Phonons in Bravais Lattices*

W. Götze†
Department of Physics, University of Illinois, Urbana, Illinois
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This work establishes some exact results in lattice dynamics. For arbitrary temperatures, an elastic sum rule is derived which expresses the minus-first moment of the displacement correlation function with respect to the frequency in terms of the isothermal elastic constants, and yields the asymptotic form of the structure factor of the lattice for small wave numbers. It is shown that at zero temperature the low-lying excitations of the crystal are sound waves, the velocity of which can be expressed by the second derivatives of the ground-state energy with respect to homogeneous deformations. This implies that the specific heat in the limit of temperatures tending to zero follows a Debye law of the same form as for a gas of noninteracting phonons. These results are derived for an ideal Bravais lattice by taking into account the entire anharmonicity of the dynamics. As a mathematical tool, a diagram technique is developed which avoids the concept of the harmonic approximation as a zeroth-order step.

I. INTRODUCTION

THE purpose of this paper is to demonstrate for an ideal Bravais lattice the connections between the isothermal elastic constants, the displacement reponse function in the long-wavelength limit, the low-lying excitations, and the asymptotic behavior of the specific heat at small temperatures. We will show that one can generalize the relevant results which have been derived in the harmonic approximation in such a way that the nonlinear dynamics is completely taken into account. These generalizations are of interest because they establish exact relations between experimental quantities and because they can be used as a powerful check on the consistency of approximations.

To handle the anharmonic effects, extensive use is made of diagrams as well as functional derivatives of diagrams to express the interesting quantities like the free energy, phonon propagator, etc. It is shown to all orders of the perturbation expansion that at zero temperature the long-wavelength excitations are phonons, the velocity of which is given in the usual way by the elastic constants. This in turn yields the Debye law for the specific heat of the crystal. The anharmonic effects do not influence the general connections between the derivatives of the ground-state energy with respect to homogeneous deformations, the excitation spectrum, and the specific heat; they only renormalize the numerical values of the elastic constants. Furthermore, we can express the static self-energy of the phonons of small momenta at arbitrary temperature by the isothermal elastic constants. This yields an elastic sum rule for the displacement-displacement response function as well as the asymptotic behavior of the static correlation function of the lattice for large separations.

This paper is divided into four major sections. First (Sec. II), the diagrammatic expansion for the free energy, the Green's functions, etc., is reported. The perturbation theory for anharmonic crystals has been developed to a large extent.[1–3] In those treatments, the harmonic part of the interaction always plays a distinguished role. For our purpose it is much more convenient to handle the whole interaction on the same footing; for this reason we start the diagrammatic expansion by using an artificial Einstein model as the unperturbed Hamiltonian. Renormalization of the perturbation theory is necessary in order to introduce the physical propagators and in order to use strains instead of forces as the independent variables. These renormalizations are carried out in the same fashion as that of De Dominicis and Martin[4] in another context.

In Sec. III we define the stress tensor in terms of the forces acting on the surface of the crystal. It is shown that this tensor equals the derivative of the free energy with respect to the lattice deformations. The elastic constants which are essentially defined as the second derivatives of the free energy with respect to homogeneous deformations are expressed by the asymptotic values of the phonon self-energy operator. The equilibrium conditions studied by Huang[5] are derived in any order of the anharmonic contributions. Section III closes with a brief discussion of the problem of constructing consistent approximations, i.e., approximations yielding identical results for the elastic constants independent of whether they are calculated as differential quotients of the free energy or by determining the self-energy diagrams for the phonons.

In Sec. IV, a sum rule is derived which expresses the minus-first moment of the imaginary part of the phonon Green's function in terms of the isothermal elastic constants. This elastic sum rule, together with the f sum rule, yields the asymptotic form for the structure factor of the lattice which diverges for small wave numbers. Furthermore, it is shown that at zero temperature the

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Green's function for small momenta and small energies has the same form as in the harmonic approximation; the anharmonic effects enter the values for the elastic constants only. We also discuss why the last result is not valid at nonzero temperature.

Finally (Sec. V), it is shown that the specific heat for temperatures tending to zero has the same form as for the gas of noninteracting phonons. This result is a generalization to arbitrary order in the anharmonic effects of the corresponding proof carried out by Barron and Klein[6] in first-order perturbation theory.

II. PERTURBATION THEORY

A. Notation

We want to discuss a Bravais lattice composed of N particles of mass m. The particles are labeled by integer vectors $\mathbf{n}=(n_1,n_2,n_3)$, where $n_i=0, \pm1, \pm2, \cdots R(\mathbf{n}i)$ and $\pi(\mathbf{n}i)$ denote, respectively, the ith component of the position and momentum operator of the $\mathbf{n}$th atom in the Schrödinger picture. For the sake of brevity, we shall use the notation $\lambda=(\mathbf{n}i)$.

Let us introduce a three-by-three matrix A_{ij}. The A_{ij}'s will determine the shape of the unit cell of the lattice; they enter the theory as parameters and have to be appropriately determined later. We define vectors $\mathbf{X}(\mathbf{n})$ by

$$X(\mathbf{n}i)=A_{ij}n_j. \tag{1a}$$

For the moment we imagine that $\mathbf{X}(\mathbf{n})$ is the mean equilibrium position of the $\mathbf{n}$th particle. We denote the volume of the unit cell by

$$\mathcal{V}=\det A_{ij}. \tag{1b}$$

It is more convenient not to use the $R(\lambda)$'s but to subtract the c numbers $X(\lambda)$ to get a set of independent dynamical variables $\varphi(\lambda)$:

$$R(\lambda)=X(\lambda)+m^{-1/2}\varphi(\lambda). \tag{2}$$

In terms of the displacement operators $\varphi(\lambda)$, the Hamiltonian of the system reads

$$H=H^0+\sum_{\nu=0}^{\infty}(1/\nu!)v_\nu(\lambda_1\cdots\lambda_\nu)\varphi(\lambda_1)\cdots\varphi(\lambda_\nu) \tag{3}$$

(here and in the following one has to sum over repeated indices),

$$H^0=\tfrac{1}{2}\sum_\lambda[(1/m)\pi^2(\lambda)+\epsilon^2\varphi^2(\lambda)]. \tag{4}$$

According to the adiabatic hypothesis of Born and Oppenheimer,[7] they may be written as

$$v_\nu(\lambda_1\cdots\lambda_\nu)=m^{-\nu/2}\partial_{\lambda_1}\cdots\partial_{\lambda_\nu}E^r[X(\lambda_1),\cdots,X(\lambda_N)], \quad [\partial_\lambda=\partial/\partial X(\lambda)]. \tag{5}$$

Here E^r is the energy of the N particle system where the $\mathbf{n}$th atom is fixed at $\mathbf{X}(\mathbf{n})$. In the simplest approximation, E^r is the sum of the two-body potentials. H^0 is the Hamiltonian of N independent oscillators located at $\mathbf{X}(\mathbf{n})$. Each of them has the same frequency ϵ. It is convenient to start with such an Einstein model as zeroth-order term, because we can now treat the whole interaction on the same footing. At the end of the calculations we have to let ϵ tend to zero.

The operators in the Heisenberg representation are defined as usual, e.g., ($\hbar=1$)

$$\varphi(\lambda t)=e^{iHt}\varphi(\lambda)e^{-iHt}. \tag{6}$$

Equation (3) yields $[\varphi, H-H^0]=0$; consequently, the Hermitian operators $\varphi(\lambda t)$ and $\pi(\lambda t)$ obey the relations

$$(\partial/\partial t)\varphi(\lambda t)=m^{-1/2}\pi(\lambda t), \tag{7a}$$

$$[i(\partial/\partial t)\varphi(\lambda t),\varphi(\mu t)]=\delta(\lambda,\mu). \tag{7b}$$

The phonon Green's function[1-3,8,9] of the crystal is defined by

$$D(\lambda_1t_1,\lambda_2t_2)=(-i)\,\mathrm{Tr}e^{-\beta H}\{\varphi(\lambda_1t_1)\varphi(\lambda_2t_2)\}/\mathrm{Tr}e^{-\beta H}. \tag{8a}$$

Here β is the reciprocal temperature $\beta=1/T^0$ ($k_B=1$). The times t_1 and t_2 in Eq. (8a) are pure imaginary numbers:

$$t_j=(-i)\tau_j, \quad 0\leq\tau_j\leq\beta, \tag{8b}$$

and $\{\ \}$ denotes the time ordering from 0 to $-i\beta$. The function D is of importance because its resonances in Fourier space give the excitation energies of the lattice, in particular, the acoustical phonons. These resonances can be measured almost directly, e.g., as peaks of the cross section in neutron-scattering experiments.[1,2,10] D^0 denotes the function which we obtain when H is replaced by H^0 in Eqs. (6) and (8a). Equations (7a), (7b), and (4) yield the equation of motion for D^0,

$$[(i\partial/\partial t_1)^2-\epsilon^2]D^0(\lambda_1t_1,\lambda_2t_2)=\delta(\lambda_1,\lambda_2)\delta(t_1-t_2). \tag{9}$$

