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MANY-PARTICLE THEORY OF INTERACTING
PHONONS IN A CRYSTAL

A Series of Lectures Given by
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MANY-PARTICLE THEORY OF INTERACTING PHONONS IN A CRYSTAL

by

J. J. J. Kokkedee

CHAPTER I INTRODUCTION

In this report (notes of a series of lectures given at Argonne National Laboratory) we discuss several problems concerning effects of phonon-phonon interactions in an ideal, insulating crystal, using many-particle perturbation theory and diagram techniques.

As is well-known, in the so-called harmonic approximation, in which the crystal potential energy is expanded up to quadratic terms in the displacements of the atoms from their equilibrium positions, the quantum-mechanical, vibrating crystal can be described in terms of noninteracting phonons (quanta of vibrational energy). Terms of higher order in the expansion of the potential energy (the anharmonic terms) give rise to a coupling between the phonons, which for temperatures well below the melting point is small enough to be regarded as a perturbation, whose effects can be investigated by means of perturbation theory. These phonon-phonon interactions are essential for the understanding of a number of important physical effects, such as thermal expansion, thermal resistance, and broadening and displacement of the one-phonon peaks in the neutron scattering spectrum.

There are several reasons why standard perturbation theory is inadequate for treating the interaction effects in a many-particle system such as the system of interacting phonons in a crystal. They are discussed in detail by Van Hove (see the introduction to his MIT lectures, Ref. 3) and will not be repeated here. More systematic perturbation methods are required for treating large quantum systems. These methods, developed in the past five or six years, are largely inspired by the techniques of quantum field theory.

We will apply these methods to a calculation of phonon interaction effects in a nonconducting crystal,⁽¹³⁾ when the crystal is in equilibrium at an arbitrary temperature T (but, of course, below the melting point). The problems which will be treated are the free energy, thermal averages, correlation functions, scattering of thermal neutrons, the one-phonon Green function, self-energy and lifetime of phonons and, very briefly,

lattice thermal conductivity. Typical ground-state properties will not be discussed, because they are extensively dealt with in the lectures of Van Hove.⁽³⁾ In some respects the work reported here is an extension to finite temperatures of the work of Van Hove.

In our considerations, diagrams will play a central role. Especially useful for the treatment of problems at nonzero temperatures is the concept of "diagrams on a cylinder," introduced by Bloch and de Dominicis⁽¹⁾ in the calculation of the free energy of a many-particle system. It turns out that these "diagrams on a cylinder" are also very suited for treating problems involving a time variable, such as the correlation function $\langle Q_1(t_1)Q_2(t_2) \rangle_T$.

We finally remark that the theory described here for nonconducting crystals only can be extended to conducting crystals to include the interaction between phonons and conduction electrons.⁽¹⁴⁾

CHAPTER II

THE HAMILTONIAN OF THE PHONON FIELD

Consider a finite, perfect, nonconducting crystal of volume Ω , containing N_0 unit cells. Let $\vec{r}_{sn}$ designate the positions of the atoms in the crystal. Each vector $\vec{r}_{sn}$ is the sum of an equilibrium position vector $\vec{s} + \vec{R}_{0n}$ and a displacement vector $\vec{u}_{sn}$:

$$\vec{r}_{sn} = \vec{s} + \vec{R}_{0n} + \vec{u}_{sn} \quad , \quad (1)$$

where $\vec{s}$ is a crystal translation vector and $\vec{R}_{0n}$ the equilibrium position vector of atom n in the unit cell containing the origin; n runs from 1 to n_0 , the number of atoms per unit cell.*

The Hamiltonian of the crystal consists of two parts: the kinetic energy of the atoms, and a potential energy term which depends on the positions $\vec{r}_{sn}$ of the vibrating atoms. We assume that the atomic electrons follow the nuclear motions adiabatically. Expanding the potential energy in powers of the atomic displacements $\vec{u}_{sn}$ from the equilibrium positions (see below), we can write the Hamiltonian as follows:

$$H = H^{(2)} + V \quad (2)$$

with

$$H^{(2)} = \epsilon_0 + \frac{1}{2} \sum_{\vec{s}n} M_n |\dot{\vec{u}}_{sn}|^2 + \sum_{\substack{\vec{s}\vec{s}' \\ n n' \\ \alpha \alpha'}} C_{ss',nn'\alpha\alpha'}^{(2)} u_{sn\alpha} u_{s'n'\alpha'} \quad (3)$$

$$V = \sum_{\nu=3}^{\infty} V^{(\nu)} \quad ;$$

$$V^{(\nu)} = \sum_{\vec{s}_1 \dots \vec{s}_\nu, n_1 \dots n_\nu, \alpha_1 \dots \alpha_\nu} C_{s_1 n_1 \alpha_1 \dots s_\nu n_\nu \alpha_\nu}^{(\nu)} u_{s_1 n_1 \alpha_1} \dots u_{s_\nu n_\nu \alpha_\nu} \quad , \quad (4)$$

where $\alpha_i = x, y, z$.

The harmonic energy $H^{(2)}$ includes all terms through second order in products of the displacements; the anharmonic energy V includes all terms of higher order. The coefficients $C_{\dots}^{(\nu)}$ are proportional to a ν^{th} -order derivative of the potential energy, evaluated for the equilibrium lattice at the temperature under consideration, thus including the effects of thermal expansion (compare the remarks at the end of this chapter).

*An arrow over a letter, which designates a vector, is omitted when the letter appears as a subscript.

The solution of the harmonic problem, in which V in Eq. (2) is put equal to zero, is well known.^(2,3) It gives a description of the quantum-mechanical vibrating crystal in terms of noninteracting phonons. Each phonon is characterized by a wave vector $\vec{q}$, a polarization index j , and a well-defined frequency ω_{qj} , satisfying

$$\omega_{-qj} = \omega_{qj} \quad ; \quad (5)$$

$$\omega_{qj} = \omega_q + 2\pi\tau_{,j} \quad , \quad (6)$$

where $\vec{\tau}$ is a vector of the reciprocal lattice. The vector $\vec{q}$ is only defined up to the addition of a vector $2\pi\vec{\tau}$. Summations over $\vec{q}$ are restricted to the first Brillouin zone. The polarization index j runs over all positive integers from 1 to $3n_0$, so there are $3n_0$ frequency functions ω_{qj} , which for each j can be considered as continuous functions of $\vec{q}$ (at least in the limit of an infinite crystal). Three of these functions become proportional to q as q approaches zero (acoustic phonons); the remaining $3(n_0 - 1)$ functions approach nonzero values as q approaches zero (optical phonons).

The excited states (phonon states) $|\vec{q}j, \vec{q}'j', \vec{q}''j'', \dots\rangle$ of the harmonic Hamiltonian will be defined by the following equation, which at the same time fixes the normalizing constants:

$$|\vec{q}j, \vec{q}'j', \vec{q}''j'', \dots\rangle = A_{qj}^* A_{q'j'}^* A_{q''j''}^* \dots |o\rangle \quad . \quad (7)$$

Here $|o\rangle$ designates the vacuum (no phonon) state, defined by $A_{qj}|o\rangle = 0$ for all $\vec{q}j$. We have introduced the creation and absorption operators A_{qj}^* and A_{qj} for the phonon $\vec{q}j$. They obey the usual commutation rules for bosons:

$$[A_{qj}, A_{q'j'}^*] = \delta_{jj'} \Delta(\vec{q} - \vec{q}') \quad (8)$$

in which $\Delta(\vec{q})$ is defined as follows:

$$\Delta(\vec{q}) = \frac{\Omega}{8\pi^3} \sum_{\vec{\tau}} \delta_{\vec{q}, 2\pi\vec{\tau}} \xrightarrow{\Omega \rightarrow \infty} \sum_{\vec{\tau}} \delta(\vec{q} + 2\pi\vec{\tau}) \quad . \quad (9)$$

It is nonzero only if $\vec{q}$ is equal to any vector $2\pi\vec{\tau}$ (including $\vec{\tau} = 0$). Note that $\Delta(o) = \Omega/8\pi^3$, the density of wave vectors in q -space.

From (7) and (8) it follows that the effect of an absorption operator acting on a phonon state is expressed by the following equation:

$$A_{qj}|\alpha\rangle = n_{qj}\Delta(o)|\beta\rangle \quad , \quad (10)$$

where $|\alpha\rangle$ contains n_{qj} phonons $\vec{q}j$ and where $|\beta\rangle$ has one phonon $\vec{q}j$ less than $|\alpha\rangle$ but otherwise is the same.

The displacement vector $\vec{u}_{sn}$ of the atom of type n can be written in terms of creation and absorption operators as follows:

$$\vec{u}_{sn} = \left(\frac{v_0}{16\pi^3 M_n} \right)^{1/2} \sum_j \int_{\vec{q}} \omega_{qj}^{-1/2} \vec{e}_{qj}^{(n)} [A_{qj} + A_{qj}^*] e^{i\vec{q} \cdot \vec{s}} \quad (11)$$

In this equation $\vec{e}_{qj}^{(n)}$ is a complex vector coefficient determining the phase and polarization of the wave $\vec{q}_j$, which obeys the following relations (the asterisk denotes complex conjugate):

$$e_{qj}^{(n)} = e_{q+2\pi\tau, j}^{(n)} \quad ; \quad e_{qj}^{(n)} = e_{-qj}^{(n)*} \quad ; \quad \sum_n e_{qj}^{(n)} \cdot e_{qj'}^{(n)*} = \delta_{jj'} \quad (12)$$

Furthermore, $v_0 = \Omega/N_0$ is the volume of the unit cell. The symbol $\int_{\vec{q}}$ stands for $(\Omega/8\pi^3)^{-1} \sum_{\vec{q}}$, which becomes $\int d\vec{q}$ in the limit of an infinite crystal ($\Omega \rightarrow \infty$).

The expectation value of the ν^{th} -order term $V^{(\nu)}$ in (3) and (4) is of the order $\omega(u/d)^{\nu-2}$ ($\nu = 2, 3, 4, \dots$), ω being a characteristic frequency, u being an average atomic displacement at temperature T , and d being the lattice constant.⁽⁴⁾ At temperatures well below the melting point, u/d is much smaller than 1. The terms $V^{(\nu)}$ then decrease rapidly with increasing order, and V itself can be considered as a small term in the Hamiltonian H . Under these circumstances the notion of phonons remains meaningful and V can be regarded as causing an interaction between the phonons. The effect of this interaction can be investigated by means of perturbation theory, the relative strength of the perturbation being measured by the parameter u/d . In the following we shall use this parameter to classify the various quantities as to order of magnitude. For temperatures well below the melting point the anharmonic crystal may thus be viewed as a gas of interacting phonons. Since the number of phonons is of the order of the number of atoms in the lattice, it is essentially a many-body system, in particular, it is a many-boson system.

We can express V in the creation and absorption operators A_{qj}^* and A_{qj} by substituting (11) into (4). The total Hamiltonian finally takes the following form:

$$H = \epsilon_0 + \epsilon_{zp} + H_0 + V \quad (13)$$

Here ϵ_0 and ϵ_{zp} are the rigid lattice energy and zero-point energy, respectively, and H_0 and V are given by the following equations (we have put $\hbar$ equal to 1):

$$H_0 = \sum_j \int_{\vec{q}} \omega_{qj} A_{qj}^* A_{qj} \quad ; \quad (14)$$

$$V = \sum_{\nu=3}^{\infty} V^{(\nu)} \quad , \quad (15)$$

with

$$V^{(\nu)} = \sum_{j_1 \dots j_\nu} \int_{\vec{q}_1 \dots \vec{q}_\nu} B_{q_1 j_1 \dots q_\nu j_\nu}^{(\nu)} [A_{q_1 j_1} + A_{q_1 j_1}^*] \dots [A_{q_\nu j_\nu} + A_{q_\nu j_\nu}^*] \Delta(\vec{q}_1 + \dots + \vec{q}_\nu) \quad . \quad (16)$$

The coefficients $B_{\dots}^{(\nu)}$ are given by the following expression:

$$B_{q_1 j_1 \dots q_\nu j_\nu}^{(\nu)} = \left(\frac{v_0}{8\pi^3} \right)^{\frac{\nu}{2} - 1} \frac{1}{(\omega_{q_1 j_1} \dots \omega_{q_\nu j_\nu})^{1/2}} \sum_{\vec{s}_2 \dots \vec{s}_\nu} \sum_{\alpha_1 \dots \alpha_\nu} \sum_{n_1 \dots n_\nu} C_{s_1 - s_2, s_1 - s_3, \dots, s_1 - s_\nu, n_1 \dots n_\nu, \alpha_1 \dots \alpha_\nu}^{(\nu)} \frac{1}{(2M_{n_1} \dots 2M_{n_\nu})^{1/2}} e_{q_1 j_1 \alpha_1}^{(n_1)} \dots e_{q_\nu j_\nu \alpha_\nu}^{(n_\nu)} \exp [i\vec{q}_2 \cdot (\vec{s}_2 - \vec{s}_1) + \dots + i\vec{q}_\nu \cdot (\vec{s}_\nu - \vec{s}_1)] \quad . \quad (17)$$

The coefficients $C_{\dots}^{(\nu)}$ only depend on $\vec{s}_1, \vec{s}_2, \dots, \vec{s}_\nu$ through the separation vectors $\vec{s}_1 - \vec{s}_2, \vec{s}_1 - \vec{s}_3, \dots, \vec{s}_1 - \vec{s}_\nu$ due to the invariance of the Hamiltonian with respect to translations generated by the crystal translation vector $\vec{s}$.^{*} Because of this the summation over $\vec{s}_1$ can be performed, giving rise to the Δ -function in Eq. (16), when we bear in mind the relation

$$\frac{v_0}{8\pi^3} \sum_{\vec{s}} e^{i\vec{q} \cdot \vec{s}} = \Delta(\vec{q}) \quad . \quad (18)$$

The factor $(\omega_{q_1 j_1} \dots \omega_{q_\nu j_\nu})^{-1/2}$ occurring in (17) can become infinite when one of the $\omega_{q_i j_i}$ becomes zero, that is, when $\omega_{q_i j_i}$ corresponds to an acoustical mode with $\vec{q} = o(\text{mod } 2\pi \vec{\tau})$. However, this situation corresponds to a pure translation of the lattice as a whole, which can be excluded explicitly. The coefficient $B_{\dots}^{(\nu)}$ then turns out to be a finite quantity which is, at least for a large crystal, independent of the size of the crystal. From (17) we immediately see that

$$B_{q_1 j_1 \dots q_\nu j_\nu}^{(\nu)} = B_{-q_1 j_1 \dots, -q_\nu j_\nu}^{(\nu)*} \quad . \quad (19)$$

^{*}Other symmetry properties of the coefficients $C_{\dots}^{(\nu)}$ are discussed in detail in a review by Leibfried and Ludwig.⁽⁵⁾

Note that the coefficients $B^{(\nu)}$ (including $\nu = 0$, that is, ϵ_0 ; and $\nu = 2$) and therefore the harmonic frequencies $\omega_{\mathbf{q}\mathbf{j}}$ for given $\vec{\mathbf{q}}\mathbf{j}$ are different for different temperatures, because the lattice constants, i.e., the equilibrium positions upon which these quantities depend, vary with temperature (thermal expansion). One can in principle determine the lattice constants by calculating the free energy F_β (see the next chapter) considering the lattice constants as variable parameters and for each temperature minimizing F_β with respect to these parameters. At each temperature we must expand the potential energy in powers of the displacements of the atoms from these new equilibrium positions and the expansion coefficients must be evaluated for these positions. For lattices in which each atom is a center of inversion symmetry (and in the following we will deal only with this type of lattice), the linear term in this expansion then always vanishes.⁽⁵⁾ It will be clear that by making the expansion of the Hamiltonian in this way, starting from a homogeneously expanded lattice, part of the anharmonic effects is already contained in the unperturbed "harmonic" frequencies $\omega_{\mathbf{q}\mathbf{j}}$.

We see from (16) that the ν^{th} -order term $V^{(\nu)}$ is given by a linear combination of products of ν creation and absorption operators, which, when operating on a phonon state, give either another phonon state or zero. Because of the factor $\Delta(\vec{\mathbf{q}}_1 + \dots + \vec{\mathbf{q}}_\nu)$, the new phonon state must have the same total wave vector, modulo $2\pi\vec{\mathbf{T}}$, as the initial one (conservation of pseudo-momentum).

We finally remark that the phonon-phonon interaction potential V , given by Eqs. (15) and (16), does not conserve the number of elementary excitations or phonons.

CHAPTER III

FREE ENERGY OF AN ANHARMONIC CRYSTAL

We will introduce the methods of many-particle perturbation theory by calculating the free energy of an anharmonic crystal. In this chapter we closely follow a treatment by Van Hove.^(3,4) The free energy at temperature T is given by the following equation [$\beta = (k_B T)^{-1}$]:

$$F_\beta = -\frac{1}{\beta} \ln Z(\beta) \quad , \quad (20)$$

where $Z(\beta)$ is the partition function of the system, which itself is defined by the following equation:

$$Z(\beta) = \sum_{\nu} e^{-\beta E_{\nu}} \quad .$$

The summation runs over all states of the system and E_{ν} is the energy of the system in the state ν . The energies E_{ν} are the exact eigenvalues of the total Hamiltonian H [Eq. (13)]. In view of the practical impossibility of evaluating the E_{ν} 's, we express $Z(\beta)$ by means of a "trace":

$$Z(\beta) = \sum_{\nu} e^{-\beta E_{\nu}} = \text{Tr} \{e^{-\beta H}\} \quad , \quad (21)$$

where the trace is given by

$$\text{Tr} A = \sum_n \langle \psi_n | A | \psi_n \rangle \quad . \quad (22)$$

It is required that the ψ_n , which are the exact eigenfunctions of H , form a complete orthonormal set. Since the trace is invariant under unitary transformations, we may write the trace in a representation other than that of the eigenstates $|\psi_n\rangle$. We will use the representation in which H_0 is diagonal, that is, the representation of the phonon states (7). We then have

$$Z(\beta) = e^{-\beta \epsilon_0 - \beta \epsilon_{zp}} Z_\beta \quad , \quad (23)$$

where

$$Z_\beta = \text{Tr} \left\{ e^{-\beta(H_0 + V)} \right\} = \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{j_1 \dots j_N} \int_{\vec{q}_1 \dots \vec{q}_N} \left\langle \vec{q}_N j_N \dots \vec{q}_1 j_1 \left| e^{-\beta(H_0 + V)} \right| \vec{q}_1 j_1 \dots \vec{q}_N j_N \right\rangle \quad . \quad (24)$$

The factor $1/N!$ results from the normalization and from the requirement that each state be counted only once.

In order to calculate the matrix elements on the right-hand side of (24) we need a perturbation expansion in powers of V for the temperature-dependent operator $\exp [-\beta(H_0 + V)]$. This expansion is well known; it is given by the following equation:

$$\begin{aligned}
 e^{-\beta(H_0 + V)} &= e^{-\beta H_0} + \sum_{n=1}^{\infty} (-1)^n \int_0^{\beta} d\beta_n \int_0^{\beta_n} d\beta_{n-1} \\
 &\quad \dots \int_0^{\beta_2} d\beta_1 e^{-(\beta - \beta_n)H_0} V e^{-(\beta_n - \beta_{n-1})H_0} V \\
 &\quad \dots V e^{-\beta_1 H_0} .
 \end{aligned} \tag{25}$$

At this stage it is very useful to introduce diagrams which graphically represent the matrix elements occurring in (24). In recent years diagram techniques have been used very successfully in field theory and many-particle physics. We use the following conventions: each operator V , or rather a term in some $V^{(\nu)}$, being a product of phonon creation and absorption operators, in the matrix element corresponds to a vertex in the diagram. The vertices occur in the same order from right to left as the V 's in the corresponding matrix element. This order is important; it is imposed by the ordered integrations in the expansion (25). A free phonon will be represented by a line. Each line entering a vertex (coming from the right) represents a phonon which will be annihilated at that vertex; each line leaving a vertex (going to the left) represents a phonon which has been created at that vertex. The total number of lines entering or leaving a vertex is equal to the order ν of the $V^{(\nu)}$ which corresponds to that vertex. In each vertex there is conservation of wave vector $[\text{mod } (2\pi\vec{\tau})]$. The operators $\exp [-(\beta_i - \beta_{i-1})H_0]$ act on the intermediate states between the vertices at β_i and β_{i-1} . Each diagram, just as the corresponding matrix element, has to be read from right to left, starting with the state $|\vec{q}_{NjN} \dots \vec{q}_{1j1}\rangle$ and ending with state $\langle \vec{q}_{1j1} \dots \vec{q}_{NjN}|$. The set of initial phonons is identical to the set of final phonons.

A sample diagram contributing to the matrix element in (24) is represented in Fig. 1. It is of third order in V and it corresponds to the

Fig. 1

Sample diagram contributing to Z_{β} ; 1 stands for $\vec{q}_{1j1}$, etc.

case $N = 4$; it contains two vertices corresponding to terms out of $V^{(3)}$, being of the form $A_5^* A_6^* A_1$ and $A_2^* A_5 A_6$, and one vertex corresponding to a term out of $V^{(6)}$, which is of the form $A_4^* A_4 A_7 A_7^* A_8 A_8^*$.

By continuously joining the external lines at the left and right of a diagram (each external line i at the right side onto the external line for the same phonon i at the left side), which is always possible because the set of initial phonons is identical to the set of final phonons, we can consider each diagram as being rolled onto a cylinder. We now define connectedness of a diagram or part of a diagram as connectedness on the cylinder, and call a connected part a component. According to this definition the diagram of Fig. 1 consists of two components, one containing the phonons 1, 2, 3, 5, and 6, the other containing the phonons 4, 7 and 8. Note that a diagram which is disconnected in the plane may be connected on the cylinder (see Fig. 2e).

