appears to be very promising in its ability to describe relative changes of metallic band structures with change in lattice spacing, especially in the vicinity of the Fermi energy, once a reasonably accurate potential has been found for the uncompressed metal. This conclusion seems to imply that the predominant change in band-theory potentials as the lattice spacing changes is simply due to a superposition of single-atom charge densities, while the change in these charge densities with small changes in lattice spacing is, at most, a second-order effect. Of course, this conclusion is based only on this study of the change of copper's band structure, and we hope to have the opportunity in the near future to perform similar studies on other metals.

ACKNOWLEDGMENTS

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Towards a Quantum Many-Body Theory of Lattice Dynamics. II. Collective Fluctuation Approximation

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A novel viewpoint towards the lattice dynamics of an anharmonic crystal, put forward in a previous paper of the same title, is enlarged and extended. This viewpoint first focuses attention on the motion of a single atom in a static environment, and develops the collective modes of the crystal as a whole from a superposition of the motions of the individual atoms. It is shown that of the many collective modes for a given wave vector, three are identifiable as one-phonon modes in that only these contribute to the displacement-displacement response, and a simple expression for the eigenfrequencies of these modes is exhibited. The other modes are shown to be associated with single-particle transitions, and their contribution to the neutron structure function $S(\mathbf{k},\omega)$ is derived in the special case of a purely harmonic lattice. The many-body approximation is extended to include collective fluctuations in the equilibrium state. Serious difficulties in principle are encountered, associated with maintaining translational invariance, but are partially overcome by an *ad hoc* procedure. Collective-mode frequencies renormalized in this way are compared with those obtained from an alternative theory which deals exclusively and from the outset with collective coordinates only.

I. INTRODUCTION

In a previous paper[1] of the same title, a novel viewpoint towards the lattice dynamics of a crystal was put forward. This viewpoint first focuses attention on the motion of a single atom in a static environment, and then develops the collective modes of the crystal as a whole from a superposition of the motions of the individual atoms. The philosophy is the same as that of the random phase approximation (RPA) which is also the starting point of the theory of most other many-body systems.

No assumption is made in this theoretical approach about the smallness of the atomic displacements relative to the interatomic spacing. Hence this theory is appropriate for highly anharmonic crystals, a leading example of which is helium. Here the traditional quasiharmonic theory fails, due to the light mass and weak restoring force, and consequent large zero-point motion of the atom. Yet the present picture gives a good account[2,3] of the phonon spectrum and attendant thermodynamic properties.

Despite the success of the RPA approach in giving at least qualitatively correct results for the phonon spectrum, some other aspects of the lattice dynamics are not treated adequately, notably the temperature dependence. This is because the phonon collective modes are only obtained from the response of the crystal to a disturbance. In the absence of any disturbance, i e., at equilibrium, the RPA regards the crystal as an array of nondynamically interacting atoms with a discrete single-particle excitation spectrum. Consequently, there are no Boltzmann factors of the form exp[−(phonon energy)/k_BT] as should be expected, only factors exp[−(single-particle excitation energy)/k_BT], which

[1] D. R. Fredkin and N. R. Werthamer, Phys. Rev. **138**, A1527 (1965), hereafter referred to as I. Similar ideas have also been discussed by W. Brenig, Z. Physik **171**, 60 (1963), and more recently by G. Meissner, *ibid.* **205**, 249 (1967).

[2] L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters **15**, 618 (1965).

[3] F. W. de Wette, L. H. Nosanow, and N. R. Werthamer, Phys. Rev. **162**, 824 (1967).

obviously give vastly different results. A further inadequacy of the RPA is the lack of any phonon lifetime, thus precluding any calculation of transport properties. Since phonons are not present as fluctuations in the equilibrium state, the collective response cannot be damped by the usual mechanism of decay into two or more phonons.

This paper attempts to extend the RPA treatment of crystal lattices in order to overcome these deficiencies. It is necessary, first of all, to generalize the rather *ad hoc* density matrix formalism of I in order to have a mathematical structure of sufficient power. This is done in the following section, where a suitable adaptation of the usual field-theoretical formalism is presented, and developed into a diagrammatic perturbation expansion.

The RPA results of I are then rederived in Sec. III with the new formalism. Several new results are also obtained which clarify the nature of this approximation. In particular, we are able to exhibit a simple explicit expression for the one-phonon eigenvalue equation, a result previously only conjectured.[1,2] Also, by reverting to a harmonic interatomic potential, we are able to find explicit solutions for all other collective modes in addition to the one-phonon modes. These other modes are merely independent single-particle transitions, having discrete frequencies. With the full set of modes at our disposal, we construct the structure function $S(\mathbf{k},\omega)$ seen, for example, by neutron scattering. Besides the correct one-phonon poles, $S(\mathbf{k},\omega)$ also contains artificial poles at the discrete single-particle transition frequencies, indicating that the RPA does not contain sufficient correlation to solve the harmonic-lattice problem exactly.

The approximation we consider beyond the RPA is one in which an atom is allowed to emit and reabsorb virtual phonons in the equilibrium state. In attempting to implement diagrammatically this physical idea, we are confronted by a serious technical obstacle connected with satisfying the requirements of translational invariance. The nature of the obstacle, its ramifications for many-body theory in general, and the procedure we follow to circumvent it is the subject of Sec. IV. We there also present results for the phonon frequencies as modified by this interaction with other phonons, and which thus have a more satisfactory temperature dependence.

We conclude in Sec. V with a brief discussion of these results, and an intercomparison of this theory with an alternative formulation, which we will call the self-consistent phonon approximation, which has made several appearances in the recent literature.

II. FORMALISM

It will be the goal in this section to develop a formalism adequate for a self-consistent treatment of the crystal-lattice problem, independent of the harmonic approximation as a starting point. Indeed, as we have emphasized earlier in the Introduction, we choose to start from a single-particle representation and build up the phonons as the low-lying collective modes of a general anharmonic system, in contrast to the conventional method of using the purely harmonic solid as the lowest-order approximation to the equilibrium state. Within the context of a single-particle description, however, direct application of the methods of second quantization—in particular, the thermodynamic Green's-function approach—to the problem of the crystal lattice presents certain immediate difficulties. That this is true becomes apparent if we note that the crystalline solid exhibits the property that each particle associated with a given lattice site must be localized in a volume $\sim a^3$ ($a \equiv$ lattice constant) about that lattice site. Furthermore, there must be on the average no more than one such particle localized in this volume. Thus one is prevented at the outset from employing a single-field-operator description of the solid, since such a description introduces exchange and indistinguishability in so fundamental a way that one could not distinguish between particles associated with different lattice sites. Nor could one hope to impose in any easy way the condition that particles be created and destroyed only in those localized regions of space surrounding the lattice sites of the crystal.

In order to preserve the distinguishability of particles associated with different lattice sites, we consider Heisenberg field operators $\psi_i^\dagger(\mathbf{x}t)$, $\psi_i(\mathbf{x}t)$ as creating and destroying particles of type i (i.e., particles associated with lattice site i) and satisfying commutation relations

$$\begin{aligned}\psi_i(\mathbf{x}t)\psi_j^\dagger(\mathbf{x}'t) \mp \psi_j^\dagger(\mathbf{x}'t)\psi_i(\mathbf{x}t) &= \delta_{ij}\delta^3(\mathbf{x}-\mathbf{x}'),\\ \psi_i(\mathbf{x}t)\psi_j(\mathbf{x}'t) \mp \psi_j(\mathbf{x}'t)\psi_i(\mathbf{x}t) &= 0.\end{aligned} \tag{1}$$

The requirement of localization means that mathematically we must have some way of differentiating crystalline solutions from those solutions, for example, which might represent a *gas* of distinguishable particles. As we shall see in more detail later, in order to isolate those solutions representing an ordered solid, one must cast the equations in a form which makes explicit the property of invariance of the system with respect to translations through a lattice vector. Bounded solutions of this set of equations then automatically represent states of an ordered lattice of particles.

Once localization is assured, the problem of how to guarantee that there be *on the average* no more than one particle localized at a given lattice site is a separate question. In principle, one satisfies this requirement by assigning a chemical potential μ_i to each type of particle and in the end allowing each $\mu_i \to -\infty$. Of course, one must be careful at all times during the limiting procedure to satisfy the constraint

$$\sum_\alpha f(\epsilon_\alpha,\mu) = 1, \tag{2}$$

where $f(\epsilon_\alpha,\mu)$ is the distribution function appropriate to

the manifold of single-particle energies ϵ_α at each lattice site. The above procedure, of course, introduces distinguishability and the associated Maxwell-Boltzmann statistics. It also eliminates the possibility of introducing exchange in any fundamental way at the beginning of the calculation. However, unless one is interested in the nuclear magnetic properties of the solid, this does not constitute a serious drawback to the approach. Indeed, although actual exchange of particles may occur in a highly quantum solid such as crystalline helium, estimates of the exchange energy involved[4] indicate that the exchange contribution to the ground-state energy is negligible even in this case. Furthermore, it is possible to reintroduce exchange in an *ad hoc* but plausible way by antisymmetrizing the scattering amplitude between neighboring particles, if the magnetic properties are indeed of interest.

Let us consider, then, a system of N distinguishable particles with associated field operators $\psi_i(\mathbf{x},t)$, $\psi_i^\dagger(\mathbf{x},t)$ $(i=1,\cdots,N)$ and governed by a Hamiltonian

$$H=\sum_{l=1}^{N}\int d^3x\,\psi_l^\dagger(\mathbf{x}t)(-1/2M)\nabla^2\psi_l(\mathbf{x}t)+\tfrac{1}{2}\sum_{l,m}^{N}\int d^3x d^3x'\psi_l^\dagger(\mathbf{x}t)\psi_m^\dagger(\mathbf{x}'t)\times V_{lm}(\mathbf{x},\mathbf{x}')\psi_m(\mathbf{x}'t)\psi_l(\mathbf{x}t), \quad (3)$$

where

$$V_{lm}(\mathbf{x},\mathbf{x}')=v(\mathbf{x}-\mathbf{x}'), \quad l\neq m$$
$$=0, \quad l=m.$$

The equations of motion of the field operators $\psi_i(\mathbf{x}t)$ are calculated according to the usual prescription

$$i(\partial/\partial t)\psi_i(\mathbf{x}t)=[\psi_i(\mathbf{x}t),H]=(-1/2M)\nabla^2\psi_i(\mathbf{x}t)+\sum_l\int d^3x' V_{il}(\mathbf{x},\mathbf{x}')\times\psi_l^\dagger(\mathbf{x}'t)\psi_l(\mathbf{x}'t)\psi_i(\mathbf{x}t). \quad (4)$$

Now, by forming the time-ordered product of any number of field operators ψ with an equal number of field operators $\psi^\dagger$ and taking the appropriate statistical average, one easily constructs the typical n-particle Green's function

$$G_{l_1l_2\cdots l_n}^{(n)}(\mathbf{x}_1t_1,\mathbf{x}_2t_2,\cdots,\mathbf{x}_nt_n;\mathbf{x}_1't_1',\mathbf{x}_2't_2',\cdots,\mathbf{x}_n't_n')\equiv(-i)^n\langle(\psi_{l_1}(\mathbf{x}_1t_1)\cdots\psi_{l_n}(\mathbf{x}_nt_n)\times\psi_{l_n}^\dagger(\mathbf{x}_n't_n')\cdots\psi_{l_1}^\dagger(\mathbf{x}_1't_1'))_+\rangle. \quad (5)$$

Here, $(\cdots)_+$ denotes the time-ordering operation. The statistical average, $\langle\cdots\rangle$, we take with respect to the grand-canonical density matrix operator

$$\hat{w}=\exp\beta\left\{\sum_i\mu_i\int d^3x\psi_i^\dagger(\mathbf{x})\psi_i(\mathbf{x})-H\right\}\Big/\operatorname{Tr}\exp\beta\left\{\sum_i\mu_i\int d^3x\psi_i^\dagger(\mathbf{x})\psi_i(\mathbf{x})-H\right\}, \quad (6)$$

where $\beta=(k_BT)^{-1}$. Using the definition (5) in conjunction with the equation of motion (4), one easily writes down in the usual manner the infinite hierarchy of Green's-function equations of motion. As is well known, the hierarchy of Green's-function equations are most easily dealt with in the imaginary time interval $0\leq t\leq -i\beta$, employing the appropriate boundary conditions.[5] The one-particle Green's function $G_{ij}^{(1)}(\mathbf{x}t,\mathbf{x}'t')$, for example, satisfies the boundary condition

$$G_{ij}^{(1)}(\mathbf{x}t,\mathbf{x}'t')\,|_{\,t=0}=\pm\exp(\beta\mu_i)G_{ij}^{(1)}(\mathbf{x}t,\mathbf{x}'t')\,|_{\,t=-i\beta}, \quad (7)$$

and similar relations hold for the higher-order functions. Let us recall at this point that a convenient formal method of generating Green's-function approximations is via the functional-derivative technique.[5] In this approach one adds to the Hamiltonian of the system some arbitrary nonlocal scalar potential

$$U(t,t')\equiv\sum_{ll'}\int d^3x d^3x'\psi_l^\dagger(\mathbf{x}t)U_{ll'}(\mathbf{x}t,\mathbf{x}'t')\psi_{l'}(\mathbf{x}'t'), \quad (8)$$

and then allows the field operators to evolve in the imaginary time interval $0\leq t\leq -i\beta$. The one-particle Green's function $G^{(1)}$ is now a functional of U, and one can generate higher-order Green's functions through successive functional differentiations of $G^{(1)}(U)$. In the presence of U, in the imaginary time interval, one finds it convenient to adopt the interaction representation for the one-particle Green's function,

$$G_{ij}^{(1)}(\mathbf{x}t,\mathbf{x}'t';U)\equiv\langle(\hat{S}\psi_i(\mathbf{x}t)\psi_j^\dagger(\mathbf{x}'t'))_+\rangle/\langle(\hat{S})_+\rangle, \quad (9)$$

where

$$\hat{S}\equiv\exp\left\{-i\int_0^{-i\beta}dtdt'U(t,t')\right\}.$$

Completely analogous representations hold for the higher-order functions. One easily verifies that the boundary condition (7) holds in this more general case.

Let us consider now the equation of motion of $G_{ij}^{(1)}(U)$ written in the following symbolic form (in what follows, we denote $G^{(1)}$ simply by G):

$$\sum_l\int d\bar{2}[G_{0il}^{-1}(1\bar{2};U)-\hat{\Sigma}_{il}(1\bar{2};U)]G_{lj}(\bar{2}1';U)=\delta_{ij}\delta(1-1'), \quad (10a)$$

[4] L. H. Nosanow and W. J. Mullin, Phys. Rev. Letters **14**, 133 (1965).

