motion of the sublattices under stress, which is possible in the case of the fluorite structure.

B. Grüneisen γ's

From the values of the SOEM at room temperature and 0°K together with their pressure derivatives (Table VI), the mode Grüneisen γ's $\gamma_i (i=1, 2, 3)$ and the low- and high-temperature limits of their thermal average γ_L and γ_H may be evaluated.[4,21] The γ_i's for some directions of high symmetry are shown in Fig. 5, where ϕ denotes the azimuthal angle, θ denotes the colatitude, γ_3 refers to the longitudinal mode, and γ_1 and γ_2 refer to the slow and fast shear modes, respectively. In Table XII, γ_L and γ_H are shown together with the values deduced from thermal expansion.[16] As can be seen, there is a good agreement between the two sets for γ_L, while the values of γ_H disagree. This is also the case[1–5] for CaF_2 and BaF_2, and is probably due to the contributions of the optical modes to the thermal expansion value of γ_H.

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Self-Consistent-Field Approach to Lattice Dynamics*

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The self-consistent-field theory of lattice dynamics is examined with particular emphasis on the physical assumptions entering this approach. The solution of the basic equation is generalized beyond that of earlier treatments to include damping and the corresponding frequency shifts of the collective modes. The expressions found for the damping and frequency shifts contain renormalized anharmonic force constants but otherwise are essentially the same as those derived in conventional perturbation theory.

I. INTRODUCTION

A VARIETY of physical problems concerning the dynamics of many-body systems has been treated in a self-consistent-field (SCF) approach. In this method complicated many-body interactions are replaced by some simplifying effective field. The form of this field depends, of course, on the particular system being considered. For example in the random-phase approximation[1] for the high-density electron gas, one introduces the time-dependent self-consistent Hartree potential as the effective potential acting on an electron. In discussing the dynamics of spin systems in the molecular-field approximation,[2] one replaces the interaction between the spins by a self-consistent magnetic field acting on the individual spins. Phase transitions in ferroelectrics[3] and transitions from one lattice structure to another[4] have been handled in a similar self-consistent-field approach.

The traditional theory of lattice dynamics[5] has failed for solid helium because of the large zero-point vibrations,[6] and therefore other approaches have been proposed.[7–13] Brenig[11] was the first to suggest a SCF approach, and this has been further developed by Fredkin and Werthamer (FW)[12] and by Gillis and Werthamer (GW).[13] Because of its mathematical simplicity and its flexibility to incorporate many physical effects, it is particularly interesting to pursue this method.

The aim of this paper is first to reexamine the theory of FW and GW. By solving their basic equation in a different way, we are able to elucidate more clearly the physical assumptions going into this approach. Second we generalize our method of solving their basic equation to include phonon-damping effects.

The outline of this paper is as follows. Section II contains the formulation of the SCF approach. Our method of solving the basic equation of motion is presented in Sec. III. In order to prove that the physical assumption made in Sec. III is identical to the more mathematical assumption of GW, we briefly discuss in Sec. IV their solution of the basic equation of motion.

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In Sec. V the treatment of Sec. III is generalized to include anharmonic effects which give damping (as well as frequency shifts) of the collective modes. Comparison is made with the results from conventional perturbation treatment. Section VI contains some concluding remarks.

II. MATHEMATICAL FORMULATION

We shall closely follow FW,[12] and we introduce single-particle states characterized by eigenfunctions $\varphi_\alpha(\mathbf{x})$ and energies ϵ_α. These are determined from the static Hartree equation

$$\left\{-(\hbar^2/2M)\nabla^2+\sum_{\mathbf{R}'}{}' \int d\mathbf{x}'\, V(\mathbf{R}+\mathbf{x}-\mathbf{R}'-\mathbf{x}')\langle\rho_{\mathbf{R}'}(\mathbf{x}')\rangle_0\right\} \times\varphi_\alpha(\mathbf{x})=\epsilon_\alpha\varphi_\alpha(\mathbf{x}). \quad (2.1)$$