We are furthermore interested in the calculation of the thermodynamical potential

$$Y=\ln\mathrm{Tr}e^{-\beta H}, \tag{10}$$

because it determines the free energy F and thus the equilibrium thermodynamics,

$$F=-Y/\beta. \tag{11}$$

B. External Disturbances

It is useful[9,11] to introduce an external time-dependent field, the Hamiltonian of which is given in the

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[11] G. Baym and L. P. Kadanoff, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

Schrödinger picture by

$$H_t' = E(\lambda t)\varphi(\lambda). \tag{12}$$

In the interaction picture with respect to H_t' we write

$$S(t_1 t_2) = \exp\left(-i\int_{t_1}^{t_2} H'(\tau)d\tau\right), \tag{13}$$

and define the generating functional

$$W = \ln \mathrm{Tr} e^{-\beta H}\{S(-i\beta 0)\}, \tag{14}$$

as well as the set of the ν-point Green's functions

$$G_\nu(\lambda_1 t_1,\cdots,\lambda_\nu t_\nu) = \mathrm{Tr} e^{-\beta H}\{S(-i\beta t_1)\varphi(\lambda_1 t_1) \times S(t_1 t_2)\cdots\varphi(\lambda_\nu t_\nu)S(t_\nu 0)\}/e^W. \tag{15a}$$

Notice that $H'(\tau) = E(\lambda\tau)\varphi(\lambda\tau)$; here and in Eq. (15a), $\varphi(\lambda t)$ is defined by Eq. (6).

Let us use the abbreviations $1 = \lambda_1 t_1$, $2 = \lambda_2 t_2$, etc. Equation (15a) then reads in a more compact form

$$G_\nu(1\cdots\nu) = \mathrm{Tr} e^{-\beta H}\{S(-i\beta 0)\varphi(1)\cdots\varphi(\nu)\}/e^W. \tag{15b}$$

The first and second derivatives of W with respect to E are given by

$$[\delta/\delta(-iE(1))]W = G(1), \tag{16}$$

$$[\delta/\delta(-iE(2))]G(1) = G_2(12) - G(1)G(2) = \tilde{G}(12). \tag{17}$$

Here and in the following we drop the index of the one-point functions to simplify the notation, i.e., $G(1) = G_1(1)$. After having developed the diagrammatic technique we shall take E as time-independent and zero within the sample. We have to provide that $E \neq 0$ on the surface of the crystal in order to discuss a system under external stresses. This procedure will give us the desired functions, viz.,

$$W \to Y, \tag{18a}$$

$$G(1) \to m^{1/2}[\langle R(\lambda_1)\rangle - X(\lambda_1)], \tag{18b}$$

$$G_2(12) \to iD(\lambda_1 t_1, \lambda_2 t_2). \tag{18c}$$

C. Perturbation Expansion

In the most primitive version of a diagrammatic representation for W and for the G_ν's we treat the operator $(H - H^0 + H')$ as a perturbation. Wick's theorem yields the expansion of the interesting quantities. The diagrams are built up by ν vertices ($\nu = 1, 2, \cdots$) and by free propagators G^0, where we write $G^0 = iD^0$. The rules for evaluating and drawing diagrams are:

(i) For each ν vertex, write down $-iV(1\cdots\nu)$. Here $V(1) = v_1(\lambda_1) + E(1)$, $V(1\cdots\nu) = v_\nu(\lambda_1\cdots\lambda_\nu)\delta(t_1 t_2) \times \delta(t_2 t_3)\cdots\delta(t_{\nu-1} t_\nu)$, if $\nu \geq 2$. A ν vertex is represented by a dot with ν legs. We write $G^0(12)$ for each propagator between 1 and 2, say; it is represented by a dotted line joining those points.

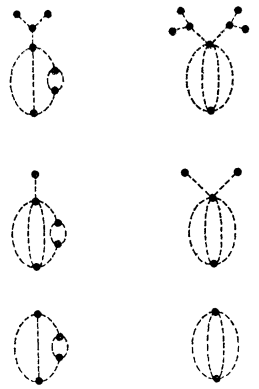

FIG. 1. Unrenormalized diagrams contributing to $W - W^0$.

(ii) Legs of vertices at which a propagator is attached are called internal points. One has to sum over all λ's and to integrate over all times between 0 and $-i\beta$ for the internal points. The other points of the vertices as well as the free ends of the propagators are called external points of the diagram. A diagram is a function of its external points.

(iii) To get the correct contribution due to a given diagram, one has to take into account some weight factors:

(a) If a propagator has both ends at the same vertex, we associate it with a factor $\frac{1}{2}$.
(b) For each set of l propagators running between the same pair of vertices, we write a factor $1/(l!)$.
(c) The diagram gets a further factor $1/\mathrm{Sy}$, where Sy is the symmetry number. To determine Sy one has to label all the vertices of the diagram; Sy is the number of permutations not changing the topological structure of the labeled graph.

A diagram with ν external points is called a ν diagram if all those ν points are ends of propagators (and not of vertices). A diagram is called linked if there is a connection between any two points of it. There are three linked cluster theorems of interest in the following, which can be derived in the standard fashion.[8,4]

$$W - W^0 = [\text{sum of all linked 0 diagrams}], \tag{19a}$$

$$G(1) = [\text{sum of all linked 1 diagrams}], \tag{19b}$$

$$\tilde{G}(12) = [\text{sum of all linked 2 diagrams}]. \tag{19c}$$

Here W^0 is the function which we obtain when $H' = 0$ and $v_\nu = 0$ for $\nu = 1, 2, \cdots$ in Eq. (14). Examples of diagrams contributing to $W - W^0$, $G(1)$, and $\tilde{G}(12)$ are shown in Figs. 1, 2, and 3, respectively. The last diagram of Fig. 3 is a graph with symmetry number $\mathrm{Sy} = 2$.

D. V_1 Renormalization

We want to use the strains $G(1)$ instead of the forces $V_1(1)$ as the independent variables of the crystal. For this reason we have to perform a generalized Legendre transformation. As far as the mathematics is concerned,

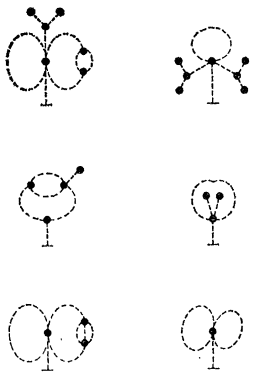

FIG. 2. Unrenormalized diagrams contributing to $G(1)$.

this problem is almost the same as the problem of replacing the 1-point sources by condensate wave functions in superfluid Bose liquids.[12] In the case of Bose liquids, the transformation mentioned has been studied at length by DeDominicis and Martin.[4] Hence we have to outline the concepts only as far as it is necessary for the discussion of the following sections. For full details the reader is referred to Ref. 4.

A propagator in a diagram is called an accumulation line if the diagram can be split into disconnected pieces by cutting this line; an accumulation line is called a trivial one, if one of those pieces is a simple V_1 vertex. A diagram is called V_1-irreducible if all its accumulation lines are trivial ones. Each of the Figs. 1, 2, and 3 shows in its first row graphs having one and two nontrivial accumulation lines, respectively. The graphs of the second rows have one and two trivial accumulation lines, respectively, while the examples given in the last rows have no accumulation line at all. Only the examples given in the first rows of those figures are not V_1-irreducible.

Every V_1 vertex is joined to the rest of the graph by a propagator; consequently, the V_1-irreducible diagrams are functionals of $-iG^0V_1=-iG^0(1\bar{1})V_1(\bar{1})$. We denote the set of all V_1-irreducible 0 diagrams by $\mathcal{K}(-iG^0V_1)$. The set of all V_1-irreducible 1 diagrams may be written as $G^0(1\bar{1})K(\bar{1};-iG^0V_1)$, because the external point is joined with the rest by a propagator. Obviously,

$$K(1;-iG^0V_1)=\{\delta/\delta[-iG^0(1\bar{1})V_1(\bar{1})]\}\mathcal{K}. \quad (20)$$

The simplest contribution to the right-hand side (RHS) of Eq. (19b) is given by $-iG^0V_1$. All the other diagrams are obtained if we replace in the set of V_1-irreducible 1 diagrams $-iG^0V_1$ by the set of all 1 diagrams, i.e., by G. Hence we get

$$G(1)=-iG^0(1\bar{1})V_1(\bar{1})+G^0(1\bar{1})K(\bar{1};G). \quad (21)$$

In Eq. (21), K appears as a functional of $G(1)$. It does not contain V_1 vertices anymore. Diagrams of this type are called V_1-renormalized graphs. The diagram rules are:

[12] I am indebted to Dr. H. Schmidt for drawing my attention to these similarities.