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

where

$$G_{0ij}^{-1}(11';U)\equiv\Big[i(\partial/\partial t_1)+(1/2M)\nabla_1^2 \mp i\sum_l\int d\bar{2}V_{il}(1\bar{2})G_{ll}(\bar{2}\bar{2}^+;U)\Big]\times\delta_{ij}\delta(1-1')-U_{ij}(11'), \quad (10b)$$

and

$$\hat{\Sigma}_{ij}(11';U)\equiv i\sum_{ll'}\int d\bar{2}d\bar{2}'V_{il}(1\bar{2})\times[\delta G_{il'}(1\bar{2}';U)/\delta U_{ll}(\bar{2}^+\bar{2})]G_{l'j}^{-1}(\bar{2}'1'U) \quad (10c)$$

is the self-energy function. In the above we have adopted the notation $2\equiv(\mathbf{x}_2,t_2)$, etc., and

$$\int d\bar{2}\equiv\int_0^{-i\beta}d\bar{t}_2\int d^3\bar{x}_2,$$

$$\delta(1-1')\equiv\delta(t_1-t_1')\delta^3(\mathbf{x}_1-\mathbf{x}_1'),$$

$$V_{ij}(11')\equiv\delta(t_1-t_1')V_{ij}(\mathbf{x}_1,\mathbf{x}_1').$$

The quantity $\delta G/\delta U$ which appears in the expression for the self-energy, when evaluated for $U=0$, defines the response of the equilibrium G to an external probe U. This leads us to define a general response function

$$L_{lm,l'm'}(12,1'2';U)\equiv\pm\delta G_{ll'}(11';U)/\delta U_{m'm}(2'2). \quad (11)$$

The form for $\hat{\Sigma}$ in terms of $\delta G/\delta U$ provides a useful starting point for the development of an iterative approximation scheme for $\hat{\Sigma}$ in terms of V and G. Neglecting $\delta G/\delta U$ altogether, for example, yields the lowest-order, or Hartree, approximation, which we will discuss in some detail later. It is clear, however, that one could arbitrarily approximate $\Sigma(U)$ by a functional of $G(U)$, say $\tilde{\Sigma}[G(U)]$, and hence from Eq. (10a) obtain a closed self-consistent equation for $G(U)$. In making such an approximate choice for $\hat{\Sigma}$, however, one must be careful to ensure that the conservation laws for particle number, energy, and momentum are preserved. Such will be the case if the approximate self-energy functional $\tilde{\Sigma}$ is derivable from a scalar functional $\Phi[G(U)]$ by the prescription[6]

$$\tilde{\Sigma}(11')=\delta\Phi/\delta G(1'1). \quad (12)$$

In practice, however, the requirement that a given approximation be conserving does not always prove to be the sole criterion for choosing an approximation appropriate to the problem under consideration. Indeed, as we shall see in Sec. IV, a seemingly obvious choice for a conserving approximation fails to give an adequate description of the solid.

Let us assume for the moment that we have chosen a $\tilde{\Sigma}[G(U)]$ suitable for approximating the exact $\hat{\Sigma}(U)$. Substituting this choice into Eq. (10a) and setting $U=0$ results in a closed self-consistent equation for G from which, in principle, all of the equilibrium thermodynamic properties of the system may be derived. Given such an equilibrium description, one can now ask how one obtains information about the response of the equilibrium state to some external probe. Such information is contained in the response function L defined in Eq. (11). Now, within the framework of our approximation, we have a closed self-consistent equation for $G(U)$; hence, from Eq. (11) it follows that we can obtain a closed equation for L, appropriate to this level of approximation, by means of a single functional differentiation of the equation for $G(U)$. Indeed, if we rewrite the equation for $G(U)$ as

$$G_{ll'}^{-1}(11';U)=G_{0ll'}^{-1}(11';U)-\tilde{\Sigma}_{ll'}[11';G(U)], \quad (13)$$

and use

$$\delta G^{-1}=-G^{-1}(\delta G)G^{-1},$$
$$\delta\tilde{\Sigma}=(\delta\tilde{\Sigma}/\delta G)\delta G,$$

we immediately obtain

$$L_{lm,l'm'}(12,1'2';U)=\pm G_{lm'}(12';U)G_{ml'}(21';U)\pm i\sum_{\bar{l}\bar{m}}G_{l\bar{l}}(1\bar{1};U)\times G_{\bar{l}l'}(\bar{1}1';U)V_{\bar{l}\bar{m}}(\bar{1}\bar{2})L_{\bar{m}m,\bar{m}m'}(\bar{2}2,\bar{2}^+2';U)+\sum_{\bar{l}\bar{l}',\bar{m}\bar{m}'}G_{l\bar{l}}(1\bar{1};U)G_{\bar{l}'l'}(\bar{1}'1';U)\times\left(\frac{\delta\tilde{\Sigma}_{\bar{l}\bar{l}'}(\bar{1}\bar{1}';U)}{\delta G_{\bar{m}\bar{m}'}(\bar{2}\bar{2}';U)}\right)L_{\bar{m}m,\bar{m}'m'}(\bar{2}2,\bar{2}'2';U). \quad (14)$$

From the above, we see that within the framework of the approximation for $\hat{\Sigma}(U)$, Eqs. (10a) and (14) yield, in principle, all of the information necessary for a complete description of the equilibrium and nonequilibrium properties of the system. The task of actually solving Eqs. (10a) and (14) in a self-consistent manner will, of course, prove to be a formidable one in practice. One can, at least, say that having chosen a suitable approximation for $\hat{\Sigma}(U)$, one has a definite prescription for determining G and L in a consistent manner.

Let us consider now the above equations within the context of the crystal-lattice problem. We will, of course, be interested in solutions for G and L in the limit $U\to 0$, i.e., for the true crystal lattice in equilibrium. In this case it is clear that the physical situation relative to a given lattice site should not be different from that with respect to any other. Hence, there exist particular solutions for G and L which have the property that

$$G_{ij}(\mathbf{x}t,\mathbf{x}'t')=\delta_{ij}G(\mathbf{x}-\mathbf{R}_i t,\mathbf{x}'-\mathbf{R}_i t'),$$
$$L_{lm,l'm'}(\mathbf{x}t,\bar{\mathbf{x}}\bar{t};\mathbf{x}'t',\bar{\mathbf{x}}'\bar{t}') \quad (15)$$
$$=\delta_{ll'}\delta_{mm'}L_{\mathbf{R}_l-\mathbf{R}_m}(\mathbf{x}-\mathbf{R}_l t,\bar{\mathbf{x}}-\mathbf{R}_m\bar{t};\mathbf{x}'-\mathbf{R}_l t',\bar{\mathbf{x}}'-\mathbf{R}_m\bar{t}'),$$

where $\mathbf{R}_l$, $\mathbf{R}_m$ are position vectors associated with lattice sites l, m, respectively. Equation (15) is essentially the

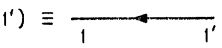
[6] G. Baym, Phys. Rev. 127, 1391 (1962).

mathematical statement of localization that we mentioned previously. The imaginary time boundary condition for the localized G takes the form

$$G(\mathbf{x}t,\mathbf{x}'t')\,|_{t=0}=\pm e^{\beta\mu}G(\mathbf{x}t,\mathbf{x}'t')\,|_{t=-i\beta}, \qquad (16)$$

with all μ_i equal to a constant μ. Now, if we introduce Eq. (15) into Eqs. (10a)–(10c) with $U=0$ we find that we may write the equation for G as

$$\int d^3\tilde{x}d\tilde{t}[G_0^{-1}(\mathbf{x}t,\tilde{\mathbf{x}}\tilde{t})-\hat{\Sigma}(\mathbf{x}t,\tilde{\mathbf{x}}\tilde{t})]G(\tilde{\mathbf{x}}\tilde{t},\mathbf{x}'t') =\delta^3(\mathbf{x}-\mathbf{x}')\delta(t-t'), \qquad (17a)$$

$G(1,1') \equiv$ 

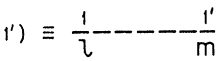
$V_{lm}(11') \equiv$ 

FIG. 1. Diagrammatic represenation of the quantities $G(1,1')$ and $V_{lm}(1,1')$.

with

$$G_0^{-1}(\mathbf{x}t,\mathbf{x}'t')=\Big[i(\partial/\partial t)+(1/2M)\nabla^2 \mp i\int d^3\tilde{\mathbf{x}}v_0(\mathbf{x}-\tilde{\mathbf{x}})G(\tilde{\mathbf{x}}0;\tilde{\mathbf{x}}0^+)\Big]\delta^3(\mathbf{x}-\mathbf{x}')\delta(t-t'), \qquad (17b)$$

and

$$\hat{\Sigma}(\mathbf{x}t,\mathbf{x}'t')=\pm\sum_{\mathbf{k}}\int d^3\tilde{x}d^3\tilde{x}'d\tilde{t}'v_{\mathbf{k}}(\mathbf{x}-\tilde{\mathbf{x}}) \times L_{\mathbf{k}}(\mathbf{x}t,\tilde{\mathbf{x}}\tilde{t};\tilde{\mathbf{x}}'\tilde{t}',\tilde{\mathbf{x}}t^+)G^{-1}(\tilde{\mathbf{x}}'\tilde{t}',\mathbf{x}'t'). \qquad (17c)$$

In the above, we have eliminated the remaining explicit

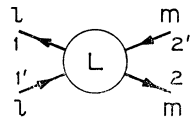
$L_{lm,l'm'}(12,1'2') \equiv$ 

FIG. 2. Diagrammatic representation of the response function $L_{lm,\,lm}(12,1'2')$.

lattice dependence by introducing the Fourier-series representation

$$v_{\mathbf{k}}(\mathbf{x}-\mathbf{x}')=\sum_{\tau\neq 0}e^{-i\mathbf{k}\cdot\tau}v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau}),$$
$$L_{\mathbf{k}}(\mathbf{x}t,\cdots)=\sum_{\tau\neq 0}e^{-i\mathbf{k}\cdot\tau}L_{\tau}(\mathbf{x}t,\cdots), \qquad (18)$$

where $\boldsymbol{\tau}$ represents a lattice translation vector. The role played by $\mathbf{k}$ will become more apparent in the next section when we consider individual approximation schemes. Suffice it to say here merely that $\mathbf{k}$ will appear as the wave vector associated with the low-lying collective modes of the system.

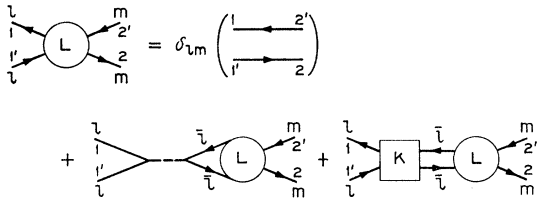


FIG. 3. Integral equation for the response function.

Employing the localization ansatz (15) one could also transform Eq. (14) for $L_{lm,l'm'}$ into an equation for $L_{\mathbf{k}}$. Rather than write out this equation explicitly, however, it is advantageous at this point to cast the equations for the localized functions into diagrammatic form. The rules for constructing Green's-function diagrams in coordinate space are well known.[5] It is easy to see that these same rules apply here with the reminder that one must be careful to keep track of lattice subscripts on interaction lines and two-particle functions. The correspondence between the basic elements of a diagram and the quantities G, V are given in Fig. 1. Thus, if we denote the response $L_{lm,lm}$ as in Fig. 2, then the equation for L may be written schematically as in Fig. 3. The effective "particle-hole" interaction K is given in

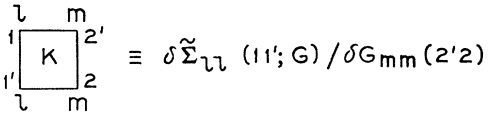


FIG. 4. Functional derivative definition of the kernel in the response function integral equation.

Fig. 4. After introducing a Fourier-series representation on the explicit lattice dependence, the above equation becomes an equation for $L_{\mathbf{k}}$ and can be written simply as in Fig. 5. In the figure we have indicated explicitly that the dashed interaction line has lattice wave vector $\mathbf{k}$.

As is well known,[5] the equations for G and L are most easily dealt with employing a Fourier-series representation for the time variable. That such a representation is possible follows from the boundary condition (16) and similar boundary conditions for the higher-order functions. The Fourier-series representation allows one to introduce equilibrium Green's functions as functions of

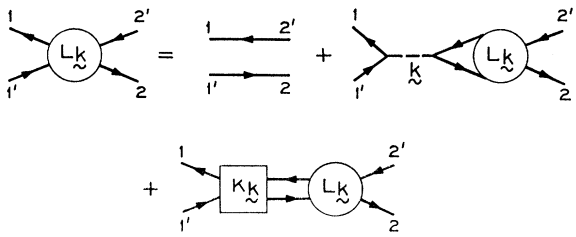


FIG. 5. Integral equation for the response function in momentum space.

a discrete imaginary frequency. Thus,

$$G(\mathbf{x}t,\mathbf{x}'t')=\frac{1}{(-i\beta)}\sum_z e^{-izt}G(\mathbf{x}\mathbf{x}',z), \tag{19}$$

where

$$z=i\pi\nu\beta^{-1}+\mu,$$
$$\nu=\text{odd integer, fermions}$$
$$=\text{even integer, bosons.}$$

The diagrammatic techniques applicable to such functions need no further discussion, since they are similar to those considered elsewhere.[5]

III. TIME-DEPENDENT HARTREE APPROXIMATION (RPA)

As a first approximation to the dynamics of a crystal, we consider in the first part of this section the time-independent Hartree description of the equilibrium state. This then provides us with a basis on which to construct the response properties of the equilibrium state to a disturbance, according to the functional-derivative prescription outlined in the previous section. It is well known, of course, that singularities in the complex frequency plane of the response function $L(\omega)$ correspond to the collective modes of the system. In particular, for the case of the general anharmonic crystal, there exists an infinite manifold of such collective modes, three of which for given wave vector can be identified as phonons.

The equation determining the response function is identical to that obtained in I employing the time-dependent Hartree approximation for the density matrix. The duplicated results are treated only briefly here, primarily as an exercise in the application of the formalism just developed. However, we are able to extend the analysis of I to show, in some detail, that all other collective modes besides the phonons are identifiable as single-particle transitions with discrete frequencies. We also exhibit an explicit expression for the neutron structure function $S(\mathbf{k},\omega)$ in order to gain additional insight into the role played by the complete manifold of collective modes in this approximation.

