P^*\right]\right\} , \qquad /5.15/$$

$$\alpha_T = \frac{k}{\ell}\,\frac{r_o}{4D}\,\{\, 1 + 2\,\frac{\theta}{D} - \frac{1}{24}\,\frac{\omega_{oL}^2}{\theta^2} - \frac{11}{12}\,P^* \,\} \qquad /5.16/$$

$$\frac{1}{N}\,E = -\,\frac{D}{2} + \theta\{\, 1 + \frac{1}{4}\,\frac{\theta}{D} + \frac{1}{24}\,\frac{\omega_{oL}^2}{\theta^2} - \frac{3P^*}{8}\,(1 + 2\,\frac{\theta}{D})\,\}\,, \qquad /5.17/$$

$$c_p = k\,\{1 - \frac{1}{24}\,\frac{\omega_{oL}^2}{\theta^2} + \frac{1}{2}\,\frac{\theta}{D}\,(1 + \frac{3}{2}\,P^*)\,\}\,. \qquad /5.18/$$

The coefficient of the linear thermal expansion, Eq. /5.16/ and also the average of the quadratic displacement, Eq. /5.13/ coincide with the result obtained in [25] using the regular perturbation theory, but the higher orders terms in the expression of the specific heat at constant pressure do not coincide with the result obtained in [25] because in the renormalized harmonic approximation all the odd terms thus e.g. the cubic term in the anharmonic interaction are missing.

5.2 Low temperature ($\tau << 1$) limit

Equation /5.3/ has a real solution for $y>o$ in the range where $\lambda>\lambda_o$ and $\theta<\theta_s$. These parameters defined previously in the case of high temperatures are now:

$$\theta_s = \frac{\omega_{oL}}{\pi e}\,\sqrt{\frac{6}{e}\,(\lambda-\lambda_o)} \quad ; \qquad \lambda_o = \frac{e}{2}\,\{\,1 - \frac{3}{2}\,(\frac{e}{2})^2\,P^*\,\}\,. \qquad /5.19/$$

The solution of Eq. /5.3/ at $\theta\leq\theta_s$ is given by

$$y(\theta\lesssim\theta_s) = 2\,\{\,1 + \frac{3e^2}{4}\,P^* - \frac{4}{e}\,(\lambda-\lambda_o) - \sqrt{\frac{4}{e}\,(\lambda-\lambda_o)(1-\theta^2/\theta_s^2)}\,\,[1 - \frac{8}{e}\,(\lambda-\lambda_o)\,] + \frac{4}{e}\,(\lambda-\lambda_o)(1-\theta^2/\theta_s^2\,)\,\}\,. \qquad /5.20/$$

The renormalized frequency ω_k near the instability point can be expressed as

$$\omega_k^2 = \left(\frac{\omega_{0k}}{e} \right)^2 \left\{ 1 - \frac{3e^2}{4} P^* + \frac{8}{e} (\lambda-\lambda_0) + \frac{4}{\sqrt{e}} \sqrt{(\lambda-\lambda_0)(1-\theta^2/\theta_s^2)} \right\} . \qquad /5.21/$$

The frequency becomes complex if $\lambda<\lambda_0$ or $\theta>\theta_s$ which shows the instability of the system. It is worth-while to emphasize, that the chain becomes unstable even at zero temperature T=0K if the zero-point energy is sufficiently high $(\omega_{0L}/2\pi) > (D/e)$. Such a situation can occur for a chain of light atoms with small binding energy /"quantum chain"/.

In the vicinity of the instability temperature $\theta \lesssim \theta_s$ the length of the chain, the internal energy and also the free energy, which can be obtained from Eqs. /5.4/, /5.5/, /5.6/ respectively, using solution /5.20/, remain finite. But the coefficient of the linear thermal expansion

$$\alpha_T = \frac{k}{a\ell} \; \frac{\theta}{\omega_{0L}^2} \; \frac{12\pi^2}{\sqrt{(\lambda-\lambda_0)(1-\theta^2/\theta_s^2)}} \quad , \qquad /5.22/$$

and the specific heat at constant pressure

$$c_p = k \frac{2\pi}{3} \; \frac{3\,\theta}{\omega_{0L}} \; \left\{ 1 + 2 \sqrt{\frac{\lambda-\lambda_0}{1-\theta^2/\theta_s^2}} \right\} \qquad /5.23/$$

tend to infinity if $\theta \to \theta_s$. The relative displacement of the atoms at the instability point in the low temperature limit is also rather small

$$\frac{\sqrt{\overline{u_s^2}}}{\ell_s} = \frac{\sqrt{y(\theta_s)}}{a\ell(\theta_s)} = \frac{\sqrt{2}}{ar_0+3} \approx 0{,}13 \quad (a\, r_0 = 6) . \qquad /5.24/$$