(i′) The V_1-renormalized diagrams are built up by vertices $V_\nu(\nu=2, 3, \cdots)$, G^0 propagators joining two points, and propagators $G(1)$ with one end 1 which has to be attached at a vertex. The $G(1)$ propagators are symbolized by a wavy line. The diagrams do not contain accumulation lines.

(ii′) The same as (ii).

(iii′) The rules (iii) (a), (b), and (c) remain valid, but we have a further prescription.

(d) Each set of n $G(1)$ propagators ending at the same vertex has associated with it the weight factor $1/(n!)$.

In Fig. 4 are shown those V_1-renormalized diagrams which can be obtained from the second rows of Figs. 1, 2, and 3, respectively, by replacing $-iG^0V_1$ by G. The examples given in the third rows of Figs. 1, 2, and 3 are also V_1-renormalized graphs.

Equation (21) is a nonlinear relation between V_1 and G. $\mathcal{K}(G)$ has been constructed as the sum of all V_1-renormalized 0 diagrams. Equation (20) yields

$$K(1)=[\delta/\delta G(1)]\mathcal{K}, \quad (22)$$

and thus $K(1)$ is the set of all V_1-renormalized diagrams having one external vertex point. The second derivative of $\mathcal{K}$,

$$M(12)=i[\delta^2/\delta G(1)\delta G(2)]\mathcal{K}, \quad (23)$$

is very important because it is the self-energy operator of the phonons. Differentiating Eq. (21) with respect to $-iE(2)$, we obtain from Eqs. (17) and (23) the Dyson equation

$$(-i)[(D^0)^{-1}(1\bar{1})-M(1\bar{1})]\tilde{G}(\bar{1}2)=\delta(12). \quad (24)$$

Here we have used the fact that $\mathcal{K}$ and K depend on $E(2)$ only implicitly via the V_1 dependence of the G's.

In the first row of Fig. 5 examples of V_1-renormalized diagrams contributing to $\mathcal{K}$ are shown. In the second and the third rows of this figure are drawn the first and second derivatives corresponding to Eqs. (22) and (23), respectively. In this figure the correct weight factors are indicated because they are changed by performing the functional derivatives.

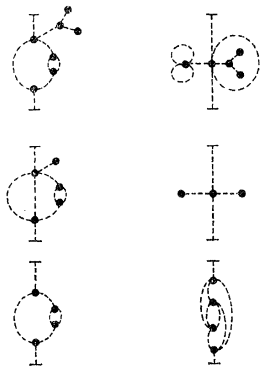

FIG. 3. Unrenormalized diagrams contributing to $\tilde{G}(12)$.

The RHS of Eq. (19a) is not simply identical with $\mathcal{K}-iV_1G$ because there are diagrams which are counted twice in this expression. The correct result is

$$W-W^0=-\tfrac{1}{2}G(1)(G^0)^{-1}(12)G(2) \\ -iV_1(1)G(1)+\mathcal{K}. \quad (25)$$

Equations (25), (21), and (24) achieve the desired Legendre transformation. $V_1(1)$ has been eliminated from all diagrams; the $G(1)$'s are now the new variables. These three equations and the underlying definitions are the necessary and sufficient tool for the analysis of the following two sections. But in order to calculate the specific heat we have to perform a further partial summation.

E. V_2 Renormalization

A sequence of $m(m\geq 2)G^0$ propagators in a V_1-renormalized diagram is called a cycle if the cutting of any two of those propagators splits the graph into disconnected parts. A graph is called a skeleton diagram if it does not contain cycles. The first diagram in the last row of Fig. 1 has a cycle with $m=2$, and the second graph in the last row is a skeleton diagram; the analogous statement is true for the diagrams of the first row of Fig. 4. The statement is also true for the graphs drawn in the last rows of Figs. 2 and 3 and the graphs of the second and third row of Fig. 4 under the condition that we amputate the propagators which join the external points with the vertices.

There is never more than one V_2 vertex in a skeleton diagram. Thus we treat V_2 separately. Let Φ denote the set of all skeleton diagrams not containing a V_2 vertex. Φ is a functional of G^0; its derivative is denoted by

$$\Sigma(12;G^0)=(2i)[\delta/\delta G^0(12)]\Phi[G^0]. \quad (26)$$

Σ is the set of all skeleton diagrams (except V_2) with two external vertex points. The simplest contribution to M in Eq. (23) is V_2. All the other contributions are obtained if one replaces G^0 in Σ by the whole set of linked 2 diagrams, i.e., by $\tilde{G}$ [compare Eq. (19c)]. Thus we obtain

$$M(12)=\Sigma(12;\tilde{G})+V_2(12). \quad (27)$$

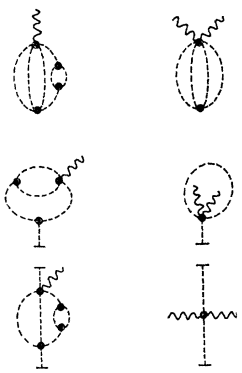

FIG. 4. V_1=renormalized diagrams contributing to $W-W^0$ (first row), $G(1)$ (second row), and $\tilde{G}(12)$ (third row).

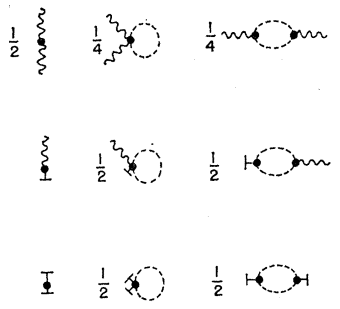

FIG. 5. In the first row, V_1-renormalized contributions to $\mathcal{K}$ are drawn. In the second and third rows the first and second functional derivatives, respectively, of those diagrams with respect to the $G(1)$ propagators are shown.

After having replaced G^0 by $\tilde{G}$ in Φ, Eq. (26) may be written as

$$\Sigma(12)=(2i)[\delta/\delta\tilde{G}(12)]\Phi[\tilde{G}]. \quad (28)$$

A similar consideration leads to

$$K(1)=-iV_2(1\bar{1})G(\bar{1})+[\delta/\delta G(1)]\Phi. \quad (29)$$

The diagrams for Φ and its derivatives just defined do not contain G^0 propagators V_2 vertices or cycles. These diagrams are called V_2-renormalized diagrams. The diagram rules are:

(i'') Each V_2-renormalized diagram is composed of V_ν vertices ($\nu=3, 4, \cdots$), propagators $\tilde{G}(12)$ joining the two points 1 and 2, and propagators $G(1)$ with one end. Only skeleton diagrams are to be considered. The $\tilde{G}$'s are represented by solid lines. Rules (ii') and (iii') remain valid.

In Fig. 6 the V_2-renormalized analogs of the first column diagrams of Figs. 1–4 are shown. The renormalization of W requires some nontrivial topological considerations and yields the formula

$$W+\beta v_0=\Phi-\Sigma(12)\tilde{G}(12)-\tfrac{1}{2}\ln[i(G^0)^{-1}-M](11) \\ -\tfrac{1}{2}G(1)[(G^0)^{-1}+iV_2](12)G(2)-iV_1(1)G(1). \quad (30)$$

[Notice that v_0 is equal to E^r for the regular arrangement of the lattice points given by Eq. (1a).]

The achievement of the V_2 renormalization has been the elimination of the G^0's from the diagrammatic expressions. Only the physical quantities $\tilde{G}$ and G occur in the final expressions, Eqs. (27), (29), and (30).

III. ELASTIC CONSTANTS

A. Invariance Properties

The lattice structure of our system has the consequence that the excitation states of the crystal form neither a representation of the group of translations nor a representation of the group of rotations. The function E^r in Eq. (5), of course, is invariant under such transformations. These symmetries and symmetry breakings, respectively, imply some relations for $M(12)$ and $K(1)$ which we want to study.

