a function of H_1^2 as have other workers at this frequency, and the fact that Kissinger and Weidner[1] found no such increase at higher frequencies indicates that this phenomena is quite possibly a frequency-dependent effect. While the dilution dependence of line 3 can be explained qualitatively, the behavior of lines 1 and 2 is anomalous and so far eludes explanation. The temperature dependence indicates that cross relaxation and direct processes are dominant over most of the temperature range, but that the transition to relaxation governed by indirect processes begins as temperatures increases to 4.2°K. The fact that Kissinger and Weidner observed no transition to indirect processes indicates that this also is a frequency-dependent effect.

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Towards a Quantum Many-Body Theory of Lattice Dynamics. I. Time-Dependent Hartree Approximation*

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The phonon is discussed as an example of a collective mode which restores a symmetry property (in this case, translational invariance) to a system whose Hamiltonian is invariant under the symmetry operation, but in whose ground state the symmetry is broken. The crystal lattice is first studied within the time-independent Hartree approximation. It is then shown that allowing small time-dependent changes in the Hartree field generates an equation for the normal modes of vibration. The three $\mathbf{k}=0$ modes with $\omega=0$ are shown to represent uniform translations of the solid, as expected. The $\mathbf{k}\neq 0$ modes are analyzed to extract those three which may be identified as one-phonon modes, and the contribution of these modes to the free energy is computed. The recent theory of Brout is found to be equivalent to the Hartree approximation with the further assumption that the atoms are infinitely heavy. No restrictions are made here on the interatomic potential other than that a hard core is absent. The reduction of the present theory to well-known results in the case of harmonic forces is demonstrated. An extension to include hard cores, analogous to the Brueckner theory, is discussed.

I. INTRODUCTION

The ordinary facts of lattice dynamics—the existence of phonons, the existence of a finite phase velocity of acoustic phonons in the infinite wavelength limit, a relation between phonons and atomic displacements, and so forth—can all be regarded as manifestations of the theory of broken symmetry. The essential idea of this theory is that it may be convenient to choose as zeroth approximation to the ground state (or equilibrium ensemble) of a system, a state (or ensemble) in which some dynamical variable $\hat{X}$ has a definite numerical value X, even though it can be rigorously shown that $\langle\hat{X}^2\rangle^{1/2}\neq X$, or even though the fluctuations of $\hat{X}$ in the true ground state (or true equilibrium ensemble) are infinite due to the uncertainty principle. When such an approximation is made, it is generally possible to study the elementary excitations of the system in such a way that all the incorrect implications of the zeroth approximation are removed and the rigorous consequences of symmetry are recovered. This usually implies a renormalization of the original approximate ground state (or equilibrium ensemble). In this paper we shall demonstrate these ideas explicitly in the case of a monatomic lattice.

In the case of a crystal lattice, the variable $\hat{X}$ is the coordinate of the center of mass of the crystal. The invariance of the Hamiltonian under arbitrary translations implies that the total momentum of the system is a good quantum number and has a definite value in equilibrium. By the uncertainty principle, the center-of-mass coordinate which is canonically conjugate to the total momentum must therefore have infinite fluctuations at equilibrium. However, any useful start-

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ing approximation for the study of lattice dynamics must assign a definite finite value of the center-of-mass coordinate.

The most common way of doing this is by taking the zero order of approximation to be one in which the kinetic energy is neglected, so that each atom sits on a definite lattice site. In the case of reasonably light atoms this is a very poor approximation because the zero point motion of the atoms must be quite large. In such cases it is tempting to use a Hartree approximation in zeroth order. This has been done for the solid rare gases by Nosanow and Shaw.[1] In fact, the Hartree approximation never gives terribly good answers for reasons which we shall indicate very briefly later on. However, it is interesting to see how, starting from the Hartree approximation, one can study the elementary excitations of the lattice and recover all the familiar facts about phonons, even though a harmonic Hamiltonian never appears in the formulas.

We shall study the elementary excitations of a lattice by the modern method of calculating the linear response of the lattice to a suitable external probe and looking for the analytic singularities of this response function. If it is found that the system is capable of absorbing energy from an external probe of definite frequency ω and crystal momentum $\mathbf{k}$, then we may conclude, at least at zero temperature, that there are excited states of the system with energy ω and crystal momentum $\mathbf{k}$ (we adopt units in which $\hbar=1$). We shall use this terminology of excited states or elementary excitations even at finite temperature, although this interpretation is perhaps less justified in that case. The term elementary excitation is really appropriate only in the case when the singularity is an isolated one, i.e., a pole. A continuum of singularities, or branch cut, obviously corresponds to multiple excitations. We shall call "phonon" an isolated singularity in which there is a finite displacement of each atom. In particular, we shall calculate the displacement response, and we shall denote by the term "phonon" an isolated singularity of that response function. One can argue quite generally that for any self-consistent calculation there must be such a singularity for $\mathbf{k}=0$, and that the frequency at which this singularity occurs must be zero. This is simply a consequence of the translational invariance of the Hamiltonian, together with the corollary fact that the total momentum commutes with the Hamiltonian. If the interaction between the atoms is not of very long range, we may expect that phonons also exist for finite k. Since this is essentially a continuity argument, it really applies only in the case of small k, that is, long wavelength or sound waves. Although we shall produce large and involved formulas which apply for arbitrary wavelengths, we cannot make any such assertion about what happens at wavelengths comparable to the lattice spacing.

Our calculation is simply an application of the time-dependent Hartree approximation. That is, it is an application to the dynamics of the crystal lattice of the ideas used by Ehrenreich and Cohen[2] in the study of the electron gas and of the ideas of Vlasov and Landau[3] in the study of classical plasmas many years ago. We make the approximation of letting each atom have its own private density matrix. We write a Liouville equation for the motion of this one-atom density matrix in the presence of a self-consistent field produced by all the other atoms. This self-consistent field is, of course, itself in motion. That is, it is consistent with the moving single-particle density matrix, not with the static or zeroth-order density matrix. It is this element of self-consistency which restores all the consequences of symmetry and therefore produces phonons to restore the translational invariance of the system. We include an external force in the Hamiltonian which has the general form of a sum of terms, each of which refers to a single atom. We calculate the (in principle self-consistent) linear response of the single-particle density matrix to this force. Through the use of the fluctuation-dissipation theorem, we are then able to obtain such things as the autocorrelation function of the atomic displacements with one another and the correlation function of the particle density with itself at different times. The displacement response quite clearly shows collective excitations or poles, which we call phonons, and higher continua of excitations, which we can alternately think of as multiple-phonon states or as localized excitations in which individual atoms oscillate in excited single-particle states. It is clear that these two descriptions overlap, and the former is the more customary one. However, in the present formalism the localized excitation point of view seems most natural, and we hope that this provides an alternate point of view to the study of multiple-phonon effects and anharmonic effects. Of course the so-called multiple-phonon effects, which occur in the displacement response function, are related to the phonon self-energy function or polarization function. Similar continua arise in the density-correlation function, or form factor, where they presumably have to do both with the single phonon polarization function and with the possibility of producing several phonons in, for example, inelastic neutron scattering.

In the next two sections we shall develop the formalism of the time-dependent Hartree approximation, using a notation which is conveniently adapted to the assumed crystal-lattice symmetry. Although the notation necessarily is somewhat cumbersome, it should be remembered that we are actually doing a very simple thing, namely, we are calculating a self-consistent time-varying single-particle density matrix. It should be borne in mind that this calculation is interesting not

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[1] L. H. Nosanow and G. L. Shaw, Phys. Rev. **128**, 546 (1962).

[2] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

[3] A. Vlasov, J. Phys. (USSR) **9**, 25 (1945); L. D. Landau, J. Phys. (USSR) **10**, 25 (1946).

merely because it shows how translational symmetry can be restored to the Hartree approximation; it also shows how, starting from a self-consistent calculation of the ground state, one can calculate response functions and therefore spectra of elementary excitations, which retain all the symmetry properties of the Hamiltonian simply by maintaining in a dynamical calculation the self-consistency that was built into the static calculation.