A. General Equation for the Collective Modes

Formally, the time-independent Hartree approximation results from neglecting the "collisional" self-energy function $\hat{\Sigma}$ in Eq. (17a). Thus the equation for $G(\mathbf{x}t,\mathbf{x}'t')$ takes the same form as that for G_0, namely

$$\left[i(\partial/\partial t)+(1/2M)\nabla^2\mp i\int d^3\tilde{x}v_0(\mathbf{x}-\tilde{\mathbf{x}})G(\tilde{\mathbf{x}}0,\tilde{\mathbf{x}}0^+)\right]$$
$$\times G(\mathbf{x}t,\mathbf{x}'t')=\delta^3(\mathbf{x}-\mathbf{x}')\delta(t-t'). \tag{20}$$

This equation is easily solved if a Fourier-series representation is introduced for the time variable, according

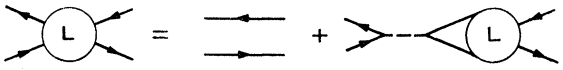


FIG. 6. Random phase approximation for the response function integral equation.

to Eq. (19). Then $G(\mathbf{x}\mathbf{x}',z)$ may be written as

$$G(\mathbf{x}\mathbf{x}',z)=\sum_\alpha(z-\epsilon_\alpha)^{-1}\varphi_\alpha(\mathbf{x})\varphi_\alpha(\mathbf{x}'), \tag{21}$$

where the $\{\varphi_\alpha(\mathbf{x})\}$ are the complete set of real basis functions diagonalizing G in coordinate space. With this form, we can explicitly evaluate the factor

$$\pm iG(\mathbf{x}0,\mathbf{x}0^+)=\pm i\sum_\alpha|\varphi_\alpha(\mathbf{x})|^2(-i\beta)^{-1}$$
$$\times\sum_z\exp(iz0^+)(z-\epsilon_\alpha)^{-1}$$
$$=\sum_\alpha|\varphi_\alpha(\mathbf{x})|^2[\exp\beta(\epsilon_\alpha-\mu)\mp1]^{-1},$$

and allow $\mu\to-\infty$ subject to the normalization condition

$$\sum_\alpha[\exp\beta(\epsilon_\alpha-\mu)\mp1]=1.$$

The eigenfunctions and eigenvalues, $\varphi_\alpha(\mathbf{x})$ and ϵ_α, are then to be determined self-consistently from

$$[(-1/2M)\nabla^2+V^H(\mathbf{x})]\varphi_\alpha(\mathbf{x})=\epsilon_\alpha\varphi_\alpha(\mathbf{x}), \tag{22}$$

with the Hartree potential

$$V^H(\mathbf{x})=\sum_{\tau\neq0}\int d^3\tilde{x}v(\mathbf{x}-\tilde{\mathbf{x}}+\tau)\sum_\alpha f_\alpha|\varphi_\alpha(\tilde{\mathbf{x}})|^2.$$

Here f_α denotes the Maxwell-Boltzmann distribution function,

$$f_\alpha\equiv\exp(-\beta\epsilon_\alpha)/\sum_\alpha\exp(-\beta\epsilon_\alpha).$$

The requirement that the Hartree approximation gives rise to a truly ordered crystal means that the representative atom is to be localized about $\mathbf{x}=0$. This in turn implies that $V^H(\mathbf{x})$ must have at least one bound state. Thus in the Hartree description, each particle moves in a potential well created by the self-consistent field of its neighbors, and in this way the description contains correlations due to the structure of the crystal. The essential feature missing in this approximation, however, is the existence of dynamic correlations due to the presence of phonon fluctuations in the equilibrium state—a feature of utmost importance in determining the correct low-temperature behavior, as discussed in the Introduction. In Sec. IV we consider in detail how the Hartree equilibrium approximation is to be improved, but first we investigate the response function appropriate to the present description.

From Fig. 5, we see that $\hat{\Sigma}=0$ implies that L satisfies the equation of Fig. 6, corresponding to a time-dependent Hartree or random-phase approximation for the response. In analyzing this equation, it is useful to introduce a time-dependent interaction $V_{ll'}(\mathbf{x}t,\mathbf{x}'t')$ analogous to the dynamically shielded interaction of an electron gas. Denoting V by a wiggly line, its definition in terms of L and the integral equation it satisfies are shown in Fig. 7. Evaluating the bubble,

$$\pm i\beta^{-1}\sum_{z'} G(\mathbf{x}\mathbf{x}', z+z')G(\mathbf{x}'\mathbf{x},z')$$
$$=i\sum_{\alpha\alpha'}\varphi_\alpha(\mathbf{x})\varphi_\alpha(\mathbf{x}')\varphi_{\alpha'}(\mathbf{x}')\varphi_{\alpha'}(\mathbf{x})f_{\alpha\alpha'}\epsilon_{\alpha\alpha'}(z^2-\epsilon_{\alpha\alpha'}{}^2)^{-1},$$

where we define

$$f_{\alpha\alpha'}\equiv f_\alpha - f_{\alpha'},\quad \epsilon_{\alpha\alpha'}\equiv\epsilon_\alpha-\epsilon_{\alpha'}.$$

It also proves convenient to define a generalized Kronecker delta

$$\delta_{\alpha\alpha',\gamma\gamma'}\equiv\tfrac{1}{2}(\delta_{\alpha,\gamma}\delta_{\alpha',\gamma'}+\delta_{\alpha,\gamma'}\delta_{\alpha',\gamma}).$$

Introducing matrix elements of V,

$$\int d^3x d^3x'\,\varphi_\alpha(\mathbf{x})\varphi_\gamma(\mathbf{x}')V_{\mathbf{k}}(\mathbf{x}t,\mathbf{x}'t')\varphi_{\alpha'}(\mathbf{x})\varphi_{\gamma'}(\mathbf{x}')$$
$$=i\beta^{-1}\sum_z \exp[-iz(t-t')]\langle\alpha\gamma|\,V_{\mathbf{k}}(z)\,|\alpha'\gamma'\rangle,$$

with

$$z=i\pi\nu\beta^{-1},\quad \nu=\text{even integer},$$

we find that $V_{\mathbf{k}}(z)$ satisfies the equation

$$\langle\alpha\gamma|\,V_{\mathbf{k}}(z)\,|\alpha'\gamma'\rangle$$
$$=\langle\alpha\gamma|\,v_{\mathbf{k}}\,|\alpha'\gamma'\rangle+\sum_{\bar\alpha\bar\alpha'}\langle\alpha\bar\alpha|\,v_{\mathbf{k}}\,|\alpha'\bar\alpha'\rangle(-f_{\bar\alpha\bar\alpha'}\epsilon_{\bar\alpha\bar\alpha'})$$
$$\times(z^2-\epsilon_{\bar\alpha\bar\alpha'}{}^2)^{-1}\langle\bar\alpha\gamma|\,V_{\mathbf{k}}(z)\,|\bar\alpha'\gamma'\rangle.$$

Using the reality of the wave functions φ_α, we may rewrite this as

$$\sum_{\bar\alpha\bar\alpha'}\langle\alpha\bar\alpha|\,V_{\mathbf{k}}(z)\,|\alpha'\bar\alpha'\rangle(z^2-\epsilon_{\bar\alpha\bar\alpha'}{}^2)^{-1}(-\epsilon_{\bar\alpha\bar\alpha'}f_{\bar\alpha\bar\alpha'})^{1/2}$$
$$\times M_{\bar\alpha\bar\alpha',\gamma\gamma'}(\mathbf{k}z)(-\epsilon_{\gamma\gamma'}f_{\gamma\gamma'})^{1/2}=\langle\alpha\gamma|\,v_{\mathbf{k}}\,|\alpha'\gamma'\rangle,\quad(23)$$

where we introduce the matrix

$$M_{\alpha\alpha',\gamma\gamma'}(\mathbf{k}z)\equiv(z^2-\epsilon_{\alpha\alpha'}{}^2)\delta_{\alpha\alpha',\gamma\gamma'}-(-\epsilon_{\alpha\alpha'}f_{\alpha\alpha'})^{1/2}$$
$$\times\langle\alpha\gamma|\,v_{\mathbf{k}}\,|\alpha'\gamma'\rangle(-\epsilon_{\gamma\gamma'}f_{\gamma\gamma'})^{1/2},\quad(24)$$

which is Hermitian under the index interchange $\alpha\alpha'\leftrightarrow\gamma\gamma'$. The matrix $M(\mathbf{k}z)$ can then be diagonalized with a unitary transformation $U(\mathbf{k})$, such that

$$\sum_{\bar\alpha\bar\alpha',\sigma\sigma'}(U^\dagger)_{\alpha\alpha',\bar\alpha\bar\alpha'}M_{\bar\alpha\bar\alpha',\sigma\sigma'}(\mathbf{k}z)U_{\sigma\sigma',\gamma\gamma'}$$
$$=[z^2-\omega_{\alpha\alpha'}{}^2(\mathbf{k})]\delta_{\alpha\alpha',\gamma\gamma'}.\quad(25)$$

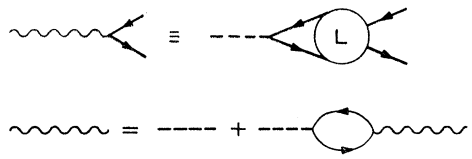


FIG. 7. Definition of, and integral equation for, the collective mode propagator (wiggly line).

It is now useful to introduce the set of matrices

$$P_{\alpha\alpha',\gamma\gamma'}{}^{(\lambda\lambda')}(\mathbf{k})\equiv U_{\alpha\alpha',\lambda\lambda'}(\mathbf{k})(U^\dagger(\mathbf{k}))_{\lambda\lambda',\gamma\gamma'},\quad(26)$$

which have the characteristics of projection operators,

$$\sum_{\bar\alpha\bar\alpha'}P_{\alpha\alpha',\bar\alpha\bar\alpha'}{}^{(\lambda\lambda')}P_{\bar\alpha\bar\alpha',\gamma\gamma'}{}^{(\delta\delta')}=\delta_{\lambda\lambda',\delta\delta'}P_{\alpha\alpha',\gamma\gamma'}{}^{(\lambda\lambda')},$$
$$\sum_{\lambda\lambda'}P_{\alpha\alpha',\gamma\gamma'}{}^{(\lambda\lambda')}=\delta_{\alpha\alpha',\gamma\gamma'},$$
$$\sum_{\alpha\alpha'}P_{\alpha\alpha',\alpha\alpha'}{}^{(\lambda\lambda')}=1.$$

The projection matrices allow us to formally invert Eq. (23) to obtain $V_{\mathbf{k}}(z)$:

$$\langle\alpha\gamma|\,V_{\mathbf{k}}(z)\,|\alpha'\gamma'\rangle$$
$$=\langle\alpha\gamma|\,v_{\mathbf{k}}\,|\alpha'\gamma'\rangle+\sum_{\lambda\lambda'}(\omega_{\lambda\lambda'}{}^2(\mathbf{k})-\epsilon_{\gamma\gamma'}{}^2)(z^2-\omega_{\lambda\lambda'}{}^2(\mathbf{k}))^{-1}$$
$$\times\sum_{\bar\alpha\bar\alpha'}\langle\alpha\bar\alpha|\,v_{\mathbf{k}}\,|\alpha'\bar\alpha'\rangle(-\epsilon_{\bar\alpha\bar\alpha'}f_{\bar\alpha\bar\alpha'})^{1/2}$$
$$\times P_{\bar\alpha\bar\alpha',\gamma\gamma'}{}^{(\lambda\lambda')}(\mathbf{k})(-\epsilon_{\gamma\gamma'}f_{\gamma\gamma'})^{-1/2}.\quad(27)$$

This is a particularly useful form with which to work, since it makes explicit the analytic structure of $V_{\mathbf{k}}(z)$ as a function of z, i.e., isolated poles at the frequencies $\pm\omega_{\lambda\lambda'}(\mathbf{k})$ along the real axis. The complete solution, of course, requires a knowledge of the $\omega_{\lambda\lambda'}(\mathbf{k})$ and $P^{(\lambda\lambda')}(\mathbf{k})$ which, in turn, are to be determined from the eigenvalue equation (25).

Before turning to an analysis of this equation, however, let us also write down the formal solution for the response. We consider the particular case of a local disturbance, for which

$$L_{\mathbf{k}}(\mathbf{x}t,\mathbf{x}'t';\,\mathbf{x}t,\mathbf{x}'t')$$
$$=\sum_{\alpha\alpha',\gamma\gamma'}\varphi_\alpha(\mathbf{x})\varphi_{\gamma'}(\mathbf{x}')\varphi_{\alpha'}(\mathbf{x})\varphi_\gamma(\mathbf{x}')$$
$$\times i\beta^{-1}\sum_z e^{iz(t-t')}\langle\alpha\gamma|\,L_{\mathbf{k}}(z)\,|\alpha'\gamma'\rangle.\quad(28)$$

Then from the equations of Figs. 6 and 7 it is found that

$$\langle\alpha\gamma|\,L_{\mathbf{k}}(z)\,|\alpha'\gamma'\rangle$$
$$=\sum_{\lambda\lambda'}[z^2-\omega_{\lambda\lambda'}{}^2(\mathbf{k})]^{-1}$$
$$\times(-\epsilon_{\alpha\alpha'}f_{\alpha\alpha'})^{1/2}P_{\alpha\alpha',\gamma\gamma'}{}^{(\lambda\lambda')}(\mathbf{k})(-\epsilon_{\gamma\gamma'}f_{\gamma\gamma'})^{1/2}.\quad(29)$$

This form for L will be useful later in constructing the

displacement-displacement response function and the neutron structure function.

B. Collective Modes in the Case of Harmonic Forces

Returning now to an examination of the solutions to Eq. (25), we examine first the case where the potential is harmonic, corresponding to a parabolic Hartree well. This analysis will provide us with an insight into the structure and proper classification of the infinite manifold of solutions in the general anharmonic situation. Even in the general case, we will be able to project out the three modes to be identified as the one-phonon modes.