Translational invariance means

$$E^r[\mathbf{X}_1,\cdots,\mathbf{X}_N]=E^r[X_1+\mathbf{a},\cdots,\mathbf{X}_N+\mathbf{a}] \quad (31a)$$

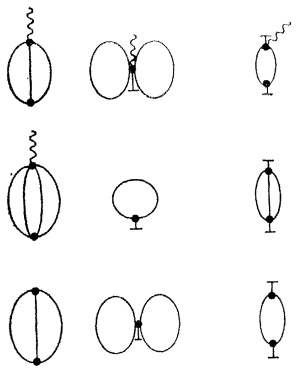

FIG. 6. V_2-renormalized diagrams contributing to Φ, $K(1)$, and $M(12)$, respectively.

for an arbitrary vector **a**. Hence Eq. (5) yields the invariance property for the vertices

$$\sum_{\mathbf{n}_1} v_\nu(\mathbf{n}_1 i_1 \lambda_2 \cdots \lambda_\nu) = 0. \tag{31b}$$

In every diagram for $M(12)$ in Eq. (23) the external points 1 and 2 are attached to some vertex and hence we get from Eq. (31b)

$$\sum_{\mathbf{n}_1} M(\mathbf{n}_1 i_1 t_1, \mathbf{n}_2 i_2 t_2) = 0. \tag{32}$$

Rotational invariance means

$$E^r(\mathbf{Z}_1, \cdots, \mathbf{Z}_N] = E^r[\mathbf{\Omega}\mathbf{Z}_1, \cdots, \mathbf{\Omega}\mathbf{Z}_N] \tag{33a}$$

for an arbitrary rotation matrix $\mathbf{\Omega}$. Equation (5) yields

$$v_\nu(\mathbf{n}_1 i_1 \cdots \mathbf{n}_\nu i_\nu; \mathbf{\Omega}\mathbf{Z}_1, \cdots, \mathbf{\Omega}\mathbf{Z}_N) = \Omega_{i_1 j_1} \cdots \Omega_{i_\nu j_\nu} v_\nu(\mathbf{n}_1 j_1 \cdots \mathbf{n}_\nu j_\nu; \mathbf{Z}_1, \cdots \mathbf{Z}_N). \tag{33b}$$

Here we have generalized the definitions of Sec. II in a trivial fashion, because we do not impose the condition (1a) for the points $\mathbf{Z}_i$ at which the derivatives have to be performed. One can write $\mathbf{Z}_i$ as the sum of $\mathbf{X}(\mathbf{n})$ and an appropriate 1-point function, this being indicated by the notation

$$v_\nu{}^G(\lambda_1 \cdots \lambda_\nu) = v_\nu[\lambda_1 \cdots \lambda_\nu; X(\lambda_1) + m^{-1/2} G(\lambda_1), \cdots, X(\lambda_N) + m^{-1/2} G(\lambda_N)]. \tag{33c}$$

The $v_\nu{}^G$'s are the vertices of the deformed lattice.

Let L be a diagram of $\mathcal{K}$ which does not contain any one-point function and Let $\mathcal{K}^L$ be the family of all diagrams of $\mathcal{K}$ which differ from L by G's only. Figure 7 shows the three such families; L's are written in the column. The diagram rules (iii') lead to

$$\mathcal{K}^L(v_\nu, G^0, G) = L(v_\nu{}^G, G^0), \tag{34a}$$

because the diagrams of the $\mathcal{K}^L$ family are obtained by performing the Taylor expansion of the $v_\nu{}^G$'s in Eq. (33c) at the points $(\mathbf{X}_1, \cdots, \mathbf{X}_N)$. For the sake of clarity we have indicated in Eq. (34a) all quantities which $\mathcal{K}$ and L depend on. The same argument which gave Eq. (34a) yields

$$-\beta v_0 - i v_1(1) G(1) + \mathcal{K}^0(v_\nu, G) = -\beta v_0{}^G. \tag{34b}$$

Here $\mathcal{K}^0$ is the set of all diagrams of $\mathcal{K}$ which do not contain G^0 propagators, Obviously, families belonging to different L's have no common element and

$$\mathcal{K} = \mathcal{K}^0 + \sum_L \mathcal{K}^L, \tag{34c}$$

where one has to sum over all different diagrams L.

Let us write the rotation matrix $\mathbf{\Omega}$ as the sum $\mathbf{\Omega} = \mathbf{1} + \boldsymbol{\omega}$. We introduce the notation

$$G_\omega(\mathbf{n}it) = G(\mathbf{n}it) + \omega_{ij}[m^{1/2} X(\mathbf{n}j) + G(\mathbf{n}jt)], \tag{35a}$$

and obtain from Eq. (34a)

$$\begin{aligned} \mathcal{K}^L(v_\nu, G^0, G_\omega) &= L(v_\nu{}^G, \mathbf{\Omega}^{-1} G^0 \mathbf{\Omega}) \\ &= L(v_\nu{}^G, G^0) \\ &= \mathcal{K}^L(v_\nu, G^0, G). \end{aligned} \tag{35b}$$

The first equality sign is a consequence of Eq. (33b) ($Z = X + G$) and the fact that each vertex point of L is joint with some other internal point; hence one can shift the $\mathbf{\Omega}$'s from the vertices to the propagators. The second equality sign is a consequence of the diagonality of G^0: $G^0(n_1 i, n_2 j) \propto \delta_{ij}$. A similar equation holds for $\mathcal{K}^0$. Using Eq. (34c) we get

$$-i v_1(1) G_\omega(1) + \mathcal{K}(G_\omega) = \mathcal{K}(G) - i v_1(1) G(1). \tag{35c}$$

Here again we have not written out the v_ν and G^0 dependence of $\mathcal{K}$ explicitly.

Let us consider an infinitesimal rotation now. To evaluate Eq. (35c) up to first order in ω, we use Eqs. (35a) and (22) and find

$$[-i v_1(\mathbf{n}i) + K(\mathbf{n}it)]\omega_{ij}[X(\mathbf{n}j) + m^{-1/2} G(\mathbf{n}jt)] = 0. \tag{36}$$

If we perform the derivative of Eq. (35c) with respect to $G(1)$, we obtain [compare Eqs. (35a) and (22)]

$$[-i v_1(\mathbf{n}_1 j_1) + K(\mathbf{n}_1 j_1 t_1)]\Omega_{j_1 i_1} = [-i v_1(\mathbf{n}_1 i_1) + K(\mathbf{n}_1 i_1 t_1; G)].$$

To evaluate this equation also up to first order in ω we use Eq. (23) and get

$$[-i v_1(\mathbf{n}_1 j_1) + K(\mathbf{n}_1 j_1 t_1)]\omega_{j_1 i_1} = i M(\mathbf{n}_1 i_1 t_1, \mathbf{n}_2 j_2 t_2)\omega_{j_2 i_2}[m^{1/2} X(\mathbf{n}_2 i_2) + G(\mathbf{n}_2 i_2 t_2)]. \tag{37}$$

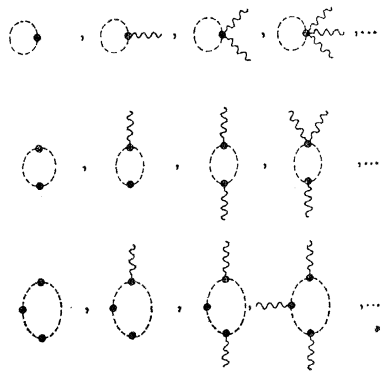

FIG. 7. The first members of three $\mathcal{K}^L$ families.

In Eqs. (36) and (37), ω_{ij} is an arbitrary skew-symmetric matrix. Notice that the summation convention applies not only to the indices of ω but also for repeated t's and n's.

B. Equilibrium Conditions

Up to now, we have not used the assumption that our system is a crystal. This assumption can be formulated as follows: For a given temperature T^0 and for given time-independent surface forces $E(\lambda)$, we can choose a matrix $A_{ij}{}^0$ in Eq. (1a) such that the equations of motion are solved by $G(1)=0$ for all points $\mathbf{X}(\mathbf{n})$ reasonably far from the surface. Because of Eq. (2) this is equivalent to the statement that (up to surface strains) the equilibrium positions of the atoms are arranged in a regular array. There is, of course, no possibility of proving such a general assumption; one can only check its consistency and analyze its consequences.

In the following, we assume that A_{ij} in Eq. (1a) agrees with $A^0{}_{ij}$. This is for convenience. But this convention is not necessary, because one could express the arrangement of the $\langle R(\lambda)\rangle$'s in Eq. (2) also by choosing appropriate 1-point functions $G(\lambda)$. A change of A_{ij}, e.g.,

$$\delta A_{ik}=A_{ik}-A^0{}_{ik}, \tag{38a}$$

can also be represented by introducing the displacements

$$G_u(\mathbf{n}i)=m^{1/2}u_{ij}X(\mathbf{n}j), \tag{38b}$$

where the deformation matrix u_{ij} is given by

$$u_{ij}=\delta A_{ik}(A^0)^{-1}{}_{kj}. \tag{38c}$$

Equation (21) with $G=0$ yields $-iV_1+K=0$ or

$$E(\lambda)=-i[-iv_1(\lambda)+K(\lambda)]. \tag{39}$$

The stress tensor for the lattice is defined by

$$\sigma_{ij}=-[m^{1/2}/(N\mathcal{V})]\sum_{\mathbf{n}} E(\mathbf{n}i)X(\mathbf{n}j), \tag{40}$$

so that Eq. (39) yields

$$\sigma_{ij}=i[m^{1/2}/(N\mathcal{V})]\sum_{\mathbf{n}}[-iv_1(\mathbf{n}i)+K(\mathbf{n}i)]X(\mathbf{n}j). \tag{41}$$

Because of Eq. (36), we conclude that the stress tensor is a symmetrical matrix: $\sigma_{ij}=\sigma_{ji}$. We remark that Eq. (39) does not hold for points on the surface of the crystal; but those points do not contribute to Eqs. (40) and (41) in the limit $N\to\infty$.