Here the atom in the $\mathbf{R}$th cell is assumed to move in the static self-consistent field of the surrounding atoms. $\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle_0$ is the mean particle density in the $\mathbf{R}$th cell, averaged over an equilibrium ensemble, so that

$$\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle_0=\sum_\beta f_\beta|\varphi_\beta(\mathbf{x})|^2, \quad (2.2)$$

with

$$f_\beta=\exp(-\epsilon_\beta/k_BT)/\sum_\gamma \exp(-\epsilon_\gamma/k_BT).$$

$V(\mathbf{x})$ is the interparticle potential, and M is the atomic mass. For simplicity we consider a Bravais lattice; the generalization to other cases is straightforward.

The collective modes will be introduced in the spirit of a SCF approximation. Following FW, we apply an arbitrary weak external potential $V_{\mathbf{R}}^{\mathrm{ext}}(\mathbf{x},t)$ which acts on the $\mathbf{R}$th atom, and we calculate the induced change in the single-particle density matrix

$$\langle\rho_{\mathbf{R}}(\mathbf{x},\mathbf{x}',t)\rangle=\langle\psi_{\mathbf{R}}^\dagger(\mathbf{x}',t)\psi_{\mathbf{R}}(\mathbf{x},t)\rangle. \quad (2.3)$$

$\psi_{\mathbf{R}}^\dagger(\mathbf{x},t)$ and $\psi_{\mathbf{R}}(\mathbf{x},t)$ are the creation and annihilation operators, respectively, of a particle in the $\mathbf{R}$th cell. In the SCF approximation here, the effective potential acting on the $\mathbf{R}$th atom is assumed to be

$$V_{\mathbf{R}}^{\mathrm{eff}}(\mathbf{x},t)=V_{\mathbf{R}}^{\mathrm{ext}}(\mathbf{x},t)+\sum_{\mathbf{R}'}{}'\int d\mathbf{x}'\, V(\mathbf{R}+\mathbf{x}-\mathbf{R}'-\mathbf{x}') \times\langle\rho_{\mathbf{R}'}(\mathbf{x}',\mathbf{x}',t)\rangle_{\mathrm{ind}}, \quad (2.4)$$

where the subscript ind denotes the change in the density matrix due to the external disturbance. The linear response of the density matrix is then given by

$$\langle\rho_{\mathbf{R}}(\mathbf{x},\mathbf{x}',t)\rangle_{\mathrm{ind}}=\int_{-\infty}^{\infty}dt_1\int d\mathbf{x}_1\chi_1^{(0)}(\mathbf{x}\mathbf{x}'t;\,\mathbf{x}_1t_1) \times V_{\mathbf{R}}^{\mathrm{eff}}(\mathbf{x}_1,t_1), \quad (2.5)$$

where the retarded response function is

$$\chi_1^{(0)}(\mathbf{x}\mathbf{x}'t;\,\mathbf{x}_1t_1)=(i\hbar)^{-1}\theta(t-t_1) \times\langle[\rho_{\mathbf{R}}(\mathbf{x},\mathbf{x}',t),\rho_{\mathbf{R}}(\mathbf{x}_1,\mathbf{x}_1,t_1)]\rangle_0. \quad (2.6)$$

$[A,B]$ is a commutator, and $\theta(t)$ is the unit step function, being unity for $t>0$ and zero for $t<0$. The zero subscript means that both the thermal average and the time evolution of the operators are to be calculated within the static Hartree approximation.

We notice that this response function refers to only one atom and its value is independent of the lattice position $\mathbf{R}$. For the reason that we have started from single-particle states, given in Eq. (2.1), the coupling of the motion of the individual atoms enters only through the effective potential in Eq. (2.4). In a more general treatment the response function would depend on two lattice sites, and it would contain collective effects besides the single-particle effects.