From Eq. (24), the matrix $M_{\alpha\alpha',\gamma\gamma'}(\mathbf{k}\omega)$ takes the simple form in the harmonic limit,

$$M_{\alpha\alpha',\gamma\gamma'}(\mathbf{k}\omega)=(\omega^2-\epsilon_{\alpha\alpha'}{}^2)\delta_{\alpha\alpha',\gamma\gamma'} +\mathbf{X}_{\alpha\alpha'}\cdot\nabla\nabla v_{\mathbf{k}}(0)\cdot\mathbf{X}_{\gamma\gamma'}, \quad (30)$$

where

$$\mathbf{X}_{\alpha\alpha'}\equiv(-\epsilon_{\alpha\alpha'}f_{\alpha\alpha'})^{1/2}\langle\alpha|\mathbf{x}|\alpha'\rangle. \quad (31)$$

Equation (22) shows that the set of basis functions $\varphi_\alpha(\mathbf{x})$ are harmonic-oscillator wave functions, with energies (cubic symmetry is assumed, for simplicity)

$$\epsilon_\alpha=(\alpha_1+\alpha_2+\alpha_3+\tfrac{3}{2})\Omega+\text{const}, \qquad \Omega=[(3M)^{-1}\nabla^2 v_0(0)], \quad (32)$$

and quantum numbers α_1, α_2, $\alpha_3=0, 1, 2, \cdots$. The eigenvalues $\omega_{\lambda\lambda'}{}^2$ and eigenvectors $U_{\alpha\alpha'}{}^{(\lambda\lambda')}$ satisfy

$$\sum_{\bar\alpha\bar\alpha'} M_{\alpha\alpha',\bar\alpha\bar\alpha'}(\mathbf{k}\omega)U_{\bar\alpha\bar\alpha'}{}^{(\lambda\lambda')}=(\omega^2-\omega_{\lambda\lambda'}{}^2)U_{\alpha\alpha'}{}^{(\lambda\lambda')}. \quad (33)$$

Introducing principal quantum numbers $A\equiv\alpha_1+\alpha_2+\alpha_3$ and $\Lambda\equiv\lambda_1+\lambda_2+\lambda_3$, it is found that the matrix elements $\mathbf{X}_{\alpha\alpha'}$ are nonvanishing only for dipole transitions,

$$\mathbf{X}_{\alpha\alpha'}\propto\delta_{|A-A'|,1}.$$

Hence the eigensolutions are characterized by the value of $\Lambda-\Lambda'$, and for $\Lambda-\Lambda'\neq1$, the solutions are verified by inspection:

$$\begin{aligned}
&U_{\alpha\alpha'}{}^{(\lambda\lambda')}=\bar U_{\alpha\alpha'}{}^{(\lambda\lambda')}\delta_{A,A'}, \quad \omega_{\lambda\lambda'}{}^2=0, \quad \Lambda-\Lambda'=0\\
&U_{\alpha\alpha'}{}^{(\lambda\lambda')}=\bar U_{\alpha\alpha'}{}^{(\lambda\lambda')}2^{-1/2}(\delta_{A-A',\Lambda-\Lambda'}-\delta_{A-A',\Lambda'-\Lambda}),\\
&\qquad\qquad \omega_{\lambda\lambda'}{}^2=0, \quad \Lambda-\Lambda'<0 \quad (34)\\
&U_{\alpha\alpha'}{}^{(\lambda\lambda')}=\bar U_{\alpha\alpha'}{}^{(\lambda\lambda')}2^{-1/2}(\delta_{A-A',\Lambda-\Lambda'}+\delta_{A-A',\Lambda'-\Lambda}),\\
&\qquad\qquad \omega_{\lambda\lambda'}{}^2=\epsilon_{\lambda\lambda'}{}^2=(\Lambda-\Lambda')^2\Omega^2, \quad \Lambda-\Lambda'>1.
\end{aligned}$$

The eigenvectors $\bar U_{\alpha\alpha'}{}^{(\lambda\lambda')}$ for a fixed value of $\Lambda-\Lambda'$, since the eigenvectors are degenerate, are arbitrary except for the requirement of orthonormality within the subset. Note that these eigenvectors and eigenvalues are independent of $\mathbf{k}$.

The case of $\Lambda-\Lambda'=1$ demands special consideration. We introduce a complete orthogonal set of unit vectors $\mathbf{e}_{\mathbf{k}\nu}$, $\nu=1, 2, 3$, which diagonalizes $\nabla\nabla v_{\mathbf{k}}(0)$ in the 3×3 space of its Cartesian indices, so that

$$\nabla\nabla v_{\mathbf{k}}(0)=\sum_\nu \mathbf{e}_{\mathbf{k}\nu}(\mathbf{e}_{\mathbf{k}\nu}\cdot\nabla\nabla v_{\mathbf{k}}(0)\cdot\mathbf{e}_{\mathbf{k}\nu})\mathbf{e}_{\mathbf{k}\nu}; \quad (35)$$

then three of the eigenvectors $U^{(\lambda\lambda')}$ for $\Lambda-\Lambda'=1$ are given by

$$U_{\alpha\alpha'}{}^{(\lambda\lambda')}=M^{1/2}\mathbf{e}_{\mathbf{k}\nu}\cdot\mathbf{X}_{\alpha\alpha'}, \quad (36)$$

as can be verified from the sum rule

$$\sum_{\alpha\alpha'}\mathbf{e}_{\mathbf{k}\nu}\cdot\mathbf{X}_{\alpha\alpha'}\mathbf{X}_{\alpha\alpha'}\cdot\mathbf{e}_{\mathbf{k}\nu'}=\delta_{\nu,\nu'}.$$

The corresponding eigenvalues are

$$\omega_{\lambda\lambda'}{}^2\equiv\omega_{\mathbf{k}\nu}{}^2=\Omega^2-\mathbf{e}_{\mathbf{k}\nu}\cdot M^{-1}\nabla\nabla v_{\mathbf{k}}(0)\cdot\mathbf{e}_{\mathbf{k}\nu}, \quad (37)$$

or using the definitions of Ω and $v_{\mathbf{k}}$,

$$\omega_{\mathbf{k}\nu}{}^2\delta_{\nu,\nu'}=\mathbf{e}_{\mathbf{k}\nu}\cdot M^{-1}\sum_\tau(1-\cos\mathbf{k}\cdot\boldsymbol{\tau})\nabla\nabla v(\boldsymbol{\tau})\cdot\mathbf{e}_{\mathbf{k}\nu'}. \quad (38)$$

This is just the usual eigenvalue equation for harmonic phonons, and we naturally identify these three modes as the one-phonon modes. The remaining eigenvectors $U^{(\lambda\lambda')}$ are again arbitrary except for the requirement of orthonormality within the full subset $\Lambda-\Lambda'=1$; they thus depend parametrically on $\mathbf{k}$. The corresponding eigenvalues are $\omega_{\lambda\lambda'}{}^2=\Omega^2$.

Inspection of the solutions show that the one-phonon modes are built up out of a coherent superposition of single-particle transitions, from a set of states $\{\alpha\}$ via the dipole matrix elements to the states $\{\alpha'\}$ of energy level just above or below, $A'=A\pm1$. All the remaining modes correspond to purely single-particle transitions, with a discrete spectrum at integer multiples of the level spacing Ω. These are the modes which would exist in the absence of any interaction between the atoms other than the static self-consistent Hartree field. Although the one-phonon frequencies are given correctly, the RPA does not build in sufficient correlation to remove entirely the additional single-particle–like modes, which of course are not present in the exact solution.

C. One-Phonon Modes in the General Anharmonic Case

We have not been able to construct a complete explicit solution for all the collective modes in the general case of an arbitrary interatomic potential. Nevertheless, it was shown in I that of these modes there are exactly three which can still be identified as phonons, in the sense of contributing to the displacement-displacement response. The three modes of zero wave vector and zero frequency were exhibited in I, and demonstrated to correspond to uniform translations of the crystal as a whole.

This analysis can be extended to an arbitrary wave vector, and the three one-phonon modes can be projected out explicitly. We begin by claiming that the re-

quired eigenvectors are just the generalization of Eq. (36),

$$U_{\alpha\alpha'}(\mathbf{k}\nu)=M^{1/2}(-\epsilon_{\alpha\alpha'}f_{\alpha\alpha'})^{1/2}\langle\alpha|\,\mathbf{e}_{\mathbf{k}\nu}\cdot\mathbf{x}\,|\alpha'\rangle. \quad (39)$$

The states $|\alpha\rangle$ are here the exact Hartree single-particle levels, without assumption concerning harmonicity of the interatomic forces. The vectors $\mathbf{e}_{\mathbf{k}\nu}$, $\nu=1, 2, 3$ are again orthonormal, although at this point need not be further specified, and as a consequence the $U_{\alpha\alpha'}(\mathbf{k}\nu)$ are also orthonormal. To verify our claim, we substitute these eigenvectors into Eq. (25), so that

$$\begin{aligned}\omega_{\mathbf{k}\nu}^2\delta_{\nu,\nu'}=M\sum_{\alpha\alpha',\gamma\gamma'}&\langle\alpha|\,\mathbf{e}_{\mathbf{k}\nu}\cdot\mathbf{x}\,|\alpha'\rangle\\ &\times[\epsilon_{\alpha\alpha'}{}^2\delta_{\alpha\alpha',\gamma\gamma'}(-\epsilon_{\alpha\alpha'}f_{\alpha\alpha'})+(-\epsilon_{\alpha\alpha'}f_{\alpha\alpha'})\\ &\times\langle\alpha\gamma|\,v_{\mathbf{k}}\,|\alpha'\gamma'\rangle(-\epsilon_{\gamma\gamma'}f_{\gamma\gamma'})]\langle\gamma|\,\mathbf{e}_{\mathbf{k}\nu'}\cdot\mathbf{x}\,|\gamma'\rangle. \quad (40)\end{aligned}$$

Making use of the important relations

$$\epsilon_{\alpha\alpha'}\langle\alpha|\,\mathbf{x}\,|\alpha'\rangle=-M^{-1}\langle\alpha|\,\nabla\,|\alpha'\rangle, \quad (41)$$

$$\begin{aligned}-\epsilon_{\alpha\alpha'}\langle\alpha|\,\nabla\,|\alpha'\rangle&=\langle\alpha|\,\nabla V^H(\mathbf{x})\,|\alpha'\rangle\\ &=\sum_\gamma f_\gamma\langle\alpha\gamma|\,\nabla v_0(\mathbf{x}-\mathbf{x}')\,|\alpha'\gamma\rangle, \quad (42)\end{aligned}$$

Eq. (40) can be reduced to the simple form

$$\begin{aligned}\omega_{\mathbf{k}\nu}^2\delta_{\nu,\nu'}=\mathbf{e}_{\mathbf{k}\nu}\cdot M^{-1}\sum_{\alpha\gamma}&f_\alpha f_\gamma\langle\alpha\gamma|\,\nabla\nabla(v_0(\mathbf{x}-\mathbf{x}')\\ &-v_{\mathbf{k}}(\mathbf{x}-\mathbf{x}'))\,|\alpha\gamma\rangle\cdot\mathbf{e}_{\mathbf{k}\nu'}. \quad (43a)\end{aligned}$$

A particularly suggestive alternative form is

$$\begin{aligned}\omega_{\mathbf{k}\nu}^2\delta_{\nu,\nu'}=\mathbf{e}_{\mathbf{k}\nu}\cdot M^{-1}\sum_\tau&(1-\cos\mathbf{k}\cdot\boldsymbol{\tau})\\ &\times\nabla\nabla\langle\langle v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})\rangle\rangle\cdot\mathbf{e}_{\mathbf{k}\nu'}, \quad (43b)\end{aligned}$$

where the double brackets denote thermal average over both $\mathbf{x}$ and $\mathbf{x}'$ separately.

Equation (43) represents a basic result of this section in that it determines the frequencies of the low-lying collective modes (which can be identified as phonons) exactly within the context of the RPA, independent of any assumption about the harmonicity of the interaction. By comparison with Eq. (38), we note that the equation has the same form as the harmonic phonon eigenvalue equation, but with effective force constants $\nabla\nabla\langle\langle v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})\rangle\rangle$ in place of the usual harmonic force constants $\nabla\nabla v(\boldsymbol{\tau})$. Already this is a significant improvement over the conventional harmonic approximation, since it introduces a "smearing" at each of the lattice sites coming from the mean zero-point and thermal motion of the atoms. This description, as opposed to the harmonic description, more closely resembles the actual situation existing in real solids, especially in those crystals for which the zero-point motion is large. Indeed, calculations carried out on crystalline helium employing Eq. (43) produce[2,3] reasonably good agreement with experiment.

In order to verify the remainder of our claim, that the modes we have exhibited are indeed one-phonon modes, we construct the displacement-displacement response function. This is defined in terms of the general response function L by

$$\mathbf{D}(\mathbf{k}z)\equiv\int d^3x d^3x'\,\mathbf{x}L_{\mathbf{k}}(\mathbf{x}\mathbf{x}',\mathbf{x}\mathbf{x}';z)\mathbf{x}',$$

or using definition (28),

$$\mathbf{D}(\mathbf{k}z)=\sum_{\alpha\alpha',\gamma\gamma'}\langle\alpha|\,\mathbf{x}\,|\alpha'\rangle\langle\alpha\gamma|\,L_{\mathbf{k}}(z)\,|\alpha'\gamma'\rangle\langle\gamma|\,\mathbf{x}\,|\gamma'\rangle.$$

But substituting Eq. (29) for $L_{\mathbf{k}}(z)$, rearranging factors, and making use of expression (39) leads to

$$\begin{aligned}\mathbf{D}(\mathbf{k}z)=M^{-1}\sum_{\lambda\lambda'}[z^2-\omega_{\lambda\lambda'}{}^2(\mathbf{k})]^{-1}&\sum_{\alpha\alpha',\gamma\gamma'}\sum_{\nu\nu'}\mathbf{e}_{\mathbf{k}\nu}U_{\alpha\alpha'}(\mathbf{k}\nu)\\ &\times P_{\alpha\alpha',\gamma\gamma'}{}^{(\lambda\lambda')}(\mathbf{k})U_{\gamma\gamma'}(\mathbf{k}\nu')\mathbf{e}_{\mathbf{k}\nu'}.\end{aligned}$$

Since the mode eigenvectors are orthonormal, only the three modes $(\lambda\lambda')=\nu$ contribute to $\mathbf{D}$:

$$\mathbf{D}(\mathbf{k}z)=M^{-1}\sum_\nu\mathbf{e}_{\mathbf{k}\nu}(z^2-\omega_{\mathbf{k}\nu}{}^2)^{-1}\mathbf{e}_{\mathbf{k}\nu}. \quad (44)$$

Because these are the only modes contributing to the displacement-displacement response, it is justified to identify them as the one-phonon modes. The form of $\mathbf{D}$ is identical to that for the phonon propagator in the usual harmonic theory, but of course with modified frequencies.