Fig. 2. Sample diagrams contributing to the trace in (26).

As a further example we now investigate the diagrams involved in the calculation of the following expression, entering the calculation of Z_β :

$$\begin{aligned}
& \text{Tr} \left\{ \int_0^\beta d\beta_2 \int_0^{\beta_2} d\beta_1 e^{-(\beta-\beta_2)H_0} V(3) e^{-(\beta_2-\beta_1)H_0} V(3) e^{-\beta_1 H_0} \right\} = \\
& \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{j_1 \dots j_N} \int_{\vec{q}_1 \dots \vec{q}_N} \left\langle \vec{q}_N j_N \dots \vec{q}_1 j_1 \left| \int_0^\beta d\beta_2 \int_0^{\beta_2} d\beta_1 e^{-(\beta-\beta_2)H_0} \right. \right. \\
& \left. \left. V(3) e^{-(\beta_2-\beta_1)H_0} V(3) e^{-\beta_1 H_0} \right| \vec{q}_1 j_1 \dots \vec{q}_N j_N \right\rangle \quad (26)
\end{aligned}$$

in which the operator in the matrix element comes from the second order term in the expansion of $\exp[-\beta(H_0 + V)]$. In Fig. 2 we have drawn some diagrams which contribute to the matrix elements in (26). In this figure, diagrams a, b, c, d, e, f, k, l, and m are one-component (connected) diagrams. The remaining ones are disconnected: diagrams g and h are two-component diagrams, while diagram i consists of three components.

Let us first consider the one-component diagrams a-f. By examination of these diagrams we notice the following important point. Consider diagram a, which has no external lines ($N=0$). Diagrams b-f can be imagined to be constructed from diagram a by breaking one or more of the internal lines and letting them run around the cylinder an arbitrary number of times before returning them to the other vertex. For instance, in diagrams b, c, and d the internal lines corresponding to phonon 1 have one, two, and three "turns," respectively. Moreover, in diagrams b and c phonon 1 is created at the left vertex and absorbed at the right vertex, in contrast with the situation in diagrams a and d. In diagram e all internal lines are broken, each line having one turn. In diagram f line 1 has two turns, just as line 3. We shall call a diagram having no external lines, such as diagram a, a "basic" diagram and all other diagrams such as b, c, d, e, and f which only differ from a in the occurrence of turns, "related" diagrams belonging to a. There is an infinite number of related diagrams belonging to a certain basic diagram.

It is now straightforward to prove the following theorem: Consider a basic diagram, i.e., a diagram without external lines,* together with its family of all different related diagrams. The total contribution to Z_β of all of these diagrams can be calculated by just calculating the basic diagram but replacing each factor $e^{-\Delta\beta\omega_{q_{ij}i}}$ - being the factor corresponding to the internal phonon line i between the vertices at β_k and β_l with $\Delta\beta = \beta_k - \beta_l$ - by $D_{q_{ij}i}^{(0)}(\Delta\beta)$, the phonon propagator, which is given by

$$D_{q_{ij}i}^{(0)}(\Delta\beta) = \frac{e^{-\Delta\beta\omega_{q_{ij}i}} + e^{-(\beta-\Delta\beta)\omega_{q_{ij}i}}}{1 - e^{-\beta\omega_{q_{ij}i}}} \quad (27)$$

*Note that a basic diagram has at least one vertex.

This theorem holds generally for our diagrams. For a detailed proof compare the lecture notes of Van Hove.^(3,4) The new propagator (27) now explicitly contains a correction for the presence of thermal phonons in the system.

By application of the above theorem, the total contribution to the trace in (26) from all processes characterized by diagram a in Fig. 2 and by its family of related diagrams, which includes diagrams b-f, is now simply

$$F_{\beta}^{(1)} = 6 \cdot \frac{\Omega}{8\pi^3} \sum_{j_1 j_2 j_3} \int_{\vec{q}_1 \vec{q}_2 \vec{q}_3} \left| B_{q_1 j_1, q_2 j_2, q_3 j_3}^{(3)} \right|^2 \Delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3) \cdot \int_0^{\beta} d\beta_2 \int_0^{\beta_2} d\beta_1 D_{q_1 j_1}^{(0)}(\beta_2 - \beta_1) D_{q_2 j_2}^{(0)}(\beta_2 - \beta_1) D_{q_3 j_3}^{(0)}(\beta_2 - \beta_1) . \quad (28)$$

Use has been made of Eqs. (16) and (19). The factor 6 gives the number of inequivalent ways in which the internal lines can be coupled together. According to Eq. (16) two terms $V^{(3)}$ together involve six integrations over wave vectors, only three of which are actually used in (28). The three unused summations give a factor $(\Omega/8\pi^3)^{-3}$. It is canceled exactly by a factor $(\Omega/8\pi^3)^3$ coming from the three annihilations [compare Eq. (10)]. In obtaining (28) we have further used the identity

$$[\Delta(\vec{q})]^2 = \Delta(o)\Delta(\vec{q}) \quad (29)$$

in which $\Delta(o) = \Omega/8\pi^3$. This latter factor gives the volume dependence of expression (28). Except for this factor, $F_{\beta}^{(1)}$ is essentially independent of the size of the crystal in the limit of an infinite crystal.

Another class of contributions to the matrix elements in (26) is represented by the diagrams which can be constructed from the diagrams treated above (diagram a and its family of related diagrams) by adding components consisting of single lines around the cylinder (see Fig. 2 g, h, i). The contributions to Z_{β} of the disconnected diagrams g, h, and i can be written as follows (we imagine the upper components as representing the complete family belonging to a.):

$$g) \quad F_{\beta}^{(1)} \cdot \left(\frac{\Omega}{8\pi^3} \sum_j \int_{\vec{q}} e^{-\beta\omega_{qj}} \right) ; \quad (30)$$

$$h) \quad F_{\beta}^{(1)} \cdot \left(\frac{1}{2} \frac{\Omega}{8\pi^3} \sum_j \int_{\vec{q}} e^{-2\beta\omega_{qj}} \right) ; \quad (31)$$

$$i) \quad F_{\beta}^{(1)} \cdot \frac{1}{3!} \left(\frac{\Omega}{8\pi^3} \sum_j \int_{\vec{q}} e^{-\beta\omega_{qj}} \right) \left(\frac{\Omega}{8\pi^3} \sum_j \int_{\vec{q}} e^{-2\beta\omega_{qj}} \right) . \quad (32)$$

The important thing to note is that the contributions of the two-component diagrams g and h are proportional to Ω^2 and the contribution of the three-component diagram i is proportional to Ω^3 . This is a completely general rule which also holds for more complicated diagrams. The contribution to Z_β of a diagram with n connected components is Ω^n times a quantity with finite limit for $\Omega \rightarrow \infty$. It is therefore clear that the matrix element of an operator which contains many $V(\nu)$'s can have contributions proportional to high powers of Ω . Such matrix elements appear in the high-order terms of standard perturbation theory and, because of these high powers of Ω , the terms in question are important, even when the phonon interaction is small, leading to an exceptionally bad convergence of the perturbation series.

The physical quantities which we want to calculate have a simple Ω -dependence. They are either linear in Ω (extensive quantities such as the free energy) or independent of Ω (intensive quantities such as the self-energy of a phonon due to phonon-phonon coupling). Hence, these high powers of Ω have to cancel in the final result, which, in general, only occurs after carrying out standard perturbation theory to infinite order. The observation that the high powers of Ω result from disconnected diagrams helps point the way out of these difficulties, however, as will be seen in the following.

Another type of basic diagram contributing to the trace in (26) is drawn in Fig. 2k; diagrams which are related to this diagram are represented in Fig. 2l and 2m. A new feature is the occurrence of what will be called an instantaneous phonon (loop), a phonon which is created and annihilated at the same vertex. Again such an internal instantaneous phonon line can be broken and run around the cylinder (diagrams l and m). Just as in the foregoing, we can fully account for these turns by adding to each loop in a basic diagram a factor

$$\eta_{\mathbf{qj}} = \frac{1 + e^{-\beta\omega_{\mathbf{qj}}}}{1 - e^{-\beta\omega_{\mathbf{qj}}}} \quad (33)$$

which derives from the right-hand side of (27) by letting $\Delta\beta$ go to zero. We find the contribution to Z_β of all the processes characterized by the basic diagram k, thus including the related diagrams:

$$F_\beta^{(2)} = 9 \cdot \frac{\Omega}{8\pi^3} \sum_{j_1 j_2 j_3} \int_{\vec{q}_1 \vec{q}_2 \vec{q}_3} B_{\mathbf{q}_1 j_1, -\mathbf{q}_1 j_1, \mathbf{q}_2 j_2}^{(3)} B_{\mathbf{q}_3 j_3, -\mathbf{q}_3 j_3, \mathbf{q}_2 j_2}^{(3)} \cdot \Delta(\vec{q}_2) \eta_{\mathbf{q}_1 j_1} \eta_{\mathbf{q}_3 j_3} \int_0^\beta d\beta_2 \int_0^{\beta_2} d\beta_1 D_{\mathbf{q}_2 j_2}^{(0)}(\beta_2 - \beta_1) \quad (34)$$

According to the factor $\Delta(\vec{q}_2)$ in this expression, the intermediate phonon $\vec{q}_{2j_2}$ must have a wave vector of zero or $2\pi\vec{\tau}$. The only intermediate phonons of interest are the optical phonons, therefore, because acoustical phonons with wave vectors of zero only describe pure translations of the crystal. Hence, for Bravais lattices the diagrams of this type give no contributions.* The vertex at the right of diagram k corresponds to a term in $V^{(3)}$ which is of the form $A_2^* A_3 A_3^*$. There are three such terms, namely, $A_2^* A_3 A_3^*$, $A_3 A_2^* A_3^*$, and $A_3 A_3^* A_2^*$, and similarly three terms for the left vertex. This accounts for the factor 9 in (34). Note that $F_{\beta}^{(2)}$ is again proportional to Ω , as should be for a class of connected diagrams. There are other diagrams which give contributions to the matrix element of this example, but for the sake of brevity they are not considered here.

Before proceeding we make the following two remarks:

a. Diagrams which only differ from one another by permutations of the indices of their external phonons (the same permutations on the right and left of a diagram), such that the roles of the phonons are interchanged, are taken to be different. Such diagrams, however, which thus are topologically equivalent on the cylinder, all give the same contribution to the partition function. An example has been drawn in Fig. 3; the two diagrams in this figure only differ in the interchange of the roles of the phonons 1 and 2.

Fig. 3. Two different diagrams giving the same contribution to Z_{β} .

b. Up to now we have, in calculating the contribution of a particular diagram, not considered explicitly the special cases in which two or more of the intermediate phonons are identical (for instance, in diagram a in Fig. 2). We have performed the summation over intermediate phonons without including correction factors for identities of the phonons. It has been proved by Wick,^(3,6) however, that this procedure is rigorously correct when the contributions from all diagrams are added together. The result is due to a compensation of errors.

We now discuss a theorem which is of fundamental importance in diagram analysis and which makes it possible to express the contributions of disconnected diagrams in terms of their connected parts. For the diagrams at hand this theorem is as follows:

Consider a set of diagrams which all contain the same components and which differ from one another only in the relative order of the vertices of the different components, leaving this ordering unchanged within each

*Compare the end of this chapter.

component. Then the sum of the contributions to Z_β from all the diagrams in this set is equal to the following expression:

$$\frac{1}{N!} \sum_{j_1 \dots j_N} \int_{\vec{q}_1 \dots \vec{q}_N} \prod_{\delta_i} \left\langle \vec{q}_{n_i j_{n_i}} \dots \vec{q}_{1 j_1} \left| \left\{ e^{-\beta(H_0 + V)} \right\}_{\delta_i} \right| \vec{q}_{1 j_1} \dots \vec{q}_{n_i j_{n_i}} \right\rangle. \quad (35)$$

Here δ_i designates the i 'th component in the set of components which makes up each diagram. The matrix element represents the contribution from component δ_i ; $\vec{q}_{1 j_1}, \dots, \vec{q}_{n_i j_{n_i}}$ are the external phonons of this component. Except for the combinatorial factor, expression (35) is a product of the contributions of the different components. Finally, N is the total number of initial or final phonons in one complete diagram ($N = \sum_i n_i$).

We shall briefly illustrate this theorem by a simple example which will indicate its general validity. Consider the diagrams represented in Fig. 4, consisting of two components. These diagrams only differ in the relative order of the vertex in component δ_1 with respect to the vertices in component δ_2 . In general, the contribution of a disconnected diagram does not factor simply into a product of the contributions of its components because of the occurrence of the ordered β -integrations in the expansion of $e^{-\beta(H_0 + V)}$ [see (25)]. For instance, in the first diagram of Fig. 4 one should always have $\beta_1 \leq \beta_2 \leq \beta_3 \leq \beta$, so that the integration of β_2 cannot be performed unrestrictedly. However, we can get rid of this "coupling" between the two components by taking the three diagrams of Fig. 4 together. Their total contribution to Z_β can be written as follows:

$$\frac{1}{2!} \left[\int_0^\beta d\beta_3 \int_0^{\beta_3} d\beta_2 \int_0^{\beta_2} d\beta_1 + \int_0^\beta d\beta_2 \int_0^{\beta_2} d\beta_3 \int_0^{\beta_3} d\beta_1 + \int_0^\beta d\beta_3 \int_0^{\beta_3} d\beta_1 \int_0^{\beta_1} d\beta_2 \right] K_{\delta_1}(\beta_2) K_{\delta_2}(\beta_1, \beta_3). \quad (36)$$

In K_{δ_i} we have lumped together all factors belonging to component δ_i alone; it contains a summation over the appropriate wave vectors and polarizations. Each K_{δ_i} will be proportional to the volume in the limit $\Omega \rightarrow \infty$. We now immediately see that the above sum of integrals factors into a product of two integrals, one corresponding to δ_1 , the other corresponding to δ_2 , as follows:

$$\frac{1}{2!} \left[\int_0^\beta d\beta_3 \int_0^{\beta_3} d\beta_1 K_{\delta_2}(\beta_1, \beta_3) \right] \left[\int_0^\beta d\beta_2 K_{\delta_1}(\beta_2) \right],$$

whereby we have achieved the desired result.

Fig. 4. Two-component diagrams which differ in the relative locations of the vertices of their components.

With the aid of this rule it is now possible to write out Z_β in terms of just connected diagrams. Since the number of possibilities for dividing N phonons into subgroups containing $n_1, n_2, \dots, n_i, \dots$ phonons is just $N!/\prod_i (n_i!)$, we can express Z_β as follows [see (35)]:

$$Z_\beta = \sum_s \frac{1}{\prod_i (n_i!) \prod_\alpha (n_\alpha!)} \prod_{\delta_i} \sum_{j_1 \dots j_{n_i}} \int_{\vec{q}_1 \dots \vec{q}_{n_i}} \left\langle \vec{q}_{n_i j_{n_i}} \dots \vec{q}_{1 j_1} \left| \left\{ e^{-\beta(H_0 + V)} \right\}_{\delta_i} \right| \vec{q}_{1 j_1} \dots \vec{q}_{n_i j_{n_i}} \right\rangle, \quad (37)$$

in which $\sum_s$ means a summation over sets of connected diagrams which differ by more than just the relative order of the diagrams, and δ_i designates one of the components in a particular set. We have included a factor $\prod_\alpha (n_\alpha!)$, in which n_α is the number of components in a particular set which are identical and have the form α , to take account of the fact that two diagrams which differ from one another in the relative location of two identical components, as in Fig. 5, are identical in shape, since the top to bottom ordering of lines in a diagram is irrelevant. In the expression for Z_β as a sum over diagrams, however, only mutually different diagrams have to be taken, so that we have to correct for situations as those shown in Fig. 5.

Fig. 5. Two diagrams which are identical in shape.

We now take together, in the sum in (37), the terms belonging to connected diagrams, those belonging to two-component diagrams, to three-component diagrams, etc. Bearing again in mind that the top to bottom ordering of lines in a diagram is irrelevant, we easily find the following expression for Z_β [$n(\delta)$ is the number of initial or final phonons in the connected diagram δ]:

$$Z_\beta = \exp \left[\sum_{\delta}^{\text{conn.}} \frac{1}{n(\delta)!} \sum_{j_1 \dots j_{n(\delta)}} \int_{\vec{q}_1 \dots \vec{q}_{n(\delta)}} \left\langle \vec{q}_{n(\delta)} j_{n(\delta)} \dots \vec{q}_1 j_1 \left| \left\{ e^{-\beta(H_0+V)} \right\}_{\delta} \right| \vec{q}_1 j_1 \dots \vec{q}_{n(\delta)} j_{n(\delta)} \right\rangle \right] , \quad (38)$$

which we write briefly as follows

$$Z_\beta = \exp \left[\text{Tr} \left\{ e^{-\beta(H_0+V)} \right\}_C \right] . \quad (39)$$

The subscript C in this last expression indicates that in calculating the trace only connected diagrams must be used. It is to be understood that this trace is expressed in the basis of phonon states. The first factor in the expansion of the exponential corresponds to the contribution $\langle 0 | \exp(-\beta H_0) | 0 \rangle = 1$.

From (20), (23), and (39) we obtain the following exact formula for the free energy:

$$F_\beta = \epsilon_0 + \epsilon_{zp} - \frac{1}{\beta} \text{Tr} \left\{ e^{-\beta(H_0+V)} \right\}_C . \quad (40)$$

We have now written F_β in a form which involves the contributions from connected diagrams only. Since we have seen that in the limit of a large crystal a connected diagram gives a contribution which is proportional to Ω , the free energy given by (40) has the proper volume dependence. This reduction to connected diagrams by grouping of terms, which in fact amounts to carrying out standard perturbation theory to infinite order, is a very general and important feature of many-particle perturbation theory.

We first calculate the free energy for a harmonic crystal $F_\beta^{(0)}$. In this case the diagrams that contribute to the trace in (40) have the following form:

Fig. 6. Diagrams contributing to the free energy in the harmonic approximation.

Note that there are $(n-1)!$ different connected diagrams with n initial phonons, which differ by permutations of phonon indices. One easily finds

$$\begin{aligned}
 F_{\beta}^{(0)} &= \epsilon_0 + \epsilon_{zp} - \frac{1}{\beta} \frac{\Omega}{8\pi^3} \sum_j \int_{\vec{q}} \left[\sum_n \frac{1}{n} e^{-n\beta\omega_{\vec{q}j}} \right] \\
 &= \epsilon_0 + \epsilon_{zp} + \frac{1}{\beta} \frac{\Omega}{8\pi^3} \sum_j \int_{\vec{q}} \ln \left[1 - e^{-\beta\omega_{\vec{q}j}} \right] . \quad (41)
 \end{aligned}$$

To calculate anharmonic corrections to $F_{\beta}^{(0)}$ we have to consider connected diagrams which contain one or more vertices. It was demonstrated in the foregoing (see the theorem on page 13) that in this case we can restrict ourselves to just so-called basic diagrams (diagrams without external lines), provided we substitute for each internal line in a basic diagram the propagator (27) and for each loop the factor (33). With this limitation (together with the limitation to connected diagrams) only a finite number of diagrams are required for a calculation of F_{β} to a given order in powers of u/d . To first nonvanishing order in the phonon-phonon coupling, i.e., to order $(u/d)^2$, the following three diagrams contribute to F_{β} , giving the first order anharmonic correction to the free energy:

Fig. 7. First order basic diagrams contributing to F_{β} .

The contributions of diagrams a and b have been calculated previously [see Eqs. (28) and (34)]. They only involve cubic anharmonic terms. The lowest-order quartic contribution, represented by diagram c, can be written down immediately to give

$$F_{\beta}^{(3)} = - 3 \frac{\Omega}{8\pi^3} \beta \sum_{j_1 j_2} \int_{\vec{q}_1 \vec{q}_2} B_{q_1 j_1, q_2 j_2, -q_1 j_1, -q_2 j_2}^{(4)} \eta_{q_1 j_1} \eta_{q_2 j_2} . \quad (42)$$

To summarize, we have obtained for the free energy the following explicit expression, valid to order $(u/d)^2$:

$$F_{\beta} = F_{\beta}^{(0)} - \frac{1}{\beta} F_{\beta}^{(1)} - \frac{1}{\beta} F_{\beta}^{(2)} - \frac{1}{\beta} F_{\beta}^{(3)} , \quad (43)$$

where $F_{\beta}^{(0)}$, $F_{\beta}^{(1)}$, $F_{\beta}^{(2)}$, and $F_{\beta}^{(3)}$ are given by the formulas (41), (28), (34), and (42), respectively, in terms of the parameters of the lattice. Note that $F_{\beta}^{(2)}$, corresponding to diagram b in Fig. 7, is zero for parameter-free lattices (see below). A numerical evaluation of formula (43) has been performed by Maradudin and co-workers⁽⁷⁾ for a simple model of a lattice.

Higher-order corrections to the free energy can be obtained by considering more complicated basic diagrams. Examples may be found in Fig. 8a and b, which give contributions of orders $(u/d)^6$ and $(u/d)^8$, respectively.

Fig. 8. Higher order basic diagrams contributing to F_{β} .