A second equilibrium condition is obtained if we consider a change of the free energy F under the deformations (38c). Equations (11), (18a), (25), and (38b) yield

$$(\partial/\partial u_{ij})F=(-T^0)(\partial/\partial u_{ij})\times[\mathcal{K}(G_u)-iV_1(1)G_u(1)]. \tag{42a}$$

Using Eqs. (22) and (41), we arrive at

$$(N\mathcal{V})^{-1}(\partial/\partial u_{ij})F=\sigma_{ij},\quad (u_{ij}=0). \tag{42b}$$

The derivative of F with respect to the deformations u_{ij} for $u_{ij}=0$ has to be equal to the stress tensor. This equation can be used to calculate $A^0{}_{ij}$ for given σ_{ij} and that transformation from the stresses to the strains is a special case of the transformation discussed in Sec. IID.

A further necessary condition for equilibrium follows from Eq. (37) after multiplication with $X(\mathbf{n}_1 j)$ and summation over $\mathbf{n}_1$ [we use Eq. (41)]:

$$-i(N\mathcal{V}/m)\sigma_{j_1 j}\omega_{j_1 i_1}=i\omega_{j_2 i_2}\int_0^{-i\beta} dt_2 M(\mathbf{n}_1 i_1 t_1,\mathbf{n}_2 j_2 t_2)X(\mathbf{n}_2 i_2)X(\mathbf{n}_1 j).$$

We have explicitly indicated the time integration to avoid confusion. If we introduce the matrix

$$S_{ij,kl}=[m/(N\mathcal{V})]\int dt_2\times\sum_{\mathbf{n}_1\mathbf{n}_2} M(\mathbf{n}_1 i t_1,\mathbf{n}_2 k t_2)X(\mathbf{n}_1 j)X(\mathbf{n}_2 1), \tag{43}$$

we may write the foregoing equation in the form

$$S_{ij,kl}-S_{ij,lk}=\sigma_{lj}\delta_{ki}-\sigma_{kj}\delta_{li}. \tag{44}$$

We want to calculate the second derivative of the free energy with respect to the deformations now. Equations (42a), (38b), and (23) yield

$$(\partial^2/\partial u_{ij}\partial u_{kl})F=(imT^0)\int dt_1 dt_2\times\sum_{\mathbf{n}_1\mathbf{n}_2} M(\mathbf{n}_1 i t_1,\mathbf{n}_2 k t_2)X(\mathbf{n}_1 j)X(\mathbf{n}_2 l).$$

$M(12)$ depends on the time difference t_1-t_2 only. Hence comparison of the last expression with Eq. (43) leads to

$$(N\mathcal{V})^{-1}(\partial^2/\partial u_{ij}\partial u_{kl})F=S_{ij,kl},\quad (u_{ij}=0). \tag{45}$$

C. Representation of the Elastic Constants

It would be complicated to continue the discussion for a general stress tensor σ_{ij}; therefore, we restrict ourselves to the most important case of an applied pressure p^0, i.e.,

$$\sigma_{ij}=-p^0\delta_{ij}. \tag{46}$$

We introduce the matrix

$$X_{ik,jl}=-p^0(\delta_{ij}\delta_{kl}-\delta_{il}\delta_{jk}), \tag{47a}$$

and define the isothermal elastic constants of the lattice by

$$C_{ij,kl}=S_{ij,kl}-X_{ik,jl}. \tag{47b}$$

The condition (44) and the trivial symmetry $S_{ij,kl}=S_{kl,ij}$ [compare Eq. (43)] yield the usual symmetry relations[5] for C;

$$C_{ij,kl}=C_{ji,kl}=C_{ij,lk}=C_{kl,ij}. \tag{47c}$$

Equation (43) may be used to get a representation of the elastic constants other than Eqs. (45), (47b). To figure this out, we introduce Fourier transforms in the usual way[8,9,11]:

$$F(\omega_1,\cdots,\omega_\nu)=\int_0^{-i\beta} dt_1\cdots dt_\nu e^{i(\omega_1 t_1+\cdots+\omega_\nu t_\nu)} \times F(t_1,\cdots,t_\nu), \quad (48a)$$

$$F(\mathbf{q}_1,\cdots,\mathbf{q}_\nu)=\sum_{\mathbf{n}_1\cdots\mathbf{n}_\nu} e^{-i[\mathbf{q}_1\mathbf{X}(\mathbf{n}_1)+\cdots+\mathbf{q}_\nu\mathbf{X}(\mathbf{n}_\nu)]} \times F(\mathbf{n}_1,\cdots,\mathbf{n}_\nu), \quad (48b)$$

for any function $F(1\cdots\nu)$. Here $\omega_1=(2\pi iT^0)\alpha_1$, $\alpha_1=0$, ±1, etc., and $\mathbf{q}_i$ is a vector of the first Brillouin zone. Because of the invariance of our functions under time translations, we may write, e.g.,

$$M(\mathbf{q}_1\omega_1 i_1,\mathbf{q}_2\omega_2 i_2)=(-i\beta)\delta_{\omega_1+\omega_2,0}M(\mathbf{q}_1 i_1,\mathbf{q}_2 i_2;\omega_1). \quad (49a)$$

If the volume of the crystal tends to infinity, we may neglect surface contributions. Hence the invariance under discrete translations yields

$$M(\mathbf{q}_1 i_1,\mathbf{q}_2 i_2;\omega_1)=N\Delta(\mathbf{q}_1+\mathbf{q}_2)M_{i_1 i_2}(\mathbf{q}_1,\omega_1), \quad (49b)$$

where

$$\Delta(\mathbf{q})=\sum_\tau \delta_{\mathbf{q},\tau} \quad (49c)$$

and τ runs over the reciprocal lattice [$\tau\mathbf{X}(\mathbf{n})/2\pi$ is an integer].

Using the reflection symmetry of the interaction and Eq. (32), we may write for the self-energy operator

$$M_{ik}(\mathbf{q},\omega)=(-2)\sum_{\mathbf{n}} \sin^2[\mathbf{q}\mathbf{X}(\mathbf{n})/2]\int dt \times M(\mathbf{n}i0,\mathbf{0}kt)e^{i\omega t}. \quad (50)$$

$M_{ik}(\mathbf{q},\omega)$ vanishes for $\mathbf{q}=0$. For small momenta and zero frequency, we write

$$M_{ik}(\mathbf{q},0)=Z_{ik,jl}q_j q_l+o(q^4). \quad (51)$$

The coefficients $Z_{ik,jl}$ are symmetric with respect to interchanging i and k or j and l. Equation (50) yields

$$Z_{ij,kl}=-\tfrac{1}{2}\sum_{\mathbf{n}}\int dt\, M(\mathbf{n}i0,\mathbf{0}kt)X(\mathbf{n}j)X(\mathbf{n}l). \quad (52)$$

On the other hand, we obtain from Eq. (43)

$$S_{ij,kl}+S_{il,kj}=[m/(N\mathcal{V})]\int dt\{-\sum_{\mathbf{n}_1\mathbf{n}_2} M(\mathbf{n}_1 i0,\mathbf{n}_2 kt)[X(\mathbf{n}_1 j)-X(\mathbf{n}_2 j)][X(\mathbf{n}_1 l)-X(\mathbf{n}_2 l)] +\sum_{\mathbf{n}_1} X(\mathbf{n}_1 j)X(\mathbf{n}_1 l)\sum_{\mathbf{n}_2} M(\mathbf{n}_1 i0,\mathbf{n}_2 kt)+\sum_{\mathbf{n}_2} X(\mathbf{n}_2 j)X(\mathbf{n}_2 l)\sum_{\mathbf{n}_1} M(\mathbf{n}_1 i0,\mathbf{n}_2 kt)\}.$$

In this expression we can perform the limit to an infinite crystal; this would not be possible in Eq. (43). The last two terms vanish because of Eq. (32) and in the limit $N\to\infty$ comparison with Eq. (52) yields

$$S_{ij,kl}+S_{il,kj}=2(m/\mathcal{V})Z_{ik,jl}. \quad (53a)$$

This formula, together with the definitions (47a) and (47b), yields

$$C_{ij,kl}+C_{il,kj}=2(m/\mathcal{V})Z_{ik,jl}. \quad (53b)$$

The symmetry relations (47c) and Eq. (53b) lead to the final result

$$C_{ij,kl}=(m/\mathcal{V})(Z_{ik,jl}+Z_{jk,il}-Z_{ji,kl}). \quad (54)$$

D. Consistency of Approximations

The equations derived do more than establish an exact relation between the derivatives $S_{ij,kl}$ of the free energy and the limiting values $Z_{ik,jl}$ of the phonon self-energy. The given proof is also of relevance as far as approximations are concerned. If one performs an approximation A^F, say, to calculate the free energy F, one can use Eqs. (45) and (47b) to get approximate expressions for the elastic constants. On the other hand, one can start with an approximation A^M for the self-energy and use Eqs. (51) and (54) to get the $C_{ij,kl}$. It is not a trivial problem to choose the approximations in such a manner that the results for the elastic constants calculated by method A^F and A^M, respectively, are the same.