D. Density-Density Response and Neutron Structure Function

Another quantity of interest in the present discussion is the density-density response function, which is directly related to the familiar neutron structure function $S(\mathbf{k}\omega)$. All of the collective modes are expected to play a role in the density-density response, and hence relevant information can be learned from considering the form of $S(\mathbf{k}\omega)$ in some detail. Within the context of the present formalism, $S(\mathbf{k}\omega)$ is given in terms of the general response L as

$$\begin{aligned}S(\mathbf{k}\omega)&\equiv\int d^3x d^3x' e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')-i\omega(t-t')}N^{-1}[\langle\rho(\mathbf{x}t)\rho(\mathbf{x}'t')\rangle-\langle\rho(\mathbf{x})\rangle\langle\rho(\mathbf{x}')\rangle]\\ &=-\sum_\tau\int d^3x d^3x' e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}'+\tau)}L_\tau{}^>(\mathbf{x}\mathbf{x}',\mathbf{x}\mathbf{x}';\omega)\\ &=-(1-e^{-\beta\omega})^{-1}\sum_{\alpha\alpha',\gamma\gamma'}\langle\alpha|\,e^{i\mathbf{k}\cdot\mathbf{x}}\,|\alpha'\rangle\langle\alpha\gamma|\,[L_{\mathbf{k}}(\omega+i0)-L_{\mathbf{k}}(\omega-i0)]\,|\alpha'\gamma'\rangle\langle\gamma|\,e^{-i\mathbf{k}\cdot\mathbf{x}}\,|\gamma'\rangle.\end{aligned}$$

Employing Eq. (29) for $L_{\mathbf{k}}(z)$, we then obtain

$$S(\mathbf{k}\omega)=\sum_{\lambda\lambda'}\frac{\pi}{\omega_{\lambda\lambda'}(\mathbf{k})}\left[\frac{\delta(\omega-\omega_{\lambda\lambda'}(\mathbf{k}))}{1-\exp(-\beta\omega_{\lambda\lambda'}(\mathbf{k}))}+\frac{\delta(\omega+\omega_{\lambda\lambda'}(\mathbf{k}))}{\exp(\beta\omega_{\lambda\lambda'}(\mathbf{k}))-1}\right]\left|\sum_{\alpha\alpha'}\langle\alpha|e^{i\mathbf{k}\cdot\mathbf{x}}|\alpha'\rangle(-\epsilon_{\alpha\alpha'}f_{\alpha\alpha'})^{1/2}U_{\alpha\alpha'}{}^{(\lambda\lambda')}(\mathbf{k})\right|^2. \quad (45)$$

Since we already know explicitly the eigenvectors $U_{\alpha\alpha'}(\mathbf{k}\nu)$ for the three-phonon modes, it is straightforward to work out their contribution to $S(\mathbf{k}\omega)$. More worthwhile, however, is to revert to the harmonic approximation where the complete solution for all the modes is available. It is easiest to build up the three-dimensional case by recognizing that for harmonic oscillators it is simply the product of three one-dimensional situations. Then for one dimension, using the results of Sec. III B,

$$S(k\omega)=\sum_{\Lambda=1}^{\infty}\sum_{\lambda=0}^{\infty}\frac{\pi}{\Lambda\Omega}\left[\frac{\delta(\omega-\Lambda\Omega)}{1-\exp(-\beta\Lambda\Omega)}+\frac{\delta(\omega+\Lambda\Omega)}{\exp(\beta\Lambda\Omega)-1}\right]|\langle\lambda|e^{ikx}|\lambda+\Lambda\rangle|^2\Lambda\Omega(1-e^{-\beta\Omega})e^{-\beta\lambda\Omega}(1-e^{-\beta\Lambda\Omega})$$

$$+\left\{\frac{\pi}{\omega_k}\left[\frac{\delta(\omega-\omega_k)}{1-\exp(-\beta\omega_k)}+\frac{\delta(\omega+\omega_k)}{\exp(\beta\omega_k)-1}\right]-\frac{\pi}{\Omega}\left[\frac{\delta(\omega-\Omega)}{1-\exp(-\beta\Omega)}+\frac{\delta(\omega+\Omega)}{\exp(\beta\Omega)-1}\right]\right\}$$

$$\times\left|2\sum_{\alpha=0}^{\infty}\langle\alpha|e^{ikx}|\alpha+1\rangle\Omega(1-e^{-\beta\Omega})^2e^{-\beta\alpha\Omega}M^{1/2}\langle\alpha|x|\alpha+1\rangle\right|^2. \quad (46)$$

The first term represents what would be the entire result, purely single-particle-transition modes, if there were no interparticle interaction other than the static Hartree field. The remaining terms represent the phonon contribution, with enough single-particle contribution subtracted off so as not to violate the familiar sum rule

$$(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\omega S(k\omega)=k^2/2M. \quad (47)$$

The subsidiary sums on λ and α can be carried out into closed form, relying heavily on the matrix elements being taken with respect to a harmonic-oscillator basis set, using an analysis detailed in the Appendix. The final result proved there, and generalized to three dimensions, is that

$$S(\mathbf{k}\omega)=\exp\left(\frac{-k^2}{2M\Omega}\coth\tfrac{1}{2}\beta\Omega\right)\left\{\sum_{\nu=1}^{3}\frac{(\mathbf{e}_{\mathbf{k}\nu}\cdot\mathbf{k})^2}{M\omega_{\mathbf{k}\nu}}\pi\left(\frac{\delta(\omega-\omega_{\mathbf{k}\nu})}{1-\exp(-\beta\omega_{\mathbf{k}\nu})}+\frac{\delta(\omega+\omega_{\mathbf{k}\nu})}{\exp(\beta\omega_{\mathbf{k}\nu})-1}\right)\right.$$

$$\left.+\sum_{\Lambda=1}^{\infty}\pi(\delta(\omega-\Lambda\Omega)e^{\beta\Lambda\Omega/2}+\delta(\omega+\Lambda\Omega)e^{-\beta\Lambda\Omega/2})\left[I_\Lambda\left(\frac{k^2/2M\Omega}{\sinh\frac{1}{2}\beta\Omega}\right)-\delta_{\Lambda,1}\left(\frac{k^2/2M\Omega}{\sinh\frac{1}{2}\beta\Omega}\right)\right]\right\}, \quad (48)$$

where I_Λ is a modified Bessel function.

This expression is to be compared with the exact result well-known for the harmonic approximation,

$$S(\mathbf{k}\omega)_h=\exp\left(-\frac{1}{N}\sum_{\mathbf{k}\nu}\frac{(\mathbf{e}_{\mathbf{k}\nu}\cdot\mathbf{k})^2}{2M\omega_{\mathbf{k}\nu}}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\nu}\right)\left\{\sum_{\nu=1}^{3}\frac{(\mathbf{e}_{\mathbf{k}\nu}\cdot\mathbf{k})^2}{M\omega_{\mathbf{k}\nu}}\pi\left(\frac{\delta(\omega-\omega_{\mathbf{k}\nu})}{1-\exp(-\beta\omega_{\mathbf{k}\nu})}+\frac{\delta(\omega+\omega_{\mathbf{k}\nu})}{\exp(\beta\omega_{\mathbf{k}\nu})-1}\right)\right.$$

$$\left.+(\text{incoherent background})\right\}. \quad (49)$$

The two major points of difference are, first, that the single-particle transitions contribute δ-function peaks to $S(\mathbf{k}\omega)$ rather than the smooth background in $S(\mathbf{k}\omega)_h$ and, second, that the Debye-Waller factor contains a thermal factor involving the single-particle level spacing Ω rather than the phonon frequencies themselves. Again it can be seen that the Hartree approximation contains insufficient correlation to fully suppress all the single-particle aspects in this response. Another way to understand the difference between the two expressions is to recognize that it is precisely Eq. (48) which is obtained if, in the Debye-Waller factor and incoherent background term of Eq. (49), the true phonon spectrum is replaced by an Einstein spectrum of frequency Ω. The true incoherent background is a smooth function of ω, without δ functions, only because the true phonon spectrum contains a spread of frequencies. From this point of view, the Hartree ap-

proximation is one which treats the one-phonon states exactly, but treats the multiphonon states in the Einstein spectrum model.

Because it is only the multiphonon states which are incorrect in the Hartree approximation, the errors in $S(\mathbf{k}\omega)$ are not overwhelmingly large numerically. The weight of the δ functions at $\omega=\Lambda\Omega$ relative to the weight of the one-phonon peaks is of order $(k^2/2M\Omega)^2$ for $k^2\ll 2M\Omega$, and varies as $e^{-\beta\Omega}$ for $\beta\Omega\gg 1$. The more serious problem is the temperature dependence, especially of the Debye-Waller factor which varies exponentially as $e^{-\beta\Omega}$ at low temperatures associated with the Einstein model, rather than as the correct T^2 power law. Furthermore, although Ω does equal the rms phonon frequency in the harmonic approximation,

$$\Omega^2=(3N)^{-1}\sum_{\mathbf{k}\nu}\omega_{\mathbf{k}\nu}^2,$$

the quantity $\Omega^{-1}\coth\frac{1}{2}\beta\Omega$ is always greater than the average over the phonon spectrum of the same function,

$$\Omega^{-1}\coth\tfrac{1}{2}\beta\Omega>(3N)^{-1}\sum_{\mathbf{k}\nu}\omega_{\mathbf{k}\nu}^{-1}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\nu},$$

by a factor which might typically be of order two.

FIG. 8. Diagrammatic approximation for the single-particle self-energy.

IV. COLLECTIVE FLUCTUATION APPROXIMATION

A. Equilibrium State

The analysis of the previous section makes it abundantly clear that although the Hartree approximation achieves success with the one-phonon modes, it does not include sufficient correlation to modify the single-particle–like collective modes into multiphonon modes, or alternatively to modify the discrete Einstein-mode spectrum of the background into a continuous spectrum. As a consequence, the low-temperature properties of the crystal have qualitatively incorrect temperature dependence, and other quantitative discrepancies appear. Furthermore, the Hartree approximation does not allow for a finite phonon lifetime, which should arise from the decay of the phonon into two or more other phonons of the incoherent background.

For these reasons, we attempt an improvement to the equilibrium description which we might term the collective fluctuation approximation. Diagrammatically, this is represented by the approximation for $\hat{\Sigma}$ illustrated in Fig. 8. The wiggly line is intended to denote a collective mode, and the approximation is meant to take account of an atom's being able to fluctuate by emission and reabsorption of these virtual modes. The solid line is the renormalized propagator G for which $\hat{\Sigma}$ is the self-energy, via the Dyson equation (10a).

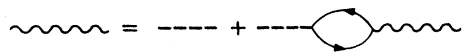


FIG. 9. Defining equation for the wiggly line in Fig. 8.

Difficulty is immediately encountered in making a more precise definition of the wiggly line, V. The most natural choice is just the same sum of bubbles which produced the phonon in the RPA; namely, the integral equation of Fig. 9. The corresponding response is then given by Fig. 10. Although identical topologically to Fig. 7(b), the equation of Fig. 9 differs in that the solid lines are again the renormalized propagators with $\hat{\Sigma}$ as in Fig. 8. But such a choice very likely leads to disaster, since it seems unavoidable that the poles of V, which ought to give the phonon frequencies $\omega_{\mathbf{k}\nu}$, are no longer momentum-conserving, or "acoustic," because $\omega_{0\nu}\neq 0$.

To understand the problem involved, let us return temporarily to the RPA and examine how the phonon spectrum there is indeed acoustic, with $\omega_{\mathbf{k}\nu}\propto k$ for small k. Considering the steps leading from Eq. (40) to Eq. (43), it can be seen that there is a nontrivial cancellation which takes place between matrix elements of $v_{\mathbf{k}}$ and the single-particle energy differences $\epsilon_{\alpha\alpha'}$, such that only the combination $v_0-v_{\mathbf{k}}$ results. This cancellation takes place particularly because of the sum-rule equation (42), which in turn is a consequence of the single-particle energies being taken with respect to the Hartree potential.

The integral equation of Fig. 9 makes this cancellation unlikely by modifying the energy differences, because of the addition of a nonvanishing self-energy $\hat{\Sigma}$, without a corresponding modification in the interatomic potential. In more formal language, the single-particle propagators are renormalized without a compensating vertex renormalization. In this particular physical situation, it seems crucial for fulfilling the requirement of translational invariance to satisfy exactly the Ward's identities between propagator and vertex renormalizations.

This difficulty calls again into question a problem in many-body theory which is usually believed to have been settled; namely, the problem of constructing a criterion for insuring that a given approximation satisfies the conservation laws. As discussed in Sec. II, the work of Baym and Kadanoff[6,7] shows that in order to obtain

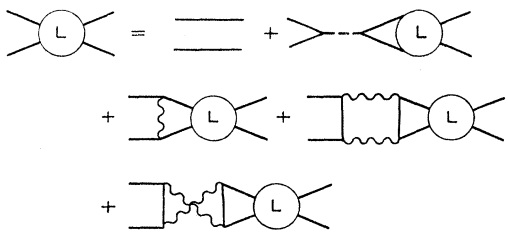


FIG. 10. Integral equation for the response function in the collective fluctuation approximation.

[7] G. Baym and L. P. Kadanoff, Phys. Rev. 124, 287 (1961).

an approximation for the response of a system to a disturbance from equilibrium which is conserving, it is sufficient to define the approximation by specifying a functional $\Phi\{G\}$ of the single-particle propagator. The self-energy $\Sigma\{G\}$ of that propagator is then to be determined from the functional derivative (schematically) $\Sigma=\delta\Phi/\delta G$, and the response in turn is related to the second functional derivative, $\delta^2\Phi/\delta G^2$, as in Eq. (14). Although the collective modes contained within this approximate response are indeed conserving, it will not in general be true that the collective-mode fluctuations within the equilibrium Σ are conserving. Such a situation also occurs in the interacting Bose gas, where it is known as the difficulty of maintaining the Hugenholtz-Pines theorem on the single-particle spectrum together with particle-number conservation.

One might be tempted to enforce conservation in both equilibrium collective fluctuations and response by requiring that the modes be represented by precisely the same diagrams in both places. That is, the approximation is to be such that Σ and L are consistent with each other. However, since L is conserving if it is given by a functional derivative of Σ, the requirement of consistency between Σ and L defines a nonlinear functional differential equation. Such an equation can be constructed by combining Eqs. (17) and Figs. 3 and 4 from Sec. II; it has also been derived by de Dominicis and Martin[8] [their Eq. (47)]. Unfortunately, this equation cannot be satisfied by any perturbation-theoretic approximation. In fact, the equation *defines* the *exact* perturbation-theoretic solution, in the sense that the iteration of the equation generates *all* perturbation-theory diagrams.[9] Thus there cannot exist any sequence of diagrammatic approximations which satisfy the consistency equation; if such a sequence did exist, perturbation theory itself would be non-unique. Our conclusion, then, is that it does not appear possible to develop any diagrammatic approximation for which both the equilibrium fluctuations as well as the response are simultaneously and automatically exactly conserving, because such a requirement is equivalent to a definition of the exact solution.