Also in Sec. III, a number of properties of the equations are discussed; in particular, the symmetry-restoring $\mathbf{k}=0$ phonon is shown to exist with zero frequency. It is further shown that ω^2 is always real, where ω is the energy of an elementary excitation, and (in an Appendix) that ω^2 is positive (ω itself is real) if the static Hartree calculation gave a local minimum of the free energy.

In Sec. IV it is shown how the results of the dynamical calculation just discussed can be used to obtain an improved estimate of the free energy. It is conjectured that the improved value is, in fact, always less than the value calculated by the ordinary Hartree approximation. However, reasons will be given why this improvement in energy is not expected to be particularly significant, and the method of calculating the free energy given in this paper is not expected to solve all the difficulties of calculating the free energy of systems such as solid helium. Finally, in Sec. V, in order to make contact with the standard textbook results, the interatomic potential is expanded in powers of the displacements of the atoms from their equilibrium positions, and the usual results are obtained.

Because we are working in the Hartree approximation, there is no possibility of including the effects of statistics on lattice dynamics. In a sense, this means that we are in no way making a more truly quantum theory of lattice dynamics than is standardly given. It also means that it would be quite pointless to burden ourselves notationally with the presence of spin, and so we shall neglect this feature which to some extent distinguishes the lattice dynamics of solid He^3 from He^4. However, as has been repeatedly stated, we hope that the method presented in this paper does represent a step in the right direction toward a true quantum theory of lattice dynamics. It is entirely possible, although somewhat more complicated, to apply the self-consistent techniques exemplified here to calculations in which the effects of statistics are taken into account. When this is done in the case of solid He^3, we may expect to obtain a sensible calculation of the dynamical magnetic properties of that solid. In the last section of this paper some discussion of the possibilities for the future along these lines is given. In addition, some discussion is also devoted to the prospects for using the techniques of this paper to treat anharmonic effects without making an expansion in powers of the atomic displacements.

II. REVIEW OF THE TIME-INDEPENDENT HARTREE APPROXIMATION

We first review the time-independent finite-temperature Hartree approximation, leading to single-particle wave functions and to an upper bound on the system free energy. In the present context, the Hartree approximation consists in writing the system density matrix $P(\mathbf{x}_1,\cdots,\mathbf{x}_N;\,\mathbf{x}_1',\cdots,\mathbf{x}_N')$ as a factored product of one-particle density matrices:

$$P_H(\mathbf{x}_1,\cdots,\mathbf{x}_N;\,\mathbf{x}_1',\cdots,\mathbf{x}_N')=\prod_i\rho_i(\mathbf{x}_i,\mathbf{x}_i'). \tag{1}$$

We choose a Hamiltonian for the system

$$\mathcal{H}=\sum_i \mathcal{K}_i+\tfrac{1}{2}\sum_{i,j}\mathcal{V}_{ij}, \tag{2}$$

where, in the coordinate representation,

$$\mathcal{K}_i=-(\hbar^2/2M)\nabla_i^2,\quad \mathcal{V}_{ij}=v(\mathbf{x}_i-\mathbf{x}_j), \tag{3}$$

and we assume central forces. The Liouville equation for the time-independent system density matrix is just

$$[P_H,\mathcal{H}]=0. \tag{4}$$

Taking the trace of this equation over all but one pair of coordinates gives us the single-particle equation,

$$[\rho_i,\mathcal{H}_i^{(H)}]=0, \tag{5}$$

where $\mathcal{H}_i^{(H)}$ is the Hartree Hamiltonian for the ith atom,

$$\mathcal{H}_i^{(H)}(\mathbf{x}_i)=-(\hbar^2/2M)\nabla_i^2+\sum_{j\neq i}\int d^3x_j\rho_j(\mathbf{x}_j,\mathbf{x}_j)v(\mathbf{x}_i-\mathbf{x}_j). \tag{6}$$

At this point we must recognize that we are interested in solutions of Eqs. (5) and (6) which describe an ordered crystal. That is, we expect the ith atom to be localized to the immediate neighborhood of the ith site of the crystal lattice labeled by position vector $\mathbf{R}_i$. Except for this localization of each atom to its own individual site, we should expect the motion of the atoms about their sites to be similar. Thus, we make a coordinate transformation and set

$$\rho_i(\mathbf{x}_i,\mathbf{x}_i')=\rho(\mathbf{x}_i-\mathbf{R}_i,\,\mathbf{x}_i'-\mathbf{R}_i). \tag{7}$$

The transformed one-particle density matrix satisfies

$$[\rho,\mathcal{H}^{(H)}]=0, \tag{8}$$

$$\mathcal{H}^{(H)}(\mathbf{x})=-(\hbar^2/2M)\nabla^2+\sum_{\tau\neq 0}\int d^3x'\rho(\mathbf{x}',\mathbf{x}')v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau}), \tag{9}$$

where $\boldsymbol{\tau}$ is a lattice translation vector and we assume, for simplicity, a Bravais lattice. If we are correct in our assumption that the system indeed forms a crystal lattice, then the Hartree Hamiltonian $\mathcal{H}^{(H)}$ will have eigenfunctions $\varphi_\alpha(\mathbf{x})$, of which at least the lowest must be localized to the region $\mathbf{x}\approx 0$. Correspondingly, at least one of the eigenvalues Ω_α must be discrete.

We find that ρ satisfies Eq. (8) if it is diagonal in the α representation:

$$\rho(\mathbf{x},\mathbf{x}')=\sum_\alpha \varphi_\alpha(\mathbf{x})\varphi_\alpha^*(\mathbf{x}')f_\alpha. \tag{10}$$

It is well known that the lowest value for the free energy, with respect to the class of density matrices (10), is obtained when the distribution f_α has the thermal equilibrium value

$$f_\alpha=e^{-\beta\Omega_\alpha}/\sum_\alpha e^{-\beta\Omega_\alpha}. \tag{11}$$

Equations (9) and (10) take a somewhat simpler form in the limit of zero temperature. Then

$$\mathcal{H}^{(H)}=-(\hbar^2/2M)\nabla^2 +\sum_{\tau\neq 0}\int d^3x'\,|\varphi_0(\mathbf{x}')|^2 v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau}), \tag{12}$$

and we see that only the ground state Hartree function φ_0 must be determined self-consistently.

If the interparticle potential $v(\mathbf{x}_i-\mathbf{x}_j)$ is integrable, so that $\mathcal{V}^{(H)}$ is everywhere finite, then the φ_α form an orthonormal set complete over all space. Also, the spectrum Ω_α will then have a continuum above a certain number of discrete levels. On the other hand, for interparticle potentials with a hard core, the Hartree potential is infinite everywhere outside the Wigner-Seitz cell. The spectrum is now purely discrete. Because of this and other complications associated with hard core potentials, we reserve the treatment of them to a later publication and here only consider integrable potentials.

The system free energy computed with the Hartree density matrix is

$$\begin{aligned} F_H&=E-TS=\mathrm{Tr}\{P_H(\mathcal{H}+\beta^{-1}\ln P_H)\}\\ &=\mathrm{Tr}\{\sum_i \rho_i\mathcal{K}_i+\tfrac{1}{2}\sum_{i\neq j}\rho_i\rho_j\mathcal{V}_{ij}+\beta^{-1}\sum_i \rho_i\ln\rho_i\},\\ \frac{F_H}{N}&=-\beta^{-1}\ln\sum_\alpha e^{-\beta\Omega_\alpha}\\ &\quad-\tfrac{1}{2}\sum_{\alpha\alpha'}f_\alpha f_{\alpha'}\int d^3x d^3x'\,|\varphi_\alpha(\mathbf{x})|^2|\varphi_{\alpha'}(\mathbf{x}')|^2\\ &\qquad\times\sum_{\tau\neq 0}v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau}). \end{aligned} \tag{13}$$

The first term is just the free energy of a particle with energy spectrum Ω_α, while the second term is the usual Hartree correction to avoid overcounting the interactions. In the zero-temperature limit, we obtain the ground state energy.