The basic diagrams which contribute to F_{β} fall into two categories: a) diagrams which cannot be divided into two parts by cutting one single phonon line (examples are Fig. 7 a,c and Fig. 8a); and b) diagrams for which this is possible (examples are Fig. 7b and Fig. 8b). In the latter case, the single phonon line which after being cut makes the diagram disconnected carries pseudo-momentum zero, as follows from the rules for conservation of pseudo-momentum in each vertex. This means that such a line corresponds to an optical phonon, because acoustic modes with $\vec{q}$ equal to zero correspond to pure translations of the crystal as a whole. From this it follows that the diagrams of the second category do not contribute in the case of Bravais lattices. However, they also give vanishing contributions for lattices with more than one atom per unit cell, as long as each atom in the lattice is a center of symmetry (so-called parameter-free lattices). This is a result of the fact that for parameter-free lattices the quantity $B_{q_1 j_1 \dots q_{\nu} j_{\nu}}^{(\nu)} \Delta(\vec{q}_1 + \dots + \vec{q}_{\nu})$ becomes zero if one of the wave vectors $\vec{q}_1, \dots, \vec{q}_{\nu}$ becomes identically equal to zero (see the argument at the end of Chapter IV). The general form of the diagrams belonging to the above-mentioned two categories are schematically represented in Fig. 9. The shaded areas represent parts of the diagram which do not involve phonon lines carrying pseudo-momentum zero.

Fig. 9. General form of the two categories of diagrams, which contribute to F_{β} .

CHAPTER IV

TIME-INDEPENDENT THERMAL AVERAGES

In this chapter we present some further illustrations of the use of the techniques explained in the previous chapter. Let Q be some operator function of the phonon creation and absorption operators A_{qj}^* and A_{qj} . We are interested in the ensemble average of this quantity:

$$\langle Q \rangle_T = \frac{1}{Z_\beta} \text{Tr} \left\{ e^{-\beta(H_0 + V)} Q \right\} \quad (44)$$

Examples are the mean square displacement $\langle u_{sn}^2 \rangle_T$ or the atomic shift $\langle \vec{u}_{sn} \rangle_T$. In the first case Q involves products of two creation and/or absorption operators; for instance, $A_{qj}^* A_{q'j'}$. In the second case Q is linear in A_{qj} or A_{qj}^* .

Just as in the calculation of Z_β in Chapter III, we can write out the trace in the basis of phonon states, substitute the expansion (25), and introduce diagrams for representing the various matrix elements. The diagrams contributing to $\text{Tr} \{ \exp[-\beta(H_0 + V)] Q \}$ look exactly like those for the partition function except for the presence of one additional vertex on the right of the diagrams, corresponding to the operator Q (Q -vertex). At such a Q -vertex, one phonon line may leave or enter (when Q is linear in A_{qj}^* or A_{qj}), two phonon lines join (when Q is quadratic in these operators), etc.

In general, a particular diagram contributing to the trace in (44) will consist of a number of connected components. Just one of these components will contain the Q -vertex. Consider a one-component diagram containing a Q -vertex, and consider all the other diagrams which can be constructed from the first by adding components without Q -vertices in all possible ways. According to the theorem on disconnected diagrams, discussed in Chapter III, the sum of the contributions to the trace in (44) of all these diagrams is equal to just the contribution of the first diagram times a factor Z_β . In view of this result, we can write down the following equation:

$$\begin{aligned} \langle Q \rangle_T &= \frac{1}{Z_\beta} \text{Tr} \left\{ e^{-\beta(H_0 + V)} Q \right\} = \frac{1}{Z_\beta} \text{Tr} \left\{ e^{-\beta(H_0 + V)} Q \right\}_C Z_\beta \\ &= \text{Tr} \left\{ e^{-\beta(H_0 + V)} Q \right\}_C, \end{aligned} \quad (45)$$

where again the subscript C indicates that in calculating the trace only connected diagrams containing the Q -vertex are involved. The trace should be expressed in the basis of phonon states.

We remark that, although the trace is expressed in terms of connected diagrams, it is not necessarily linear in the volume in the limit $\Omega \rightarrow \infty$, as in the case of the free energy [Eq. (40)]. The volume dependence depends on the nature of Q . This is obvious, because Q may correspond to an intensive as well as to an extensive quantity. In the first case, the diagrams contributing to $\text{Tr}\{\exp[-\beta(H_0 + V)]Q\}_C$ turn out to be independent of Ω (see for instance the following calculation of $\langle u_{sn}^2 \rangle_T$); in the second case they are linear in Ω (for instance when $Q = A_{qj}^* A_{qj}$).

Let us first apply the general formula (45) to calculate the mean square displacement $\langle u_{sn}^2 \rangle_T$. From (11) and (45) we find

$$\begin{aligned} \langle u_{sn}^2 \rangle_T = & \frac{v_0}{16\pi^3 M_n} \sum_{jj'} \int_{\vec{q}\vec{q}'} \frac{1}{(\omega_{qj}\omega_{q'j'})^{1/2}} \left(\vec{e}_{qj}^{(n)} \cdot \vec{e}_{q'j'}^{(n)*} \right) e^{i\vec{s} \cdot (\vec{q} - \vec{q}')} \\ & \cdot \text{Tr} \left\{ e^{-\beta(H_0 + V)} (A_{qj} + A_{-qj}^*) (A_{q'j'}^* + A_{-q'j'}) \right\}_C \end{aligned} \quad (46)$$

Fig. 10. Diagrams contributing to the trace in (46) for a harmonic lattice

We have to calculate the trace occurring in (46). In the harmonic approximation things become very simple. For this case some examples of diagrams contributing to the trace in (46) are displayed in Fig. 10. The Q -vertex, corresponding to the operator $(A_{qj} + A_{-qj}^*)(A_{q'j'}^* + A_{-q'j'})$, is designated by the symbol $\odot$. Note that the contributions of these diagrams are nonzero only if $\vec{q}' = \vec{q} \pmod{2\pi\vec{\tau}}$ and $j' = j$.

Just as in the calculation of the free energy we can consider the first diagram in this figure as a basic diagram and the other ones as related diagrams in the sense described in Chapter III. In fact, in complete analogy with the treatment of the loops in the diagrams for the free energy, it can be easily shown that the total contribution of all "harmonic" diagrams to the trace in (46) can be obtained by just calculating the contribution of the basic diagram in Fig. 10, provided we substitute for the loop in this diagram a factor η_{qj} given by Eq. (33). By doing this, we find for the mean square displacement in the harmonic approximation the familiar result

$$\langle u_{sn}^2 \rangle_T^{(0)} = \frac{v_0}{16\pi^3 M_n} \sum_j \int_{\vec{q}} \frac{1}{\omega_{qj}} \left(\vec{e}_{qj}^{(n)} \cdot \vec{e}_{qj}^{(n)*} \right) \frac{1 + e^{-\beta\omega_{qj}}}{1 - e^{-\beta\omega_{qj}}} \quad (47)$$

For a Bravais lattice this becomes, by virtue of (12),

$$\langle u_s^2 \rangle_T^{(0)} = \frac{v_0}{16\pi^3 M} \sum_j \int_{\vec{q}} \frac{1}{\omega_{qj}} \frac{1 + e^{-\beta\omega_{qj}}}{1 - e^{-\beta\omega_{qj}}} \quad (48)$$

In these equations $\langle \dots \rangle_T^{(0)}$ means $\text{Tr} \{ e^{-\beta H_0} \dots \} / \text{Tr} \{ e^{-\beta H_0} \}$.

To calculate interaction corrections to these formulas we have to consider more involved diagrams. In order to obtain the first-order anharmonic correction to the mean square displacement, which is of order $(u/d)^2$, the following basic diagrams have to be calculated:

Fig. 11. First-order basic diagrams for the calculation of $\langle u_{sn}^2 \rangle_T$

Using (27), (33), and the rules described in the previous chapter, we find from these diagrams the following correction to (47):

$$\begin{aligned} \langle u_{sn}^2 \rangle_T^{(1)} = & \frac{v_0}{16\pi^3 M_n} \left\{ 36 \sum_{jj'j_1j_2} \int_{\vec{q}\vec{q}_1\vec{q}_2} \frac{1}{(\omega_{qj}\omega_{qj'})^{1/2}} B_{-qj',q_1j_1,q_2j_2}^{(3)} B_{qj,-q_1j_1,-q_2j_2}^{(3)} \right. \\ & \cdot \left(\vec{e}_{qj}^{(n)} \cdot \vec{e}_{qj'}^{(n)*} \right) \Delta(\vec{q} - \vec{q}_1 - \vec{q}_2) \int_0^\beta d\beta_2 \int_0^{\beta_2} d\beta_1 D_{qj'}^{(0)}(\beta_2) D_{q_1j_1}^{(0)}(\beta_2 - \beta_1) D_{q_2j_2}^{(0)}(\beta_2 - \beta_1) D_{qj}^{(0)}(\beta_1) \\ & - 6 \sum_{jj'j_1} \int_{\vec{q}\vec{q}_1} \frac{1}{(\omega_{qj}\omega_{qj'})^{1/2}} B_{q_1j_1,-q_1j_1,qj,-qj'}^{(4)} \left(\vec{e}_{qj}^{(n)} \cdot \vec{e}_{qj'}^{(n)*} \right) \cdot \eta_{q_1j_1} \int_0^\beta d\beta_1 D_{qj'}^{(0)}(\beta_1) D_{qj}^{(0)}(\beta_1) \\ & + 24 \sum_{jj'j_1j_2} \int_{\vec{q}\vec{q}_1\vec{q}_2} \frac{1}{(\omega_{qj}\omega_{qj'})^{1/2}} B_{q_1j_1,-q_1j_1,-q_2j_2}^{(3)} B_{qj,-qj',q_2j_2}^{(3)} \\ & \cdot \left(\vec{e}_{qj}^{(n)} \cdot \vec{e}_{qj'}^{(n)*} \right) \Delta(\vec{q}_2) \eta_{q_1j_1} \int_0^\beta d\beta_2 \int_0^{\beta_2} d\beta_1 D_{q_2j_2}^{(0)}(\beta_2 - \beta_1) D_{qj}^{(0)}(\beta_1) D_{qj'}^{(0)}(\beta_1) \left. \right\} \quad (49) \end{aligned}$$

In this formula the first term corresponds to diagrams a and b, the second to diagram c, and the third to diagrams d and e. Notice that the expressions (47), (48), and (49) for the mean square displacement are independent of $\vec{s}$, as should be expected. In the case of a Bravais lattice, (49) can be much simplified; the third term then is zero due to the factor $\Delta(\vec{q}_2)$, while according to (12) the factor $(\vec{e}_{\vec{q}j}^{(n)} \cdot \vec{e}_{\vec{q}j'}^{(n)*})$ becomes $\delta_{jj'}$. For this case (49) has recently also been derived by Maradudin and Flinn⁽⁸⁾ by quite different methods. These authors also present some numerical evaluations.

Another quantity of interest is the average of the exponential $\exp(i\vec{k} \cdot \vec{u}_{sn})$, where $\vec{k}$ is some constant vector. This quantity is of great importance in the theory of X-ray and neutron scattering from crystals. From (45) we have

$$\begin{aligned} \langle e^{i\vec{k} \cdot \vec{u}_{sn}} \rangle_T &= \text{Tr} \left\{ e^{-\beta(H_0 + V)} e^{i\vec{k} \cdot \vec{u}_{sn}} \right\}_C \\ &= \text{Tr} \left\{ e^{-\beta(H_0 + V)} \left[1 + i\vec{k} \cdot \vec{u}_{sn} + \frac{1}{2} (i\vec{k} \cdot \vec{u}_{sn})^2 + \dots + \frac{1}{m!} (i\vec{k} \cdot \vec{u}_{sn})^m + \dots \right] \right\}_C \end{aligned} \quad (50)$$

in which

$$\vec{k} \cdot \vec{u}_{sn} = \left(\frac{v_0}{16\pi^3 M_n} \right)^{1/2} \sum_j \int_{\vec{q}} \omega_{\vec{q}j}^{-1/2} \left(\vec{e}_{\vec{q}j}^{(n)} \cdot \vec{k} \right) \left[A_{\vec{q}j} + A_{\vec{q}j}^* \right] e^{i\vec{q} \cdot \vec{s}}. \quad (51)$$

The trace in (50) is expressed in terms of connected diagrams containing the Q-vertex. From (50) and (51) it is clear that the Q-operator is a linear combination of products of phonon creation and absorption operators. In the Q-vertex corresponding to the term $(i\vec{k} \cdot \vec{u}_{sn})^m/m!$, just m phonon lines enter and/or emerge.

In the harmonic case, obviously only the even powers of $i\vec{k} \cdot \vec{u}_{sn}$ give nonzero contributions, and the basic diagrams have the following form:

Fig. 12

Diagrams contributing to the trace in (50) for a harmonic lattice

Again we have designated the Q-vertex by the symbol $\odot$. The diagrams consist of a Q-vertex with a number of loops (instantaneous phonons).

Consider the basic diagram which contains ℓ loops corresponding to the term $1/(2\ell)! (i\vec{k} \cdot \vec{u}_{sn})^{2\ell}$ in the expansion of $\exp(i\vec{k} \cdot \vec{u}_{sn})$. These

loops are completely independent of one another, so each loop corresponds to a factor $(i\vec{\kappa} \cdot \vec{u}_{sn})^2$ and each loop independently contributes a factor $\text{Tr} \{e^{-\beta H_0} (i\vec{\kappa} \cdot \vec{u}_{sn})^2\}_C$. There is a combinatorial factor equal to $(2\ell)!/2^\ell \ell!$, counting the number of inequivalent ways in which the creation and absorption operators can be coupled together to form the loops. In view of this, the contribution of the diagram with ℓ loops takes the form [we make use of Eq. (45)]:

$$\begin{aligned} \frac{(-1)^\ell}{(2\ell)!} \frac{(2\ell)!}{2^\ell \ell!} \left[\text{Tr} \{e^{-\beta H_0} (\vec{\kappa} \cdot \vec{u}_{sn})^2\}_C \right]^\ell &= \frac{1}{\ell!} \left[-\frac{1}{2} \frac{\text{Tr} \{e^{-\beta H_0} (\vec{\kappa} \cdot \vec{u}_{sn})^2\}}{\text{Tr} \{e^{-\beta H_0}\}} \right]^\ell \\ &= \frac{1}{\ell!} \left[-\frac{1}{2} \left\langle (\vec{\kappa} \cdot \vec{u}_{sn})^2 \right\rangle_T^{(0)} \right]^\ell, \end{aligned} \quad (52)$$

where, as before, $\langle \dots \rangle_T^{(0)}$ means $\text{Tr} \{e^{-\beta H_0} \dots\} / \text{Tr} \{e^{-\beta H_0}\}$.

Summing over ℓ from zero to infinity, we find the well-known formula

$$\left\langle e^{i\vec{\kappa} \cdot \vec{u}_{sn}} \right\rangle_T^{(0)} = \exp \left[-\frac{1}{2} \left\langle (\vec{\kappa} \cdot \vec{u}_{sn})^2 \right\rangle_T^{(0)} \right], \quad (53)$$

which is known as Bloch's theorem.⁽⁹⁾ It states that the equilibrium distribution of linear combinations of coordinates of independent harmonic oscillators is Gaussian.

The squared modulus $|\langle \exp(i\vec{\kappa} \cdot \vec{u}_{sn}) \rangle_T|^2$, which according to (53) for a harmonic lattice is equal to $\exp \left[-\langle (\vec{\kappa} \cdot \vec{u}_{sn})^2 \rangle_T^{(0)} \right]$, is called the Debye-Waller factor. It appears in X-ray and neutron scattering problems (compare Chapter VI), and describes the influence of the lattice thermal motion on the intensity of the scattering. Furthermore, it determines the probability of the Mössbauer effect in a harmonic lattice.

Anharmonic corrections to the Debye-Waller factor can be obtained by considering diagrams which differ from those of Fig. 12 by the presence of vertices. The most simple class of diagrams consists of the "harmonic" diagrams (Fig. 12) and those which can be constructed from the "harmonic" diagrams by the insertion of "bubbles" in the loops. An example is shown in Fig. 13a.

Fig. 13. Diagrams contributing to (50)

It is a straightforward process to show that this class of diagrams just contributes a factor* $\exp \left[-\langle (\vec{\kappa} \cdot \vec{u}_{sn})^2 \rangle_T \right]$ to the Debye-Waller factor, because each loop is again independent of the others except for the relative ordering of the vertices in different loops. However, just as in the case of disconnected diagrams, we can disentangle different loops by considering groups of diagrams which only differ from one another in the relative order of the vertices in different loops.

More complicated diagrams are shown in Fig. 13b and c. Including these and similar diagrams, we finally find for the Debye-Waller factor for an anharmonic Bravais crystal (see also the end of Chapter V):

$$e^{-2W(\vec{\kappa})} = \left| \langle \exp(i\vec{\kappa} \cdot \vec{u}_s) \rangle_T \right|^2$$

$$= \exp \left\{ -\langle (\vec{\kappa} \cdot \vec{u}_s)^2 \rangle_T + \frac{1}{12} \left[\langle (\vec{\kappa} \cdot \vec{u}_s)^4 \rangle_T - 3 \langle (\vec{\kappa} \cdot \vec{u}_s)^2 \rangle_T^2 \right] + \dots \right\} \quad (54)$$

The first term in the exponent, describing the Gaussian behavior, corresponds to the simple class of diagrams represented by the diagrams in Fig. 12 and Fig. 13a. The terms proportional to κ^4 , κ^6 , ... in the exponent, which describe the deviation from Gaussian behavior, correspond to the diagrams such as b and c in Fig. 13. Numerical calculations by Maradudin *et al.*⁽⁸⁾ seem to indicate that these non-Gaussian terms are very small (less than a few per cent) compared with the Gaussian term. A first-order expression for the quantity $\langle (\vec{\kappa} \cdot \vec{u}_s)^2 \rangle_T$ may be obtained from Eqs. (47) and (49).

As a final example in this series, we consider the quantity $\langle \vec{u}_{sn} \rangle_T$, the mean atomic displacement at temperature T. It is evident from (11) that in order to find $\langle \vec{u}_{sn} \rangle_T$ we have to calculate $\langle A_{-qj} + A_{qj}^* \rangle_T$. On the basis of (45), we have

$$\langle A_{-qj} + A_{qj}^* \rangle_T = \text{Tr} \left\{ e^{-\beta(H_0 + V)} (A_{-qj} + A_{qj}^*) \right\}_C$$

There are no contributions to this trace in the harmonic approximation. In the anharmonic case the general structure of the basic diagrams is as shown in the following figure:

Fig. 14

Structure of the diagrams involved in the calculation of $\langle \vec{u}_{sn} \rangle_T$

*Note that this factor can be obtained from the harmonic Debye-Waller factor, as written down above, by simply replacing H_0 by $H_0 + V$.

The cross-hatched circle represents an arbitrary set of vertices and lines connected to the Q-vertex [in the present case the $(A_{-qj} + A_{qj}^*)$ -vertex] by means of the phonon line $\vec{q}j$. The V_{qj} -vertex is the first vertex which the line $\vec{q}j$ meets, starting at the Q-vertex. The lowest-order basic diagram is shown explicitly.

Taking the total contribution of these diagrams, we find [see (27)]

$$\langle A_{-qj} + A_{qj}^* \rangle_T = - \int_0^\beta d\beta_1 \text{Tr} \left\{ e^{-(\beta - \beta_1)(H_0 + V)} V_{qj} e^{-\beta_1 H_0} \right\}_C D_{qj}^{(0)}(\beta_1) ,$$

in which [see (16)]

$$V_{qj} = \sum_{\nu=3}^{\infty} V_{qj}^{(\nu)} ;$$

$$V_{qj}^{(\nu)} = \int_{\vec{q}_2 \dots \vec{q}_\nu} \sum_{j_2 \dots j_\nu} B_{qj, q_2 j_2, \dots, q_\nu j_\nu}^{(\nu)} \Delta(\vec{q} + \vec{q}_2 + \dots + \vec{q}_\nu) \\ \cdot \left[A_{q_2 j_2} + A_{-q_2 j_2}^* \right] \dots \left[A_{q_\nu j_\nu} + A_{-q_\nu j_\nu}^* \right] .$$

The trace in this expression corresponds to the cross-hatched region in Fig. 14.

From the conservation of pseudo-momentum for the total diagram it follows at once that $\vec{q}$ is zero (modulo $2\pi\vec{T}$). In view of this and of the cyclic invariance of the trace, we get, after performing the integration over β_1 ,

$$\langle A_{-qj} + A_{qj}^* \rangle_T = - \frac{2}{\omega_{qj}} \Delta(\vec{q}) \text{Tr} \left\{ e^{-\beta(H_0 + V)} V_{0j} \right\}_C ,$$

in which V_{0j} is obtained from V_{qj} by putting $\vec{q}$ equal to zero (modulo $2\pi\vec{T}$).^{*} For the atomic shift we then find the following general expression:

$$\langle \vec{u}_{sn} \rangle_T = - \sum_j \left(\frac{v_0}{4\pi^3 M_n \omega_{0j}^3} \right)^{1/2} \vec{e}_{0j}^{(n)} \text{Tr} \left\{ e^{-\beta(H_0 + V)} V_{0j} \right\}_C .$$

^{*}Note, however, that $V_{qj} = V_{q+2\pi T, j}$.

Since acoustical modes with $\vec{q} = 0$ (modulo $2\pi\vec{T}$) lead only to pure translations of the crystal, the summation over j in this expression runs over optical modes only. Notice that the right-hand side is independent of $\vec{s}$, corresponding to the fact that $\langle \vec{u}_{sn} \rangle_T$ will describe only relative changes within the unit cell.