It should also be remarked that the area of lattice dynamics is not the only physical context where collective fluctuations are significant. Diagrams similar to those of Figs. 8–10 have been used to calculate the plasmon lifetime in an electron gas[10] and electron-phonon interactions in a "jellium" metal.[11] In such contexts, the approximation has been referred to[7] as the shielded-interaction approximation. Related considerations have been applied to the interaction of fermions with collective spin waves.[12] Despite this widespread usage, however, the problem of properly defining the collective mode does not seem to have become widely appreciated.

In order to make further progress, we are forced to commit some violence to the approximation under consideration. The tactic we adopt is to specify the wiggly line in Fig. 8 algebraically rather than diagrammatically. We take Eq. (27) as a defining relationship, particularly insofar as the singularities of $V_k(z)$ are poles at the collective-mode frequencies $\pm\omega_{\lambda\lambda'}(\mathbf{k})$ given by the RPA, three of which are indeed acoustic phonons. However, the single-particle eigenfunctions $|\alpha\rangle$ and eigenvalues ϵ_α are allowed to differ from their Hartree values, so as to be consistent with the renormalization induced by the improved choice of $\hat{\Sigma}$.

The Dyson equation (17a) for G is clearly nonlinear, since both G_0^{-1} of Eq. (17b) and $\hat{\Sigma}$ of Fig. 8 themselves depend on G. In order to solve this set, then, it is necessary to make an ansatz for G which can be substituted into the internal lines of G_0^{-1} and $\hat{\Sigma}$, the ansatz then to be justified *a posteriori* by inversion of Eq. (17a). Since the singularities of $G(z)$ are at single-particle energies in the absence of $\hat{\Sigma}$, it is natural to assume in the presence of $\hat{\Sigma}$ that $G(z)$ would continue to have poles at renormalized single-particle energies, but of course with smaller residue. If we denote the renormalized single-particle energies by E_α, then the residue of $G(z)$ at E is diminished by the usual renormalization factor,

$$Z=[1-\hat{\Sigma}'(E)]^{-1}. \tag{50}$$

The remaining spectral weight $1-Z$ is made up by the branch cut induced in $G(z)$ by the branch cut of $\hat{\Sigma}(z)$. Thus the singularities of $\hat{\Sigma}(z)$ are of vital importance for maintaining conservation of probability.

Nevertheless, we have been unable to construct an ansatz for the G of internal lines which accurately represents the branch cut. Instead, for most internal lines, we make a "quasiparticle" ansatz in which we assume $G(z)$ merely to have poles at the E_α, with no further singularities. In order to conserve probability, it is necessary to ignore wave-function renormalization, i.e., $Z\to 1$. The quasiparticle propagator is thus

$$\langle\alpha|G^{QP}(z)|\alpha'\rangle=(z-E_\alpha)^{-1}\delta_{\alpha,\alpha'}. \tag{51}$$

But as will be detailed later, this ansatz is not everywhere sufficient, and where necessary we approximate the branch cut by a lowest-order iteration; schematically,

$$G(z)\cong G^{QP}(z)+G^{QP}(z)(\hat{\Sigma}(z)-\hat{\Sigma}(E))G^{QP}(z). \tag{52}$$

Enough comment has now been supplied and ground rules laid to plunge into the actual evaluation of $\hat{\Sigma}(z)$. Collecting the analytical expressions which are being assumed for each element of the diagram of Fig. 8—namely, Eqs. (27) and (51)—we construct the

[8] C. de Dominicis and P. C. Martin, J. Math. Phys. **5**, 14 (1964).
[9] P. C. Martin (private communication).
[10] D. F. Du Bois, V. Gilinsky, and M. G. Kivelson, Phys. Rev. **129**, 2376 (1963).
[11] T. Holstein, Ann. Phys. (N. Y.) **29**, 410 (1964).
[12] N. F. Berk and J. R. Schrieffer, Phys. Rev. Letters **17**, 433 (1966); S. Doniach and S. Engelsberg, *ibid.* **17**, 750 (1966).

formula

$$\langle\alpha|\hat{\Sigma}(z)|\alpha'\rangle = \frac{i}{N}\sum_{\mathbf{k}}\sum_{\bar{\alpha}}\frac{i}{\beta}\sum_{z'}\frac{1}{z'-E_{\bar{\alpha}}}\sum_{\gamma\gamma'}\langle\alpha\gamma|v_{\mathbf{k}}|\bar{\alpha}\gamma'\rangle \times\sum_{\lambda\lambda'}P_{\gamma\gamma',\alpha'\bar{\alpha}}{}^{(\lambda\lambda')}(\mathbf{k})\left(\frac{-E_{\gamma\gamma'}f_{\gamma\gamma'}}{-E_{\alpha'\bar{\alpha}}f_{\alpha'\bar{\alpha}}}\right)^{1/2} \times\frac{\omega_{\lambda\lambda'}{}^2(\mathbf{k})-E_{\alpha'\bar{\alpha}}{}^2}{(z-z')^2-\omega_{\lambda\lambda'}{}^2(\mathbf{k})}. \quad (53)$$

Use has been made of the relationship

$$\sum_{\mathbf{k}} v_{\mathbf{k}}=0. \quad (54)$$

Alternatively, $\langle\alpha|\hat{\Sigma}(z)|\alpha'\rangle$ can be given equally well by the expression (53) in which α and α' are interchanged on the right-hand side. Carrying out the sum over z and letting $\mu\rightarrow-\infty$, we find

$$\langle\alpha|\hat{\Sigma}(z)|\alpha'\rangle = N^{-1}\sum_{\mathbf{k}\lambda\lambda'}\sum_{\bar{\alpha}\gamma\gamma'}\langle\alpha\gamma|v_{\mathbf{k}}|\bar{\alpha}\gamma'\rangle P_{\gamma\gamma',\alpha'\bar{\alpha}}{}^{(\lambda\lambda')}(\mathbf{k}) \times\left(\frac{-E_{\gamma\gamma'}f_{\gamma\gamma'}}{-E_{\alpha'\bar{\alpha}}f_{\alpha'\bar{\alpha}}}\right)^{1/2}\frac{\omega_{\lambda\lambda'}{}^2(\mathbf{k})-E_{\alpha'\bar{\alpha}}{}^2}{(z-E_{\bar{\alpha}})^2-\omega_{\lambda\lambda'}{}^2(\mathbf{k})} \times\left((z-E_{\bar{\alpha}})\frac{\coth\frac{1}{2}\beta\omega_{\lambda\lambda'}(\mathbf{k})}{2\omega_{\lambda\lambda'}(\mathbf{k})}-\frac{1}{2}\right), \quad (55)$$

or alternatively an expression with $\alpha\leftrightarrow\alpha'$.

The energy renormalization is obtained by putting $\hat{\Sigma}(z)$ onto the mass shell. We evaluate $\langle\alpha|\hat{\Sigma}(z)|\alpha'\rangle$ at $z=E_{\alpha'}$ and $\langle\alpha'|\hat{\Sigma}(z)|\alpha\rangle$ at $z=E_{\alpha}$, and then average the two results. It is important to note that

$$\sum_{\mathbf{k}\lambda\lambda'} v_{\mathbf{k}}P^{(\lambda\lambda')}(\mathbf{k})=0, \quad (56)$$

because of Eqs. (26) and (54). The result is that

$$\langle\alpha|\hat{\Sigma}(E)|\alpha'\rangle \equiv\tfrac{1}{2}\langle\alpha|\left(\hat{\Sigma}(E_\alpha)+\hat{\Sigma}(E_{\alpha'})\right)|\alpha'\rangle = -\frac{1}{N}\sum_{\mathbf{k}\lambda\lambda'}\frac{\coth\frac{1}{2}\beta\omega_{\lambda\lambda'}(\mathbf{k})}{2\omega_{\lambda\lambda'}(\mathbf{k})} \times\sum_{\bar{\alpha}\gamma\gamma'}\tfrac{1}{2}\{\langle\alpha\gamma|v_{\mathbf{k}}|\bar{\alpha}\gamma'\rangle P_{\gamma\gamma',\alpha'\bar{\alpha}}{}^{(\lambda\lambda')}(\mathbf{k}) \times E_{\alpha'\bar{\alpha}}(-E_{\gamma\gamma'}f_{\gamma\gamma'}/-E_{\alpha'\bar{\alpha}}f_{\alpha'\bar{\alpha}})^{1/2}+(\alpha\leftrightarrow\alpha')\}. \quad (57)$$

It is evident that $\langle\alpha|\hat{\Sigma}(E)|\alpha'\rangle$ is purely real, so that no quasiparticle lifetime appears in this approximation. This feature is consistent with the ansatz for G [Eq. (51)].

The contribution to Eq. (57) from the one-phonon modes can be evaluated, since the projection operators and frequencies are known via Eqs. (39) and (43). Keeping just the one-phonon modes, and applying the sum rule (41) vigorously,

$$\langle\alpha|\hat{\Sigma}(E)|\alpha'\rangle\cong-\frac{1}{2N}\sum_{\mathbf{k}\nu}\frac{\coth\frac{1}{2}\beta\omega_{\mathbf{k}\nu}}{2M\omega_{\mathbf{k}\nu}}\mathbf{e}_{\mathbf{k}\nu}\mathbf{e}_{\mathbf{k}\nu}: \sum_{\gamma} f_\gamma\langle\alpha\gamma|\nabla\nabla v_{\mathbf{k}}|\alpha'\gamma\rangle. \quad (58)$$

This expression is more easily interpreted by recognizing within it a displacement-displacement correlation function [related to the phonon propagator, Eq. (44)], so that

$$\langle\alpha|\hat{\Sigma}(E)|\alpha'\rangle=-\tfrac{1}{2}\sum_{\tau}\langle\mathbf{u}_\tau\mathbf{u}_0\rangle: \sum_{\gamma} f_\gamma\langle\alpha\gamma|\nabla\nabla v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})|\alpha'\gamma\rangle. \quad (59)$$

We denote a phonon dynamical displacement coordinate by $\mathbf{u}$. If we also insert the quasiparticle propagator G^{QP} into the expression (17b) for G_0^{-1}, then we obtain the simple form

$$\langle\alpha|G_0^{-1}(z)|\alpha'\rangle=\langle\alpha|z-(-1/2M)\nabla^2|\alpha'\rangle -\sum_{\gamma} f_\gamma\langle\alpha\gamma|v_0|\alpha'\gamma\rangle. \quad (60)$$

Combining Eqs. (59) and (60) into the Dyson equation (17a), it would seem that the quasiparticle ansatz for $G(z)$ is consistent provided only that the renormalized single-particle eigenfunctions and eigenvalues satisfy the renormalized Hartree equation,

$$\Big[(-1/2M)\nabla^2+\sum_{\tau}\sum_{\gamma} f_\gamma\int d^3x'\,|\varphi_\alpha(\mathbf{x}')|^2 \times(1-\tfrac{1}{2}\langle\mathbf{u}_\tau\mathbf{u}_0\rangle:\nabla\nabla)v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})\Big]\varphi_\alpha(\mathbf{x}) =E_\alpha\varphi_\alpha(\mathbf{x}). \quad (61)$$

While this form does show many of the physical features which the diagram approximation was intended to incorporate, and which will be discussed shortly, there is one serious flaw which must be attented to first. The problem is that expression (59) is not translationally invariant; i.e., a uniform translation of the crystal as a whole does not leave $\langle\mathbf{u}_\tau\mathbf{u}_0\rangle$ invariant, since it is not a function solely of the coordinate difference $\mathbf{u}_\tau-\mathbf{u}_0$. The cause of this defect is subtle, but can be traced to the inadequacy of the quasiparticle ansatz for the G internal line occurring in G_0^{-1}. The trouble can be corrected by appending to G^{QP} a contribution of the branch cut, with the iterative expansion equation (52) being sufficient for this purpose. Thus there is the

additional contribution to the single-particle self-energy shown in Fig. 11, and given by

$$\langle\alpha|\delta G_0^{-1}|\alpha'\rangle=\pm i\sum_{\gamma\gamma'}\langle\alpha\gamma|v_0|\alpha'\gamma'\rangle i\beta^{-1}\sum_z(z-E_\gamma)^{-1}(z-E_{\gamma'})^{-1}\langle\gamma|\hat{\Sigma}(z)-\hat{\Sigma}(E)|\gamma'\rangle.$$

Substituting Eq. (55) for $\langle\gamma|\hat{\Sigma}(z)|\gamma'\rangle$, and for brevity dropping all arguments $\mathbf{k}$ and $\lambda\lambda'$,

$$\langle\alpha|\delta G_0^{-1}|\alpha'\rangle=\pm i\sum_{\gamma\gamma'}\langle\alpha\gamma|v_0|\alpha'\gamma'\rangle i\beta^{-1}\sum_z(z-E_\gamma)^{-1}(z-E_{\gamma'})^{-1}\Big\{-\langle\gamma|\hat{\Sigma}(E)|\gamma'\rangle+\frac{1}{N}\sum_{\mathbf{k}\lambda\lambda'}\sum_{\bar{\alpha}\sigma\sigma'}\frac{\omega^2-E_{\gamma'\bar{\alpha}}{}^2}{2\omega}$$
$$\times\Big[\frac{n(\omega)}{z-E_{\bar{\alpha}}+\omega}+\frac{n(-\omega)}{z-E_{\bar{\alpha}}-\omega}\Big]\Big(\frac{-E_{\sigma\sigma'}f_{\sigma\sigma'}}{-E_{\gamma'\bar{\alpha}}f_{\gamma'\bar{\alpha}}}\Big)^{1/2}\langle\gamma\sigma|v_{\mathbf{k}}|\bar{\alpha}\sigma'\rangle P_{\sigma\sigma',\gamma'\bar{\alpha}}\Big\},$$

where $n(\omega)\equiv(\exp(\beta\omega)-1)^{-1}$ is the boson thermal weight factor. Next, the sum over z can be carried out:

$$\langle\alpha|\delta G_0^{-1}|\alpha'\rangle=\sum_{\gamma\gamma'}\langle\alpha\gamma|v_0|\alpha'\gamma'\rangle\Big\{-\frac{f_{\gamma\gamma'}}{E_{\gamma\gamma'}}\langle\gamma|\hat{\Sigma}(E)|\gamma'\rangle+\frac{1}{N}\sum_{\mathbf{k}\lambda\lambda'}\sum_{\bar{\alpha}\sigma\sigma'}\frac{\omega^2-E_{\gamma'\bar{\alpha}}{}^2}{2\omega}$$
$$\times\Big[\Big(\frac{f_\gamma n(\omega)}{E_{\gamma\gamma'}(E_{\gamma\bar{\alpha}}+\omega)}-\frac{f_{\gamma'}n(\omega)}{E_{\gamma\gamma'}(E_{\gamma'\bar{\alpha}}+\omega)}+\frac{f(E_{\bar{\alpha}}-\omega)n(\omega)}{(E_{\bar{\alpha}\gamma}-\omega)(E_{\alpha\gamma'}-\omega)}\Big)+(\omega\to-\omega)\Big]$$
$$\times\Big(\frac{-E_{\sigma\sigma'}f_{\sigma\sigma'}}{-E_{\gamma'\bar{\alpha}}f_{\gamma'\bar{\alpha}}}\Big)^{1/2}\langle\gamma\sigma|v_{\mathbf{k}}|\bar{\alpha}\sigma'\rangle P_{\sigma\sigma',\gamma'\bar{\alpha}}\Big\}.$$