III. SOLUTION IN POSITION REPRESENTATION

FW[12] and also GW[13] solve Eqs. (2.4) and (2.5) by changing from the position representation to the representation defined by the eigenstates $\{\varphi_\alpha(\mathbf{x})\}$ of the Hartree Hamiltonian. In order to elucidate more easily the physical assumptions made by these authors, we shall here continue in the position representation. We need then to consider only the induced density $\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle_{\mathrm{ind}}$.

Putting $\mathbf{x}=\mathbf{x}'$ in Eq. (2.5) and using Eq. (2.4), we get

$$\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle_{\mathrm{ind}}-\sum_{\mathbf{R}_1}{}'\int_{-\infty}^{\infty}dt_1\int d\mathbf{x}_1\,d\mathbf{x}''\,\chi^{(0)}(\mathbf{x}t;\,\mathbf{x}''t_1) \times V(\mathbf{R}-\mathbf{R}_1+\mathbf{x}''-\mathbf{x}_1)\langle\rho_{\mathbf{R}_1}(\mathbf{x}_1,t_1)\rangle_{\mathrm{ind}} =\int_{-\infty}^{\infty}dt_1\int d\mathbf{x}_1\,\chi^{(0)}(\mathbf{x}t;\,\mathbf{x}_1t_1)V_{\mathbf{R}}^{\mathrm{ext}}(\mathbf{x}_1,t_1), \quad (3.1)$$

where

$$\chi^{(0)}(\mathbf{x}t;\,\mathbf{x}_1t_1)=\chi_1^{(0)}(\mathbf{x}\mathbf{x}t;\,\mathbf{x}_1t_1) \quad (3.2)$$

is the retarded equilibrium density-density response function in the static Hartree approximation. The corresponding response function for the fully interacting system is given by

$$\delta\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle/\delta V_{\mathbf{R}'}^{\mathrm{ext}}(\mathbf{x}',t')=(i\hbar)^{-1}\theta(t-t') \times\langle[\rho_{\mathbf{R}}(\mathbf{x},t),\rho_{\mathbf{R}'}(\mathbf{x}',t')]\rangle. \quad (3.3)$$

Note that the microscopic density operator in Eq. (3.3) can be written as

$$\rho_{\mathbf{R}}(\mathbf{x},t)=\delta(\mathbf{x}-\mathbf{u}(\mathbf{R},t)). \quad (3.4)$$

The functional derivative above is evaluated for zero external potential, and it gives the equilibrium response function, which we denote by $\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\,\mathbf{x}'t')$. By taking the functional derivative of Eq. (3.1), we obtain the following equation for $\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')$:

$$\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')-\sum_{\mathbf{R}_1}{}'\int_{-\infty}^{\infty}dt_1\int d\mathbf{x}_1\,d\mathbf{x}''\,\chi^{(0)}(\mathbf{x}t;\mathbf{x}''t_1)\times V(\mathbf{R}-\mathbf{R}_1+\mathbf{x}''-\mathbf{x}_1)\chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1t_1;\mathbf{x}'t')=\delta_{\mathbf{R}\mathbf{R}'}\chi^{(0)}(\mathbf{x}t;\mathbf{x}'t'). \quad (3.5)$$

From Eq. (3.4) follows

$$\mathbf{u}(\mathbf{R},t)=\int d\mathbf{x}\,\mathbf{x}\rho_{\mathbf{R}}(\mathbf{x},t), \quad (3.6)$$

and consequently the retarded equilibrium displacement-displacement response function, denoted $\mathbf{D}(\mathbf{R}-\mathbf{R}',t-t')$, is given by[14]

$$\mathbf{D}(\mathbf{R}-\mathbf{R}',t-t')=-\int d\mathbf{x}\,d\mathbf{x}'\,\mathbf{x}\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')\mathbf{x}' \quad (3.7)$$

$$=-(i\hbar)^{-1}\theta(t-t')\langle[\mathbf{u}(\mathbf{R},t),\mathbf{u}(\mathbf{R}',t')]\rangle. \quad (3.8)$$

Similarly, we introduce

$$\mathbf{D}^{(0)}(t-t')=-\int d\mathbf{x}\,d\mathbf{x}'\,\mathbf{x}\chi^{(0)}(\mathbf{x}t;\mathbf{x}'t')\mathbf{x}', \quad (3.9)$$

which is the corresponding response function in the static Hartree approximation.