III. THE TIME-DEPENDENT HARTREE APPROXIMATION

A. Response to a Disturbance

We now consider the application of an infinitesimal disturbance to the system, and examine the response to this disturbance. We expect that the response will be determined by the free modes of vibration of the system about its equilibrium configuration and by the relative strength with which the disturbance excites these various modes. Stated differently, we expect the linear response function to exhibit singularities, which correspond to the low-lying excitations or collective modes of the system. In the case of a crystal lattice, the collective modes are traditionally termed phonons, and their character is well known. We should hope to be able to separate the collective modes found in our formalism into those identifiable as single-phonon excitations and those corresponding to multiple-phonon excitations. In particular, phonons of zero wave number have zero frequency and represent uniform translations of the lattice as a whole, whereas multiple-phonon excitations of zero total wave number have finite frequency and do not lead to any mean atom displacement.

To discuss the system response and low-lying excitations, we introduce an additional term in the Hamiltonian, coupling an externally imposed time-dependent perturbation to a one-particle operator. Thus,

$$\mathcal{H}=\sum_i \mathcal{K}_i+\tfrac{1}{2}\sum_{i,j}\mathcal{V}_{ij}+\sum_i \mathcal{H}_i^e(\mathbf{x}_i-\mathbf{R}_i,t). \tag{14}$$

The perturbation of most interest in the present context is a force acting on each atom, for which

$$\mathcal{H}_i^e(\mathbf{x}_i-\mathbf{R}_i,t)=-\mathbf{F}_i(t)\cdot(\mathbf{x}_i-\mathbf{R}_i). \tag{15}$$

We again assume that the density matrix can be written in product form

$$P_H(\mathbf{x}_1,\cdots,\mathbf{x}_N;\mathbf{x}_1',\cdots,\mathbf{x}_N';t) =\prod_i \rho_i(\mathbf{x}_i-\mathbf{R}_i,\mathbf{x}_i'-\mathbf{R}_i;t). \tag{16}$$

The formal procedure now follows closely that of Ehrenreich and Cohen,[2] who used the density matrix and time-dependent self-consistent field approximation in a study of the electron gas. We write the Liouville equation for ρ_i:

$$i\partial\rho_i/\partial t=[\mathcal{K}_i+\mathcal{V}_i^{(H)}+\mathcal{H}_i^e,\rho_i]. \tag{17}$$

It proves convenient to introduce a Fourier transform with respect to the remaining lattice position dependence

$$\rho_i(\mathbf{x},\mathbf{x}';t)=N^{-1}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_i}\rho_{\mathbf{k}}(\mathbf{x},\mathbf{x}';t), \tag{18}$$

and

$$\mathcal{V}_i^{(H)}(\mathbf{x},t)=N^{-1}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_i}\mathcal{V}_{\mathbf{k}}(\mathbf{x},t), \tag{19}$$

where

$$\mathcal{V}_{\mathbf{k}}(\mathbf{x},t)=\sum_{\tau\neq 0} e^{-i\mathbf{k}\cdot\tau}\int d^3x'\rho_{\mathbf{k}}(\mathbf{x}',\mathbf{x}';t)v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau}),$$

$$\equiv\int d^3x'\rho_{\mathbf{k}}(\mathbf{x}',\mathbf{x}';t)v_{\mathbf{k}}(\mathbf{x}-\mathbf{x}'). \tag{20}$$

The Liouville equation then becomes

$$i\partial\rho_{\mathbf{k}}/\partial t=[\mathcal{K},\rho_{\mathbf{k}}]+N^{-1}\sum_{\mathbf{k}'}[\mathcal{V}_{\mathbf{k}-\mathbf{k}'}+\mathcal{H}_{\mathbf{k}-\mathbf{k}'}{}^{e},\rho_{\mathbf{k}'}]. \tag{21}$$

Since we are only interested in disturbances and responses which are infinitesimal, we set

$$\rho_{\mathbf{k}}(\mathbf{x},\mathbf{x}';t)=N\delta_{\mathbf{k},0}\rho(\mathbf{x},\mathbf{x}')+\delta\rho_{\mathbf{k}}(\mathbf{x},\mathbf{x}';t), \tag{22}$$

where $\rho(\mathbf{x},\mathbf{x}')$ is the equilibrium density matrix given by Eqs. (10) and (11), and we linearize the Liouville equation with respect to $\delta\rho$. Now that the equation is linear, it is useful to Fourier transform the time dependence, so that

$$\omega\delta\rho_{\mathbf{k}}=[\mathcal{H}^{(H)},\delta\rho_{\mathbf{k}}]+[\delta\mathcal{V}_{\mathbf{k}}+\mathcal{H}_{\mathbf{k}}{}^{e},\rho], \tag{23}$$

where all the subscripted quantities now also depend on ω. Taking matrix elements of this equation in the Hartree basis, we find

$$\omega\langle\alpha|\delta\rho_{\mathbf{k}}|\alpha'\rangle=(\Omega_\alpha-\Omega_{\alpha'})\langle\alpha|\delta\rho_{\mathbf{k}}|\alpha'\rangle$$
$$+(f_{\alpha'}-f_\alpha)\sum_{\gamma\gamma'}\langle\alpha\gamma|v_{\mathbf{k}}|\alpha'\gamma'\rangle\langle\gamma'|\delta\rho_{\mathbf{k}}|\gamma\rangle$$
$$+(f_{\alpha'}-f_\alpha)\langle\alpha|\mathcal{H}_{\mathbf{k}}{}^{e}|\alpha'\rangle. \tag{24}$$

It is worth noting the explicit expression for $\langle\alpha|\mathcal{H}_{\mathbf{k}}{}^{e}|\alpha'\rangle$ in the particular case of the displacement coupling: If

$$\mathbf{F}_i(t)=(2\pi N)^{-1}\sum_{\mathbf{k}}\int d\omega e^{i\mathbf{k}\cdot\mathbf{R}_i-i\omega t}\mathbf{F}_{\mathbf{k}}(\omega), \tag{25}$$

then from Eq. (15),

$$\langle\alpha|\mathcal{H}_{\mathbf{k}}{}^{e}|\alpha'\rangle=-\mathbf{F}_{\mathbf{k}}(\omega)\cdot\langle\alpha|\mathbf{x}|\alpha'\rangle. \tag{26}$$

We may simplify Eq. (24) if we assume that the wave functions φ_α are real. This is guaranteed by the choice of standing-wave boundary conditions. Then it proves convenient to divide $\langle\alpha|\delta\rho|\alpha'\rangle$ into an "even" and "odd" part:

$$\langle\alpha|\delta\rho|\alpha'\rangle=\xi_{\alpha\alpha'}+\eta_{\alpha\alpha'},\quad \langle\alpha'|\delta\rho|\alpha\rangle=\xi_{\alpha\alpha'}-\eta_{\alpha\alpha'}, \tag{27}$$

where (ξ,η) depend on $(\mathbf{k},\omega)$. With the further notation

$$\Omega_{\alpha\alpha'}\equiv\Omega_\alpha-\Omega_{\alpha'},\quad f_{\alpha\alpha'}\equiv f_\alpha-f_{\alpha'},$$

we have the simultaneous equations

$$(\omega-\Omega_{\alpha\alpha'})(\xi_{\alpha\alpha'}+\eta_{\alpha\alpha'})+f_{\alpha\alpha'}\sum_{\gamma\gamma'}\langle\alpha\gamma|v_{\mathbf{k}}|\alpha'\gamma'\rangle\xi_{\gamma\gamma'}$$
$$=-f_{\alpha\alpha'}\langle\alpha|\mathcal{H}_{\mathbf{k}}{}^{e}|\alpha'\rangle, \tag{28}$$
$$(\omega+\Omega_{\alpha\alpha'})(\xi_{\alpha\alpha'}-\eta_{\alpha\alpha'})-f_{\alpha\alpha'}\sum_{\gamma\gamma'}\langle\alpha\gamma|v_{\mathbf{k}}|\alpha'\gamma'\rangle\xi_{\gamma\gamma'}$$
$$=+f_{\alpha\alpha'}\langle\alpha|\mathcal{H}_{\mathbf{k}}{}^{e}|\alpha'\rangle.$$