But $f(E-\omega)n(\omega)=f(E)n(-\omega)$, and hence some rearrangement gives

$$\langle\alpha|\delta G_0^{-1}|\alpha'\rangle=\sum_{\gamma\gamma'}\langle\alpha\gamma|v_0|\alpha'\gamma'\rangle\Big\{-\frac{f_{\gamma\gamma'}}{E_{\gamma\gamma'}}\langle\gamma|\hat{\Sigma}(E)|\gamma'\rangle+\frac{1}{N}\sum_{\mathbf{k}\lambda\lambda'}\sum_{\bar{\alpha}\sigma\sigma'}\Big\{\Big[\frac{\coth\frac{1}{2}\beta\omega}{2\omega}\Big(\frac{f_{\gamma'}E_{\gamma'\bar{\alpha}}}{E_{\gamma\gamma'}}-f_{\bar{\alpha}}\frac{\omega^2+E_{\gamma\bar{\alpha}}E_{\gamma'\bar{\alpha}}}{E_{\gamma\bar{\alpha}}{}^2-E_{\gamma'\bar{\alpha}}{}^2}\Big)-\frac{f_{\gamma'\bar{\alpha}}}{2E_{\gamma\gamma'}}\Big]$$
$$\times\Big(\frac{-E_{\sigma\sigma'}f_{\sigma\sigma'}}{-E_{\gamma'\bar{\alpha}}f_{\gamma'\bar{\alpha}}}\Big)^{1/2}\langle\gamma\sigma|v_{\mathbf{k}}|\bar{\alpha}\sigma'\rangle P_{\sigma\sigma',\gamma'\bar{\alpha}}+(\gamma\leftrightarrow\gamma')\Big\}\Big\}.$$

The term not containing the factor $\coth\frac{1}{2}\beta\omega$ vanishes according to Eq. (56). Substituting Eq. (57) for $\langle\alpha|\hat{\Sigma}(E)|\gamma'\rangle$, we obtain

$$\langle\alpha|\delta G_0^{-1}|\alpha'\rangle=\sum_{\gamma\gamma'}\langle\alpha\gamma|v_0|\alpha'\gamma'\rangle\frac{1}{N}\sum_{\mathbf{k}\lambda\lambda'}\frac{\coth\frac{1}{2}\beta\omega}{2\omega}\sum_{\bar{\alpha}\sigma\sigma'}\Big\{\Big(\frac{f_\gamma+f_{\gamma'}}{2E_{\gamma\gamma'}}E_{\gamma'\bar{\alpha}}-f_{\bar{\alpha}}\frac{\omega^2+E_{\gamma\bar{\alpha}}E_{\gamma'\bar{\alpha}}}{E_{\gamma\bar{\alpha}}{}^2-E_{\gamma'\bar{\alpha}}{}^2}\Big)$$
$$\times\Big(\frac{-E_{\sigma\sigma'}f_{\sigma\sigma'}}{-E_{\gamma'\bar{\alpha}}f_{\gamma'\bar{\alpha}}}\Big)^{1/2}\langle\gamma\sigma|v_{\mathbf{k}}|\bar{\alpha}\sigma'\rangle P_{\sigma\sigma',\gamma'\bar{\alpha}}+(\gamma\leftrightarrow\gamma')\Big\}.$$

Finally, using the collective-mode eigenvalue equation to eliminate $v_{\mathbf{k}}$,

$$\langle\alpha|\delta G_0^{-1}|\alpha'\rangle=\sum_{\bar{\alpha}\gamma\gamma'}\langle\alpha\gamma|v_0|\alpha'\gamma'\rangle\frac{1}{N}\sum_{\mathbf{k}\lambda\lambda'}\frac{\coth\frac{1}{2}\beta\omega}{\beta\omega}\frac{P_{\gamma\bar{\alpha},\gamma'\bar{\alpha}}}{(E_{\gamma\bar{\alpha}}f_{\gamma\bar{\alpha}}E_{\gamma'\bar{\alpha}}f_{\gamma'\bar{\alpha}})^{1/2}}$$
$$\times\Big[(\omega^2-E_{\gamma\bar{\alpha}}{}^2)\Big(\frac{f_\gamma+f_{\gamma'}}{2E_{\gamma\gamma'}}E_{\gamma'\bar{\alpha}}-f_{\bar{\alpha}}\frac{\omega^2+E_{\gamma\bar{\alpha}}E_{\gamma'\bar{\alpha}}}{E_{\gamma\bar{\alpha}}{}^2-E_{\gamma'\bar{\alpha}}{}^2}\Big)+(\gamma\leftrightarrow\gamma')\Big]$$
$$=\frac{1}{N}\sum_{\mathbf{k}\lambda\lambda'}\frac{\coth\frac{1}{2}\beta\omega_{\lambda\lambda'}(\mathbf{k})}{2\omega_{\lambda\lambda'}(\mathbf{k})}\sum_{\bar{\alpha}\gamma\gamma'}\langle\alpha\gamma|v_0|\alpha'\gamma'\rangle P_{\gamma\bar{\alpha},\gamma'\bar{\alpha}}{}^{(\lambda\lambda')}(\mathbf{k})\Big(1+\frac{\omega_{\lambda\lambda'}{}^2(\mathbf{k})}{E_{\gamma\bar{\alpha}}E_{\gamma'\bar{\alpha}}}\Big)$$
$$\times\tfrac{1}{2}[E_{\gamma\bar{\alpha}}(-E_{\gamma'\bar{\alpha}}f_{\gamma'\bar{\alpha}}/-E_{\gamma\bar{\alpha}}f_{\gamma\bar{\alpha}})^{1/2}+(\gamma\leftrightarrow\gamma')]. \quad (62)$$

While this expression does not seem to resemble very closely the $\langle\alpha|\hat{\Sigma}(E)|\alpha'\rangle$ as given by Eq. (57), the one-phonon contribution becomes more familiar:

$$\langle\alpha|\delta G_0^{-1}|\alpha'\rangle\cong\frac{1}{2N}\sum_{\mathbf{k}\nu}\frac{\coth\frac{1}{2}\beta\omega_{\mathbf{k}\nu}}{\beta M\omega_{\mathbf{k}\nu}}\mathbf{e}_{\mathbf{k}\nu}\mathbf{e}_{\mathbf{k}\nu}:\sum_\gamma f_\gamma\langle\alpha\gamma|\nabla\nabla v_0|\alpha'\gamma\rangle. \quad (63)$$

This term is just what is needed to restore translational invariance to the total self-energy, such that

$$\begin{aligned}&\langle\alpha|\delta G_0^{-1}+\hat{\Sigma}(E)|\alpha'\rangle\\&=\frac{1}{2N}\sum_{\mathbf{k}\nu}\frac{\coth\frac{1}{2}\beta\omega_{\mathbf{k}\nu}}{2\omega_{\mathbf{k}\nu}}\mathbf{e}_{\mathbf{k}\nu}\mathbf{e}_{\mathbf{k}\nu}:\sum_\gamma f_\gamma\langle\alpha\gamma|\nabla\nabla(v_0-v_{\mathbf{k}})|\alpha'\gamma\rangle\\&=\tfrac{1}{2}\sum_\tau\langle(\mathbf{u}_\tau-\mathbf{u}_0)(\mathbf{u}_\tau-\mathbf{u}_0)\rangle:\sum_\gamma f_\gamma\langle\alpha\gamma|\nabla\nabla v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})|\alpha'\gamma\rangle,\end{aligned}$$

which is a function only of coordinate differences as desired. Thus the single-particle wave functions and energies are consistent if they are determined from the more satisfactory renormalized Hartree equation

$$\Big[(-1/2M)\nabla^2+\sum_\tau\sum_\gamma f_\gamma\int d^3x'\,|\varphi_\gamma(\mathbf{x}')|^2\times(1+\tfrac{1}{2}\langle(\mathbf{u}_\tau-\mathbf{u}_0)(\mathbf{u}_\tau-\mathbf{u}_0)\rangle:\nabla\nabla)\times v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})\Big]\varphi_\alpha(\mathbf{x})=E_\alpha\varphi_\alpha(\mathbf{x}), \quad (64)$$

rather than from Eq. (61).

This equation has a simple and important physical interpretation. It indicates that a single-particle behavior of a given atom is determined from a modified interatomic potential, in this case

$$v_\tau(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})\equiv(1+\tfrac{1}{2}\langle(\mathbf{u}_\tau-\mathbf{u}_0)(\mathbf{u}_\tau-\mathbf{u}_0)\rangle:\nabla\nabla)v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau}), \quad (65)$$

which incorporates the correlation in position between a given pair of atoms due to the thermal occupation of phonon collective modes. As a consequence, the modification provides a more reasonable temperature dependence for physical quantities: The displacement-displacement correlation function varies as T^4 for temperatures well below the Debye temperature, in contrast to the $e^{-\beta\Omega}$ dependence from single-particle excitations. The T^4 dependence has already been deduced by Kaplan[13] from physical considerations in analogy to those of Keffer and Loudon[14] concerning the temperature dependence of spin-wave interactions.

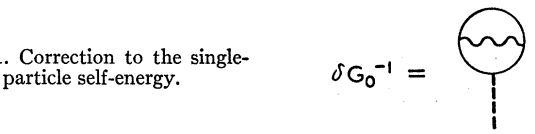


FIG. 11. Correction to the single-particle self-energy.

The interpretation of the modified potential is reinforced by the following speculation. Although we have not been able to exhibit the complete set of collective modes in full generality, it is likely from the analysis of Sec. III for the harmonic approximation that the modes other than the three one-phonon modes are in a one-to-one correspondence with multiphonon modes. Hence it is possible if the complete set of modes could be used to evaluate Eqs. (57) and (62), rather than just the one-phonon contribution, that a density-density correlation would result. That is, the modified potential of Eq. (65) might rather have something like the exponentiated, many-phonon form

$$v_\tau(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})=\exp(\tfrac{1}{2}\langle(\mathbf{u}_\tau-\mathbf{u}_0)(\mathbf{u}_\tau-\mathbf{u}_0)\rangle:\nabla\nabla)v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau}). \quad (66)$$

If this were so, then well-known theorems about functions of phonon dynamical coordinates would lead to

$$\begin{aligned}v_\tau(\mathbf{x}-\mathbf{x}+\boldsymbol{\tau})&=\langle\exp(\mathbf{u}_\tau-\mathbf{u}_0)\cdot\nabla\rangle v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})\\&=\langle v((\mathbf{x}+\mathbf{u}_\tau+\boldsymbol{\tau})-(\mathbf{x}'+\mathbf{u}_0))\rangle. \quad (67)\end{aligned}$$

This last expression shows quite clearly that two atoms at lattice sites separated by $\boldsymbol{\tau}$ would interact via a correlated potential, allowing for relative displacements which are consistent with a thermal-equilibrium population of phonons.

Another significant feature of Eq. (64) is that the smearing of the potential due to thermal phonon vibrations is *superimposed upon* the smearing already present from the Hartree approximation due to single-particle, thermal excitations. In the present approximation the introduction of collective fluctuations does not transform away the single-particle representation. Of course it might be argued that this result was forced artificially by the nature of the single-particle ansatz G^{Qp}, which deliberately inserted into internal lines a propagator with discrete spectrum without any renormalization factor Z different from unity. It is certainly true that $\hat{\Sigma}'(E)$, evaluated from Eq. (55), does not vanish; and furthermore it was just shown that some attention to the continuous spectrum is required to preserve translational invariance. On the other hand, even if the $G(z)$ for each and every internal line was allowed to have a continuous spectrum, it is unlikely that the single-particle poles would be suppressed entirely, with $Z=0$.

[13] J. I. Kaplan, Phys. Letters **17**, 227 (1965).

[14] F. Keffer and R. Loudon, J. Appl. Phys. Suppl. **32**, 25 (1961).

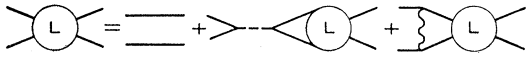


FIG. 12. Integral equation for the response function with ladder vertex correction.

It is more probable that a balance between single-particle and collective motion is established, and that both types of thermal average appear in an equation like (64) but with relative weights adding to unity. An important goal for future investigation is to obtain a definite answer to this question.

B. Response from the Equilibrium State

As shown in the previous subsection, reasonable success has been achieved in circumventing the difficulty of defining a conserving collective fluctuation in the equilibrium single-particle self-energy. However, the difficulty is compounded when attention is turned to the response to a disturbance from the equilibrium state.

As the RPA demonstrated, maintaining the translational invariance of the collective modes is decidely nontrivial. Furthermore, the correct wave-vector dependence of the mode frequencies in a given approximation cannot be verified at a glance, but can only be confirmed through the detailed application of sum rules. Thus it is necessary to generate approximations only by means which automatically guarantee that the conservation laws are satisfied. The "Φ-derivable" criterion of Baym[6] is the only approximation procedure to our knowledge which does this systematically.

Repeating briefly the discussion of Sec. II, the Φ-derivable criterion states that a response is fully conserving if it is obtained from the second functional derivative of a functional $\Phi\{G\}$, where G is the Green's function whose self-energy is the first functional derivative [see Eq. (12)]. This criterion implies that approximations must be specified entirely as *functionals*, not as functions. But in contradiction, we have been forced to define the equilibrium collective fluctuation algebraically, rather than diagrammatically. As a consequence, we cannot use the Φ-derivable criterion to write down with certainty the correct conserving response to this approximate equilibrium state.

We can, however, make some educated guesses, based on the Φ-derivable approximation of Figs. 8–10, even though the approximation is not adequate for the equilibrium state. Referring to Fig. 10, it can be seen that the first term in the kernel for L arises from functionally differentiating with respect to the G contained in G_0; the second term in the kernel arises similarly from the explicit G line in the $\hat{\Sigma}$ of Fig. 8; and the last two terms in the kernel arise from the two G lines in the bubble of Fig. 9. The first two terms in the kernel would have essentially the same structure even if the entire problem were being solved exactly, whereas the last two terms are doubtful since they are a direct consequence of the bare-bubble sum (Fig. 9) for the collective fluctuations, which is itself certainly inadequate.