From this general expression for $\langle \vec{u}_{sn} \rangle_T$ we can derive an interesting property of the coefficients $B_{q_1 j_1, \dots, q_\nu j_\nu}^{(\nu)}$. For lattices containing more than one atom per unit cell, but with the property that each atom is a center of symmetry, $\langle \vec{u}_{sn} \rangle_T$ must be zero to all orders in the anharmonic coupling and for all $\vec{s}$ and n , excluding pure translations of the crystal as a whole. This is evident because $\vec{u}_{sn}$ is defined as the displacement of atom $\vec{s}n$ from the actual equilibrium positions at temperature T , that is, the displacement from the thermally expanded lattice (compare the remarks at the end of Chapter II). From the last expression for $\langle \vec{u}_{sn} \rangle_T$ it can be easily shown that $\langle \vec{u}_{sn} \rangle_T = 0$ implies

$$B_{0j, q_2 j_2, \dots, q_\nu j_\nu}^{(\nu)} \Delta(\vec{q}_2 + \dots + \vec{q}_\nu) = 0 \quad . \quad (54a)$$

This property holds for parameter-free lattices (lattices in which each atom is a center of symmetry). For Bravais lattices $B_{0j, q_2 j_2, \dots, q_\nu j_\nu}^{(\nu)}$ is equal to zero by definition, so that in (54a) both j , as well as $j_2, \dots, j_\nu$, cover the acoustical and optical branches of the vibration spectrum. It is to be understood that $B_{0j, q_2 j_2, \dots, q_\nu j_\nu}^{(\nu)}$ at each temperature has to be calculated for the thermally expanded equilibrium lattice corresponding to that temperature.

Special cases of (54a) are:

$$B_{0j, q'j', -q'j'}^{(3)} = 0 \quad ;$$

$$B_{0j, q'j', -q'j', q''j'', -q''j''}^{(5)} = 0 \quad .$$

The first one was quoted by Peierls⁽¹⁰⁾ and by Maradudin *et al.*⁽⁸⁾

For more general lattices $\langle \vec{u}_{sn} \rangle_T$ is nonzero. However, we must remember that for these lattices the linear term in the expansion of the crystal potential energy does not vanish, due to possible relative displacements of sublattices. This means that in this case our starting point [Eqs. (2), (3), and (4)] is incorrect.

CHAPTER V

TIME-DEPENDENT CORRELATION FUNCTIONS

Up to now we have calculated quantities which did not depend on the time. In this chapter we will extend our considerations to studying quantities which involve a time variable. This considerably complicates the problem.

Of great interest for all kinds of problems is the function

$$\langle Q_1(t') Q_2(t) \rangle_T, \quad (55)$$

which measures the correlation between a quantity represented by the operator Q_1 at time t' and a quantity represented by the operator Q_2 at time t . In general, Q_1 and Q_2 are linear combinations of products of phonon creation and absorption operators A_{qj}^* and A_{qj} . An important example is provided by the function

$$\langle u_{s'n'\alpha'}(t') u_{sn\alpha}(t) \rangle_T \quad (56)$$

describing the correlation between the position of atom $\vec{s}n$ at time t and atom $\vec{s}'n'$ at time t' . From (11) it will be clear that the calculation of this correlation function amounts to the calculation of the function

$$\left\langle \left\{ A_{q'j'}(t') + A_{-q'j'}^*(t') \right\} \left\{ A_{qj}(t) + A_{-qj}^*(t) \right\} \right\rangle_T, \quad (57)$$

which may be referred to as one-phonon Green function. We will consider it in detail in the following chapters. It will be seen that these functions contain valuable information about the elementary excitations, i.e., the phonons, in the system. Moreover, there is a close relationship between these functions and the so-called one-phonon scattering of thermal neutrons by a crystal.

In neutron scattering problems the following, more general correlation function is of utmost importance:

$$\langle T_{-\kappa}(t') T_{\kappa}(t) \rangle_T \quad (58)$$

in which

$$T_{\kappa} = \sum_{\vec{s}n} e^{i\vec{\kappa} \cdot \vec{r}_{sn}} \quad (59)$$

and where $\vec{\kappa}$ is some constant vector.

Still another example is given by

$$\langle N_{q'j'}(t') N_{qj}(t) \rangle_T \quad (60)$$

with $N_{qj} = A_{qj} A_{qj}^*$, a two-phonon Green function, which one encounters in the theory of lattice thermal conductivity (Chapter IX).

According to the usual definitions, (55) may be written out as follows:

$$\begin{aligned} \langle Q_1(t') Q_2(t) \rangle_T &= \frac{1}{Z(\beta)} \text{Tr} \left\{ e^{-\beta H + it'H} Q_1 e^{-i(t' - t)H} Q_2 e^{-itH} \right\} \\ &= \frac{1}{Z(\beta)} \text{Tr} \left\{ e^{-\beta H} e^{-i(t - t')H} Q_1 e^{i(t - t')H} Q_2 \right\}, \end{aligned} \quad (61)$$

where we made use of the invariance of the trace against cyclic permutations: $\text{Tr}\{AB\} = \text{Tr}\{BA\}$. We see that $\langle Q_1(t') Q_2(t) \rangle_T$ only depends on the time difference $t - t'$. Without loss of generality we can therefore put t' equal to zero. We thus have, writing Q_1 for $Q_1(0)$ and using (23);

$$\langle Q_1 Q_2(t) \rangle_T = \frac{1}{Z_\beta} \text{Tr} \left\{ U_{-\beta} U_{-it} Q_1 U_{it} Q_2 \right\}, \quad (62)$$

where we have introduced the notations $U_{-\beta} = e^{-\beta(H_0 + V)}$ and $U_{\pm it} = e^{\pm it(H_0 + V)}$.

As the next step the time-development operators $U_{\pm it}$ in the curly brackets should be expanded in powers of the operator V , analogous to the expansion of $U_{-\beta}$ given by (25). One has

$$\begin{aligned} U_{-it} &= e^{-itH_0} + \sum_{n=1}^{\infty} (-i)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1} \dots \int_0^{t_2} dt_1 \\ &\quad \cdot e^{-i(t - t_n)H_0} V e^{-i(t_n - t_{n-1})H_0} V \dots V e^{-it_1 H_0} \end{aligned} \quad (63)$$

and

$$\begin{aligned} U_{it} &= e^{itH_0} + \sum_{n=1}^{\infty} i^n \int_0^t dt_n \int_0^{t_n} dt_{n-1} \dots \int_0^{t_2} dt_1 \\ &\quad \cdot e^{it_1 H_0} V \dots V e^{i(t_n - t_{n-1})H_0} V e^{i(t - t_n)H_0} \end{aligned} \quad (64)$$

The trace in (62) can now be analyzed in terms of diagrams which are essentially the same as those used in the previous chapters. In the present case, each diagram contains two Q -vertices in addition to the ordinary vertices, and each diagram has three different regions in which the three operators U_{it} , U_{-it} , and $U_{-\beta}$ act (two "time regions" and one "temperature region"). But in other respects each diagram can be drawn like a diagram for Z_{β} .

Fig. 15

Sample diagram contributing to the trace in (62) for the special case $Q_1 = A_{qj}$ and $Q_2 = A_{qj}^*$

In Fig 15 we have shown an example for the particular case $Q_1 = A_{qj}$ and $Q_2 = A_{qj}^*$. The above-mentioned three regions are indicated and separated by dashed lines. The vertices Q_1 and Q_2 are again designated by the symbol $\odot$. Note that the right to left order of the operators Q_2 , U_{it} , Q_1 , U_{-it} , and $U_{-\beta}$ is, of course, precisely the same as in the trace in (62). The above diagram is an example of a diagram that contributes to the following matrix element:

$$\begin{aligned}
 & \left\langle \vec{q}_{1j1}, \vec{q}_{2j2} \left| \left\{ - \int_0^{\beta} d\beta_1 e^{-(\beta - \beta_1)H_0} V e^{-\beta_1 H_0} \right\} \right. \right. \\
 & \quad \cdot \left\{ - \int_0^t dt_2' \int_0^{t_2'} dt_1' e^{-i(t - t_2')H_0} V e^{-i(t_2' - t_1')H_0} V e^{-it_1' H_0} \right\} A_{qj} \\
 & \quad \cdot \left\{ - i \int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 e^{it_1 H_0} V e^{i(t_2 - t_1)H_0} V e^{i(t_3 - t_2)H_0} V e^{i(t - t_3)H_0} \right\} A_{qj}^* \left| \vec{q}_{2j2}, \vec{q}_{1j1} \right\rangle
 \end{aligned} \tag{64a}$$

The diagrams can again be imagined as diagrams on a cylinder, and the concept of connectedness on the cylinder can be invoked again. The fundamental theorem (page 16) on disconnected diagrams remains true with minor modifications. To disentangle the ordered integrations we have to take sets of diagrams together which only differ in the relative order of the ordinary vertices of the different components, leaving this ordering unchanged within each component, with the restriction that only those vertices are permuted with respect to each other which are in the same region. Or, in other words, in changing the right to left order of the vertices in different components crossing of the boundaries between the regions is prohibited, because we only have to disentangle parts of diagrams which are situated within the same region.

As an example, consider the diagram shown in Fig. 15, in which the right to left order of the vertices is fixed by the symbol

$$\{0 \leq \beta_1 \leq \beta; \quad 0 \leq t'_1 \leq t'_2 \leq t; \quad 0 \leq t_1 \leq t_2 \leq t_3 \leq t\} \quad .$$

The total contribution to the trace in (62) of this diagram together with the five diagrams which only differ from the first one in having the following ordering of the vertices:

$$\{0 \leq \beta_1 \leq \beta; \quad 0 \leq t'_2 \leq t'_1 \leq t; \quad 0 \leq t_1 \leq t_2 \leq t_3 \leq t\}$$

$$\{0 \leq \beta_1 \leq \beta; \quad 0 \leq t'_1 \leq t'_2 \leq t; \quad 0 \leq t_2 \leq t_1 \leq t_3 \leq t\}$$

$$\{0 \leq \beta_1 \leq \beta; \quad 0 \leq t'_2 \leq t'_1 \leq t; \quad 0 \leq t_2 \leq t_1 \leq t_3 \leq t\}$$

$$\{0 \leq \beta_1 \leq \beta; \quad 0 \leq t'_1 \leq t'_2 \leq t; \quad 0 \leq t_1 \leq t_3 \leq t_2 \leq t\}$$

$$\{0 \leq \beta_1 \leq \beta; \quad 0 \leq t'_2 \leq t'_1 \leq t; \quad 0 \leq t_1 \leq t_3 \leq t_2 \leq t\}$$

is equal to $1/2!$ times the product of the contributions of the two components in Fig. 15.

We use this theorem to eliminate the factor $1/Z_\beta$ in Eq. (62), just as we did in Chapter IV. A diagram in the present problem can contain components with Q-vertices, as well as components which do not involve Q-vertices (see Fig. 15). Consider a diagram which contains only components with Q-vertices (such a diagram consists of either one or two components), and consider all other diagrams which can be constructed from the first one by just adding components without Q-vertices. According to the above theorem, the total contribution to the trace in (62) from all of these diagrams (together with the diagrams which only differ from these in the renumbering of the external phonons in one component with respect to those in the other components) is equal to the contribution of the original one times a factor $\text{Tr}\{U_{-\beta} U_{-it} U_{it}\} = \text{Tr}\{U_{-\beta}\} = Z_\beta$. This factor Z_β cancels the factor Z_β in the denominator of expression (62), giving

$$\langle Q_1 Q_2(t) \rangle_T = \text{Tr}\{U_{-\beta} U_{-it} Q_1 U_{it} Q_2\}_Q \quad . \quad (65)$$

Here the subscript Q outside the curly brackets means that the trace, which should be expressed in terms of phonon states, has to be calculated for diagrams which contain only components with Q-vertices.

These diagrams can be classified into two types: a) diagrams that consist of two components, each component containing one Q-vertex,

and b) diagrams that consist of a single component which involves both of the Q -vertices. In Fig. 16 we have schematically represented the two types.

Fig. 16. The two types of diagrams which contribute to the trace in (65)

By using once more the fundamental theorem, it will be clear that the contribution of all possible diagrams of type a to the right-hand side of (65) is equal to the product of the contributions of the components, that is,

$$\text{Tr} \{ U_{-\beta} U_{-it} U_{it} Q_2 \}_C = \text{Tr} \{ U_{-\beta} U_{-it} Q_1 U_{it} \}_C ,$$

which can be written as follows [compare Eq. (45)]:

$$\frac{1}{Z_\beta} \text{Tr} \{ U_{-\beta} Q_1 \} = \frac{1}{Z_\beta} \text{Tr} \{ U_{-\beta} Q_2 \} = \langle Q_1 \rangle_T = \langle Q_2 \rangle_T , \quad (66)$$

use having been made of the cyclic invariance of the trace. We see that the total contribution of these diagrams is independent of time and simply equals the product of the averages of Q_1 and Q_2 . It represents the asymptotic value, for large t , of the correlation function $\langle Q_1 Q_2(t) \rangle_T$, for which it is expected that Q_1 and Q_2 are statistically independent. It will be seen below that, in the case of neutron scattering, diagrams of this type describe the elastic-scattering processes.

In view of these results, we can write for the correlation function

$$\langle Q_1 Q_2(t) \rangle_T = \langle Q_1 \rangle_T \langle Q_2 \rangle_T + \text{Tr} \{ U_{-\beta} U_{-it} Q_1 U_{it} Q_2 \}_C , \quad (67)$$

in which the trace now involves only connected diagrams containing the Q -vertices (Fig. 16b).

This is as far as one can get without specifying the operators Q_1 and Q_2 . To calculate the right-hand side of Eq. (67), one has to substitute the explicit form of Q_1 and Q_2 in terms of phonon creation and absorption operators.

It is interesting to note that (67) can be easily extended to averages of products of more than two operators, for instance, $\langle Q_1(t_1) Q_2(t_2) Q_3(t_3) \rangle_T$,

and, in general, $\langle Q_1(t_1) Q_2(t_2) \dots Q_n(t_n) \rangle_T$. The diagrams that correspond to these quantities only differ from the diagrams described above in the number of Q -vertices and time regions. By applying the fundamental theorem, one can again restrict oneself to diagrams which only contain components involving one or more Q -vertices. Then one can distinguish these remaining diagrams into several types: a) diagrams that consist of n components, each component containing one Q -vertex; b) diagrams that consist of $n-1$ components, one component containing two Q -vertices and the remaining $n-2$ components containing one Q -vertex each; etc.

One finds

$$\begin{aligned} \langle Q_1 Q_2 \dots Q_n \rangle_T = & \langle Q_1 \rangle_C \langle Q_2 \rangle_C \dots \langle Q_n \rangle_C + \langle Q_1 \rangle_C \langle Q_2 \dots Q_n \rangle_C \\ & + \langle Q_2 \rangle_C \langle Q_1 \dots Q_n \rangle_C + \dots + \langle Q_1 Q_2 \rangle_C \langle Q_3 \dots Q_n \rangle_C \\ & + \dots + \langle Q_1 Q_2 \dots Q_n \rangle_C, \end{aligned} \quad (67a)$$

which is a generalization of (67) [see also (45)]. Here Q_i stands for $Q_i(t_i)$ and $\langle \dots \rangle_C$ means $\text{Tr} \{ U_{-\beta} \dots \}_C$. Let us formally denote the product $Q_1(t_1) Q_2(t_2) \dots Q_n(t_n)$ by Q^n ; the $(n+1)^{\text{th}}$ term in the expansion of $\exp Q$ then is $Q^n/n! = Q_1(t_1) \dots Q_n(t_n)/n!$. It can be easily verified that (67a) can be obtained by equating the terms with y^n on the right and left of the following formal relation: *

$$\langle \exp(yQ) \rangle_T = \exp \left[\sum_{n=1}^{\infty} \frac{y^n}{n!} \langle Q^n \rangle_C \right]. \quad (67b)$$

Observe the formal similarity between this relation and the expansion in semi-invariants (cumulants) in mathematical statistics.⁽¹¹⁾ This correspondence between the methods of semi-invariants in mathematical statistics, on the one hand, and of connected diagrams in statistical mechanics, on the other hand, seems to be of a very general nature.⁽¹²⁾

A particular case of (67b) is that in which $y = i\vec{\kappa}$ and $Q_1 = Q_2 = \dots = Q_n = \vec{u}_{\text{sn}}$. We then immediately find (54), taking the squared modulus of (67b). For a harmonic lattice (67b) reduces in this case to Bloch's theorem (Chapter IV).

*Note the difference between the symbols $\langle \dots \rangle_C$ and $\langle \dots \rangle_T$;

$\langle \dots \rangle_C = \text{Tr} \{ U_{-\beta} \dots \}_C$, while $\langle \dots \rangle_T = \frac{1}{Z_\beta} \text{Tr} \{ U_{-\beta} \dots \}$.

CHAPTER VI

SCATTERING OF THERMAL NEUTRONS BY CRYSTALS

As an important application of many-particle perturbation theory and diagram analysis we consider in this chapter the coherent scattering of thermal neutrons by the nuclei of a perfect, single crystal at an arbitrary temperature. In particular, we wish to investigate the influence of phonon interactions on the scattering process.(3,13,14)

The differential scattering cross section at temperature T per unit of solid angle $d\Omega$ and per unit interval of outgoing energy $d\epsilon$ of the neutron for coherent scattering in the first Born approximation is given by(15)

$$\frac{d^2\sigma_T}{d\Omega d\epsilon} = a^2 \frac{|\vec{k}|}{|\vec{k}_0|} S_T(\vec{k}, \omega) \quad , \quad (68)$$

in which a is the scattering length, which we assume the same for each nucleus in the crystal, and in which the so-called scattering function $S_T(\vec{k}, \omega)$ has the following form:

$$S_T(\vec{k}, \omega) = \frac{1}{Z(\beta)} \sum_{\nu_0} e^{-\beta E_{\nu_0}} \sum_{\nu} |\langle \psi_{\nu} | T_{\kappa} | \psi_{\nu_0} \rangle|^2 \delta(\omega + E_{\nu_0} - E_{\nu}) \quad . \quad (69)$$

In these equations $|\psi_{\nu_0}\rangle$ and $|\psi_{\nu}\rangle$ are initial and final excited states of the crystal. They are eigenstates of the total Hamiltonian H , given by (13), with corresponding eigenvalues E_{ν_0} and E_{ν} . The scattering function depends on $\vec{k} = \vec{k}_0 - \vec{k}$ and ω , the momentum and energy transferred from the neutron to the crystal ($\vec{k}_0$ and $\vec{k}$ are the momenta of incident and scattered neutron, respectively). The operator T_{κ} is defined by Eq. (59). The delta function in (69) ensures conservation of energy during a scattering process. Equation (68) is derived under the assumption that the neutron-nucleus interaction may be represented by a pseudo-potential which is proportional to a delta function.

The scattering function (69) as it stands is very unpractical for a diagrammatic analysis, because it explicitly involves the exact, but completely unknown, eigenstates of the anharmonic crystal. To get a more convenient representation, we introduce the relation

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{it\omega} \quad , \quad (70)$$

and find, using (23) and noting that $T_{\kappa}^* = T_{-\kappa}$,

$$\begin{aligned}
 S_T(\vec{\kappa}, \omega) &= \frac{1}{2\pi Z(\beta)} \int_{-\infty}^{\infty} dt e^{-i\omega t} \left\{ \sum_{\nu, \nu_0} e^{-(\beta + it)E_{\nu_0}} \langle \psi_{\nu_0} | T_{-\kappa} | \psi_{\nu} \rangle \cdot e^{itE_{\nu}} \langle \psi_{\nu} | T_{\kappa} | \psi_{\nu_0} \rangle \right\} \\
 &= \frac{1}{2\pi Z_{\beta}} \int_{-\infty}^{\infty} dt e^{-i\omega t} \text{Tr} \left\{ U_{-\beta} U_{-it} T_{-\kappa} U_{it} T_{\kappa} \right\} .
 \end{aligned} \tag{71}$$

The appearance of the trace in this expression shows that this result no longer involves the exact eigenstates $|\psi_{\nu}\rangle$. As before, we represent the trace in the basis of phonon states. From (58) and (62) we see that the scattering function is expressed as the Fourier transform of a time-dependent correlation function in the sense of the previous chapter for the particular case $Q_1 = T_{-\kappa}$ and $Q_2 = T_{\kappa}$. The Q -vertices in the corresponding diagrams, representing the operators T_{κ} and $T_{-\kappa}$, will be called neutron vertices.

From (59) and (1) we have

$$T_{\pm\kappa} = \sum_{\vec{s}, \vec{n}} e^{\pm i\vec{\kappa} \cdot (\vec{s} + \vec{R}_{0n} + \vec{u}_{sn})} . \tag{72}$$

Expanding the operators $\exp[\pm i\vec{\kappa} \cdot \vec{u}_{sn}]$ as in Eqs. (50) and (51), we see that each operator T_{κ} and $T_{-\kappa}$ is a linear combination of products of creation and absorption operators A_{qj}^* and A_{qj} . In the neutron vertex corresponding to the term $\pm(i\vec{\kappa} \cdot \vec{u}_{sn})^m$, just m phonon lines enter and/or emerge. We see from (18), (50), (51), and (72) that, due to the summation over $\vec{s}$, each product of creation and absorption operators that occurs in the expansion of $T_{\pm\kappa}$ contains a factor $\Delta(\pm\vec{\kappa} - \Sigma\vec{q})$, where $\Sigma\vec{q}$ is the sum of the wave vectors of the phonons created by $T_{\pm\kappa}$ minus the sum of the wave vectors of the phonons absorbed by $T_{\pm\kappa}$.

From the general theory of the previous chapter, and in particular from Eq. (67), it follows that the scattering function can be written as follows:

$$S_T(\vec{\kappa}, \omega) = | \langle T_{\kappa} \rangle_T |^2 \delta(\omega) + \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \text{Tr} \left\{ U_{-\beta} U_{-it} T_{-\kappa} U_{it} T_{\kappa} \right\}_C . \tag{73}$$

We see that the first term on the right-hand side of (73), which arises from diagrams of type a in Fig. 16, describes the elastic scattering in which no energy is exchanged between neutron and crystal. The second term, corresponding to diagrams of type b in Fig. 16, gives the inelastic spectrum, as will be seen below.