Eliminating $\eta_{\alpha\alpha'}$,

$$(\omega^2-\Omega_{\alpha\alpha'}{}^2)\xi_{\alpha\alpha'}+\Omega_{\alpha\alpha'}f_{\alpha\alpha'}\sum_{\gamma\gamma'}\langle\alpha\gamma|v_{\mathbf{k}}|\alpha'\gamma'\rangle\xi_{\gamma\gamma'}$$
$$=-\Omega_{\alpha\alpha'}f_{\alpha\alpha'}\langle\alpha|\mathcal{H}_{\mathbf{k}}{}^{e}|\alpha'\rangle. \tag{29}$$

We may solve this formally for $\xi_{\alpha\alpha'}$:

$$\xi_{\alpha\alpha'}=-\sum_{\gamma\gamma'}(\mathcal{M}^{-1})_{\alpha\alpha',\gamma\gamma'}\Omega_{\gamma\gamma'}f_{\gamma\gamma'}\langle\gamma|\mathcal{H}_{\mathbf{k}}{}^{e}|\gamma'\rangle, \tag{30}$$

where

$$\mathcal{M}_{\alpha\alpha',\gamma\gamma'}(\mathbf{k}\omega)\equiv(\omega^2-\Omega_{\alpha\alpha'}{}^2)\delta_{\alpha\alpha',\gamma\gamma'}$$
$$+\Omega_{\alpha\alpha'}f_{\alpha\alpha'}\langle\alpha\gamma|v_{\mathbf{k}}|\alpha'\gamma'\rangle. \tag{31}$$

Thus, the displacement of atom i, due to a driving force at atom j, is given by

$$\delta\langle\langle\mathbf{x}_i-\mathbf{R}_i\rangle\rangle_t/\delta\mathbf{F}_j(t')$$
$$=-(2\pi N)^{-1}\sum_{\mathbf{k}}\int d\omega e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)-i\omega(t-t')}$$
$$\times\mathbf{R}(\mathbf{k},\omega+i0+), \tag{32}$$

where

$$\mathbf{R}(\mathbf{k},\omega)\equiv-\sum_{\alpha\alpha',\gamma\gamma'}\langle\alpha|\mathbf{x}|\alpha'\rangle(\mathcal{M}^{-1})_{\alpha\alpha',\gamma\gamma'}$$
$$\times\Omega_{\gamma\gamma'}f_{\gamma\gamma'}\langle\gamma|\mathbf{x}|\gamma'\rangle. \tag{33}$$

B. Normal Modes

Equation (29) determines the response $\xi_{\alpha\alpha'}$ in terms of the disturbance $\langle\alpha|\mathcal{H}^{e}|\alpha'\rangle$. In the absence of any disturbance the homogeneous form of Eq. (29), (which we may call 29h) yields the normal modes of free oscillation of the system about its equilibrium configuration. Thus, the response $\xi(\mathbf{k}\omega)$ will have poles when ω equals the frequency of a collective mode of wave number $\mathbf{k}$. Equation (29h) shows immediately that if ω is an eigenfrequency, then so is $-\omega$. It is also straightforward to prove from Eq. (29h) that if $\omega_{\mathbf{k}}$ is an eigenfrequency, then $\omega_{\mathbf{k}}=\omega_{-\mathbf{k}}$. These are properties we would expect of phonon excitations.

It can also be shown that all eigenfrequencies of Eq. (29h) have real squares, so that ω is either real or pure imaginary.[4] To demonstrate this, it is most convenient

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[4] It may be objected that similar mathematics could be used to prove the reality of the plasmon frequency in the electron gas, whereas it is well known that at finite temperature, or at zero temperature for sufficiently short wavelengths, the plasmon frequency is complex (Landau damping). An easy, if not particularly enlightening, reply is that the stability theorem proved in the Appendix shows that the roots of Eq. (29h) are real, without appeal to the argument in the body of the paper. A more proper answer is that a complex plasmon frequency appears only upon passing to the limit of infinite volume. Only then does the dielectric function acquire a branch cut and hence an analytic continuation off the "physical sheet." The plasmon pole appears on an unphysical sheet, whereas the stability theorem refers only to the physical sheet. In the present case, according to the remarks following Eq. (9), there is a finite gap in the spectrum of the time-independent Hartree Hamiltonian, even in the limit of infinite volume. Therefore, for long wavelengths there is no opportunity for the phonon pole to appear on an unphysical sheet, given that it is at the origin of the physical sheet for $\mathbf{k}=0$. A second objection to the simple argument in the text is that it leans on the choice of real one-particle orbitals, which may be impossible in the presence of spin-orbit coupling; in such a case, we must appeal to the stability theorem.

to divide Eq. (29h) by $(-\Omega_{\alpha\alpha'}f_{\alpha\alpha'})^{1/2}$, which is real, and to define $\hat{\xi}_{\alpha\alpha'}\equiv\xi_{\alpha\alpha'}(-\Omega_{\alpha\alpha'}f_{\alpha\alpha'})^{1/2}$. Then

$$(\omega^2-\Omega_{\alpha\alpha'}{}^2)\hat{\xi}_{\alpha\alpha'}-\sum_{\gamma\gamma'}(-\Omega_{\alpha\alpha'}f_{\alpha\alpha'})^{1/2}\langle\alpha\gamma|v_{\mathrm{k}}|\alpha'\gamma'\rangle \times(-\Omega_{\gamma\gamma'}f_{\gamma\gamma'})^{1/2}\hat{\xi}_{\gamma\gamma'}=0. \quad (34)$$

It is now readily verified that the kernel of Eq. (34) is Hermitian, so that the eigenfrequencies ω^2 are real as stated. Furthermore, the possibility of $\omega^2<0$ is eliminated by the argument of the Appendix. There it is proved that the normal modes about a thermal equilibrium configuration have real frequencies if the configuration, corresponding to a free energy stationary point, is actually a local minimum and not a maximum or saddle point. We have tacitly assumed throughout that the crystal symmetry and lattice constants, chosen for a calculation of the Hartree basis functions, do in fact lead to a minimum of the Hartree free energy. Normal modes with imaginary frequencies signal an instability in the system, such that there is an alternative configuration of lower free energy which can be reached through an infinitesimal fluctuation.

C. Atomic Displacements and One-Phonon Normal Modes

We note that Eq. (29h) is a multidimensional matrix equation, and for any given $\mathbf{k}$ will have many eigenfrequencies. In order to pick from this large set the three representing one-phonon modes, we consider the mean value of the atom displacements associated with each mode. The mean displacement of the ith atom is given by

$$\langle\langle\mathbf{x}_i-\mathbf{R}_i\rangle\rangle_t\equiv\mathrm{Tr}\{(\mathbf{x}_i-\mathbf{R}_i)\rho_i(t)\}$$

$$=(2\pi N)^{-1}\sum_{\mathbf{k}}\int d\omega e^{i\mathbf{k}\cdot\mathbf{R}_i-i\omega t}\boldsymbol{\varepsilon}_{\mathrm{k}}(\omega), \quad (35)$$

$$\boldsymbol{\varepsilon}_{\mathrm{k}}(\omega)\equiv\sum_{\alpha\alpha'}\langle\alpha|\mathbf{x}|\alpha'\rangle\xi_{\alpha\alpha'}(\mathbf{k}\omega). \quad (36)$$

Multiplying the eigenvalue equation (29h) through by $\langle\alpha|\mathbf{x}|\alpha'\rangle$ and summing over α, α', one obtains

$$\omega^2\boldsymbol{\varepsilon}_{\mathrm{k}}+\sum_{\alpha\alpha'}\{-\langle\alpha|\mathbf{x}|\alpha'\rangle\Omega_{\alpha\alpha'}{}^2\xi_{\alpha\alpha'} +\langle\alpha|\mathbf{x}|\alpha'\rangle\Omega_{\alpha\alpha'}f_{\alpha\alpha'}\sum_{\gamma\gamma'}\langle\alpha\gamma|v_{\mathrm{k}}|\alpha'\gamma'\rangle\xi_{\gamma\gamma'}\}=0. \quad (37)$$