For $\lambda \gg 1$ the solution of Eq. /5.3/ has the following form:

$$y = \frac{1}{\lambda} \{ 1 + \frac{1}{2\lambda} + \gamma (1 + \frac{2}{\lambda}) - \frac{3P^*}{8} (1 + \frac{2}{\lambda}) \} , \qquad /5.25/$$

from which we see, that $y \ll 1$.

Using this solution the renormalized frequency ω_k, the equilibrium separation of the neighbouring atoms ℓ, the linear thermal expansion α_T , the internal energy $(1/N)E$, and the specific heat at constant pressure c_p can be written as

$$\omega_k^2 = \omega_{ok}^2 \{ 1 + \frac{P^*}{3} - \frac{1}{\lambda} (1 + \gamma - \frac{3}{2} P^*) \} , \qquad /5.26/$$

$$\ell = r_o \{ 1 - \frac{P^*}{54} + \frac{1}{4} \frac{\omega_{oL}}{\pi D} [1 + \frac{\omega_{oL}}{2\pi D} + \frac{\pi^2}{3} \frac{\theta^2}{\omega_{oL}^2} (1 + \frac{2\omega_{oL}}{\pi D}) - \frac{13}{24} P^* \} , \qquad /5.27/$$

$$\alpha_T = \frac{kr_o}{6\ \ell} \frac{\theta}{\omega_{oL}} \frac{\pi}{D} (1 + \frac{2\omega_{oL}}{\pi D}) , \qquad /5.28/$$

$$\frac{1}{N} E = - \frac{D}{2} + \frac{\omega_{oL}}{\pi} \{ 1 - \frac{1}{4} \frac{\omega_{oL}}{\pi D} + \frac{\pi^2 \theta^2}{3\ \omega_{oL}^2} (1 + 2 \frac{\omega_{oL}}{\pi D}) \} , \qquad /5.29/$$

$$c_p = k \frac{2\pi}{3} \frac{\theta}{\omega_{oL}} \{ 1 + 2 \frac{\omega_{oL}}{\pi D} \} , \qquad /5.30/$$

The expressions /5.26/-/5.30/ characterize the behaviour of a weakly anharmonic linear chain in the low temperature limit. Using the ordinary perturbation theory this expressions can be obtained.

6. CONCLUSIONS

The SCPT reviewed shortly in Section 3 can be used for investigating the properties of strongly anharmonic crystals in a wide range of temperature and external pressure. It is obvious also that in the limit of weak anharmonicity the SCPT gives the same results as the usual perturbation theory. It is interesting to point out that the method of double-time thermodynamic Green's function in the SCPT appears to be more simple and effective in the derivation of the main results in comparison with the other methods, cited in Section 1. We think, that the investigation of a simple model, the anharmonic linear chain with nearest neighbour central force interaction in the first order of SCPT, given in the Sections 4 and 5 has confirmed our opinion. This simple model was investigated also in the second order of SCPT [26]. The results obtained in the second order coincidence with those of the renormalized harmonic approximation except for numerical coefficients, which are somewhat different. In second order the instability temperature becomes smaller and the dimensionless coupling constant becomes higher than in the first order of SCPT.

This variant of the SCPT was applied for the investigation of a simple model of three-dimensional anharmonic crystals too /see [12] and references quoted therein/. It is worth-while to point out also several applications of the SCPT to more complicated systems, where the interaction of lattice vibrations with other subsystems plays on essential role in the lattice instability, e.g. in the electron-phonon system of metals and semiconductors, magnetic systems with spin-phonon interaction, molecular crystals with rotational degrees of freedom, ferroelectric crystals, etc.