Multiplying Eq. (3.5) by $\mathbf{x}$ and $\mathbf{x}'$, and integrating over these variables, we obtain

$$\mathbf{D}(\mathbf{R}-\mathbf{R}',t-t')+\sum_{\mathbf{R}_1}{}'\int_{-\infty}^{\infty}dt_1\int d\mathbf{x}_1\,d\mathbf{x}''\times\left\{\int d\mathbf{x}\,\mathbf{x}\chi^{(0)}(\mathbf{x}t;\mathbf{x}''t_1)\right\}V(\mathbf{R}-\mathbf{R}_1+\mathbf{x}''-\mathbf{x}_1)\times\left\{\int d\mathbf{x}'\,\chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1t_1;\mathbf{x}'t')\mathbf{x}'\right\}=\delta_{\mathbf{R}\mathbf{R}'}\mathbf{D}^{(0)}(t-t'). \quad (3.10)$$

We shall now introduce the assumptions on the fluctuations in the system that are necessary to recover the results of FW and of GW. First we write the *nonequilibrium* mean density in the form

$$\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle=(2\pi)^{-3}\int d\mathbf{q}\langle\exp\{i\mathbf{q}\cdot[\mathbf{x}-\mathbf{u}(\mathbf{R},t)]\}\rangle$$

$$=(2\pi)^{-3}\int d\mathbf{q}\,\exp[i\mathbf{q}\cdot(\mathbf{x}-\langle\mathbf{u}(\mathbf{R},t)\rangle)]\times\exp[-\tfrac{1}{2}\mathbf{q}\cdot\langle\mathbf{u}(\mathbf{R},t)\mathbf{u}(\mathbf{R},t)\rangle_c\cdot\mathbf{q}+\cdots], \quad (3.11)$$

utilizing the cumulant expansion. The subscript c indicates a cumulant, e.g., $\langle\mathbf{uu}\rangle_c=\langle\mathbf{uu}\rangle-\langle\mathbf{u}\rangle\langle\mathbf{u}\rangle$. We assume that only the mean displacements $\langle\mathbf{u}(\mathbf{R},t)\rangle$ change as a result of the external disturbance and that all the other cumulants retain their equilibrium values. It then follows that

$$\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle_{\rm ind}=\langle\rho_{\mathbf{R}}(\mathbf{x}-\langle\mathbf{u}(\mathbf{R},t)\rangle)\rangle_0-\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle_0=-\nabla_{\mathbf{x}}\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle_0\cdot\langle\mathbf{u}(\mathbf{R},t)\rangle, \quad (3.12)$$

ignoring the difference between the equilibrium Hartree value of $\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle$ and the fully self-consistent value. The second line of Eq. (3.12) follows from the fact that the external disturbance is considered infinitesimal. Physically the assumption above can be stated as follows:

The density distribution associated with each atom is displaced rigidly due to the external disturbance, and any distortion of the shape of the distribution is neglected.