But

$$\langle\alpha|\mathbf{x}|\alpha'\rangle\Omega_{\alpha\alpha'}=\langle\alpha|[\mathcal{H}^{(H)},\mathbf{x}]|\alpha'\rangle=-i\langle\alpha|\mathbf{p}|\alpha'\rangle/M, \quad (38)$$

and

$$\langle\alpha|\mathbf{p}|\alpha'\rangle\Omega_{\alpha\alpha'}=\langle\alpha|[\mathcal{H}^{(H)},\mathbf{p}]|\alpha'\rangle =\sum_{\gamma\gamma'}f_{\gamma\gamma'}\langle\alpha\gamma|v_0|\alpha'\gamma'\rangle\langle\gamma|\mathbf{p}|\gamma'\rangle. \quad (39)$$

Inserting Eqs. (38) and (39) into (37), we find

$$\omega^2\boldsymbol{\varepsilon}_{\mathrm{k}}-iM^{-1}\sum_{\alpha\alpha'\gamma\gamma'}\langle\alpha|\mathbf{p}|\alpha'\rangle \times f_{\alpha\alpha'}\langle\alpha\gamma|(v_{\mathrm{k}}-v_0)|\alpha'\gamma'\rangle\xi_{\gamma\gamma'}=0. \quad (40)$$

We thus learn that for the $\mathbf{k}=0$ modes, either $\omega=0$ or the mode does not lead to a mean atom displacement. In addition, the eigenvectors of the $\mathbf{k}=0$, $\omega=0$ modes may be exhibited explicitly:

$$\xi_{\alpha\alpha'}(\mathbf{k}\omega)=iN\delta_{\mathrm{k},0}2\pi\delta(\omega)f_{\alpha\alpha'}\langle\alpha|\mathbf{p}|\alpha'\rangle\cdot\mathbf{d}, \quad (41)$$

where $\mathbf{d}$ is an arbitrary vector. Substitution into Eq. (29h), together with Eq. (39), confirms that expression (41) is indeed an eigenvector, while Eqs. (35) and (36) show that it represents, as expected, a uniform displacement of the entire crystal by a distance $\mathbf{d}$:

$$\langle\langle\mathbf{x}_i-\mathbf{R}_i\rangle\rangle=\mathbf{d}. \quad (42)$$

We further note that there are only three such modes which are linearly independent, and we identify these modes as the $\mathbf{k}=0$ phonons. We may tentatively identify as multiple-phonon excitations the large number of other modes with $\mathbf{k}=0$ but $\omega\neq0$; they would have, for example, $\langle\langle\mathbf{x}_i-\mathbf{R}_i\rangle\rangle=0$ but $\langle\langle(\mathbf{x}_i-\mathbf{R}_i)^2\rangle\rangle\neq0$. Extending this argument by continuity to $\mathbf{k}\neq0$, we should expect that only the three one-phonon excitations would appear as poles in the displacement response,[5] whereas all normal modes, both one- and multiple-phonon excitations, would enter into other responses such as the density response.

IV. FREE ENERGY INCLUDING NORMAL MODES

One useful application of the response functions is to generate a better expression for the system free energy than that given by the Hartree approximation, Eq. (13). This is because correctly including the zero point motion of the collective modes must give a lower free energy than when the collective modes are ignored.

The derivation of the free energy, using the response functions, is analogous to that given by Englert and Brout[6] for the case of a gas, where the potential energy is small compared to the kinetic energy. In the case of a crystal lattice the opposite is true, so we differentiate the free energy with respect to the inverse mass (instead of the interparticle coupling constant, as they did):

$$\partial F/\partial(1/M)=\langle\langle\tfrac{1}{2}\sum_i p_i{}^2\rangle\rangle. \quad (43)$$

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[5] This can be proved by introducing the projection operator A:

$$A_{\alpha\alpha',\gamma\gamma'}\equiv if_{\alpha\alpha'}\langle\alpha|\mathbf{p}|\alpha'\rangle\cdot\langle\gamma|\mathbf{x}|\gamma'\rangle,$$

which leaves the displacements $\langle\alpha|\mathbf{x}|\alpha'\rangle$ invariant. Since $\mathrm{Tr}A=3$, only three poles contribute to the displacement-displacement response function. These relationships can also be seen from Eqs. (33) and (53) together with (38), from which we learn that the free energy depends on

$$\mathrm{tr}\mathbf{R}=M^{-1}\sum_{\alpha\alpha',\gamma\gamma'}A_{\gamma\gamma',\alpha\alpha'}(\mathfrak{M}^{-1})_{\alpha\alpha',\gamma\gamma'}=M^{-1}\,\mathrm{Tr}A\mathfrak{M}^{-1}.$$

[6] F. Englert and R. Brout, Phys. Rev. **120**, 1085 (1960).

Hence

$$F(M)-F(\infty)=\int_0^{1/M} d(1/M')\langle\langle \tfrac{1}{2}\sum_i p_i^2\rangle\rangle_{M'}\,, \tag{44}$$

with the thermal average taken in a system with mass M'. The right-hand side of Eq. (44) gives the free energy arising from the collective modes.

One's initial reaction is to interpret $F(\infty)$ as just the free energy of the system in which each atom is held rigidly fixed to its lattice site, and which is readily calculated as a lattice sum of the potential energy. Upon further thought, however, one is tempted to regard $F(\infty)$ as the free energy merely neglecting kinetic energy, so that an ensemble of static positional configurations must be considered. Thus the Hartree equation, with $M\rightarrow\infty$ in Eq. (9), becomes

$$\mathcal{V}^{(H)}(\mathbf{x})\varphi_\alpha(\mathbf{x})=\Omega_\alpha\varphi_\alpha(\mathbf{x})\,. \tag{45}$$

The eigenfunctions are

$$\varphi_\alpha(\mathbf{x})\propto\delta^3(\mathbf{x}-\boldsymbol{\alpha})\,,$$

where the index $\boldsymbol{\alpha}$ becomes a position vector lying within the Wigner-Seitz cell. Furthermore, the eigenvalues satisfy

$$\begin{aligned}\Omega_\alpha=\mathcal{V}^{(H)}(\boldsymbol{\alpha})&=\sum_{\tau\neq 0}\int d^3\alpha' f_{\alpha'} v(\boldsymbol{\alpha}-\boldsymbol{\alpha}'+\boldsymbol{\tau})\\ &=\sum_{\tau\neq0}\int d^3\alpha' v(\boldsymbol{\alpha}-\boldsymbol{\alpha}'+\boldsymbol{\tau})\exp(-\beta\Omega_{\alpha'})\Big/\\ &\qquad\int d^3\alpha\exp(-\beta\Omega_\alpha)\,.\end{aligned} \tag{46}$$

The nonlinear, self-consistent Eq. (46) for Ω_α is identical to that proposed recently by Brout.[7,8] The corresponding result for $F(\infty)$ is found from Eq. (13),

$$\begin{aligned}F_{\text{cl}}&\equiv F(\infty)-\tfrac{3}{2}\beta^{-1}\ln(M/2\pi\hbar^2\beta)\\ &=-\beta^{-1}\ln\int d^3\alpha\exp(-\beta\Omega_\alpha)-\frac{1}{2}\int d^3\alpha d^3\alpha' f_\alpha f_{\alpha'}\\ &\qquad\times\sum_{\tau\neq0}v(\boldsymbol{\alpha}-\boldsymbol{\alpha}'+\boldsymbol{\tau})\,.\end{aligned} \tag{47}$$

The quantity F_{cl}, the classical Hartree free energy excluding the uninteresting kinetic zero-point contribution, is just Eq. (5) of Ref. 8.