For the elastic scattering function $S_T^{(0)}(\vec{\kappa}, \omega)$ we thus have

$$S_T^{(0)}(\vec{\kappa}, \omega) = |\langle T_{\kappa} \rangle_T|^2 \delta(\omega) = \left| \sum_{\vec{s}, n} e^{i\vec{\kappa} \cdot (\vec{s} + \vec{R}_{0n})} \langle e^{i\vec{\kappa} \cdot \vec{u}_{sn}} \rangle_T \right|^2 \delta(\omega) .$$

The quantity $\langle \exp(i\vec{\kappa} \cdot \vec{u}_{sn}) \rangle_T$ was discussed in Chapter IV. From the structure of the diagrams that contribute to this quantity (see Fig. 12 and 13), it is immediately clear that it does not depend on $\vec{s}$, because for these diagrams $\Sigma \vec{q}$ is zero [see the remarks following Eq. (72)]. By virtue of this result and of Eqs. (18) and (29), we find

$$S_T^{(0)}(\vec{\kappa}, \omega) = \frac{8\pi^3 N_0}{v_0} \left| \sum_n e^{i\vec{\kappa} \cdot \vec{R}_{0n}} \langle e^{i\vec{\kappa} \cdot \vec{u}_{0n}} \rangle_T \right|^2 \delta(\omega) \Delta(\vec{\kappa}) . \quad (74)$$

This expression is exact. We conclude that also for an anharmonic crystal the Bragg-conditions, $\omega = 0$ and $\vec{\kappa} = 0 \pmod{2\pi\vec{\tau}}$, are exactly valid. Phonon-phonon interactions only affect the intensity of the scattering determined by the quantity within absolute value signs, the structure factor. In the case of a Bravais lattice, we get simply

$$S_T^{(0)}(\vec{\kappa}, \omega) = \frac{8\pi^3 N_0}{v_0} e^{-2W(\vec{\kappa})} \delta(\omega) \Delta(\vec{\kappa}) , \quad (75)$$

in which $e^{-2W(\vec{\kappa})}$ is the Debye-Waller factor for an anharmonic crystal, defined by Eq. (54).

It is worth noting that also the cross section for resonance absorption or emission of γ rays by the nuclei composing the lattice can be expressed in terms of a correlation function⁽³³⁾ similar to (71). When we apply the general formula (67), the first term on the right of this equation, corresponding to Fig. 16a, describes in this case the recoilless resonance absorption or emission of γ rays (Mössbauer effect). A formula analogous to (74) can be derived which shows that phonon-phonon interactions only affect the intensity of the Mössbauer line. For the case of a Bravais lattice, this intensity is determined by $\exp[-2W(\vec{\kappa})]$ [Eq. (54)], in which $\vec{\kappa}$ now is the wave vector of the γ quantum. The second term on the right of (67), corresponding to Fig. 16b, produces the wings of the Mössbauer line.

We next turn to a discussion of the inelastic scattering processes, described by the second term on the right of (73). We first briefly consider scattering by a harmonic crystal. For that case, some examples of diagrams that contribute to the trace in (73) are drawn in Fig. 17.

Fig. 17

Diagrams for the calculation of the inelastic neutron scattering spectrum in the case of a harmonic lattice

Let us first consider the loops (instantaneous phonons) on the neutron vertices (see Fig. 17c and d). In view of the results of Chapter IV it is straightforward to show that the contribution of all possible loops of this kind on a particular diagram is completely taken into account by including a factor

$$\left\langle e^{i\vec{\kappa} \cdot \vec{u}_{0n}} \right\rangle_T^{(0)} = \exp \left[-\frac{1}{2} \left\langle (\vec{\kappa} \cdot \vec{u}_{0n})^2 \right\rangle_T^{(0)} \right]$$

for each neutron vertex in the calculation of that diagram. The product of these two factors is precisely the Debye-Waller factor.

The remaining phonon lines in the diagrams are lines which run from one neutron vertex to the other, either directly (for instance, diagrams a and e) or after having encircled the cylinder once or more (for instance, diagram b). Just as in the calculation of the free energy, we can restrict ourselves to considering only basic diagrams (diagrams without external lines) by partially summing those diagrams which only differ from one another in the number of turns of a particular phonon line.

For instance, writing down only the exponential factors:

$$\begin{aligned}
 & \text{Diagram a} + \text{Diagram b} + \text{Diagram c} + \dots \\
 & + \text{Diagram d} + \dots \\
 & = e^{it\omega_{qj}} + e^{-\beta\omega_{qj}} e^{it\omega_{qj}} + e^{-2\beta\omega_{qj}} e^{it\omega_{qj}} + \dots \\
 & + e^{-\beta\omega_{qj}} e^{-it\omega_{qj}} + e^{-2\beta\omega_{qj}} e^{-it\omega_{qj}} + \dots \\
 & = \frac{e^{it\omega_{qj}} + e^{-\beta\omega_{qj}} e^{-it\omega_{qj}}}{1 - e^{-\beta\omega_{qj}}} \quad .
 \end{aligned} \tag{76}$$

In the diagram in this series, which contains n external phonon lines, there is a factor $1/n!$ according to the definition of the trace. However, this is just canceled by a factor $n!$ which is the number of ways in which these external lines can be renumbered. Equation (76) is the propagator function for an internal phonon line in a basic diagram. The basic diagrams have a very simple form (see Fig. 17a and e). They consist of the two neutron vertices and one, two, three, ... internal phonon lines, each phonon line being associated with a propagator function (76). The diagram with one internal phonon line describes the so-called one-phonon processes, in which one phonon is emitted or absorbed by the neutron per single scattering event. This follows directly from (73) and (76) by performing the integration over t , which gives a factor

$$\frac{\delta(\omega - \omega_{qj}) + e^{-\beta\omega_{qj}} \delta(\omega + \omega_{qj})}{1 - e^{-\beta\omega_{qj}}} \quad (77)$$

Note that the contribution of this one-phonon diagram is nonzero only if $\vec{q} = \vec{\kappa} \pmod{2\pi\vec{T}}$ due to the $\Delta(\vec{\kappa} - \vec{q})$ -function connected with a neutron vertex.

The one-phonon processes produce delta-function peaks in the energy spectrum of the scattered neutrons. In general there are two peaks for each j , one corresponding to emission ($\omega = \omega_{qj}$) and one corresponding to absorption of a phonon by the neutron ($\omega = -\omega_{qj}$). We see from (77) that in the limit $T \rightarrow 0$ ($\beta \rightarrow \infty$) the absorption peaks vanish, reflecting the fact that no energy can be absorbed from a crystal in its ground state. The delta-function peaks in the spectrum are particularly interesting, because they correspond to one-phonon processes and because their locations, which follow simply from the conservation rules of energy and momentum, can be investigated experimentally. This provides a direct method of obtaining the frequency vs. wave vector relationship of a phonon, which in turn may yield valuable information about the interatomic forces. (16-18)

The peaks are superposed on a smooth background caused by the so-called multiphonon processes, in which more than one phonon is involved per single scattering event. These latter processes are described by the basic diagrams with more than one internal phonon line. In particular, the diagram containing n internal lines just describes the n -phonon processes. It corresponds to the n -th term in the so-called phonon expansion, shown in Fig. 18.

$$S_T^{\text{inel.}}(\vec{\kappa}, \omega) = \text{---} \bigcirc \text{---} \bigcirc \text{---} + \text{---} \bigcirc \text{---} \bigcirc \text{---} + \text{---} \bigcirc \text{---} \bigcirc \text{---} + \dots$$

Fig. 18. Graphical representation of the phonon expansion for scattering by a harmonic crystal

The diagrams can be easily calculated, giving immediately the familiar expressions for the differential scattering cross section for scattering of neutrons by a harmonic lattice.^(17,19)

Much of the remaining part of these lectures will be devoted to a study of the influence of phonon interactions on the inelastic coherent neutron scattering processes.⁽¹³⁾ In particular, we will consider the shifting and broadening of the one-phonon peaks in the scattering spectrum as a result of phonon-phonon coupling. This amounts to studying the self-energy and lifetime of a phonon due to the presence of the interaction.

We saw in the foregoing that, as predicted by harmonic theory, the coherent inelastic energy spectrum of neutrons, scattered by a single crystal, for any particular angle of scattering consists of a number of delta-function peaks superposed on a continuous background. Phonon-phonon interactions show up in a most interesting way in the one-phonon peaks, producing a temperature-dependent displacement of each peak from the harmonic position, and a temperature-dependent broadening. There are two contributions which make the positions of the peaks vary with temperature. In the first place, we must notice that the unperturbed frequencies are themselves temperature-dependent due to the effect of thermal expansion, which is a purely anharmonic effect (compare Chapter II). In the second place, there is an interaction-produced self-energy of the appropriate phonon, which also depends on temperature. Since the effects of phonon-phonon interaction are dissipative in character, the presence of these interactions furthermore results in a finite lifetime of the phonon (the self-energy is complex), giving rise to a broadening of the corresponding one-phonon peak in the scattering spectrum. Recently, these effects of shifting and broadening have been observed experimentally by Larsson et al.⁽²⁰⁾ with aluminum and by Brockhouse et al. with lead.⁽²¹⁾ We remark that in conducting crystals there is an additional contribution to the displacement and broadening of the peaks as a result of the interaction between phonons and conduction electrons.⁽¹⁴⁾

In the following we will study the self-energy and lifetime of a phonon as a result of phonon-phonon interaction, supposing that for any temperature the harmonic problem has been solved with the correct values of the lattice parameters, thus including effects of thermal expansion.* Since the phonon self-energy and lifetime effects show up in the shifting and broadening of the scattering peaks in the neutron scattering spectrum, and are thus accessible to measurement, a systematic calculation of these effects is of interest in itself as a means of checking the general predictions of many-particle perturbation theory.

*For a calculation of the frequency shift due to thermal expansion, see reference 25.

The inelastic scattering spectrum is described by the second term on the right of Eq. (73):

$$S_T^{\text{inel}}(\vec{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \text{Tr} \{U_{-\beta} U_{-it} T_{-\kappa} U_{it} T_{\kappa}\}_C, \quad (78)$$

in which only connected diagrams containing both of the neutron vertices contribute to the trace. Some examples of diagrams are shown in Fig. 19.

Fig. 19

Examples of diagrams which contribute to the trace in (78); b and c are examples of one-phonon diagrams

Since we are primarily interested in the peaks of the inelastic scattering spectrum, and not in the complete spectrum, it is important to construct a theory which yields information about just the peaks. This only makes sense if the peaks are distinguishable from the background, so that they can be treated as separate from it. Therefore our treatment is restricted to the case in which, independent of the strength of the interaction, the width of a peak is small compared to the value of the frequency at its center. Only then the peaks can be considered as being well defined with respect to the background to higher order in the interaction, thus allowing a separate treatment of the one-phonon peaks. Such a treatment amounts to neglecting the influence of the background ("multi-phonon processes") on the shape of the peaks. From the experimental results of Larsson and Brockhouse, mentioned above, we expect that the case of sharply distinguishable peaks is realized for temperatures well below the melting point and/or values of the phonon wave vector which are sufficiently small.

The part $S_T^{(1)}(\vec{k}, \omega)$ of the total inelastic scattering function $S_T^{\text{inel}}(\vec{k}, \omega)$, which under the circumstances described above can be expected to describe the peaks correctly, can be obtained from Eq. (78) by further restricting the summation over the diagrams involved to so-called one-phonon diagrams, which will be defined as follows.

Consider Fig. 19. What is the minimum number of phonon lines that has to be broken in such a way that the two neutron vertices become disconnected from one another on the cylinder? In diagram a this number is clearly three, but in diagrams b and c only one phonon line has to be cut in order to achieve this result. In the latter case such a phonon line is called a κ -line, because it corresponds to a phonon with wave vector $\vec{\kappa}$ or $-\vec{\kappa}$ (modulo $2\pi\vec{\tau}$), as will be clear from the rules of conservation of wave vector in the vertices of our diagrams. Diagrams b and c have three and two κ -lines, respectively. We now define one-phonon diagrams as diagrams which have at least one κ -line in the regions U_{it} or U_{-it} . Hence, diagrams b and c of Fig. 19 are one-phonon diagrams, while diagram a is not. In the harmonic approximation the one-phonon diagrams are simply the diagrams with one phonon line between the neutron vertices (the first diagram in Fig. 18). We have seen that they produce delta-function peaks in the spectrum. The one-phonon diagrams defined above are the generalization for the perturbed system of these simple harmonic diagrams. Note, however, that the term "one-phonon diagram" is somewhat misleading for the anharmonic case in the sense that these diagrams do not rigorously describe "one-phonon processes," as they do in the harmonic case. When phonon-phonon interactions are present, it is in principle not possible to make a phonon expansion analogous to the one in Fig. 18, which means that it is not rigorously possible to effect a separation into "one-phonon processes" and "multiphonon processes," i.e., into peaks and background.

We will now investigate the structure of the one-phonon diagrams. From its definition it will be clear that the general form of a one-phonon diagram is a chain of so-called proper parts, which themselves do not contain any κ -line, connected by κ -lines. The chain, hanging on the neutron vertices, is broken by cutting one of the κ -lines. Diagram c of Fig. 19, for instance, has two proper parts: one containing the vertices a and b, the other containing the vertices c, d, e, and $T_{-\kappa}$. From this example we see that two different proper parts of a diagram may overlap on the cylinder, giving rise to a "coupling" between these proper parts induced by the ordering of the vertices. In much the same way as in the case of the theorem on disconnected diagrams (see page 16) we can disentangle different proper parts by a suitable permutation of the vertices. For instance, in our example we should like to have the integrations over the variables corresponding to the vertices a and b independent of those corresponding to the vertices c, d, and e. This can be achieved by taking the following six diagrams together: diagram c plus the diagrams that only differ from it in the order of vertex b with respect to vertices d and e, and of vertex a with respect to vertex c. In the appendix we have illustrated the disentanglement process by working out a simple example.

After having performed the disentanglement process in this way, we are now able to write down the general expression for the contribution

of all proper parts that can be drawn "between" two fixed V_{κ} -vertices, being the vertices at which the κ -lines enter and/or leave the proper part (see Fig. 20).

Fig. 20. Schematic representation of proper parts (the shaded areas) and examples of diagrams that are contained in these proper parts

Consider Fig. 20a. In this figure the shaded area represents the totality of all possible proper diagrams "between" t_1 and t_2 , a few examples of which are shown. The contribution of all these diagrams can be expressed as follows:

$$\text{Tr}\{U_{-\beta}U_{-it}U_{it}V_{-\kappa j}U_i(t_2-t_1)V_{\kappa j'}U_i(t-t_2)\}_p = \text{Tr}\{U_{-\beta}U_{-i(t_2-t_1)}V_{-\kappa j}U_i(t_2-t_1)V_{\kappa j'}\}_p \quad (79)$$

Use has been made of the cyclic invariance of the trace. The operators $V_{-\kappa j}$ and $V_{\kappa j'}$ correspond to the vertices at which the κ -lines, carrying polarization indices j and j' , are attached to the proper part (the dots in the figure). One has

$$V_{\kappa j} = \sum_{\nu=3}^{\infty} V_{\kappa j}^{(\nu)} \quad ;$$

$$V_{\kappa j}^{(\nu)} = \int_{\vec{q}_2 \dots \vec{q}_\nu} \sum_{j_2 \dots j_\nu} B_{\kappa j, q_2 j_2, \dots, q_\nu j_\nu}^{(\nu)} \left[A_{q_2 j_2} + A_{-q_2 j_2}^* \right] \dots \left[A_{q_\nu j_\nu} + A_{-q_\nu j_\nu}^* \right] \Delta(\vec{\kappa} + \vec{q}_2 + \dots + \vec{q}_\nu) \quad (80)$$

The κ -line attached to the vertex $V_{\kappa j}$ either comes from the right, corresponding to a phonon $\vec{\kappa}_j$ which will be absorbed at that vertex, or runs to the left, corresponding to a phonon $-\vec{\kappa}_j$ which is created at $V_{\kappa j}$. The factor $A_{\kappa j} + A_{-\kappa j}^*$ does not appear in (80); it belongs to the κ -line [see for instance (93)]; $\vec{q}_2, \dots, \vec{q}_\nu$ correspond to phonons belonging to the proper part. The suffix "p" in expression (79) indicates that the trace has to be

calculated for proper diagrams only, that is, for diagrams which do not involve any κ -line, so that at least two lines within the proper part have to be cut to separate the $V_{-\kappa j}$ -vertex from the $V_{\kappa j'}$ -vertex on the cylinder.

In the same way we have for the proper part of the type shown in Fig. 20b, in which the two κ -lines enter and/or leave the proper part in the same vertex:

$$\text{Tr}\{U_{-\beta} V_{-\kappa j, \kappa j'}\}_p \quad (81)$$

with

$$V_{-\kappa j, \kappa j'} = \sum_{\nu=3}^{\infty} V_{-\kappa j, \kappa j'}^{(\nu)} ;$$

$$V_{-\kappa j, \kappa j'}^{(\nu)} = \int_{\vec{q}_3 \dots \vec{q}_\nu} \sum_{j_3 \dots j_\nu} B_{-\kappa j, \kappa j', q_3 j_3, \dots, q_\nu j_\nu}^{(\nu)} \left[A_{q_3 j_3} + A_{-q_3 j_3}^* \right] \dots \left[A_{q_\nu j_\nu} + A_{-q_\nu j_\nu}^* \right] \Delta(\vec{q}_3 + \dots + \vec{q}_\nu) . \quad (82)$$

In addition to the proper parts just treated, which contain only V-vertices, proper parts exist which involve one neutron vertex (T_κ or $T_{-\kappa}$). We will meet them in the following (compare Fig. 21). Such parts will be called neutron bubbles. Formulae analogous to (79) and (81) can be written down for this case, and also for those cases in which the $V_{\pm\kappa}$ -vertices are situated in different regions. Proper parts containing only V-vertices are also called self-energy parts, because, similarly to the situation in quantum electrodynamics, they describe self-energy effects which renormalize the energies of the phonons (see the next chapter). Due to the dissipative character of the interaction, however, the self-energy parts in this case also involve lifetime effects (the self-energy is complex).

At this stage we must remark that, in order to be able to write the contribution of a proper part in the form of a trace, as in expressions (79) and (81), it still must be proven that we have the correct combinatorial factor. This is quite easy, however, and follows from the fact that the number of possibilities for dividing N phonons (corresponding to the N external lines of the total diagram) into $k + 1$ groups of $n, n_1, n_2, \dots, n_k$ phonons ($n_1, \dots, n_k$ being the numbers of external lines of the k proper parts in the diagram, n being the number of external κ -lines) is just $N! / n! n_1! \dots n_k!$. Together with the original factor $1/N!$ in the trace for the total diagram this gives the required factor $1/n! n_1! n_2! \dots n_k!$. Hence, for the i -th proper part having n_i external lines we have the correct factor $1/n_i!$.

In view of the above results the general form of the one-phonon diagrams can now be represented schematically as in Fig. 21. Note that diagram c in Fig. 19 is contained in diagram b of the following figure.

Fig. 21

General form of the one-phonon diagrams

We now perform the summation of the one-phonon diagrams to obtain an expression for $S_T^{(1)}(\vec{\kappa}, \omega)$ in terms of the contributions of the proper parts. We first isolate the contributions of the neutron bubbles. According to the location of the $V_{\kappa j}$ -vertex belonging to the neutron bubble which contains $T_{-\kappa}$, we subdivide the set of one-phonon diagrams into four groups represented by Fig. 22.

Fig. 22

The four groups of one-phonon diagrams defined in the text

The heavy dashed lines represent the remaining parts of the diagrams (the one-phonon diagrams minus the $T_{-\kappa}$ -bubble). Each of these parts is attached to the $V_{\kappa j}$ -vertex by means of a κ -line. Let us consider the group of diagrams represented by Fig. 22b. The two parts into which we have divided the diagrams in this group (the $T_{-\kappa}$ -bubble and the rest) are linked at the $V_{\kappa j}$ -vertex. However, in addition to this direct coupling there is still an indirect coupling between the two parts, induced by the ordered integrations in the expansions of the operators $U_{-\beta}$ and $U_{\pm it}$. In a particular diagram vertices belonging to one part have a definite order with respect to vertices of the other part. In completely the same way as in the foregoing, however, we can disentangle the two parts by shifting the vertices in one part with respect to the appropriate vertices in the other part, keeping the position of $V_{\kappa j}$ fixed, and taking sets of diagrams together which only differ from one another in the relative ordering of these vertices. In view of this, we have for the total contribution of all diagrams of the group under consideration to $S_T^{(1)}(\vec{\kappa}, \omega)$ for the case $t > 0$ [see (64)]:

$$\frac{(8\pi^3)^2 \Delta(0)}{2\pi v_0^2} \sum_j \int_0^\infty dt e^{-i\omega t} \int_0^t dt_1 i \text{Tr} \{U_{-\beta} U_{-it_1} T'_{-\kappa} U_{it_1} V_{\kappa j}\}_p$$

$$\cdot \text{Tr} \{U_{-\beta} U_{-i(t-t_1)} (A_{\kappa j} + A_{-\kappa j}^*) U_{i(t-t_1)} T'_\kappa\}_C \quad . \quad (83)$$

The two traces in this expression correspond to the two above-mentioned parts of the diagrams [compare (79)]. The operators $T'_{\pm\kappa}$ are equal to $T_{\pm\kappa}$ except for the Δ function arising from the summation over $\vec{s}$ [see remarks following Eq. (72)]:

$$T'_{\pm\kappa} = \sum_n e^{\pm i\vec{\kappa} \cdot (\vec{R}_{0n} + \vec{u}_{0n})} \quad . \quad (84)$$

The first factor in (83) arises from applying the relations (18) and (29).