The response of the mean density to an external force can be expressed through Eq. (3.12) in terms of the corresponding response of the mean displacement $\mathbf{D}(\mathbf{R}-\mathbf{R}',t-t')$ as follows (see Appendix A for details):

$$\int d\mathbf{x}'\,\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')\mathbf{x}'=\nabla_{\mathbf{x}}\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle_0\cdot\mathbf{D}(\mathbf{R}-\mathbf{R}',t-t'). \quad (3.13)$$

Applying the same kind of argument to the nonequilibrium mean density $\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle_0$ in the static Hartree approximation, we obtain the same relation as above with χ and $\mathbf{D}$ replaced by $\chi^{(0)}$ and $\mathbf{D}^{(0)}$, respectively. As shown in Appendix B we also have

$$\int d\mathbf{x}\,\mathbf{x}\chi^{(0)}(\mathbf{x}t;\mathbf{x}'t')=\mathbf{D}^{(0)}(t-t')\cdot\nabla_{\mathbf{x}'}\langle\rho_{\mathbf{R}}(\mathbf{x}')\rangle_0. \quad (3.14)$$

If we now insert Eqs. (3.13) and (3.14) into Eq. (3.10) and perform some partial integrations, we obtain the following equation for the displacement response function:

$$\mathbf{D}(\mathbf{R}-\mathbf{R}',t-t')-\sum_{\mathbf{R}_1}{}'\int_{-\infty}^{\infty}dt_1\,\mathbf{D}^{(0)}(t-t_1)\cdot\langle\nabla_{\mathbf{R}}\nabla_{\mathbf{R}}V(\mathbf{R}-\mathbf{R}_1)\rangle_0\cdot\mathbf{D}(\mathbf{R}_1-\mathbf{R}',t_1-t')=\delta_{\mathbf{R}\mathbf{R}'}\mathbf{D}^{(0)}(t-t'), \quad (3.15)$$

where

$$\langle\nabla_{\mathbf{R}}\nabla_{\mathbf{R}}V(\mathbf{R}-\mathbf{R}_1)\rangle_0=\int d\mathbf{x}\,d\mathbf{x}_1\,\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle_0\times\nabla_{\mathbf{R}}\nabla_{\mathbf{R}}V(\mathbf{R}-\mathbf{R}_1+\mathbf{x}-\mathbf{x}_1)\langle\rho_{\mathbf{R}_1}(\mathbf{x}_1)\rangle_0. \quad (3.16)$$

These quantities can be interpreted as renormalized harmonic force constants.

[14] The minus signs in Eqs. (3.7) and (3.9) arise because $\mathbf{D}$ and $\mathbf{D}^{(0)}$ are defined to give the response to an external force. Our definitions differ in sign from those in FW and GW.

Equation (3.15) is most easily solved by going over to the Fourier space, introducing

$$\mathbf{D}^{(0)}(\omega)=\int_{-\infty}^{\infty} dt\, e^{i\omega t}\mathbf{D}^{(0)}(t)\,, \qquad (3.17)$$

$$\mathbf{D}(\mathbf{q},\omega)=\sum_{\mathbf{R}}\int_{-\infty}^{\infty} dt\, e^{-i(\mathbf{q}\cdot\mathbf{R}-\omega t)}\mathbf{D}(\mathbf{R},t)\,, \qquad (3.18)$$

and

$$\mathbf{T}(\mathbf{q})=\sum_{\mathbf{R}\neq 0} e^{-i\mathbf{q}\cdot\mathbf{R}}\langle\nabla_{\mathbf{R}}\nabla_{\mathbf{R}}V(\mathbf{R})\rangle_0\,. \qquad (3.19)$$

We then get

$$\{[\mathbf{D}^{(0)}(\omega)]^{-1}-\mathbf{T}(\mathbf{q})\}\cdot\mathbf{D}(\mathbf{q},\omega)=\mathbf{I}\,. \qquad (3.20)$$