In deriving the results for the elastic constants, we have not used the complete information of the equations of Sec. IID; essentially we have only applied the Eqs. (21), (22), (23), and (25). Hence we conclude: To get a consistent scheme of approximations one can start by approximating the functional $\mathcal{K}$. The corresponding approximation A^M for M and K is obtained by performing the derivatives of Eqs. (22) and (23). The approximation A^F is then given by Eq. (25). In approximating $\mathcal{K}$, one has to fulfill Eq. (35c), i.e., one must not approximate $\mathcal{K}$ by a set of graphs which violates the rotational symmetry of the system. This can be achieved by choosing the desired set of L graphs (diagrams not containing one-point propagators) and then approximating $\mathcal{K}$ by the sum of all $\mathcal{K}^L$ classes [diagrams obtained from L by attaching $G(1)$ propagators in all possible ways] generated by those L's.

The simplest approximation is given by $\mathcal{K}^0$, i.e., by the set of all diagrams not containing any G^0 propagator. According to our convention $G(1)=0$, we obtain $\mathcal{K}=0$, $M(\lambda_1 t_1,\lambda_2 t_2)=v_2(\lambda_1\lambda_2)\delta(t_1 t_2)$ (compare with the first column of Fig. 5). Equation (25) yields $F=v_0$. The free energy is approximated by the energy of the rigid lattice

and the self-energy of the phonons is given by the second derivatives of E^r. This is the classical harmonic approximation for the lattice. The equilibrium conditions of Sec. IIIB have first been discussed by Huang[5] and by Leibfried and Ludwig[13] for this approximation.

Another interesting approximation is given, if we choose as the set of L diagrams all rings which can be constructed with only V_2 vertices and G^0 propagators (Fig. 7). The contribution to Y is

$$Y_s=\sum_{\mathbf{q}\alpha} \ln\{2\sinh[\tfrac{1}{2}\beta\omega(\mathbf{q}\alpha)]\}, \tag{55}$$

where the phonon frequencies $\omega(\mathbf{q}\alpha)$ are given as the roots of the eigenvalues of $v_2(\mathbf{q})$. This is the quasiharmonic approximation[14] for the lattice. The approximation for M which is consistent with Eq. (55) is indicated by the last two diagrams of Fig. 5; the propagators occurring there have to be replaced by the ones of the harmonic approximation. The evaluation of the expression (55) or of the corresponding diagrams for M [15] is very difficult; therefore, further approximations have been applied.[16,17] We remark that the approximate evaluation of Eq. (45) for the quasiharmonic approximation carried out by Salter[17] is equivalent to a replacement of the propagators in the two diagrams for M (Fig. 5) by Green's functions for an Einstein model.

IV. THE GREEN'S FUNCTION FOR SMALL MOMENTA

A. Elastic Sum Rule

We introduce the usual spectral representation[8,9] for the response function [Eqs. (8a), (49a), (49b)]:

$$D_{ij}(\mathbf{q},z)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\chi_{ij}(\mathbf{q},\omega)}{z-\omega}. \tag{56}$$

The spectral function χ_{ij} is the Fourier transform of the commutator of the field operators. χ_{ij} is a Hermitian three-by-three matrix, because the $\varphi(\lambda t)$'s are Hermitian operators; it is a real matrix because of the time-reversal symmetry of the Hamiltonian. $\chi_{ij}(\mathbf{q},\omega)$ is a symmetric function of $\mathbf{q}$ because of the invariance of the system under space reflections. It is an antisymmetric function of ω and it is a positive matrix for $\omega>0$ as follows from its definition.

The Dyson equation (24) reads in Fourier space ($\epsilon\to 0$)

$$[z^2\delta_{ik}-M_{ik}(\mathbf{q},z)]D_{kn}(\mathbf{q},z)=\delta_{in}. \tag{57}$$

Using Eq. (51), we obtain

$$-[Z_{ik,jl}q_jq_l+o(q^4)]D_{kn}(\mathbf{q},0)=\delta_{in}, \tag{58a}$$

or, if we apply Eqs. (53a), (47b), and (47a),

$$-(\mathcal{V}/m)[C_{ij,kl}q_jq_l+o(q^4)]D_{kn}(q,0)=\delta_{in}. \tag{58b}$$

This equation shows that the restoring force for static, long-wavelength deformations is given by the isothermal elastic constants. From Eq. (56) we derive

$$(\mathcal{V}/m)C_{ij,kl}\lim_{\mathbf{q}\to 0}\left[q_jq_l\int_0^{\infty}d\omega\,\omega^{-1}\chi_{kn}(\mathbf{q},\omega)\right]=\pi\delta_{in}. \tag{59}$$

The ω^{-1} moment of the spectral function is thus given by the isothermal elastic constants. This elastic sum rule is a generalization of the compressibility sum rule[18] for liquids. The ω moment can also be calculated by using Eq. (7b); this yields the f sum rule[9]

$$\int_0^{\infty}d\omega\,\omega\chi_{in}(\mathbf{q},\omega)=\pi\delta_{in}. \tag{60}$$

The foregoing results determine the structure factor $F_{ij}(\mathbf{q})$ of the lattice which is defined by

$$F_{ij}(\mathbf{q})=(1/m)\sum_{\mathbf{n}}e^{-i\mathbf{q}\mathbf{x}(\mathbf{n})}\langle\varphi(ni)\varphi(0j)\rangle. \tag{61}$$

The fluctuation-dissipation theorem relates F_{ij} and χ_{ij}:

$$F_{kn}(\mathbf{q})=(1/m)\int_0^{\infty}d\omega\coth(\beta\omega/2)\chi_{kn}(\mathbf{q},\omega)/(2\pi). \tag{62}$$

The inequality

$$0\le\int_0^{\infty}[(\omega\beta/2)\coth(\tfrac{1}{2}\beta\omega)-1]\omega^{-1}\chi_{kn}(\mathbf{q},\omega)\le\text{const}\times\int_0^{\infty}d\omega\,\omega\chi_{kn}(\mathbf{q},\omega)$$

implies, because of Eq. (60),

$$\lim_{q\to 0}q_jq_l\int_0^{\infty}d\omega(\beta/2)\coth(\tfrac{1}{2}\beta\omega)\chi_{kn}(\mathbf{q},\omega)=\lim_{q\to 0}q_jq_l\int_0^{\infty}d\omega\,\omega^{-1}\chi_{kn}(\mathbf{q},\omega).$$

Hence we obtain for $F_{kn}(\mathbf{q})$ in Eq. (62), using Eq. (59),

$$\lim_{\mathbf{q}\to 0}\mathcal{V}C_{ij,kl}F_{kn}(\mathbf{q})q_jq_l=T^0\delta_{in}. \tag{63}$$

The structure factor increases to infinity if $\mathbf{q}$ tends to zero. The fact that $F_{ij}(\mathbf{q})$ diverges proportional to $(1/q^2)$ can be derived[19] under less restrictive assump-

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tions than we made in Sec. IIA. The achievement of formula (63) lies in the determination of the complete asymptotic form of $F_{ij}(\mathbf{q})$ for $\mathbf{q}\to 0$, which is given by the isothermal elastic constants.

B. Phonons at Zero Temperature

The self-energy $M_{ij}(\mathbf{q},z)$ is an even function of $\mathbf{q}$ and z and it vanishes for $\mathbf{q}=0$. Let us assume that M is a function not too singular for small z and $\mathbf{q}$ so that we may write the expansion [compare Eq. (51)]

$$M_{ij}(\mathbf{q},z)=Z_{ij,kl}q_kq_l+q^4\zeta_1(\mathbf{q},z)+q^2z^2\zeta_2(\mathbf{q},z)\,, \quad (64)$$

where ζ_1 and ζ_2 are finite for $q\to 0$ and $z\to 0$. We will see later that this assumption is justified for zero temperature only; for $T^0\neq 0$, an expansion like Eq. (64) is impossible.