ACKNOWLEDGEMENT

The author wishes to thank the Institute for Physics, University of Lodz for the hospitality.

REFERENCES

[1] M. Born, K. Huang, Dynamical Theory of Crystal Lattices, Oxford Univ. Press /Clarendon/, New-York and London, 1954.

[2] A.A. Maradudin, E.W. Montroll, G.H. Weiss, I.P. Ipatova, Solid State Physics, Supplement 3, second ed., Theory of Lattice Dynamics in the Harmonic Approximation, Academic Press, New-York and London, 1971.

[3] G. Leibfried, in Handbuch der Physik, edited by S. Flügge, 2-nd ed. Vol. 7., part 1., p. 104, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1955.

[4] G. Leibfried, W. Ludwig, in Solid State Physics, edited by F. Seitz and D.Turnbull, Vol. 12., p. 275, Academic Press, New-York and London, 1961.

[5] G.K. Horton, Rare Gas Solids - A Century of Excitement and Progress, in Rare Gas Solids, edited by M.L. Klein and J.A. Venables, Vol. 1. Chap. 1., p. 1, Academic Press,London-New-York-San Francisco, 1976.

[6] M.Born, in Festschrift zur Feier des zweihundertjährigen Bestehens der Academie der Wissenschaften in Göttingen: I. Matematisch-physikalische Klasse, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1951.

[7] N.R. Werthamer, Am. J. Phys., 37, 763, 1969.
Phys. Rev., B1, 572, 1970.

[8] Ph. F. Choquard, The Anharmonic Crystals, W.A. Benjamin Inc., New-York, 1967.

[9] N.M. Plakida, T. Siklós, Acta Phys. Hung. 25, 17, 1968.

[10] N.M. Plakida, T. Siklós, phys. stat. sol. 33, 103, 1969.

[11] N.M. Plakida, Teor. i Mat. Fiz., 12, 135, 1972.

[12] N.M. Plakida, T. Siklós, Acta Phys. Hung. 45, 37, 1978.

[13] N.N. Bogoliubov, S.V. Tyablikov, Dokl. Akad. Nauk SSSR, 126, 53, 1959.

[14] D.N. Zubarev, Sov. Phys.-Uspekhi 3, 320, 1960;
Non-equilibrium Statistical Mechanics, §. 16., Plenum Press, New-York, 1974.

[15] W. Götze, K.H. Michel, Z. Phys. 217, 170, 1968.

[16] A.A. Abrikosov, L.P. Gorkov, I.E. Dzyaloshinski, Methods of Quantum Field Theory in Statistical Physics, Prentice-Hall, Inc., Englewood Cliffs, New-York, 1963.

[17] L.J. Sham, Phys. Rev., 139, A 1189, 1965.

[18] N.M. Plakida, Theor. i mat. fiz. 5, 147, 1970.

[19] N.M. Plakida, Theor. i mat. fiz. 12, 135, 1972.

[20] H.R. Glyde, M.L. Klein, Critical Review in Solid St. Sc. 2, 181, 1971.

[21] H. Horner, Strongly Anharmonic Crystals with Hard Core Interaction, in Dynamical Properties of Solids, edited by G.K. Horton and A.A. Maradudin, Vol. 1., Ch. 8., p. 451, North-Holland Publ. Comp. Amsterdam, 1974.

[22] N.M. Plakida, T. Siklós, Phys. Lett. 26A, 342, 1968. Acta Phys. Hung. 26, 387, 1969.

[23] T. Siklós, Acta Phys. Hung., 30, 181, 1971.

[24] T. Siklós, Acta Phys. Hung., 30, 301, 1971.

[25] J.S. Dugdale, D.K. MacDonald, Phys. Rev. 96, 57, 1954.

[26] N.M. Plakida, T. Siklós, phys. stat. sol. 33, 113, 1969.

Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Kroó Norbert
Szakmai lektor: Sólyom Jenő
Nyelvi lektor: Sólyom Jenő
Példányszám: 490 Törzsszám: 81-351
Készült a KFKI sokszorositó üzemében
Felelős vezető: Nagy Károly
Budapest, 1981. junius hó