We introduce new time variables as follows:

$$t - t_1 = \tau \quad ; \quad t_1 = \tau' \quad ; \quad \tau \geq 0 \quad ; \quad \tau' \geq 0 \quad . \quad (85)$$

With these variables we can replace $\int_0^\infty dt \int_0^t dt_1$ by $\int_0^\infty d\tau \int_0^\infty d\tau'$ and we get for (83) (N_0 is the number of unit cells):

$$\frac{8\pi^3 N_0}{2\pi v_0} \sum_j i \int_0^\infty d\tau' e^{-i\omega\tau'} \text{Tr} \{U_{-\beta} U_{-i\tau'} T'_{-\kappa} U_{i\tau'} V_{\kappa j}\}_p$$

$$\cdot \int_0^\infty d\tau e^{-i\omega\tau} \text{Tr} \{U_{-\beta} U_{-i\tau} (A_{\kappa j} + A_{-\kappa j}^*) U_{i\tau} T'_\kappa\}_C \quad , \quad (86)$$

so that we simply have obtained a product of integrals, one corresponding to the neutron bubble, the other corresponding to the rest of the diagrams (dashed line in Fig. 22b). In the same way we find analogous expressions for the contributions of the groups of diagrams represented by Fig. 22a and c. We get the following expression for the contribution of the groups a, b, and c to $S_T^{(1)}(\vec{\kappa}, \omega)$ for the case $t > 0$:

$$\frac{8\pi^3 N_0}{2\pi v_0} \sum_j N^+(\vec{\kappa}, \omega_j) \int_0^\infty d\tau e^{-i\omega\tau} \text{Tr} \{U_{-\beta} U_{-i\tau} (A_{\kappa j} + A_{-\kappa j}^*) U_{i\tau} T'_\kappa\}_C \quad , \quad (87)$$

in which $N^+(\vec{\kappa}\omega_j)$, the contribution of the neutron bubbles containing $T_{-\kappa}$ in Fig. 22a, b, and c, is given by the following expression:

$$N^+(\vec{\kappa}\omega_j) = \text{Tr} \{U_{-\beta} T''_{-\kappa}\}_p + i \int_0^\infty d\tau e^{-i\omega\tau} \text{Tr} \{U_{-\beta} U_{-i\tau} T'_{-\kappa} U_{i\tau} V_{\kappa j}\}_p \\ - i \int_0^\infty d\tau e^{-i\omega\tau} \text{Tr} \{U_{-\beta} U_{i\tau} V_{\kappa j} U_{-i\tau} T'_{-\kappa}\}_p \quad . \quad (88)$$

In this expression the operator $T''_{-\kappa}$ in the first term on the right, representing the contribution of the neutron bubble in Fig. 22a, is defined by

$$T''_{-\kappa} = -i \sum_n \left(\frac{v_0}{16\pi^3 M_n \omega_{\kappa j}} \right)^{1/2} \left(\vec{\kappa} \cdot \vec{e}_{\kappa j}^{(n)} \right) e^{i\vec{\kappa} \cdot (\vec{R}_{0n} + \vec{u}_{0n})} \quad . \quad (89)$$

We next consider the integral in expression (87). The diagrams that contribute to the trace in this integral are the diagrams of Fig. 21 without the $T_{-\kappa}$ -bubble. To isolate the contribution of the T_{κ} -bubble, we again subdivide these diagrams into four groups characterized by the location of the V_{κ} -vertex belonging to the T_{κ} -bubble, directly analogous to what we did in Fig. 22. Treating these groups of diagrams in a way similar to that demonstrated above and repeating the calculation for the case $t < 0$, we are led to the following expression for the partial scattering function $S_T^{(1)}(\vec{\kappa}\omega)$, valid to general order in the interaction:

$$S_T^{(1)}(\vec{\kappa}\omega) = \frac{8\pi^3 N_0}{v_0} \sum_{jj'} [N^+(\vec{\kappa}\omega_j) C^+(\vec{\kappa}\omega_{jj'}) N^{-*}(\vec{\kappa}\omega_{j'}) + N^-(\vec{\kappa}\omega_j) C^-(\vec{\kappa}\omega_{jj'}) N^{+*}(\vec{\kappa}\omega_{j'})] + \Lambda(\vec{\kappa}\omega) \quad (90)$$

The function $N^-(\vec{\kappa}\omega_j)$ can be obtained from $N^+(\vec{\kappa}\omega_j)$, given by Eq. (88), by

replacing $\int_0^\infty$ by $\int_0^{-\infty}$. The star denotes complex conjugate. Note that we

have $T_{\kappa}''^* = T_{-\kappa}''$, $T_{\kappa}'^* = T_{-\kappa}'$, and $V_{\kappa j}^* = V_{-\kappa j}$. The last relation follows from (80) and (19). Recall that the N-functions represent contributions from neutron bubbles.* They only affect the intensity of the scattering, but do not contain information about the line shift and broadening effects. They are independent

*All quantities, such as $N^\pm(\vec{\kappa}\omega_j)$, $C^\pm(\vec{\kappa}\omega_{jj'})$, $G^\pm(\vec{\kappa}\omega_{jj'})$, etc. (see below), depend on temperature. We shall not explicitly indicate this temperature dependence.

of Ω in the limit of large Ω , and they do not have peaks of the type that are presently sought. From each N in (90) a factor $e^{-W(\vec{\kappa})}$ can be extracted (Bravais lattice), where $e^{-2W(\vec{\kappa})}$ is the anharmonic Debye-Waller factor given by Eq. (54).

The functions $C^{\pm}(\vec{\kappa}\omega jj')$ in Eq. (90) have the following form:

$$C^{\pm}(\vec{\kappa}\omega jj') = \pm \frac{1}{2\pi} \int_0^{\pm\infty} d\tau e^{-i\omega\tau} \text{Tr}\{U_{-\beta} U_{-i\tau} (A_{\kappa j} + A_{-\kappa j}^*) U_{i\tau} (A_{-\kappa j'} + A_{\kappa j'}^*)\} C \quad (91)$$

The diagrams that correspond to the trace in this expression are the one-phonon diagrams without the neutron bubbles (for examples see the next chapter). The trace in (91) is what is called the one-phonon Green function. It is this function which contains the effects we are looking for, as will be seen in the next chapter.

Finally, the quantity $\Lambda(\vec{\kappa}\omega)$, appearing in Eq. (90), needs our attention. This function represents the contribution of those one-phonon diagrams or parts of one-phonon diagrams which do not contribute to the scattering peaks. It is, in general, a smooth function of ω , and it does not have peaks of the type under study. In other words, it contributes to the background of the scattering spectrum. For instance, $\Lambda(\vec{\kappa}\omega)$ includes the group of one-phonon diagrams shown in Fig. 22d. Writing out the contribution of this group we immediately see that it does not involve the functions $C^{\pm}(\vec{\kappa}\omega jj')$ defined above.

In obtaining the above expression for $S_T^{(1)}(\vec{\kappa}\omega)$ we have achieved our goal: the isolation of the contributions containing the information about the scattering peaks [the first term on the right of (90) involving the Fourier transforms of the Green function] from the contributions which correspond to the background (the function $\Lambda(\vec{\kappa}\omega)$ and the contributions of all those diagrams which do not belong to the class of one-phonon diagrams). We recall once more that such an isolation is only meaningful as long as the width of a peak is small with respect to the value of the frequency at its center.

In the next chapter we will study the functions $C^{\pm}(\vec{\kappa}\omega jj')$ in detail and return to the neutron scattering problem at the end of that chapter.

CHAPTER VII

THE ONE-PHONON GREEN FUNCTION

In this chapter we shall give a diagrammatic analysis of the important functions $C^\pm(\vec{q}\omega jj')$, defined by Eq. (91). Since for a parameter-free lattice $\langle A_{\vec{q}j} + A_{-\vec{q}j}^* \rangle_T = 0$ (see the end of Chapter IV), we have in this case

$$C^\pm(\vec{q}\omega jj') = \pm \frac{1}{2\pi} \int_0^{\pm\infty} dt e^{-i\omega t} \left\langle \left(A_{\vec{q}j} + A_{-\vec{q}j}^* \right) \left(A_{-\vec{q}j'}(t) + A_{\vec{q}j'}^*(t) \right) \right\rangle_T, \quad (92)$$

as follows from (67). We see that $C = C^+ + C^-$ is the Fourier transform of the one-phonon Green function. As such, it contains valuable information about the shift and spread of the phonon energies due to phonon-phonon interactions (self-energy and lifetime effects). Therefore, a calculation of these functions is theoretically interesting on its own merits.⁽²²⁾

We have seen in the foregoing chapter that the general form of the diagrams which contribute to the trace in the expression for $C^\pm(\vec{q}\omega jj')$ consists of a chain of proper parts (self-energy parts) connected by single lines (q-lines) carrying wave vector $\vec{q}$ or $-\vec{q}$. The chain is broken by cutting one of the q-lines. In Fig. 23 we have presented a few examples; the crosses represent the operators $A_{\vec{q}j}(A_{-\vec{q}j}^*)$ and $A_{-\vec{q}j'}(A_{\vec{q}j'}^*)$.

Fig. 23. Examples of diagrams contributing to $C^\pm(\vec{q}\omega jj')$

Our task is to sum all these diagrams and write their total contribution in terms of the contributions of the self-energy parts, represented by the shaded areas. This can be done exactly, as will be shown now.*

In the first place, we can restrict ourselves to considering only diagrams without external q -lines (see Fig. 23 a and c) by performing the summation over turns on the cylinder, such as in Fig. 23b in completely the same way as we did in the foregoing [Eqs. (27) and (76)]. We then have to associate with each q -line in such a diagram a propagator function such as (27) or (76), or a mixture of them when a q -line lies partly in a $U_{\pm it}$ -region and partly in a $U_{-\beta}$ -region. For instance, for a q -line in U_{it} between t_1 and t_2 , we have the propagator

$$D_{qj}^{(0)}(t_2-t_1) = \text{Tr} \left\{ U_{-\beta}^{(0)} U_{-i(t_2-t_1)}^{(0)} (A_{qj} + A_{-qj}^*) U_{i(t_2-t_1)}^{(0)} (A_{-qj} + A_{qj}^*) \right\}_C$$

$$= \frac{e^{i(t_2-t_1)\omega_{qj}} + e^{-\beta\omega_{qj}} e^{-i(t_2-t_1)\omega_{qj}}}{1 - e^{-\beta\omega_{qj}}}, \quad (93)$$

in which $U_{-\beta}^{(0)} = e^{-\beta H_0}$, etc.

According to the location of the V_{-qj} -vertex, being the vertex at which the q -line corresponding to the phonon $\pm \vec{qj}$ is attached (this q -line has its other endpoint at the left cross), we now subdivide this reduced set of diagrams into the following four classes (see Fig. 24):

- A: diagrams with no V -vertices at all;
- B: diagrams in which the V_{-qj} -vertex is located in the U_{it} -region;
- C: diagrams in which the V_{-qj} -vertex is located in the U_{-it} -region;
- D: diagrams in which the V_{-qj} -vertex is located in the $U_{-\beta}$ -region.

For instance, diagrams a and c of Fig. 23 belong to class B, whereas diagram b belongs to class C.

Fig. 24

Schematic representation of the four classes of diagrams defined in the text. The dots are the V_{-qj} -vertices; the heavy dotted lines represent the remaining parts of the diagrams "between" the V_{-qj} -vertex and the cross at the right.

*See references 13 and 22. The notation in these papers differs somewhat from the notation used here.

Let us first consider the diagrams of class A. They are the "harmonic" diagrams of our problem. According to (93), their contribution to $C^\pm(\vec{q}\omega_{jj'})$ is equal to $C_{(0)}^\pm(\vec{q}\omega_{jj'})\delta_{jj'}$, with

$$\begin{aligned} C_{(0)}^\pm(\vec{q}\omega_{jj'}) &= \pm \frac{1}{2\pi} \int_0^{\pm\infty} dt e^{-i\omega t} D_{qj}^{(0)}(t) \\ &= \pm \frac{1}{2\pi i} \frac{(\omega - \omega_{qj} \mp i0)^{-1} + e^{-\beta\omega_{qj}} (\omega + \omega_{qj} \mp i0)^{-1}}{1 - e^{-\beta\omega_{qj}}} \quad , \quad (94) \end{aligned}$$

where we have used the formal relations

$$\int_0^{\pm\infty} dt e^{i\omega t} = \frac{i}{\omega \pm i0} \quad . \quad (96)$$

Either the upper sign has to be taken or the lower sign. The function $D_{qj}^{(0)}(t)$ in the above integrands, explicitly given by Eq. (93), is the unperturbed one-phonon Green function.

We next turn to a discussion of the diagrams of class B. The total contribution $C_B^+(\vec{q}\omega_{jj'})$ to $C^+(\vec{q}\omega_{jj'})$ of this class of diagrams can be written as follows:

$$\begin{aligned} C_B^+(\vec{q}\omega_{jj'}) &= \frac{1}{2\pi} \int_0^\infty dt \int_0^t dt_1 e^{-i\omega t} D_{qj}^{(0)}(t_1) \\ &\quad \cdot i \text{Tr} \left\{ U_{-\beta} U_{-i(t-t_1)} V_{-qj} U_{i(t-t_1)} (A_{-qj'} + A_{qj'}^*) \right\} C \quad . \quad (97) \end{aligned}$$

Here, the trace corresponds to the part of diagram B designated by the dotted line. It involves all possible diagrams that are attached to V_{-qj} and to the cross at the right (representing $A_{-qj'} + A_{qj'}^*$). The factor i originates from the expansion of U_{it} [see (64)].

Introducing in (97) new time variables as before:

$$t - t_1 = \tau \quad ; \quad t_1 = \tau' \quad ; \quad \tau \geq 0 \quad ; \quad \tau' \geq 0 \quad , \quad (98)$$

we see that $\int_0^\infty dt \int_0^t dt_1$ can be replaced by $\int_0^\infty d\tau \int_0^\infty d\tau'$. This gives

$$C_B^+(\vec{q}\omega_{jj'}) = C_{(0)}^+(\vec{q}\omega_j) i \int_0^\infty d\tau e^{-i\omega\tau} \text{Tr} \left\{ U_{-\beta} U_{-i\tau} V_{-qj} U_{i\tau} (A_{-qj'} + A_{qj'}^*) \right\}_C . \quad (99)$$

Each of the diagrams contributing to the trace in the last expression will be divided into two parts: the self-energy part belonging to the V_{-qj} -vertex and the rest of the diagram, which by itself is a chain of self-energy parts with "points of suspension" at $V_{qj''}$ and at the cross at the right (see Fig. 25). The four different ways in which this is possible are displayed in Fig. 25. As before, the shaded areas represent the self-energy parts; the thick lines represent the rest of the diagrams (the chains).

Fig. 25

The four groups of diagrams contributing to the trace in (99)

In the diagrams of the form c, the vertices V_{-qj} and $V_{qj''}$ are identical to give the vertex $V_{-qj, qj''}$, in which phonon $\vec{q}j$ is created (or equivalently $-\vec{q}j$ is absorbed) and phonon $\vec{q}j''$ is absorbed (or equivalently $-\vec{q}j''$ is created). An example of a diagram from this group is diagram a in Fig. 23 (without the line $\vec{q}j$); diagram c in Fig. 23 is contained in the group represented by Fig. 25a.

Disentangling the two parts of the diagrams as in the previous chapter, we can write for the total contribution of all diagrams represented by Fig. 25 a and b to the integral on the right of expression (99),

$$i \sum_{j''} \int_0^\infty d\tau \int_0^\tau d\tau_1 e^{-i\omega\tau} \left[\text{Tr} \left\{ U_{-\beta} U_{-i\tau_1} V_{-qj} U_{i\tau_1} V_{qj''} \right\}_p - \text{Tr} \left\{ U_{-\beta} U_{i\tau_1} V_{qj''} U_{-i\tau_1} V_{-qj} \right\}_p \right] \\ \cdot \text{Tr} \left\{ U_{-\beta} U_{-i(\tau-\tau_1)} (A_{qj''} + A_{qj''}^*) U_{i(\tau-\tau_1)} (A_{-qj'} + A_{qj'}^*) \right\}_C . \quad (100)$$

If a change of variables in this expression analogously to (98) is made, this contribution, together with the corresponding contribution of diagram c in Fig. 25, becomes [compare Eq. (91)]

$$2\pi \sum_{j''} G^+(\vec{q}\omega_{jj''}) C^+(\vec{q}\omega_{j''j'}) \quad , \quad (101)$$

in which the self-energy function $G^+(\vec{q}\omega_{jj'})$, representing the contributions of the self-energy parts in Fig. 25a, b, and c, is defined by the following equation:

$$\begin{aligned} G^+(\vec{q}\omega_{jj''}) = & i \int_0^\infty d\tau e^{-i\omega\tau} \text{Tr} \left\{ U_{-\beta} U_{-i\tau} V_{-qj} U_{i\tau} V_{qj''} \right\}_p \\ & - i \int_0^\infty d\tau e^{-i\omega\tau} \text{Tr} \left\{ U_{-\beta} U_{i\tau} V_{qj''} U_{-i\tau} V_{-qj} \right\}_p \\ & + \text{Tr} \left\{ U_{-\beta} V_{-qj, qj''} \right\}_p \quad . \end{aligned} \quad (102)$$

The total contribution to the integral in (99) of the diagrams of type d in Fig. 25 will be denoted by $F^+(\vec{q}\omega_{jj'})$. Its explicit expression is not needed for our purpose, because it will turn out not to appear in the final result.

We thus finally find for $C_B^+(\vec{q}\omega_{jj'})$ the following expression:

$$\begin{aligned} C_B^+(\vec{q}\omega_{jj'}) = & 2\pi i C_{(0)}^+(\vec{q}\omega_j) \sum_{j''} G^+(\vec{q}\omega_{jj''}) C^+(q\omega_{j''j'}) \\ & + i C_{(0)}^+(\vec{q}\omega_j) F^+(q\omega_{jj'}) \quad . \end{aligned} \quad (103)$$

In completely the same way one finds for $C_C^+(\vec{q}\omega_{jj'})$, representing the contributions of all diagrams of class C (see Fig. 24) to $C^+(\vec{q}\omega_{jj'})$,

$$\begin{aligned} C_C^+(\vec{q}\omega_{jj'}) = & - 2\pi i C_{(0)}^-(\vec{q}, -\omega_j) \sum_{j''} G^+(\vec{q}\omega_{jj''}) C^+(\vec{q}\omega_{j''j'}) \\ & - i C_{(0)}^-(\vec{q}, -\omega_j) F^+(\vec{q}\omega_{jj'}) \quad . \end{aligned} \quad (104)$$

Finally, the sum of the contributions to $C^+(\vec{q}\omega_{jj'})$ of the diagrams of class D will be called $H^+(\vec{q}\omega_{jj'})$, which will not be written down explicitly. Just as $F^+(\vec{q}\omega_{jj'})$ it does not enter into the final result, as will be seen below.

Summarizing, the following equation for $C^+(\vec{q}\omega_{jj'})$ has been obtained:

$$\begin{aligned}
C^+(\vec{q}\omega_{jj'}) &= C_{(0)}^+(\vec{q}\omega_j)\delta_{jj'} + C_B^+(\vec{q}\omega_{jj'}) + C_C^+(\vec{q}\omega_{jj'}) + H^+(\vec{q}\omega_{jj'}) \\
&= C_{(0)}^+(\vec{q}\omega_j)\delta_{jj'} + i\left[C_{(0)}^+(\vec{q}\omega_j) - C_{(0)}^-(\vec{q}, -\omega_j)\right] F^+(\vec{q}\omega_{jj'}) + H^+(\vec{q}\omega_{jj'}) \\
&\quad + 2\pi i \left[C_{(0)}^+(\vec{q}\omega_j) - C_{(0)}^-(\vec{q}, -\omega_j)\right] \sum_{j''} G^+(\vec{q}\omega_{jj''}) C^+(\vec{q}\omega_{jj''}) \quad , \\
\end{aligned} \tag{105}$$

which, after some algebraic manipulation, can be put into the form

$$\begin{aligned}
2\pi i \sum_{j'} \left[\delta_{jj'}(\omega^2 - \omega_{qj'}^2) - 2\omega_{qj} G^+(\vec{q}\omega_{jj'}) \right] C^+(\vec{q}\omega_{jj''}) = \\
2\pi i (\omega^2 - \omega_{qj}^2) C_{(0)}^+(\vec{q}\omega_j)\delta_{jj''} + 2\omega_{qj} F^+(\vec{q}\omega_{jj''}) + 2\pi i (\omega^2 - \omega_{qj}^2) H^+(\vec{q}\omega_{jj''}) \quad . \\
\end{aligned} \tag{106}$$

For reasons which will become clear in a moment, it is advantageous to introduce the auxiliary function $C^-(-\vec{q}, -\omega_j'j)$, defined as follows:

$$C^-(-\vec{q}, -\omega_j'j) = -\frac{1}{2\pi} \int_0^{-\infty} dt e^{i\omega t} \text{Tr} \left\{ U_{-\beta} U_{-it} (A_{-qj'} + A_{qj'}^*) U_{it} (A_{qj} + A_{-qj}^*) \right\}_C \quad . \tag{107}$$

Using the same procedure as in the derivation of Eq. (106), the following equation for $C^-(-\vec{q}, -\omega_j'j)$ can be obtained:

$$\begin{aligned}
2\pi i \sum_{j'} \left[\delta_{jj'}(\omega^2 - \omega_{qj'}^2) - 2\omega_{qj} G^+(\vec{q}\omega_{jj'}) \right] C^-(-\vec{q}, -\omega_j''j') = \\
2\pi i (\omega^2 - \omega_{qj}^2) C_{(0)}^-(\vec{q}, -\omega_j)\delta_{jj''} + 2\omega_{qj} F^+(\vec{q}\omega_{jj''}) + 2\pi i (\omega^2 - \omega_{qj}^2) H^+(\vec{q}\omega_{jj''}) \quad . \\
\end{aligned} \tag{108}$$

Subtracting (108) from (106), we get

$$\begin{aligned}
2\pi i \sum_{j'} \left[\delta_{jj'}(\omega^2 - \omega_{qj'}^2) - 2\omega_{qj} G^+(\vec{q}\omega_{jj'}) \right] \left[C^+(\vec{q}\omega_{jj''}) - C^-(-\vec{q}, -\omega_j''j') \right] \\
= 2\omega_{qj} \delta_{jj''} \quad . \\
\end{aligned} \tag{109}$$

We see that the quantities F^+ and H^+ no longer appear in this equation. From this equation we set up a new equation for $C^+(\vec{q}\omega_{jj'})$ by considering the following function:

$$A^+(\vec{q}\omega_{jj'}) = \frac{1}{2\pi} \int_0^{\infty} dt e^{-i\omega t} \left\langle \left[(A_{qj} + A_{-qj}^*), (A_{-qj'}(t) + A_{qj'}^*(t)) \right] \right\rangle_T \quad . \tag{110}$$

On the basis of (67) and (92), we have

$$A^+(\vec{q}\omega_{jj'}) = C^+(\vec{q}\omega_{jj'}) - \frac{1}{2\pi} \int_0^\infty dt e^{-i\omega t} \text{Tr} \left\{ U_{-\beta} U_{it} (A_{-qj'} + A_{qj'}^*) U_{-it} (A_{qj} + A_{-qj}^*) \right\}_C, \quad (111)$$

which, on the one hand, in view of the cyclic invariance of the trace, can be written as follows:

$$A^+(\vec{q}\omega_{jj'}) = C^+(\vec{q}\omega_{jj'}) - \frac{e^{-\beta\omega}}{2\pi} \int_{i\beta}^{\infty+i\beta} d(t+i\beta) e^{-i\omega(t+i\beta)} \text{Tr} \left\{ U_{-\beta} U_{-i(t+i\beta)} (A_{qj} + A_{-qj}^*) U_{i(t+i\beta)} (A_{-qj'} + A_{qj'}^*) \right\}_C. \quad (112)$$

Assuming the trace to be analytic in the region $0 \leq \text{Im}t \leq \beta$; $t > 0$ of the complex t -plane, we find, according to Cauchy's theorem,

$$A^+(\vec{q}\omega_{jj'}) = (1 - e^{-\beta\omega}) C^+(\vec{q}\omega_{jj'}) + B(\vec{q}\omega_{jj'}) \quad (113)$$

Here $B(\vec{q}\omega_{jj'})$ is the contribution to the integral in (112) of the part of the imaginary axis between zero and $i\beta$ (for which $t = 0$). The integral in infinity vanishes due to dissipation [the trace behaves as $\exp(-\Gamma(\vec{q}j)|t|)$, see below].