The asymptotic form for $D_{ij}(\mathbf{q},z)$ is obtained if we substitute Eq. (64) into Eq. (57). We neglect all but the second-order terms. Using Eqs. (53a), (47b), and (47a) we arrive at

$$[z^2\delta_{ik}-(\mathcal{V}/m)C_{ij,kl}q_jq_l]D_{kn}(\mathbf{q},z)=\delta_{in}. \quad (65)$$

Hence, we conclude: The low-lying excitations of the lattice at zero temperature are phonons. The velocities of the sound waves are given by the elastic constants as they are in the harmonic approximation. The anharmonic effects do not change the connection between the derivatives of the ground-state energy with respect to homogeneous deformations and the restoring forces for displacement fluctuations; they renormalize the elastic constants only, so that quantum effects are included.

To evaluate $F_{ij}(\mathbf{q})$, we write the solution of Eq. (65) as

$$D_{kn}(\mathbf{q},z)=\sum_\alpha e_k{}^\alpha(\mathbf{q})[z^2-\omega^2(\mathbf{q}\alpha)]^{-1}e_n{}^\alpha(\mathbf{q})\,, \quad (66a)$$

where $\mathbf{e}^\alpha(\mathbf{q})$ ($\alpha=1, 2, 3$) are the polarization vectors of the three sound branches, while

$$\omega(\mathbf{q}\alpha)=c_\alpha(\Omega)q\,, \quad (66b)$$

with $c_\alpha(\Omega)$ as the sound velocity of branch α in direction $\Omega=\mathbf{q}/q(q=|\mathbf{q}|)$. From Eq. (62), we find

$$F_{kn}(\mathbf{q})=\frac{1}{2mq}\sum_\alpha e_k{}^\alpha(\mathbf{q})e_n{}^\alpha(\mathbf{q})/c_\alpha(\Omega)\,, \quad (\mathbf{q}\to 0) \quad (67)$$

i.e., at zero temperature the structure function diverges like $(1/q)$ if $\mathbf{q}$ tends to zero. Again, the asymptotic behavior is determined by the elastic constants.

C. Analytic Properties of $M(q,z)$

We write the self-energy of the phonons as the sum of two contributions:

$$M_{ij}(\mathbf{q},z)=M_{ij}{}^0(\mathbf{q})+M_{ij}{}^c(\mathbf{q},z)\,. \quad (68)$$

Here M^0 is independent of z. The V_4 diagram of Fig. 5 is an example of a contribution to M^0. M^0 may be considered as a renormalization of the V_2 term of the harmonic approximation. It allows an expansion of the kind formulated in Eq. (64); hence it is uninteresting in the following. $M_{ij}{}^c(\mathbf{q},z)$ is an analytic function on the whole plane with the possible exception of the real axis. It decreases like z^{-2} if z tends to infinity. Therefore, we may write the spectral representation[9] similarly to Eq. (56);

$$M_{ij}{}^c(\mathbf{q},z)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\Gamma_{ij}(\mathbf{q},\omega)}{z-\omega}\,, \quad (69a)$$

and

$$\Gamma_{ij}(\mathbf{q},\omega)=i[M_{ij}(\mathbf{q},\omega+i\eta)-M_{ij}(\mathbf{q},\omega-i\eta)]\,, \quad \eta\to 0+\,. \quad (69b)$$

Γ_{ij} has the same symmetry properties as χ_{ij}; it is a real function also. The simplest contribution to M^c is the last diagram of Fig. 5;

$$M^c(12)=(\tfrac{1}{2}i)V_3(1\bar{1}\bar{2})D(\bar{1}\bar{1}')D(\bar{2}\bar{2}')V_3(\bar{1}'\bar{2}'2)\,. \quad (70a)$$

To evaluate this expression[2,3] we use the harmonic approximation for D, i.e., we use the representation Eq. (66a), where the $\omega^2(\mathbf{q}\alpha)$'s and $\mathbf{e}^\alpha(\mathbf{q})$'s are the eigenvalues and eigenvectors of the classical secular matrix and where $\mathbf{q}$ runs over the first Brillouin zone. The Fourier transform of v_3, which is defined according to Eq. (48b), may be written as [compare Eqs. (49b) and (49c)]

$$v_3(\mathbf{q}i,\mathbf{k}_1i_1,\mathbf{k}_2i_2)=N\Delta(\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2)b(\mathbf{q}i,\mathbf{k}_1i_1,\mathbf{k}_2i_2)\,. \quad (70b)$$

We introduce

$$v(\mathbf{q}\alpha,\mathbf{k}_1\gamma_1,\mathbf{k}_2\gamma_2)=e_i{}^\alpha(\mathbf{q})e_{i_1}{}^{\gamma_1}(\mathbf{k}_1)e_{i_2}{}^{\gamma_2}(\mathbf{k}_2)b(\mathbf{q}i,\mathbf{k}_1i_1,\mathbf{k}_2i_2) \quad (70c)$$

and the distribution functions

$$f(\mathbf{q}\alpha)=[\exp(\omega(\mathbf{q}\alpha)/T^0)-1]^{-1}, \quad (70d)$$

and get from Eq. (70a) after some algebra

$$M_{ij}{}^c(\mathbf{q},z)=e_i{}^\alpha(\mathbf{q})[m_{\alpha\beta}(\mathbf{q}z)+m_{\alpha\beta}(\mathbf{q}-z)]e_j{}^\beta(\mathbf{q})\,. \quad (71a)$$

Here we used the notations

$$m_{\alpha\beta}(\mathbf{q}z)=m_{\alpha\beta}{}^r(\mathbf{q}z)+m_{\alpha\beta}{}^s(\mathbf{q}z)\,, \quad (71b)$$

with

$$m_{\alpha\beta}{}^r(\mathbf{q}z)=(1/8N)\sum_{\mathbf{k}_1\mathbf{k}_2}v(\mathbf{q}\alpha,\mathbf{k}_1\gamma_1,\mathbf{k}_2\gamma_2)\Delta(\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2)v(\mathbf{k}_2\gamma_2,\mathbf{k}_1\gamma_1,\mathbf{q}\beta)\left(\frac{1}{\omega(\mathbf{k}_1\gamma_1)\omega(\mathbf{k}_2\mathbf{k}_2)}\right)\frac{1+f(\mathbf{k}_1\gamma_1)+f(\mathbf{k}_2\gamma_2)}{z-\omega(\mathbf{k}_1\gamma_1)-\omega(\mathbf{k}_2\gamma_2)}\,, \quad (71c)$$

and

$$m_{\alpha\beta}{}^{s}(\mathbf{q}z)=(1/8N)\sum_{\mathbf{k}_1\mathbf{k}_2} v(\mathbf{q}\alpha,\mathbf{k}_1\gamma_1,\mathbf{k}_2\gamma_2)\Delta(\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2)v(\mathbf{k}_2\gamma_2,\mathbf{k}_1\gamma_1,\mathbf{q}\beta)\left(\frac{1}{\omega(\mathbf{k}_1\gamma_1)\omega(\mathbf{k}_2\gamma_2)}\right)\frac{f(\mathbf{k}_2\gamma_2)-f(\mathbf{k}_1\gamma_1)}{z+\omega(\mathbf{k}_2\gamma_2)-\omega(\mathbf{k}_1\gamma_1)}. \quad (71d)$$

First we consider the zero-temperature case, i.e., $f(\mathbf{k}\gamma)=0$. We obtain $m_{\alpha\beta}{}^{s}=0$ and, according to Eqs. (69b), (71a), and (71c), we find for $\omega>0$ the contribution to Γ_{ij}

$$\Gamma_{ij}(\mathbf{q},\omega)=(\pi/4N)\sum_{\mathbf{k}_1\mathbf{k}_2} e_i{}^{\alpha}(\mathbf{q})v(\mathbf{q}\alpha,\mathbf{k}_1\gamma_1,\mathbf{k}_2\gamma_2)\Delta(\mathbf{q}+\mathbf{k}_1+\mathbf{k}_2)$$
$$\times v(\mathbf{k}_2\gamma_2,\mathbf{k}_1\gamma_1,\mathbf{q}\beta)e_j{}^{\beta}(\mathbf{q})/[\omega(\mathbf{k}_1\gamma_1)\omega(\mathbf{k}_2\gamma_2)]\delta[\omega-\omega(\mathbf{k}_1\gamma_1)-\omega(\mathbf{k}_2\gamma_2)]. \quad (72a)$$

For small ω, no umklapp processes contribute to Eq. (72a). Because of Eq. (31b), v in Eq. (72a) vanishes if one of the arguments $\mathbf{q}$, $\mathbf{k}_1$, or $\mathbf{k}_2$ tends to zero. Thus the usual phase-space discussion yields for the leading contribution to $\Gamma_{ij}(\mathbf{q},\omega)$ for $\mathbf{q}$, and ω tending to zero

$$\Gamma_{ij}(\mathbf{q}\omega)\propto q^2\omega^n, \quad (n\geq 5). \quad (72b)$$

Equation (69a) shows that the expansion of Eq. (64) is justified. More complicated diagrams do not alter this result qualitatively.