It is thus tempting, as a first approximation, to ignore the last two terms in the kernel and to consider only the equation of Fig. 12. This truncated equation cannot any longer be guaranteed conserving, but we believe that translational invariance is maintained to the same degree of accuracy as the algebraic definition of the wiggly line. We do not attempt an exact solution even of this simplified equation, however, because of the uncertainties detailed in the previous subsection as to the exact analytic structure of $G(z)$. Nevertheless, we can extrapolate the partial solution for $G(z)$ to speculate about the solution for L. We note that the quasiparticle pole in $G(z)$ was a consequence of a subtle interplay between G_0^{-1} and $\hat{\Sigma}$, leading ultimately merely to the replacement

$$v(\mathbf{x}-\mathbf{x}'+\tau)\rightarrow v_\tau(\mathbf{x}-\mathbf{x}'+\tau). \tag{68}$$

Furthermore, since the two terms in the kernel of Fig. 12 are functional derivatives of G_0^{-1} and $\hat{\Sigma}$, respectively, it is likely that they combine in a similar way. If so, then the ladder vertex corrections generated by the second term merely affect the alteration (68) in the first term. We thus argue that an approximate solution of Fig. 12 would have the same structure as the solution (29) [together with Eqs. (24) and (25)] of Fig. 6, except for the replacement (68) in Eq. (24). In particular, the modified phonon frequencies would then be given by the generalization of Eq. (43),

$$\omega_{\mathbf{k}\nu}^2\delta_{\nu,\nu'}=\mathbf{e}_{\mathbf{k}\nu}\cdot M^{-1}\sum_\tau(1-\cos\mathbf{k}\cdot\tau)\times(1+\tfrac{1}{2}\langle(\mathbf{u}_\tau-\mathbf{u}_0)(\mathbf{u}_\tau-\mathbf{u}_0)\rangle:\nabla\nabla)\times\nabla\nabla\langle\langle v(\mathbf{x}-\mathbf{x}'+\tau)\rangle\rangle\cdot\mathbf{e}_{\mathbf{k}\nu'}, \tag{69}$$

with

$$\langle(\mathbf{u}_\tau-\mathbf{u}_0)(\mathbf{u}_\tau-\mathbf{u}_0)\rangle=\sum_{\mathbf{k}\nu}(2M\omega_{\mathbf{k}\nu})^{-1}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\nu}(1-\cos\mathbf{k}\cdot\tau)\mathbf{e}_{\mathbf{k}\nu}\mathbf{e}_{\mathbf{k}\nu}. \tag{70}$$

At the present stage, the phonon frequencies and polarizations in Eq. (70) are those given by the RPA, and are not the same as those determined by Eq. (69). However, there is nothing in the philosophy of defining the equilibrium collective fluctuations algebraically which forbids us from altering the definition so that the frequencies and polarizations are identical in the two equations, and hence are determined self-consistently. Indeed, this alternative procedure would seem more in keeping with the ideal of consistency between equilibrium fluctuations and nonequilibrium response.

Since we are not yet in a position to do more than speculate about the response equation of Fig. 12, we certainly are not yet ready to attack Fig. 10. Nonetheless, it should be remarked that the third term in the

kernel for L introduces the lowest-order contribution to a finite phonon lifetime. By putting intermediate states onto the energy shell, it can be seen that this term contributes to the process of one phonon decaying into two, with an effective matrix element involving three separate single-particle level transitions by an individual atom. It is certainly an important goal of a many-body theory of lattice dynamics to calculate this decay process in detail, but such a calculation must await more satisfactory answers to the other questions of principle raised in this section.

V. DISCUSSION: COMPARISON WITH THE SELF-CONSISTENT PHONON THEORY

Both the results demonstrated in the previous section and the speculations extrapolated from them bear an important resemblance to an alternative many-body theory of lattice dynamics which we might term the self-consistent phonon theory. This alternative theory has been derived independently by several recent authors, using a variety of techniques. Variational principles have been employed by Koehler[15] at zero temperature and by Boccara and Sarma[16] at finite temperatures. A diagrammatic expansion and resummation procedure has been used by Choquard and Ranninger,[17] and by Horner.[18] An intercomparison and summary of the different techniques has been given by Gillis, Werthamer, and Koehler.[19] The key result of this theory is that phonon modes are determined to lowest order by the eigenvalue equation

$$\omega_{\mathbf{k}\nu}^2\mathbf{e}_{\mathbf{k}\nu}=M^{-1}\sum_{\tau}(1-\cos\mathbf{k}\cdot\boldsymbol{\tau})\langle\nabla\nabla v(\mathbf{u}_\tau-\mathbf{u}_0+\boldsymbol{\tau})\rangle\cdot\mathbf{e}_{\mathbf{k}\nu}, \quad (71)$$

where the brackets denote thermal average with respect to phonon dynamical displacements $\mathbf{u}$, in the same sense as Eqs. (67) and (70). The theory is self-consistent in that the phonon thermal average employs the same frequencies and polarizations as Eq. (71) determines.

The most significant feature of this result is that it incorporates a smearing of the potential due to phonon excitational motion, in a manner similar to that of the collective fluctuations just considered, but it does not contain any trace of single-particle motion. In fact, an assumption underlying all the derivations of Eq. (71) is that the dynamics of the crystal can be described entirely in terms of phonon normal modes, without any attention to single-particle excitations. The apparent contradiction between these two approaches is a major paradox for many-body theory of lattice dynamics at its present stage of development. It is certainly true that both approaches, if they could be worked out exactly to all orders, would necessarily give identical answers, since the starting Hamiltonians are equivalent. Furthermore, it is also true that the phonon modes provide a complete set of dynamical coordinates, just as the Hartree states are also a complete set. The difference between the two approaches is basically just in the choice of unperturbed representation in which to express perturbation theory. It is likely that low-order approximations in the two approaches differ primarily in the description of motion which is not merely a single phonon: motion which is alternatively typed as "multiphonon" or "single-particle" in character.

On a practical level, the self-consistent phonon theory enjoys a decided advantage over the collective-fluctuation approximation in terms of its relative ease of implementation for numerical computation.[15,18–20] However, some refinements in the physical description can probably best be treated from a single-particle wavefunction approach. One aspect in particular is the formation of vacancy-interstitial pairs at high temperatures. From the Hartree-well viewpoint, a vacancy-interstitial pair is easily interpreted as an individual atom being excited from a bound level into a continuum state above the top of the potential well. Describing such behavior in terms of multiphonon modes is difficult, if not unnatural, and is normally done using classical arguments divorced from lattice dynamics.

A second aspect of real crystals for which a single-particle representation should be useful is the short-range correlation between neighboring atoms induced by a hard-core repulsive potential. Although the work reported here has only considered nonsingular potentials, the inclusion of a set of multiple-scattering diagrams ("ladders") in close analogy with the theory of nuclear matter should be adequate to compensate for hard-core repulsion. It is not at all obvious how to accomplish this within the framework of phonon excitations, especially since the short-range correlations should interfere seriously with short-wavelength phonons. As an added benefit, the nuclear-spin exchange integral in a crystal such as He^3 should be estimated reasonably well by antisymmetrizing the scattering amplitude between nearest neighbors. Again, there does not seem to be a natural way to introduce the Pauli principle, antisymmetry, and exchange into the self-consistent phonon scheme. [*Note added in proof.* This last objection has been successfully overcome by L. H. Nosanow and C. M. Varma (unpublished).]

APPENDIX: EVALUATION OF $S(\mathbf{k}\omega)$

Beginning with Eq. (46), we first carry out the sum over λ in the first term. Using the expression for the wave functions of a harmonic oscillator in terms of

[15] T. R. Koehler, Phys. Rev. Letters **17**, 89 (1966).
[16] N. Boccara and G. Sarma, Physics **1**, 219 (1965).
[17] P. Choquard, *Equilibrium Theory of Anharmonic Crystals* (W. A. Benjamin, New York, to be published); J. Ranninger, Phys. Rev. **140**, A2031 (1965).
[18] H. Horner, Z. Physik **205**, 72 (1967).
[19] N. S. Gillis, N. R. Werthamer, and T. R. Koehler, Phys. Rev. **165**, 951 (1968).
[20] T. R. Koehler, Phys. Rev. Letters **18**, 654 (1967); Phys. Rev. **165**, 942 (1968).

Hermite polynomials, we obtain the matrix element

$$K_{\lambda,\Lambda}\equiv|\langle\lambda|e^{ikx}|\lambda+\Lambda\rangle|^2$$
$$=\left|\int_{-\infty}^{\infty}dx\frac{\exp(-\frac{1}{2}M\Omega x^2)H_\lambda((M\Omega)^{1/2}x)}{(2^\lambda\lambda!(\pi/M\Omega)^{1/2})^{1/2}}\right.$$
$$\left.\times e^{ikx}\frac{\exp(-\frac{1}{2}M\Omega x^2)H_{\lambda+\Lambda}((M\Omega)^{1/2}x)}{(2^{\lambda+\Lambda}(\lambda+\Lambda)!(\pi/M\Omega)^{1/2})^{1/2}}\right|^2$$
$$=\frac{\exp(-k^2/2M\Omega)}{2^{2\lambda+\Lambda}\lambda!(\lambda+\Lambda)!\pi}$$
$$\times\left|\int_{-\infty}^{\infty}du\exp\left[-u+\frac{\frac{1}{2}ik}{(M\Omega)^{1/2}}\right]H_\lambda(u)H_{\lambda+\Lambda}(u)\right|^2.$$

But the Hermite polynomials have the properties that

$$H_\lambda(u-u_0)=\sum_{m=0}^{\lambda}[(-2u_0)^{\lambda-m}\lambda!/m!(\lambda-m)!]H_m(u),$$

and

$$\int_{-\infty}^{\infty}du\exp(-u^2)H_m(u)H_{m'}(u)=\delta_{m,m'}2^m m!\pi^{1/2}.$$

Hence

$$K_{\lambda,\Lambda}=\exp\left(-\frac{k^2}{2M\Omega}\right)\left(\frac{k^2}{2M\Omega}\right)^\Lambda\frac{\lambda!}{(\lambda+\Lambda)!}$$
$$\times\left(\sum_{m=0}^{\lambda}\left(-\frac{k^2}{2M\Omega}\right)^m\frac{(\lambda+\Lambda)!}{m!(\lambda-m)!(m+\Lambda)!}\right)^2$$
$$=\exp\left(-\frac{k^2}{2M\Omega}\right)\left(\frac{k^2}{2M\Omega}\right)^\Lambda\frac{\lambda!}{(\lambda+\Lambda)!}\left[L_\lambda^\Lambda\left(\frac{k^2}{2M\Omega}\right)\right]^2,$$

where L_λ^Λ is an associated Laguerre polynomial. A standard formula of analysis[21] then enables us to evaluate the sum on λ,

$$\sum_{\lambda=0}^{\infty}(1-e^{-\beta\Omega})e^{-\beta\lambda\Omega}K_{\lambda,\Lambda}$$
$$=\exp\left(-\frac{k^2}{2M\Omega}\coth\tfrac{1}{2}\beta\Omega\right)e^{\beta\Lambda\Omega/2}I_\Lambda\left(\frac{k^2/2M\Omega}{\sinh\frac{1}{2}\beta\Omega}\right),$$

where I_Λ is a modified Bessel function.

[21] Bateman Manuscript Project, *Higher Transcendental Functions* (McGraw-Hill Book Co., Inc., New York, 1955), Vol. 2, p. 189.

Using other better-known theorems about harmonic oscillators together with the sum rules of Eqs. (41) and (42), the sum over α is also easily evaluated,

$$|2\sum_{\alpha=0}^{\infty}\langle\alpha|e^{ikx}|\alpha+1\rangle\Omega(1-e^{-\beta\Omega})^2e^{-\beta\alpha\Omega}M^{1/2}\langle\alpha|x|\alpha+1\rangle|^2$$
$$=|\sum_{\alpha\alpha'}\langle\alpha|e^{ikx}|\alpha'\rangle(-\epsilon_{\alpha\alpha'}f_{\alpha\alpha'})M^{1/2}\langle\alpha|x|\alpha'\rangle|^2$$
$$=(k^2/M)|\sum_\alpha f_\alpha\langle\alpha|e^{ikx}|\alpha\rangle|^2$$
$$=(k^2/M)\exp(-\tfrac{1}{2}k^2\sum_\alpha f_\alpha\langle\alpha|x^2|\alpha\rangle)$$
$$=(k^2/M)\exp(-(k^2/2M\Omega)\coth\tfrac{1}{2}\beta\Omega).$$

Putting these formulas together, we obtain the final expression for the one-dimensional $S(k\omega)$,

$$S(k\omega)=\exp\left(\frac{-k^2}{2M\Omega}\coth\tfrac{1}{2}\beta\Omega\right)$$
$$\times\left\{\frac{k^2}{M}\frac{\pi}{\omega_k}\left(\frac{\delta(\omega-\omega_k)}{1-\exp(-\beta\omega_k)}+\frac{\delta(\omega+\omega_k)}{\exp(\beta\omega_k)-1}\right)\right.$$
$$+\sum_{\Lambda=1}^{\infty}\pi[\delta(\omega-\Lambda\Omega)e^{\beta\Lambda\Omega/2}+\delta(\omega+\Lambda\Omega)e^{-\beta\Lambda\Omega/2}]$$
$$\left.\times\left[I_\Lambda\left(\frac{k^2/2M\Omega}{\sinh\frac{1}{2}\beta\Omega}\right)-\delta_{\Lambda,1}\frac{k^2/2M\Omega}{\sinh\frac{1}{2}\beta\Omega}\right]\right\}.$$

The three-dimensional expression is simply the sum of products of three such one-dimensional forms, each evaluated with k replaced by a Cartesian component of $\mathbf{k}$. The only nontrivial complexity arising is an expression of the form

$$\sum_{\Lambda_1,\Lambda_2,\Lambda_3=0}^{\infty}\delta_{\Lambda_1+\Lambda_2+\Lambda_3,\Lambda}I_{\Lambda_1}(\kappa_1^2)I_{\Lambda_2}(\kappa_2^2)I_{\Lambda_3}(\kappa_3^2)$$
$$=I_\Lambda(\kappa_1^2+\kappa_2^2+\kappa_3^2),$$

the evaluation of which is accomplished using the standard integral representation for the modified Bessel functions and a Fourier-integral representation for the δ function. The final result for $S(\mathbf{k}\omega)$ is quoted in the text [Eq. (48)].