According to general theory of lattice dynamics,[15] $\mathbf{D}(\mathbf{q},\omega)$ satisfies an equation of the form

$$[-\omega^2\mathbf{I}+\mathbf{M}(\mathbf{q},\omega)]\cdot\mathbf{D}(\mathbf{q},\omega)=M^{-1}\mathbf{I}\,, \qquad (3.21)$$

where the retarded self-energy $\mathbf{M}(\mathbf{q},\omega)$ in general is both wave-vector- and frequency-dependent. From the inversion symmetry of the lattice it follows that $\mathbf{M}(\mathbf{q},\omega)$ is an even function of $\mathbf{q}$, and from the translational invariance follows $\mathbf{M}(0,\omega)=0$. We can understand the second statement from the following reasoning: Assume the lattice to move rigidly with translational motion, which in Eq. (3.21) corresponds to a $\mathbf{q}=0$ mode with ω finite. In such a state of motion the interatomic interactions do not enter, and this means that $\mathbf{M}(0,\omega)=0$. The total inertia of the lattice is contained in the term $[-M\omega^2\mathbf{I}]$. For interatomic potentials of interest here $\mathbf{M}(\mathbf{q},\omega)$ should be a regular function of $\mathbf{q}$ around $\mathbf{q}=0$. We can therefore conclude that it is of the form $\mathbf{M}(\mathbf{q},\omega)=\mathbf{q}\cdot\mathfrak{M}(\mathbf{q},\omega)\cdot\mathbf{q}$, where $\mathfrak{M}(0,0)$ is related to the elastic constants.

In order for Eq. (3.20) to be consistent with Eq. (3.21) and with the stated properties of $\mathbf{M}(\mathbf{q},\omega)$, we have to choose

$$[\mathbf{D}^{(0)}(\omega)]^{-1}=-M\omega^2\mathbf{I}+\mathbf{T}(0)\,. \qquad (3.22)$$

This means that our basic assumption on the fluctuations of $\rho_{\mathbf{R}}(\mathbf{x},t)$ made earlier implies that the single-particle motion is harmonic with the restoring force $[\mathbf{T}(0)\cdot\mathbf{u}]$.

With this form for $[\mathbf{D}^{(0)}(\omega)]^{-1}$ inserted into Eq. (3.20) we obtain the phonon dispersion relations

$$\omega_\nu^2(\mathbf{q})=M^{-1}\mathbf{e}_{\mathbf{q}\nu}\cdot[\mathbf{T}(0)-\mathbf{T}(\mathbf{q})]\cdot\mathbf{e}_{\mathbf{q}\nu}\,,\quad \nu=1,\,2,\,3 \qquad (3.23)$$

where $\mathbf{e}_{\mathbf{q}\nu}$ are the eigenvectors of $[\mathbf{T}(0)-\mathbf{T}(\mathbf{q})]$. The displacement response function is

$$\mathbf{D}(\mathbf{q},\omega)=-M^{-1}\sum_{\nu=1}^{3}\mathbf{e}_{\mathbf{q}\nu}[\omega^2-\omega_\nu^2(\mathbf{q})]^{-1}\mathbf{e}_{\mathbf{q}\nu}\,. \qquad (3.24)$$

Both these results agree precisely with those given by FW and GW, noting that our $\mathbf{T}(\mathbf{q})$ is in the notation of GW given by

$$\mathbf{T}(\mathbf{q})=\sum_{\alpha,\gamma} f_\alpha f_\gamma\langle\alpha\gamma|\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}v_{\mathbf{q}}(\mathbf{x}-\mathbf{x}')|\alpha\gamma\rangle\,, \qquad (3.25)$$

and that a difference in sign arises from our definition in Eq. (3.7) (see Ref. 14).

From our discussion it is clear that our basic assumption, following Eq. (3.12), is essential in order to obtain the results of FW and GW. If we would relax this assumption, we would not get an equation involving only the displacement response function but would get a coupling to higher-order cumulants. In Sec. V we show that taking into account also the response of the term $\langle\mathbf{u}(\mathbf{R},t)\mathbf{u}(\mathbf{R},t)\rangle_c$ in Eq. (3.11) gives damping of the phonons.

We notice that having made our basic assumption on the density fluctuations, the single-particle motion is uniquely determined. The Hartree states introduced in the beginning enter only in the evaluation of $\mathbf{T}(\mathbf{q})$.