On the other hand, we can write $A^+(\vec{q}\omega_{jj'})$ as follows [Eqs. (107) and (111)]:

$$A^+(\vec{q}\omega_{jj'}) = C^+(\vec{q}\omega_{jj'}) - C^-(-\vec{q}, -\omega_{j'j}) ,$$

so that we get, combining this equation with Eq. (113),

$$(1 - e^{-\beta\omega}) C^+(\vec{q}\omega_{jj'}) = C^+(\vec{q}\omega_{jj'}) - C^-(-\vec{q}, -\omega_{j'j}) - B(\vec{q}\omega_{jj'}) \quad (114)$$

Combining (109) and (114) and repeating the calculation for $C^-(\vec{q}\omega_{jj'})$, we finally obtain the following general matrix equations for $C^\pm(\vec{q}\omega_{jj'})$, analogous to the Dyson equations in field theory:

$$\pm 2\pi i \sum_{j'} \left[\delta_{jj'} (\omega^2 - \omega_{qj'}^2) - 2\omega_{qj} G^\pm(\vec{q}\omega_{jj'}) \right] \left[C^\pm(\vec{q}\omega_{j'j''}) \pm \bar{B}(\vec{q}\omega_{j'j''}) \right] = 2\omega_{qj} \delta_{jj''} (1 - e^{-\beta\omega})^{-1} \quad (115)$$

Here $\bar{B}(\vec{q}\omega_{j'j''}) = (1 - e^{-\beta\omega})^{-1} B(\vec{q}\omega_{j'j''})$.

The function G^- follows from G^+ , given by Eq. (102), by replacing $\int_0^\infty$ by $\int_0^{-\infty}$. The function $\bar{B}(\vec{q}\omega_{jj'})$ is of no importance. It drops in the spectral function $C^+(\vec{q}\omega_{jj'}) + C^-(\vec{q}\omega_{jj'}) = C(\vec{q}\omega_{jj'})$, while in the neutron scattering function describing the peaks [Eq. (90)] it gives rise to terms of the form $N^+ \bar{B} N^*$, etc., which do not involve peaks of the type that are presently sought, since $\bar{B}$ does not involve such peaks. This can be shown by investigating the diagrams that contribute to $\bar{B}(\vec{q}\omega_{jj'})$. The above-mentioned terms can be considered as corresponding to traces of the background and can be taken to be incorporated in the term $\Lambda(\vec{\kappa}\omega)$ in Eq. (90). We then see that we can find $C(\vec{q}\omega_{jj'})$ once we know the self-energy function $G^\pm(\vec{q}\omega_{jj'})$, although still then the set of equations (115) has to be solved numerically. The function $G^\pm(\vec{q}\omega_{jj'})$ is completely expressed in terms of proper, connected diagrams. Therefore, an expansion of this function in powers of the coupling constant u/d is expected to converge rapidly for all values of ω , while for any particular order only a finite number of different basic diagrams has to be calculated. For instance, in lowest order [i.e., to order $(u/d)^2$] this number is three (see the next chapter). This would not be the case if we had tried to give a direct perturbation analysis of $C(\vec{q}\omega_{jj'})$ itself, starting from expression (91) and taking first all zeroth-order diagrams, then all first-order diagrams, etc. The resulting series would be very poorly convergent for ω near $\omega_{\kappa j}$. What we have done, in fact, by deriving Eq. (115), is treating this series in its entirety [compare also Van Hove's lectures⁽³⁾].

A solution of Eqs. (115), which is correct to lowest nonvanishing order in the coupling, can be easily found. Writing $G^\pm(\vec{q}\omega_j)$ for $G^\pm(\vec{q}\omega_{jj})$ we find for the spectral function $C_{(1)}(\vec{q}\omega_{jj'}) = C_{(1)}^+(\vec{q}\omega_{jj'}) + C_{(1)}^-(\vec{q}\omega_{jj'})$, where the subscript (1) denotes the lowest-order contribution:

$$2\pi i C_{(1)}(\vec{q}\omega_{jj'}) = \frac{2\omega_{qj} \delta_{jj'}}{1 - e^{-\beta\omega}} \left\{ \frac{1}{\omega^2 - \omega_{qj}^2 - 2\omega_{qj} G_{(1)}^+(\vec{q}\omega_j)} - \frac{1}{\omega^2 - \omega_{qj}^2 - 2\omega_{qj} G_{(1)}^-(\vec{q}\omega_j)} \right\}.$$

The following relations can be easily verified from the definition of $G^\pm(\vec{q}\omega_{jj'})$:

$$\begin{aligned} [G^\pm(\vec{q}\omega_{jj'})]^* &= G^\mp(\vec{q}\omega_{jj'}) \quad ; \\ G^\pm(\vec{q}\omega_{jj'}) &= G^\mp(-\vec{q}, -\omega_{jj'}) \quad . \end{aligned} \quad (116)$$

The first of these relations implies that the diagonal part ($j=j'$) of $G^\pm(\vec{q}\omega_{jj'})$ satisfies

$$G^\pm(\vec{q}\omega_j) = \text{Re } G^\pm(\vec{q}\omega_j) \pm i \text{Im } G^\pm(\vec{q}\omega_j) \quad . \quad (117)$$

Using these relations and denoting $\text{Re } G_{(1)}^+(\vec{q}\omega_j)$ by $\Delta_{(1)}(\vec{q}\omega_j)$ and $\text{Im } G_{(1)}^+(\vec{q}\omega_j)$ by $\Gamma_{(1)}(\vec{q}\omega_j)$, we can write $C_{(1)}(\vec{q}\omega_{jj'})$ in the form

$$2\pi i C_{(1)}(\vec{q}\omega_{jj'}) = \frac{2\omega_{qj} \delta_{jj'}}{1 - e^{-\beta\omega}} \cdot \left\{ \frac{1}{[\omega - \omega_{qj} - \Delta_{(1)}(\vec{q}\omega_j) - i\Gamma_{(1)}(\vec{q}\omega_j)] [\omega + \omega_{qj} + \Delta_{(1)}(\vec{q}\omega_j) + i\Gamma_{(1)}(\vec{q}\omega_j)]} - \text{c.c.} \right\} . \quad (118)$$

or, still to lowest order and for $\Gamma_{(1)}(\vec{q}\omega_j) \ll \omega_{qj}$,

$$C_{(1)}(\vec{q}\omega_{jj'}) = \frac{\pi^{-1} \delta_{jj'}}{1 - e^{-\beta\omega_{qj}}} \left\{ \frac{\Gamma_{(1)}(\vec{q}j)}{[\omega - \omega_{qj} - \Delta_{(1)}(\vec{q}j)]^2 + [\Gamma_{(1)}(\vec{q}j)]^2} + \frac{e^{-\beta\omega_{qj}} \Gamma_{(1)}(\vec{q}j)}{[\omega + \omega_{qj} + \Delta_{(1)}(\vec{q}j)]^2 + [\Gamma_{(1)}(\vec{q}j)]^2} \right\} , \quad (119)$$

where we have written $\Gamma_{(1)}(\vec{q}j)$ for $\Gamma_{(1)}(\vec{q}, \omega_{qj}, j)$, etc. In the first term on the right of (119) we have substituted $\omega = \omega_{qj}$, in the second term $\omega = -\omega_{qj}$, and we have used the fact that $\Delta_{(1)}(\vec{q}\omega_j)$ and $\Gamma_{(1)}(\vec{q}\omega_j)$ are even and uneven functions of ω , respectively [see (134) and (135)].

This result has to be compared with the unperturbed (harmonic) C-function, which, according to (94) and by applying the formal relation

$$\frac{1}{\omega + i0} - \frac{1}{\omega - i0} = 2\pi i \delta(\omega) , \quad (120)$$

has the form

$$C_{(0)}(\vec{q}\omega_j) = \frac{1}{1 - e^{-\beta\omega_{qj}}} \left\{ \delta(\omega - \omega_{qj}) + e^{-\beta\omega_{qj}} \delta(\omega + \omega_{qj}) \right\} . \quad (121)$$

In the latter case, the spectral function $C_{(0)}(\vec{q}\omega_j)$ displays delta-function singularities for $\omega = \pm\omega_{qj}$, where ω_{qj} is the unperturbed single-phonon energy. In the perturbed case (first order) these delta-function singularities have become finite peaks of Lorentzian shape with central frequencies at $\omega = \pm(\omega_{qj} + \Delta_{(1)}(\vec{q}j))$ and width at half-maximum equal to $2\Gamma_{(1)}(\vec{q}j)$. From this we conclude that $\Delta_{(1)}(\vec{q}j)$ describes the first-order shift in the energy of the phonon $\vec{q}j$ due to the interaction (self-energy), while $\Gamma_{(1)}(\vec{q}j)$ is the first-order damping rate (inverse phonon lifetime), in accord with the familiar interpretation of the poles of the Fourier-transformed one-particle Green function.⁽²³⁾

From (92) and (119) we find for the Green function for a parameter-free lattice (to first order):

$$\left\langle \left(A_{\mathbf{qj}} + A_{-\mathbf{qj}}^* \right) \left(A_{-\mathbf{qj}'}(t) + A_{\mathbf{qj}'}^*(t) \right) \right\rangle_T^{(1)} = \frac{\delta_{jj'}}{1 - e^{-\beta \omega_{\mathbf{qj}}}} \cdot \left[e^{i(\omega_{\mathbf{qj}} + \Delta_{(1)}(\vec{\mathbf{q}}))t} + e^{-\beta \omega_{\mathbf{qj}}} e^{-i(\omega_{\mathbf{qj}} + \Delta_{(1)}(\vec{\mathbf{q}}))t} \right] e^{-\Gamma_{(1)}(\vec{\mathbf{q}})|t|} \quad (122)$$

From this expression we can immediately obtain an expression for the correlation function $\langle \vec{u}_{\mathbf{sn}}(0) \cdot \vec{u}_{\mathbf{s'n'}}(t) \rangle_T$.

To general order in the interaction, an explicit solution of Eqs. (115) cannot be written down due to polarization mixing. However, when we drop the polarization indices for convenience (i.e., when we consider a Bravais lattice and put $\omega_{\mathbf{qj}} = \omega_{\mathbf{q}}$, etc.), the matrix equations (115) become algebraic equations for the functions $C^\pm(\vec{\mathbf{q}}\omega)$. One finds for $C(\vec{\mathbf{q}}\omega) = C^+(\vec{\mathbf{q}}\omega) + C^-(\vec{\mathbf{q}}\omega)$ to general order in the interaction

$$2\pi i C(\vec{\mathbf{q}}\omega) = \frac{2\omega_{\mathbf{q}}}{1 - e^{-\beta\omega}} \cdot \left\{ \frac{1}{[\omega - \omega_{\mathbf{q}} - \Delta(\vec{\mathbf{q}}\omega) - i\Gamma(\vec{\mathbf{q}}\omega)] [\omega + \omega_{\mathbf{q}} + \Delta(\vec{\mathbf{q}}\omega) + i\Gamma(\vec{\mathbf{q}}\omega)]} - \text{c.c.} \right\} \quad (123)$$

with the abbreviations

$$\Delta(\vec{\mathbf{q}}\omega) = \text{Re} \left[\omega_{\mathbf{q}} \left\{ 1 + (2 G^+(\vec{\mathbf{q}}\omega)/\omega_{\mathbf{q}}) \right\}^{1/2} - \omega_{\mathbf{q}} \right] \quad (124)$$

and

$$\Gamma(\vec{\mathbf{q}}\omega) = \text{Im} \left[\omega_{\mathbf{q}} \left\{ 1 + (2 G^+(\vec{\mathbf{q}}\omega)/\omega_{\mathbf{q}}) \right\}^{1/2} - \omega_{\mathbf{q}} \right] \quad (125)$$

We see that also to general order the shift and width of the energy states of individual phonons are determined by the complex self-energy function $G^+(\vec{\mathbf{q}}\omega)$ [or $G^+(\vec{\mathbf{q}}\omega_{\mathbf{jj}'})$ when the polarization indices are retained]. However, in higher order [to order $(u/d)^n$ with $n > 2$], the shift and width are no longer simply the real and imaginary part of this quantity as in the lowest-order case. The self-energy and damping rate are interdependent in the general case [notice that $\Delta(\vec{\mathbf{q}}\omega)$ and $\Gamma(\vec{\mathbf{q}}\omega)$ are functions of ω]. The lifetime of a phonon, being a dissipative effect, is influenced by the energy-shift effect, since energy conservation is involved in each decay. On the other hand, the peak position of the energy spectrum of a phonon may depend upon the decay probability.⁽³⁾ In order to be able to consider the phonon as a quasiparticle with wave vector $\vec{\mathbf{q}}$ also in higher order, $\Delta(\vec{\mathbf{q}}\omega)$ and $\Gamma(\vec{\mathbf{q}}\omega)$ must be slowly varying functions of ω , and $\Gamma(\vec{\mathbf{q}}\omega)/\omega$ must be

much smaller than one, independent of the strength of the interaction. We expect this latter condition to be true for temperatures well below the melting point and/or values of q which are sufficiently small. This condition of long-lived excitations in the crystal is equivalent with the condition of narrow well-defined peaks in the neutron scattering spectrum (see Chapter VI).

Let us finally return to the neutron scattering problem. Equations (90) and (115) together express the partial scattering function describing the scattering peaks entirely in terms of quantities which involve proper, connected diagrams only and which can be evaluated to arbitrarily high accuracy (at least in principle). It will be clear from the foregoing that the functions $G^\pm(\vec{q}\omega jj')$ describe the shift and broadening of the one-phonon peaks in the scattering spectrum due to phonon-phonon coupling.

For instance, to lowest nonvanishing order we find for the case of a Bravais lattice, using Eqs. (88), (89), (90), and (119), and remembering that to zeroth order

$$N^\pm(\vec{\kappa}\omega j) = -i \left(\frac{v_0}{16\pi^3 M \omega_{\kappa j}} \right)^{1/2} (\vec{\kappa} \cdot \vec{e}_{\kappa j}) e^{-W(\vec{\kappa})},$$

for the partial scattering function $S_T^{(1)}(\vec{\kappa}\omega)$:

$$S_T^{(1)}(\vec{\kappa}\omega) = \frac{N_0 e^{-2W(\vec{\kappa})}}{2\pi M} \sum_j \frac{(\vec{\kappa} \cdot \vec{e}_{\kappa j})^2}{\omega_{\kappa j} (1 - e^{-\beta\omega_{\kappa j}})}$$

$$\cdot \left\{ \frac{\Gamma_{(1)}(\vec{\kappa}j)}{[\omega - \omega_{\kappa j} - \Delta_{(1)}(\vec{\kappa}j)]^2 + [\Gamma_{(1)}(\vec{\kappa}j)]^2} + \frac{e^{-\beta\omega_{\kappa j}} \Gamma_{(1)}(\vec{\kappa}j)}{[\omega + \omega_{\kappa j} + \Delta_{(1)}(\vec{\kappa}j)]^2 + [\Gamma_{(1)}(\vec{\kappa}j)]^2} \right\}. \quad (126)$$

This lowest-order expression has recently also been obtained by a number of other authors⁽²⁴⁾ by different methods. The right-hand side of Eq. (126) describes a set of Lorentz peaks centered at $\pm(\omega_{\kappa j} + \Delta_{(1)}(\vec{\kappa}j))$ and having width at half-maximum equal to $2\Gamma_{(1)}(\vec{\kappa}j)$. They can be interpreted as emission or absorption peaks according as their central frequencies occur at positive or negative values of ω . Explicit expressions for $\Delta_{(1)}(\vec{\kappa}j)$ and $\Gamma_{(1)}(\vec{\kappa}j)$ will be derived in the next chapter. In writing down formula (126) for $S_T^{(1)}(\vec{\kappa}\omega)$ we have omitted the irrelevant quantity $\Lambda(\vec{\kappa}\omega)$ occurring in (90) because it only describes something of the continuous background.

Notice that in (126) in the limit $T \rightarrow 0$ ($\beta \rightarrow \infty$) the absorption peaks vanish, just as in the unperturbed case. This behaviour persists to general order, as can be seen from Eq. (115). The right-hand side of this equation goes to zero in the limit $T \rightarrow 0$ for $\omega < 0$, due to the factor $(1 - e^{-\beta\omega})^{-1}$. Since the quantities $G^{\pm}(\vec{\kappa}\omega jj')$ and $N^{\pm}(\vec{\kappa}\omega j)$ have finite limits for $T \rightarrow 0$ (see next chapter), this implies that the first term on the right-hand side of Eq. (90), which describes the scattering peaks, vanishes for $T = 0$ and $\omega < 0$.*

*The discussion of this point in reference (13) is incorrect.

CHAPTER VIII

SELF-ENERGY AND LIFETIME OF A PHONON

In the previous chapter we saw that the functions $G^{\pm}(\vec{q}\omega jj')$, which can be generally expressed as follows:

$$\begin{aligned}
 G^{\pm}(\vec{q}\omega jj') = & i \int_0^{\pm\infty} d\tau e^{-i\omega\tau} \text{Tr} \left\{ U_{-\beta} U_{-i\tau} V_{-qj} U_{i\tau} V_{qj'} \right\}_p \\
 & + i \int_0^{\mp\infty} d\tau e^{i\omega\tau} \text{Tr} \left\{ U_{-\beta} U_{-i\tau} V_{qj'} U_{i\tau} V_{-qj} \right\}_p \\
 & + \text{Tr} \left\{ U_{-\beta} V_{-qj, qj'} \right\}_p, \quad (127)
 \end{aligned}$$

describe the self-energy and lifetime of a phonon as a result of phonon-phonon coupling. It is completely expressed in terms of proper, connected diagrams, as is indicated by the subscript "p." The diagonal elements ($j=j'$) satisfy [see (117)]

$$G^{\pm}(\vec{q}\omega j) = \text{Re } G^{\pm}(\vec{q}\omega j) \pm i \text{Im } G^{\pm}(\vec{q}\omega j) \quad (128)$$

The real and imaginary parts of $G^{\pm}(\vec{q}\omega j)$ are not independent, but satisfy a Kramers-Kronig relation.⁽²²⁾ This follows from a theorem due to Titchmarsh,⁽²⁶⁾ often used in the theory of dispersion relations. According to this theorem, one has

$$\text{Im } G^+(\vec{q}\omega j) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\text{Re } G^+(q\omega' j) - F(\vec{q}j)}{\omega' - \omega} d\omega' \quad ; \quad (129)$$

$$\text{Re } G^+(\vec{q}\omega j) - F(\vec{q}j) = - \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\text{Im } G^+(\vec{q}\omega j)}{\omega' - \omega} d\omega' \quad , \quad (130)$$

where P denotes the Cauchy principal value. Here $F(\vec{q}j)$ stands for the diagonal element of the ω -independent term on the right of (127): $F(\vec{q}j) = \text{Tr} \left\{ U_{-\beta} V_{-qj, qj} \right\}_p$. In deriving these relations use has been made of the fact that the traces in the first two terms on the right of (127) are bounded for all values of τ and go sufficiently rapidly to zero for $\tau \rightarrow \infty$ to be square integrable functions of τ [see remarks following Eq. (132)].