Shifting temporarily into the Heisenberg picture, we can write

$$\begin{aligned}F(M)&-F(\infty)\\ &=\int_0^{1/M}d(1/M')\tfrac{1}{2}M'^2\sum_i\frac{\partial^2}{\partial t\partial t'}\langle\langle\mathbf{x}_i(t)\cdot\mathbf{x}_i(t')\rangle\rangle_{M'}\Big|_{t=t'}\,.\end{aligned} \tag{48}$$

But if we Fourier-transform the displacement-displacement correlation function,

$$\begin{aligned}\langle\langle(\mathbf{x}_i(t)&-\mathbf{R}_i)(\mathbf{x}_j(t')-\mathbf{R}_j)\rangle\rangle\\ &=(2\pi N)^{-1}\sum_{\mathbf{k}}\int d\omega e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)-i\omega(t-t')}\mathbf{C}(\mathbf{k}\omega)\,,\end{aligned} \tag{49}$$

and similarly transform the response function,

$$\begin{aligned}-i\langle\langle[(\mathbf{x}_i(t)&-\mathbf{R}_i),(\mathbf{x}_j(t')-\mathbf{R}_j)]\rangle\rangle\Theta(t-t')\\ &=(2\pi N)^{-1}\sum_{\mathbf{k}}\int d\omega e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)-i\omega'(t-t')}\mathbf{R}(\mathbf{k}\omega)\,,\end{aligned} \tag{50}$$

it is well known that $\mathbf{C}$ and $\mathbf{R}$ are related by

$$\mathbf{C}(\mathbf{k}\omega)=-2(1-e^{-\beta\omega})^{-1}\operatorname{Im}\mathbf{R}(\mathbf{k},\omega+i0+)\,. \tag{51}$$

Hence

$$\begin{aligned}F(M)-F(\infty)&=-\int_0^{1/M}d(1/M')\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{M'^2\omega^2}{1-e^{-\beta\omega}}\\ &\qquad\times\operatorname{Im}\sum_{\mathbf{k}}\operatorname{tr}\mathbf{R}(\mathbf{k},\omega+i0+)_{M'}\,.\end{aligned} \tag{52}$$

Since we can show that $\operatorname{Im}\mathbf{R}(\mathbf{k},\omega+i0+)$ is odd in ω, and introducing definition (47), we arrive at[9]

$$\begin{aligned}F(M)-F_{\text{cl}}&=-\int_M^\infty dM'\int_0^\infty d(\omega/2\pi)\\ &\qquad\times\omega^2\coth\tfrac{1}{2}\beta\omega\sum_{\mathbf{k}}\operatorname{Im}\operatorname{tr}[\mathbf{R}(\mathbf{k},\omega+i0+)_{M'}\\ &\qquad-(1/M')\lim_{M''\rightarrow\infty}M''\mathbf{R}(\mathbf{k},\omega+i0+)_{M''}]\,.\end{aligned} \tag{53}$$

The response function $\mathbf{R}(\mathbf{k}\omega)$ is exactly that of Eq. (33). Equations (53) and (33) are the desired expressions for the free energy. Further attention will be given to them in the next section, in which the harmonic approximation is developed with our formalism.

It is worth pointing out one apparent ambiguity in formula (53). The mass integration calls for the evaluation of the phonon spectrum of a system with atomic mass M', in equilibrium. But a system of mass M' in true equilibrium will have a lattice constant smaller than the same system of mass M, if $M'>M$.

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[7] R. Brout, Physica **29**, 1041 (1963).

[8] R. Brout, S. Nettel, and H. Thomas, Phys. Rev. Letters **13**, 474 (1964).

[9] It is amusing to note the coth factor in Eq. (53), showing that the free energy automatically regards the phonon modes as bosons and allows for their multiple occupation without having to postulate separately a boson field.

(The larger zero-point motion of a lighter system tends to expand the lattice.) Thus it would appear that the mass integration must also integrate over implicit changes in the lattice constant. However, all our calculations are being carried out with the constraint of constant volume. The phonon spectrum for mass M' is to be computed assuming sufficient (negative) pressure applied to keep the lattice constant fixed. If this were actually done in the laboratory, of course, the crystal might well shatter into two or more smaller pieces, but mathematically it is unlikely that the Hartree equations are subtle enough to signal this possibility by developing instabilities. The worst difficulty we should expect in using formula (53), if we were particularly unlucky, would be the development of imaginary collective mode frequencies, indicating a shift to a new crystal structure which again filled the entire volume. Nevertheless, it seems physically less likely that the constrained fixed-volume crystal would undergo symmetry changes than would the free unbounded crystal, if we were able to alter the mass.

V. REDUCTION TO THE HARMONIC APPROXIMATION

The development presented so far has, of necessity, been quite formal and nonspecific. This is because we have constructed a framework within which it is possible to discuss both one- and multiphonon processes for an arbitrary (but nonsingular) interparticle potential. The analysis of the formalism becomes much more transparent if we specialize to the harmonic approximation, and use our equations to obtain the standard results for this simple case.

The harmonic approximation consists of assuming the interparticle potential to vary slowly over distances comparable to the atom displacements, no matter how close the atoms are to each other:

$$v(\mathbf{x}-\mathbf{x}'+\boldsymbol{\tau})\cong v(\boldsymbol{\tau})+(\mathbf{x}-\mathbf{x}')\cdot\nabla v(\boldsymbol{\tau}) +\tfrac{1}{2}(\mathbf{x}-\mathbf{x}')(\mathbf{x}-\mathbf{x}'):\nabla\nabla v(\boldsymbol{\tau}), \quad (54)$$

for all $\boldsymbol{\tau}\neq 0$. With the further simplifying assumption of cubic symmetry, we then have

$$\begin{aligned}\mathcal{V}^{(H)}(x) &=\sum_{\tau\neq 0} v(\boldsymbol{\tau})+\frac{1}{2}\left[x^2+\sum_{\alpha} f_\alpha\int d^3x'\,|\varphi_\alpha(\mathbf{x}')|^2 x'^2\right]\tfrac{1}{3}\sum_{\tau\neq 0}\nabla^2 v(\boldsymbol{\tau})\\ &\equiv w_0+\tfrac{1}{2}(x^2+\langle\langle x^2\rangle\rangle)w_2. \end{aligned} \quad (55)$$

The Hartree functions φ_α are harmonic oscillator eigenfunctions, with eigenfrequencies

$$\Omega_\alpha=w_0+\tfrac{1}{2}w_2\langle\langle x^2\rangle\rangle+(\alpha+\tfrac{3}{2})(w_2/M)^{1/2}, \quad (56)$$

where α is a non-negative integer. The Hartree free energy expression (13) is readily evaluated, yielding

$$(F_H/N)_{\text{harmonic}}=\tfrac{1}{2}w_0+3\beta^{-1}\ln[2\sinh\tfrac{1}{2}\beta(w_2/M)^{1/2}]. \quad (57)$$

Proceeding to the response function, Eq. (29) reduces to

$$(\omega^2-\Omega_{\alpha\alpha'}{}^2)\,\xi_{\alpha\alpha'}-\Omega_{\alpha\alpha'}f_{\alpha\alpha'}\langle\alpha|\mathbf{x}|\alpha'\rangle \cdot\sum_{\tau\neq 0}e^{-i\mathbf{k}\cdot\tau}\nabla\nabla v(\boldsymbol{\tau})\cdot\boldsymbol{\varepsilon}_{\mathbf{k}}=-\Omega_{\alpha\alpha'}f_{\alpha\alpha'}\langle\alpha|\mathcal{H}_{\mathbf{k}}{}^e|\alpha'\rangle, \quad (58)$$

and the mean displacement $\boldsymbol{\varepsilon}_{\mathbf{k}}$ is found by a reduction similar to that leading to Eq. (40):

$$M\omega^2\boldsymbol{\varepsilon}_{\mathbf{k}}-\sum_{\tau}(e^{-i\mathbf{k}\cdot\tau}-1)\nabla\nabla v(\boldsymbol{\tau})\cdot\boldsymbol{\varepsilon}_{\mathbf{k}}=i\langle\langle[\mathbf{p},\mathcal{H}_{\mathbf{k}}{}^e]\rangle\rangle. \quad (59)$$