Second, we consider the case of a nonvanishing temperature T^0. We get a contribution due to $m_{\alpha\beta}{}^{s}$ and in contrast to $m_{\alpha\beta}{}^{r}$ it yields a very singular result. We get, on the one hand,

$$\lim_{z\to 0}\{\lim_{q\to 0} m_{\alpha\alpha}{}^{s}(\mathbf{q}z)/q^2\}=\rho, \quad (73a)$$

but we have, on the other hand,

$$\lim_{q\to 0}\{\lim_{z\to 0} m_{\alpha\alpha}{}^{s}(qz)/q^2\}=\rho+(1/8N)\sum_{\mathbf{k}\gamma}[\lim_{q\to 0} v(\mathbf{q}\alpha,\mathbf{k}-\mathbf{q}\gamma,-\mathbf{k}\gamma)/q\omega(\mathbf{k}\gamma)]^2(-1/T^0)f(\mathbf{k}\gamma)[1+f(\mathbf{k}\gamma)]\neq\rho. \quad (73b)$$

Hence $M_{ij}(\mathbf{q},z)/q^2$ is a discontinuous function for $z\to 0$ and $\mathbf{q}\to 0$. An expansion like Eq. (64) is not possible. This is the mathematical reason why Eq. (65) cannot be applied for finite temperatures.

The physical reason for the result Eqs. (73a) and (73b) is the following. If $\mathbf{q}$ and z tend to zero at fixed nonzero temperature, we enter the region where all phenomena are dominated by quasiparticle collisions. In this hydrodynamic regime, the self-energy $M_{ij}(\mathbf{q},z)$ itself has poles due to heat conduction or due to second-sound propagation.[20] No matter how small T^0 is, in the limit $z\to 0$, $\mathbf{q}\to 0$ the calculation of simple graphs[3] like Eq. (70a) does not yield reliable results for $M_{ij}(\mathbf{q},z)$, i.e., for the sound velocities or for the sound damping. The solution of integral equations of the Boltzmann type is unavoidable in this domain.

V. SPECIFIC HEAT

A. Asymptotic Expansion of W

Knowing the low-lying excitations one knows the asymptotic behavior of the entropy and thus the leading term of the specific heat for small temperature T^0. The proof of this statement follows closely the ones given in the theory of quantum liquids.[21,22]

To expand W in Eq. (30), we choose A_{ij} in Eq. (1a) as the equilibrium matrix for $T^0=0$. Because of $[\delta/\delta G(1)]W=0$ we may put $G(1)=0$ to get the leading term of W, i.e., we may neglect the thermal expansion. We indicate the temperature dependence of M and $\tilde{G}$ explicitly, putting

$$M(12,T^0)=M(12)+M'(12), \quad (74a)$$

$$\tilde{G}(12,T^0)=\tilde{G}(12)+G'(12), \quad (74b)$$

where

$$G'(12)=G(1\bar{1})M'(\bar{1}\bar{2})G(\bar{2}2)+\cdots. \quad (74c)$$

$M(12)$ and $\tilde{G}(12)$ denote the self-energy and the propagator, respectively, for zero temperature. Equation (28) yields the expansion for Φ:

$$\Phi_T[\tilde{G}(12,T^0)]=\Phi_T[\tilde{G}(12)]$$
$$+(1/2i)\Sigma(12)G'(12)+\cdots. \quad (74d)$$

Substituting Eqs. (74) into Eq. (30), we obtain

$$(2/\beta)W-2v_0=T^0\{2\Phi_T[\tilde{G}]-\Sigma(12)\tilde{G}(12)$$
$$-\ln(iG^{0-1}-M)(11)\}. \quad (75)$$

The functional $\Phi_T[\tilde{G}]$ depends on temperature because the diagrams contain the distribution function $f(\omega)=[\exp(\omega/T^0)-1]^{-1}$. The expression for $m_{\alpha\beta}{}^{r}$ in Eq. (71c), e.g., depends on T^0 even though the harmonic propagators in Eq. (70a) are T^0-independent. We write

$$f(\omega)=\lim_{T^0\to 0} f(\omega)+\hat{f}(\omega), \quad (76)$$

[20] P. C. Kwok and P. C. Martin, Phys. Rev. **142**, 495 (1966); compare formula (87b) of W. Götze and K. H. Michel, this issue, Phys. Rev. **156**, 963 (1967).
[21] J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).
[22] W. Götze and H. Wagner, Physica **31**, 475 (1965).

and expand Φ_T up to first order in $\hat{f}$. Equation (75) then reads[22]

$$(2/\beta)W-2v_0=(2T^0\Phi_T[\tilde{G}])_{T\to 0}+T^0\Big\{\Sigma(12)G(12)+\sum_{\mathbf{q}}\int d\omega[\hat{f}(\omega)/2\pi]\,\Sigma^r{}_{ij}(\mathbf{q},\omega)A_{ij}(\mathbf{q},\omega)\Big\}-T^0\ln\tilde{G}^{-1}(11)\,, \quad (77)$$

where

$$\Sigma^r{}_{ij}(\mathbf{q},\omega)=\tfrac{1}{2}[\Sigma_{ij}(\mathbf{q},\omega+i\eta)+\Sigma_{ij}(\mathbf{q},\omega-i\eta)]\,, \quad \eta=0+\,.$$

The first term on the RHS of Eq. (77) is temperature-independent. The second term yields a constant, while the leading T^0 powers of the two terms in the parentheses cancel; there is no contribution to $(T^0)^4$ due to those terms. Hence only the log term in Eq. (77) enters the free energy in Eq. (11) as the leading temperature-dependent quantity. The entropy S is

$$S\to\tfrac{1}{2}[\partial/\partial T^0]T^0\ln D^{-1}(11)\,. \quad (78)$$

B. The Debye Law

The trace in Eq. (78) can be calculated by transforming the expression into Fourier space, viz.,

$$y=T^0\ln D^{-1}(11)=T^0\sum_{\omega_\alpha}\sum_{\mathbf{q}}[\ln D^{-1}(\mathbf{q},\omega_\alpha)]_{ii}\,. \quad (79a)$$

In this equation we have to calculate the trace of the logarithm of a three-by-three matrix, which is equal to the logarithm of the determinant of this matrix. Hence we get from Eq. (57)

$$\ln D^{-1}(\mathbf{q},\omega_\alpha)_{ii}=\ln d(\mathbf{q},\omega_\alpha)\,, \quad (79b)$$

where

$$d(\mathbf{q},\omega_\alpha)=\det[\omega_\alpha{}^2\delta_{ij}-M_{ij}(\mathbf{q},\omega_\alpha)]\,. \quad (79c)$$

Transforming the sum over the discrete frequencies into an integral over the real axis Eq. (79a) yields

$$y=\left(\frac{-i}{\pi}\right)\int_0^\infty d\omega\,\hat{f}(\omega)\sum_{\mathbf{q}}\ln\left[\frac{d(\mathbf{q},\omega+i\eta)}{d(\mathbf{q},\omega-i\eta)}\right]+\text{const}\,, \quad \eta\to 0+\,. \quad (80)$$

Only the contributions due to small ω's and small $\mathbf{q}$'s enter the asymptotic form of y in Eq. (80). Hence we may use Eq. (66a) to get

$$d(\mathbf{q},\omega)=[\omega^2-c_1{}^2(\Omega)q^2][\omega^2-c_2{}^2(\Omega)q^2]\times[\omega^2-c_3{}^2(\Omega)q^2]\,. \quad (81)$$

Transforming the sum over $\mathbf{q}$ into an integral, Eqs. (80), (81), and (78) yield the final result for the entropy

$$S/N\to(4/5)\pi^4(T^0/\Theta)^3\,, \quad (82a)$$

where the Debye temperature Θ is given by

$$\Theta^{-3}=[\mathcal{V}/(18\pi^2)]\sum_\alpha\int\frac{d\Omega}{4\pi}c_\alpha{}^{-3}(\Omega)\,. \quad (82b)$$

The sum runs over the three phonon branches and the integration over the solid angle Ω has to be extended over all directions.

The entropy obeys the same Debye law Eq. (82a) as a gas of noninteracting phonons. The Debye temperature Θ is related to the sound velocities, which in turn are given via the elastic constants by the derivatives of the ground-state energy with respect to homogeneous deformations, in the same way as it is known from the harmonic approximation. The anharmonic effects do not influence these general aspects of the results; they enter the formulas by renormalization of the ground-state energy only.

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