To compute the self-energy and lifetime to first order, that is, to order $(u/d)^2$, for a parameter-free lattice, we have to calculate *

$$\begin{aligned}
 G_{(1)}^{\pm}(\vec{q}\omega jj') &= i \int_0^{\pm\infty} d\tau e^{-i\omega\tau} \text{Tr} \left\{ U_{-\beta}^{(0)} U_{-i\tau}^{(0)} V_{-qj}^{(3)} U_{i\tau}^{(0)} V_{qj'}^{(3)} \right\}_p \\
 &+ i \int_0^{\mp\infty} d\tau e^{i\omega\tau} \text{Tr} \left\{ U_{-\beta}^{(0)} U_{-i\tau}^{(0)} V_{qj'}^{(3)} U_{i\tau}^{(0)} V_{-qj}^{(3)} \right\}_p \\
 &+ \text{Tr} \left\{ U_{-\beta}^{(0)} V_{-qj, qj'}^{(4)} \right\}_p, \quad (131)
 \end{aligned}$$

in which $U_{-\beta}^{(0)} = e^{-\beta H_0}$, etc. To each trace in this expression there corresponds only one basic diagram (see Fig. 26). On the basis of the rules for calculating diagrams explained in the foregoing chapters, we easily find

$$\begin{aligned}
 G_{(1)}^{\pm}(\vec{q}\omega jj') &= 18i \int_0^{\pm\infty} d\tau e^{-i\omega\tau} \int_{\vec{q}_1, \vec{q}_2} \sum_{j_1 j_2} \Delta(\vec{q} - \vec{q}_1 - \vec{q}_2) \\
 &\cdot B_{-qj, q_1 j_1, q_2 j_2}^{(3)} B_{qj', -q_1 j_1, -q_2 j_2}^{(3)} D_{q_1 j_1}^{(0)}(\tau) D_{q_2 j_2}^{(0)}(\tau) \\
 &+ 18i \int_0^{\mp\infty} d\tau e^{i\omega\tau} \int_{\vec{q}_1, \vec{q}_2} \sum_{j_1 j_2} \Delta(\vec{q} + \vec{q}_1 + \vec{q}_2) \\
 &\cdot B_{qj', q_1 j_1, q_2 j_2}^{(3)} B_{-qj, -q_1 j_1, -q_2 j_2}^{(3)} D_{q_1 j_1}^{(0)}(\tau) D_{q_2 j_2}^{(0)}(\tau) \\
 &+ 12 \int_{\vec{q}_1} \sum_{j_1} B_{-qj, qj', q_1 j_1, -q_1 j_1}^{(4)} \eta_{q_1 j_1}. \quad (132)
 \end{aligned}$$

*For more general lattices there is, in addition to the diagram in Fig. 26c, a second diagram contributing to $\text{Tr} \left\{ U_{-\beta} V_{-qj, qj'} \right\}_p$ to order $(u/d)^2$. However, this diagram involves an intermediate optical phonon of wave vector zero (modulo $2\pi\vec{\tau}$) and hence gives vanishing contribution in the case of a parameter-free lattice (see the end of Chapter IV).

Fig. 26. Lowest-order basic diagrams for the calculation of the phonon self-energy and lifetime

Here η_{qj} and $D_{qj}^{(0)}(\tau)$ are given by Eqs. (33) and (93), respectively. Use has been made of relation (29); the factor $\Delta(o)$ induced by this relation is cancelled by the $\Delta(o)$ -factors arising from the unused summations over wave vectors and from the absorption operators according to (10). As a consequence, the right-hand side of (132) is independent of the volume in the limit $\Omega \rightarrow \infty$; this property remains true to all orders in the interaction. It expresses the fact that the energy shift and width described by $G^{\pm}(\vec{q}\omega jj')$ are intensive quantities. Notice that the integrals over $\vec{q}_1$ and $\vec{q}_2$ in the first two terms on the right of (132) become zero for $|\tau| \gg \omega_D^{-1}$ (ω_D is the Debye frequency of the lattice, i.e., the maximum frequency of the vibration spectrum), which follows from the Riemann-Lebesgue theorem. Also, this property persists to general order: the traces occurring in the first two terms on the right-hand side of Eq. (127) vanish for $|\tau| \gg \omega_D^{-1}$, such that they are square integrable with respect to τ .

To perform the integrations over τ in (132), we use the formal relation

$$\int_0^{\pm\infty} d\tau e^{i\omega\tau} = i P\left(\frac{1}{\omega}\right) \pm \pi \delta(\omega) \quad (133)$$

By means of this relation a separation of $G_{(1)}^{\pm}(\vec{q}\omega jj')$ in Hermitian and anti-Hermitian parts is accomplished. We find after some algebraic manipulation and making use of (19), the following formulas for the real and imaginary part $\Delta_{(1)}(\vec{q}\omega j)$ and $\Gamma_{(1)}(\vec{q}\omega j)$ of the diagonal elements ($j=j'$) of $G_{(1)}^{\pm}(\vec{q}\omega jj')$:

$$\begin{aligned} \Delta_{(1)}(\vec{q}\omega j) = & 18 P \int_{\vec{q}_1 \vec{q}_2} \sum_{j_1 j_2} \left| B_{qj, -q_1 j_1, -q_2 j_2}^{(3)} \right|^2 \Delta(\vec{q} - \vec{q}_1 - \vec{q}_2) \\ & \cdot \left\{ (1 + f_{q_1 j_1} + f_{q_2 j_2}) \left[(\omega - \omega_{q_1 j_1} - \omega_{q_2 j_2})^{-1} - (\omega + \omega_{q_1 j_1} + \omega_{q_2 j_2})^{-1} \right] \right. \\ & \left. + 2 (f_{q_1 j_1} - f_{q_2 j_2}) (\omega + \omega_{q_1 j_1} - \omega_{q_2 j_2})^{-1} \right\} + F_{(1)}(\vec{q}j) \quad ; \end{aligned} \quad (134)$$

$$\begin{aligned}
\Gamma_{(1)}(\vec{q}\omega_j) = & 18 \pi \int_{\vec{q}_1 \vec{q}_2} \sum_{j_1 j_2} \left| B_{\vec{q}j, -\vec{q}_1 j_1, -\vec{q}_2 j_2}^{(3)} \right|^2 \Delta(\vec{q} - \vec{q}_1 - \vec{q}_2) \\
& \cdot \left\{ \left(1 + f_{\vec{q}_1 j_1} + f_{\vec{q}_2 j_2} \right) \left[\delta(\omega - \omega_{\vec{q}_1 j_1} - \omega_{\vec{q}_2 j_2}) - \delta(\omega + \omega_{\vec{q}_1 j_1} + \omega_{\vec{q}_2 j_2}) \right] \right. \\
& \left. + 2 \left(f_{\vec{q}_1 j_1} - f_{\vec{q}_2 j_2} \right) \delta(\omega + \omega_{\vec{q}_1 j_1} - \omega_{\vec{q}_2 j_2}) \right\} . \quad (135)
\end{aligned}$$

In these equations $f_{\vec{q}j} = [\exp(\beta\omega_{\vec{q}j}) - 1]^{-1}$ and $F_{(1)}(\vec{q}j)$ is the third term on the right of (132) for $j=j'$. The expressions (134) and (135) represent the self-energy and inverse lifetime of the phonon $\vec{q}j$ to order $(u/d)^2$, or, equivalently, the shift and half-width of the peaks in the scattering spectrum. To this order we can put $\omega = \pm\omega_{\vec{q}j}$ in the right-hand sides of these expressions. Note that diagram c of Fig. 26, which involves the quartic anharmonic coefficient, only contributes to the energy shift $\Delta_{(1)}(\vec{q}\omega_j)$. We see from these formulas that for temperatures well above the Debye temperature $\Delta_{(1)}(\vec{q}\omega_j)$ and $\Gamma_{(1)}(\vec{q}\omega_j)$ are proportional to T ,* in agreement with the results of neutron scattering experiments. For T equals zero, $\Delta_{(1)}$ and $\Gamma_{(1)}$ are nonzero. Numerical evaluations of (134) and (135) for a simple model of a lattice have been carried out by Maradudin and coworkers.^(24,27)

Higher-order corrections to Eqs. (134) and (135), which are at least of order $(u/d)^4$ because it can be shown that there are no contributions to $G^{\pm}(\vec{q}\omega_{jj'})$ which are of uneven order in u/d , can be obtained from diagrams such as shown in Fig. 27. For the case of a conducting crystal the expressions must be completed by including the effects of electron-phonon interaction. It is possible to extend the theory described in the foregoing to conducting crystals where, in addition to phonon-phonon coupling, there is an interaction between phonons and conduction electrons.⁽¹⁴⁾

Fig. 27. Diagrams which contribute to $G^{\pm}(\vec{q}\omega_{jj'})$ to order $(u/d)^6$

We finally remark that some information about the phonon self-energy and lifetime can also be obtained by using more intuitive arguments based on the exponential decay of one-particle states. Such simple techniques are complicated in the phonon case by the problem of polarization mixing and, in any case, they can only be expected to give results which are valid to lowest order in the interaction, in which self-energy and lifetime effects are independent. Moreover, such procedures are unable to yield closed expressions for the complete Green function.

*This is only true if we neglect the temperature dependence of the coefficients $B_{\dots}^{(\nu)}$ and the frequencies $\omega_{\vec{q}j}$ due to thermal expansion.

CHAPTER IX

REMARKS ON LATTICE THERMAL CONDUCTIVITY

In this chapter we briefly make some remarks concerning phonon transport in a large, perfect, insulating crystal. Recently, the thermal conductivity tensor $K_{\alpha\beta}$ has been expressed in terms of an equilibrium correlation function^(28,29) analogous to the famous Kubo-formula in electrical conductivity. Under certain assumptions, the following formula holds:

$$K_{\alpha\beta} = \frac{\Omega}{k_B T^2} \int_{-\infty}^0 dt \langle J_\alpha(0) J_\beta(t) \rangle_T \quad . \quad (136)$$

Here, k_B is Boltzmann's constant and J_α is the α^{th} component of the thermal flux, which one chooses to be that for the harmonic lattice:

$$\vec{J} = \frac{1}{\Omega} \int_{\vec{q}} \sum_j \omega_{qj} \vec{v}_{qj} A_{qj}^* A_{qj} \quad , \quad (137)$$

in which $\vec{v}_{qj} = \partial \omega_{qj} / \partial \vec{q}$ is the group velocity of phonon $\vec{q}j$. We will not enter into the derivation of Eq. (136) nor into a discussion of the approximations involved. We merely take this expression as a starting point for a brief investigation by means of diagrams.

Since in equilibrium $\langle J_\alpha \rangle_T$ is equal to zero, which follows from symmetry considerations [remember that $\langle N_{qj} \rangle_T = \langle A_{qj}^* A_{qj} \rangle_T = \langle N_{-qj} \rangle_T$, $\omega_{qj} = \omega_{-qj}$, and $\vec{v}_{qj} = -\vec{v}_{-qj}$], we can, on the basis of (67), express $K_{\alpha\beta}$ in terms of connected diagrams:

$$K_{\alpha\beta} = \frac{\Omega}{k_B T^2} \int_{-\infty}^0 dt \text{Tr} \left\{ \check{U}_{-\beta} U_{-it} J_\alpha U_{it} J_\beta \right\}_C \quad . \quad (138)$$

Each diagram contributing to the trace in this expression contains both of the J-vertices. From (137) it will be clear that in each J-vertex just one phonon line comes in and one phonon line goes out, both lines carrying the same wave vector and polarization index. Some examples of diagrams are shown in Fig. 28.

Fig. 28

Examples of diagrams which contribute to the trace in Eq. (138) for $K_{\alpha\beta}$

Combining (137) and (138), we have

$$K_{\alpha\beta} = \frac{1}{\Omega k_B T^2} \int_{\vec{q} \vec{q}'} \sum_{jj'} \omega_{qj} \omega_{q'j'} v_{qj,\alpha} v_{q'j',\beta} \cdot \int_{-\infty}^0 dt \text{Tr} \left\{ U_{-\beta} U_{-it} A_{qj}^* A_{qj} U_{it} A_{q'j'}^* A_{q'j'} \right\} C \quad (139)$$

We consider the following simple class of diagrams. It contains all diagrams which consist of a closed chain of proper parts on the cylinder connected by q -lines, such that each of the J -vertices is situated on a q -line. A q -line has the property that after being cut it breaks the closed chain; it carries pseudo-momentum $\vec{q}$ or $-\vec{q}$. Examples of diagrams from this class are represented in Fig. 28c and d. For these diagrams always $\vec{q}' = \vec{q}$ or $\vec{q}' = -\vec{q}$ [see (139)]. The class in question is schematically represented by Fig. 29; diagram a corresponds to the case $\vec{q}' = \vec{q}$ (see Fig. 28c), whereas diagram b corresponds to the case $\vec{q}' = -\vec{q}$ (see Fig. 28d).

Fig. 29

Schematic representation of the special class of diagrams calculated in the text. Each of the thick lines represents one of the traces in (140).

We see that each diagram belonging to this class consists of two parts which are separated by the J -vertices. These two parts are independent of one another, except for possible relative ordering of ordinary

vertices. The two parts can be completely disentangled, however, by means of a suitable disentanglement process, analogous to the one described in the appendix. In view of this, the total contribution of our class of diagrams to the trace on the right of Eq. (139) can be written as follows:

$$\begin{aligned} & \text{Tr} \left\{ U_{-\beta} U_{-it} A_{\vec{q}j}^* U_{it} A_{\vec{q}j'} \right\}_C \text{Tr} \left\{ U_{-\beta} U_{-it} A_{\vec{q}j} U_{it} A_{\vec{q}j'}^* \right\}_C \Delta(\vec{q} - \vec{q}') \\ & + \text{Tr} \left\{ U_{-\beta} U_{-it} A_{-\vec{q}j} U_{it} A_{\vec{q}j'} \right\}_C \text{Tr} \left\{ U_{-\beta} U_{-it} A_{-\vec{q}j}^* U_{it} A_{\vec{q}j'}^* \right\}_C \Delta(\vec{q} + \vec{q}') \quad . \end{aligned} \quad (140)$$

The two terms correspond to Fig. 29a and b, respectively. Each term is a product of two one-phonon Green functions. On using the methods of Chapter VII, we can find expressions for these Green functions analogous to (122). To lowest non-vanishing order in the phonon-phonon interaction only the first term in (140) contributes. We find in this case

$$\text{Tr} \left\{ U_{-\beta} U_{-it} A_{\vec{q}j}^* U_{it} A_{\vec{q}j'} \right\}_C = \delta_{jj'} \frac{e^{-\beta\omega_{\vec{q}j}}}{1 - e^{-\beta\omega_{\vec{q}j}}} e^{-i(\omega_{\vec{q}j} + \Delta_{(1)}(\vec{q}j))t - \Gamma_{(1)}(\vec{q}j)|t|} \quad ; \quad (141)$$

$$\text{Tr} \left\{ U_{-\beta} U_{-it} A_{\vec{q}j} U_{it} A_{\vec{q}j'}^* \right\}_C = \delta_{jj'} \frac{1}{1 - e^{-\beta\omega_{\vec{q}j}}} e^{i(\omega_{\vec{q}j} + \Delta_{(1)}(\vec{q}j))t - \Gamma_{(1)}(\vec{q}j)|t|} \quad , \quad (142)$$

in which $\Delta_{(1)}(\vec{q}j)$ and $\Gamma_{(1)}(\vec{q}j)$, the lowest-order self-energy and inverse lifetime of phonon $\vec{q}j$, are given by Eqs. (134) and (135).

Substituting (140), (141), and (142) in (139), we obtain

$$K_{\alpha\beta} = \frac{1}{\Omega k_B T^2} \int_{\vec{q}} \sum_j \omega_{\vec{q}j}^2 v_{\vec{q}j,\alpha} v_{\vec{q}j,\beta} \frac{e^{-\beta\omega_{\vec{q}j}}}{(1 - e^{-\beta\omega_{\vec{q}j}})^2} \frac{1}{2} \tau_{(1)}(\vec{q}j) \quad , \quad (143)$$

where we have put $\Gamma_{(1)}(\vec{q}j)^{-1} = \tau_{(1)}(\vec{q}j)$, the lifetime of phonon $\vec{q}j$. Introducing the heat capacity per normal mode per unit volume:

$$c(\vec{q}j) = \frac{\omega_{\vec{q}j}^2 e^{-\beta\omega_{\vec{q}j}}}{\Omega k_B T^2 (1 - e^{-\beta\omega_{\vec{q}j}})^2} \quad ,$$

Eq. (143) becomes

$$K_{\alpha\beta} = \frac{1}{2} \int_{\vec{q}} \sum_j c(\vec{q}j) v_{\vec{q}j,\alpha} v_{\vec{q}j,\beta} \tau_{(1)}(\vec{q}j) \quad . \quad (144)$$

This is the usual expression for the thermal conductivity tensor $K_{\alpha\beta}$, which one obtains from the Boltzmann equation in the so-called relaxation time approximation.⁽²⁹⁻³²⁾ In this approximation it is assumed that the scattering mechanisms may be characterized by a relaxation time per vibrational mode. In our diagrammatic formulation it corresponds to neglecting all diagrams except those of the special class represented by Fig. 29. Or, expressed alternatively, it amounts to a sort of superposition approximation: the two-phonon Green function appearing in (139) is written as a sum of products of two one-phonon Green functions [Expression (140)].

Expression (144) for $K_{\alpha\beta}$ is of order $(u/d)^{-2}$; only three-phonon processes (cubic anharmonic terms) are involved in the calculation of $\tau_{(1)}(\vec{q} \ j)$ (see Fig. 26). Corrections to this expression may be obtained, in the first place, by calculating the traces in (140) to higher order and, secondly, by including those diagrams which do not belong to the special class defined above (see Fig. 28a and b). It can be shown that these corrections to $K_{\alpha\beta}$ are at least of order $(u/d)^0$. This diagrammatic analysis will be worked out in greater detail in the future.

We finally remark that Eq. (144) for $K_{\alpha\beta}$ [just as the general formula (136)] as it stands cannot be complete, because if there were only normal processes [processes which conserve pseudomomentum, $\vec{\tau} = 0$, see (9)] $K_{\alpha\beta}$ would not be infinite. The generally accepted viewpoint, however, is that normal processes alone cannot produce thermal resistance.^(10,30-32) This property of the normal processes must be explicitly taken into account, in the same way as this must be done in a calculation of the thermal conductivity starting from the Boltzmann equation. However, this point is not completely clear and needs further clarification (compare Appendix B of Ref. 32).

Appendix

In this appendix we will illustrate the disentanglement process (page 43) by means of the following simple example. Consider the diagram in Fig. 30a. It is a one-phonon diagram containing two proper parts.

Fig. 30. Diagrams to illustrate the disentanglement process

These two proper parts are entangled in the sense that the vertex at t_2 should always be on the right of the vertex at t_3 ($t_2 \leq t_3$). In order to get rid of this restriction, we take diagrams a and b in Fig. 30 together; in diagram b, t_2 is always larger than t_3 . The sum of their contributions to the trace in (78) contains (we only write down the exponential factors and the t -integrations, the remaining factors and q -integrations being the same for both diagrams; furthermore we drop the polarization indices for convenience)

$$e^{-\beta(\omega_K + \omega_3)} \left[\int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 + \int_0^t dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_1 \right] e^{-i(t-t_1)\omega_K} e^{it_1(\omega_3 - \omega_2)} . \quad (A1)$$

Since the sum of the integrals within square brackets can be written as

$$\int_0^t dt_3 \int_0^{t_3} dt_1 \int_{t_1}^t dt_2, \text{ this becomes}$$

$$-e^{-\beta(\omega_K + \omega_3)} \int_0^t dt_3 \int_0^{t_3} dt_1 e^{-i(t-t_1)\omega_K} \left[- \int_{t_1}^t dt_2 e^{it_1(\omega_3 - \omega_2)} \right] . \quad (A2)$$

The factor within square brackets now contains the "internal" time exponential factors and integrations of the proper part containing phonons 2 and 3. The integration over t_2 runs from t_1 to t independent of t_3 .

We now add to (A2) the contribution of diagram c, in which the loop at t_2 appears in the U_{it} -region. This diagram contributes

$$-e^{-\beta(\omega_K + \omega_3)} \int_0^t dt_3 \int_0^{t_3} dt_1 e^{-i(t-t_1)\omega_K} \left[\int_0^t dt_2 e^{it_1(\omega_3 - \omega_2)} \right] . \quad (A3)$$

Then (A2) + (A3) become

$$-e^{-\beta(\omega_K + \omega_3)} \int_0^t dt_3 \int_0^{t_3} dt_1 e^{-i(t-t_1)\omega_K} \left[\int_0^{t_1} dt_2 e^{it_1(\omega_3 - \omega_2)} \right] . \quad (A4)$$

The general expression corresponding to all proper parts between t_1 and T_{-K} is, according to Chapter VI, equal to $\text{Tr}\{U_{-}\beta U_{it_1} V_K U_{-it_1} T_{-K}\}_P$. Diagram d in Fig. 30, contributing to this trace, now gives rise to a factor

$$\int_0^{t_1} dt_2 e^{it_1(\omega_3 - \omega_2)}, \text{ which is just equal to the factor within square brackets}$$

in (A4). The proper diagram d with the vertex t_2 in U_{it_1} is equivalent to the proper parts of diagrams a+b+c, in which the vertex t_2 is situated in the regions $U_{-i}(t_3 - t_1)$, $U_{-i}(t - t_3)$ and U_{it} , respectively.

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