The eigenvectors $\mathbf{e}_{\mathbf{k}\lambda}$ and eigenfrequencies $\omega_{\mathbf{k}\lambda}$ of the homogeneous form of this equation

$$M\omega_{\mathbf{k}\lambda}{}^2\mathbf{e}_{\mathbf{k}\lambda}-\sum_{\tau}(e^{-i\mathbf{k}\cdot\tau}-1)\nabla\nabla v(\boldsymbol{\tau})\cdot\mathbf{e}_{\mathbf{k}\lambda}=0, \qquad \lambda=1,2,3 \quad (60)$$

are just the usual phonon polarizations and frequencies as ordinarily computed in the harmonic approximation. Thus

$$\boldsymbol{\varepsilon}_{\mathbf{k}}=\sum_{\lambda}\mathbf{e}_{\mathbf{k}\lambda}\mathbf{e}_{\mathbf{k}\lambda}{}^*(\omega^2-\omega_{\mathbf{k}\lambda}{}^2)^{-1}\cdot iM^{-1}\langle\langle[\mathbf{p},\mathcal{H}_{\mathbf{k}}{}^e]\rangle\rangle. \quad (61)$$

If the perturbation couples to the atomic displacements, Eq. (15), then the displacement-displacement response function is just the usual phonon Green's function,

$$\mathsf{R}(\mathbf{k}\omega)=-\partial\boldsymbol{\varepsilon}_{\mathbf{k}}/\partial\mathbf{F}_{\mathbf{k}}=M^{-1}\sum_{\lambda}\mathbf{e}_{\mathbf{k}\lambda}\mathbf{e}_{\mathbf{k}\lambda}{}^*(\omega^2-\omega_{\mathbf{k}\lambda}{}^2)^{-1}. \quad (62)$$

Using expression (62) in the formula (53) for the free energy, and noting from Eq. (60) that $\omega_{\mathbf{k}\lambda}\propto M^{-1/2}$, we arrive at

$$F/N=\tfrac{1}{2}w_0+N^{-1}\sum_{\mathbf{k}\lambda}\beta^{-1}\ln[2\sinh\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}]. \quad (63)$$

It is useful to compute the mean square of the phonon spectrum. Multiplying the eigenfrequency Eq. (60) by $\mathbf{e}_{\mathbf{k}\lambda}{}^*$, and summing on $\mathbf{k}$ and λ, we find

$$(3N)^{-1}\sum_{\mathbf{k}\lambda}\omega_{\mathbf{k}\lambda}{}^2=w_2/M. \quad (64)$$

Comparing with Eqs. (57) and (63), we learn that the Hartree free energy in the harmonic approximation is equivalent to that calculated from an Einstein phonon spectrum with frequency equal to the root-mean-square of the true phonon spectrum. Furthermore, since

$$g(x)\equiv\beta^{-1}\ln(2\sinh\tfrac{1}{2}\beta x)$$

is convex upwards for $x>0$, the free energy (63) is always less than the free energy (57). It is plausible that this property holds more generally, independent of the harmonic approximation. In simple models of a phonon spectrum, however, this lowering is quite small. For instance, if the phonon spectrum is assumed to be simply $\omega_{\mathbf{k}\lambda}=\sin(\pi k/2k_{\max})$, then at $T=0$ the phonon zero point energy is only $1\frac{1}{2}\%$ less than the Hartree zero point energy.

VI. DISCUSSION

The introduction and development presented thus far have been of quite a formal nature. The central issue has been the explicit demonstration of the existence of phonons, even in highly anharmonic crystals, as expected from general considerations of translational symmetry. It is natural, however, to enquire to what extent the present viewpoint and formalism can be used for actual calculations of the lattice dynamics of real anharmonic crystals. There are a number of physical systems where the traditional theoretical approach, that of expanding the potential in powers of the atomic displacements through quartic terms, is entirely inadequate. Conspicuous examples are the solid heliums and solid molecular hydrogen isotopes, where the atomic masses are very light and the zero-point motions large, or the paraelectrics of the $SrTiO_3$ family, where the polarizabilities are large due to the incipient crystal structure instability. It could be hoped that the present formulation would be applicable in these otherwise difficult cases, but not until several generalizations and extensions have been made.

The most significant generalization necessary is to take account of the hard-core potentials between atoms. As remarked earlier, the Hartree approximation in the case of hard cores confines a given atom entirely to its own Wigner-Seitz cell, with an unrealistically large kinetic energy. It seems intuitively clear that by moving its neighbors aside appropriately, an atom should be able to penetrate into adjoining unit cells. However, to achieve a complete description of these effects would require dealing with several-body correlations, a difficult task for currently available many-body techniques. A reasonable compromise program would be to construct an analog of the Brueckner theory[10] of finite nuclei, by including two-body correlations in the ladder approximation. Such a treatment would allow a pair of contiguous atoms to interact via a softened t matrix, rather than the hard-core interatomic potential, and thus to enter each other's cells and even to exchange positions entirely. Furthermore, the two atoms in interaction would be confined not just to the volume formed by the union of their cells, but rather to a larger self-consistently softened potential well formed by averaging the t matrix over the position probabilities of the remaining neighbors.

In addition, the exchange probability computed from the properly antisymmetrized t matrix might be a good first comparison (provided ring exchanges of three or more atoms simultaneously are not important) with the exchange integral obtained from nuclear resonance experiments in solid He^3. The effects of particle indistinguishability are thus being built in only to the same extent as are particle correlations, in contrast to the situation, e.g., in the theory of the high density electron gas.

It is expected that the formulation and development of such a nuclear-like theory will be the subject of the next article in this series.

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APPENDIX

We shall prove that if the time-dependent Hartree method yields a complex eigenfrequency, then the original solution of the time-independent Hartree equations does not correspond to a local minimum of the free energy. It should be noted that the converse of this statement is not true, although it is possible to completely determine the local properties of the free energy functional from a study of the solutions of the time-dependent Hartree problem. A similar result has been obtained for the Hartree-Fock-Bogoliubov approximation,[11–13] but the present conclusions cannot be deduced from that theorem.

We again choose the Hamiltonian of the form

$$\mathcal{H}=\sum_i \mathcal{K}_i+\tfrac{1}{2}\sum_{i\neq j}\mathcal{V}_{ij}. \tag{A1}$$

Although trying to conform to the notation used throughout the body of this paper, we do not here require each atom to have the same mass, and so do not Fourier-transform the site index. The density matrix is again assumed to be factored,

$$P=\prod_i \rho_i, \tag{A2}$$

and $\rho_i=\rho_i^0+\delta\rho_i$, where ρ_i^0 is the solution of the time-independent Hartree equations,

$$\rho_i^0=\exp(-\beta\mathcal{H}_i^{(H)})/\mathrm{Tr}\exp(-\beta\mathcal{H}_i^{(H)}). \tag{A3}$$

$$\mathcal{H}_i^{(H)}=\mathcal{K}_i+\sum_i \mathrm{Tr}_j\mathcal{V}_{ij}\rho_j^0. \tag{A4}$$

For each particle we introduce the orthonormal set $|\alpha^i\rangle$ of eigenvectors of $\mathcal{H}_i^{(H)}$, so that

$$\mathcal{H}_i^{(H)}|\alpha^i\rangle=\Omega_\alpha{}^i|\alpha^i\rangle, \tag{A5}$$

$$\rho_i^0=\sum_\alpha|\alpha^i\rangle f_\alpha{}^i\langle\alpha^i|, \tag{A6}$$

$$f_\alpha{}^i=\exp(-\beta\Omega_\alpha{}^i)/\sum_\alpha\exp(-\beta\Omega_\alpha{}^i). \tag{A7}$$

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[10] K. A. Brueckner and J. L. Gammel, Phys. Rev. **109**, 1023 (1958), and references contained therein.

[11] D. J. Thouless, Nucl. Phys. **21**, 225 (1960).

[12] N. D. Mermin, Ann. Phys. (N. Y.) **21**, 99 (1963).

[13] C. Bloch (private communication).

We also define

$$\Omega_{\alpha\alpha'}{}^{i}\equiv\Omega_{\alpha}{}^{i}-\Omega_{\alpha'}{}^{i},\quad f_{\alpha\alpha'}{}^{i}\equiv f_{\alpha}{}^{i}-f_{\alpha'}{}^{i}. \tag{A8}$$

The site index on the vector labels will be suppressed, since it can always be inferred from the index on the operator whose matrix elements are in question. As in Sec. III, the linearized homogeneous time-dependent Hartree equations, after Fourier analysis in time, are

$$(\omega-\Omega_{\alpha\alpha'}{}^{i})\langle\alpha|\delta\rho_i|\alpha'\rangle = -f_{\alpha\alpha'}{}^{i}\sum_{j\neq i}\sum_{\gamma\gamma'}\langle\alpha\gamma'|\mathcal{V}_{ij}|\alpha'\gamma\rangle\langle\gamma|\delta\rho_j|\gamma'\rangle. \tag{A9}$$

On the other hand, it is well known that for any positive semidefinite Hermitian operator P, with trace unity, the functional

$$F\{P\}\equiv \mathrm{Tr}P(\mathcal{H}+\beta^{-1}\ln P) \tag{A10}$$

gives an upper bound for the free energy at inverse temperature β. The Hartree method consists of adopting the ansatz (A2) and determining the ρ_i so as to minimize (A10). The usual Eqs. (A5)–(A7) result from requiring the first variation of F to be zero. To investigate whether a given solution of Eqs. (A5)–(A7) gives a local minimum of F, we must look at the second variation, $F^{(2)}$.

Using Eq. (A2), we find

$$F\{\rho_i\}=\sum_i \mathrm{Tr}_i\mathcal{K}_i\rho_i+\tfrac{1}{2}\sum_{i\neq j}\mathrm{Tr}_{i,j}\mathcal{V}_{ij}\rho_i\rho_j+\beta^{-1}\sum_i\sigma(\rho_i), \tag{A11}$$

where

$$\sigma(\rho)\equiv\mathrm{Tr}\rho\ln\rho. \tag{A12}$$

Thus the second variation of F is

$$F^{(2)}=\tfrac{1}{2}\sum_{i\neq j}\mathrm{Tr}_{i,j}\mathcal{V}_{ij}\delta\rho_i\delta\rho_j+\beta^{-1}\sum_i\sigma^{(2)}(\rho_i). \tag{A13}$$

To determine $\sigma^{(2)}(\rho)$, we write

$$\sigma(\rho)=\mathrm{Tr}\oint\frac{dz}{2\pi i}\frac{z\ln z}{z-\rho}, \tag{A14}$$

where the contour of integration encloses the real axis in the counterclockwise sense and passes infinitesimally to the right of the origin. Using the expansion

$$\frac{1}{z-\rho^0-\delta\rho}=\frac{1}{z-\rho^0}+\frac{1}{z-\rho^0}\delta\rho\frac{1}{z-\rho^0}+\frac{1}{z-\rho^0}\delta\rho\frac{1}{z-\rho^0}\delta\rho\frac{1}{z-\rho^0}+\cdots$$

in Eq. (A14), we find

$$\sigma^{(2)}(\rho)=\mathrm{Tr}\oint\frac{dz}{2\pi i}z\ln z\frac{1}{z-\rho^0}\delta\rho\frac{1}{z-\rho^0}\delta\rho\frac{1}{z-\rho^0}. \tag{A15}$$

Introducing the $|\alpha\rangle$ representation,

$$\begin{aligned}\sigma^{(2)}(\rho)&=\sum_{\alpha\alpha'}\oint\frac{dz}{2\pi i}\frac{z\ln z}{(z-f_\alpha)^2}\langle\alpha|\delta\rho|\alpha'\rangle\frac{1}{z-f_{\alpha'}}\langle\alpha'|\delta\rho|\alpha\rangle,\\&=-\tfrac{1}{2}\beta\sum_{\alpha\alpha'}(\Omega_{\alpha\alpha}/f_{\alpha\alpha'})\langle\alpha|\delta\rho|\alpha'\rangle\langle\alpha'|\delta\rho|\alpha\rangle.\end{aligned} \tag{A16}$$

Therefore

$$\begin{aligned}F^{(2)}=\tfrac{1}{2}\sum_{i\neq j}\sum_{\alpha\alpha',\gamma\gamma'}&\langle\alpha\gamma'|\mathcal{V}_{ij}|\alpha'\gamma\rangle\langle\alpha'|\delta\rho_i|\alpha\rangle\langle\gamma|\delta\rho_j|\gamma'\rangle\\&-\tfrac{1}{2}\sum_i\sum_{\alpha\alpha'}(\Omega_{\alpha\alpha'}{}^{i}/f_{\alpha\alpha'}{}^{i})\langle\alpha'|\delta\rho_i|\alpha\rangle\langle\alpha|\delta\rho_i|\alpha'\rangle.\end{aligned} \tag{A17}$$

Next, let $\langle\alpha|\delta\hat{\rho}_i|\alpha'\rangle$ be a solution of Eq. (A9) with complex eigenvalue ω. In general, $\langle\alpha|\delta\hat{\rho}_i|\alpha'\rangle$ is not a Hermitian matrix, and is therefore ineligible for substitution into $F^{(2)}$. But we can insert

$$\langle\alpha|\delta\rho_i|\alpha'\rangle\equiv\mu\langle\alpha|\delta\hat{\rho}_i|\alpha'\rangle+\mu^*\langle\alpha'|\delta\hat{\rho}_i|\alpha\rangle^*, \tag{A18}$$

into Eq. (A17), with μ an arbitrary complex number, and we find

$$F^{(2)}=-\sum_i\sum_{\alpha\alpha'}|\mu|^2\tfrac{1}{2}(\omega+\omega^*)|\langle\alpha|\delta\hat{\rho}_i|\alpha'\rangle|^2/f_{\alpha\alpha'}{}^{i}. \tag{A19}$$

This already shows that if ω is pure imaginary, then there exists an infinitesimal change in the set of density matrices ρ_i that only changes F by terms of third or higher order. Except in highly unusual circumstances (which sometimes occur because of symmetry when $\omega=0$, but not otherwise) the third-order change in F, due to the change (A18), will not vanish. By choosing μ properly, $F^{(3)}$ can be made negative. Therefore our theorem is proved for ω pure imaginary.

More generally, Eq. (A9) can be used to show that

$$\begin{aligned}\omega\sum_i\sum_{\alpha\alpha'}&|\langle\alpha|\delta\hat{\rho}_i|\alpha'\rangle|^2/f_{\alpha\alpha'}{}^{i}\\&=\sum_i\sum_{\alpha\alpha'}(\Omega_{\alpha\alpha'}{}^{i}/f_{\alpha\alpha'}{}^{i})|\langle\alpha|\delta\hat{\rho}_i|\alpha'\rangle|^2\\&\quad-\sum_{i\neq j}\sum_{\alpha\alpha',\gamma\gamma'}\langle\alpha\gamma'|\mathcal{V}_{ij}|\alpha'\gamma\rangle\langle\alpha|\delta\hat{\rho}_i|\alpha'\rangle^*\langle\gamma|\delta\hat{\rho}_j|\gamma'\rangle.\end{aligned} \tag{A20}$$

Since the right-hand side of Eq. (A20) is manifestly real, either $\mathrm{Im}\omega=0$ or

$$\sum_i\sum_{\alpha\alpha'}|\langle\alpha|\delta\hat{\rho}_i|\alpha'\rangle|^2/f_{\alpha\alpha'}{}^{i}=0. \tag{A21}$$

Comparison with Eq. (A19) shows that $F^{(2)}=0$ if $\mathrm{Im}\omega\neq0$, and so the full theorem is proved.