IV. SOLUTION IN HARTREE REPRESENTATION

By changing to the Hartree representation we shall further demonstrate that our basic assumption in Sec. III is indeed identical to the more mathematical assumption made by GW. The development in this section follows closely that of FW and GW. We can therefore be very brief in our presentation, and we refer to the above authors for more details.

We return to Eqs. (2.4) and (2.5) and write them in the representation defined by the eigenstates $\varphi_\alpha(\mathbf{x})$. We then have

$$\chi_1^{(0)}(\mathbf{x}\mathbf{x}'t;\mathbf{x}_1t_1)=-(i\hbar)^{-1}\theta(t-t_1)\sum_{\alpha,\beta}\varphi_\alpha(\mathbf{x}')\varphi_\beta(\mathbf{x})\varphi_\alpha(\mathbf{x}_1)\times\varphi_\beta(\mathbf{x}_1)f_{\beta\alpha}\exp[-i\omega_{\beta\alpha}(t-t_1)]\,, \qquad (4.1)$$

with $f_{\beta\alpha}=(f_\beta-f_\alpha)$ and $\omega_{\beta\alpha}=(\epsilon_\beta-\epsilon_\alpha)/\hbar$. Without loss of generality we can assume that the external potential has the form

$$V_{\mathbf{R}}^{\text{ext}}(\mathbf{x},t)=V^{\text{ext}}(\mathbf{x};\,\mathbf{q}\omega)\exp[i(\mathbf{q}\cdot\mathbf{R}-\omega t)]\,, \qquad (4.2)$$

and we then ask for a solution to Eq. (2.5) of the form

$$\langle\rho_{\mathbf{R}}(\mathbf{x},\mathbf{x}',t)\rangle_{\text{ind}}=\delta\rho(\mathbf{x}\mathbf{x}';\,\mathbf{q}\omega)\exp[i(\mathbf{q}\cdot\mathbf{R}-\omega t)]\,. \qquad (4.3)$$

In the $\{\varphi_\alpha\}$ representation we may write

$$\delta\rho(\mathbf{x}\mathbf{x}';\,\mathbf{q}\omega)=\sum_{\alpha,\beta}\varphi_\alpha(\mathbf{x}')\langle\alpha|\delta\rho(\mathbf{q},\omega)|\beta\rangle\varphi_\beta(\mathbf{x})\,. \qquad (4.4)$$

Substituting Eqs. (4.1)–(4.4) into Eq. (2.5), we obtain an equation for $\langle\alpha|\delta\rho(\mathbf{q},\omega)|\beta\rangle$ which is identical to that of FW [Eq. (24)]. Following FW, we separate $\langle\alpha|\delta\rho(\mathbf{q},\omega)|\beta\rangle$ into an even part $\xi_{\alpha\beta}(\mathbf{q},\omega)$ and an odd part $\eta_{\alpha\beta}(\mathbf{q},\omega)$,[16] and we obtain after some calculations

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[16] Only the even part of the density matrix will finally enter in the problem.

the following equation for $\xi_{\alpha\beta}(\mathbf{q},\omega)$:

$$\sum_{\alpha',\beta'} M_{\alpha\beta,\alpha'\beta'}(\mathbf{q},\omega)(-\omega_{\beta'\alpha'}f_{\beta'\alpha'})^{-1/2}\xi_{\alpha'\beta'}(\mathbf{q},\omega) = (-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2}\int d\mathbf{x}_1\, \varphi_\alpha(\mathbf{x}_1)\varphi_\beta(\mathbf{x}_1)V^{\text{ext}}(\mathbf{x}_1;\mathbf{q}\omega). \quad (4.5)$$

The matrix $M_{\alpha\beta,\alpha'\beta'}(\mathbf{q},\omega)$ is given by

$$M_{\alpha\beta,\alpha'\beta'}(\mathbf{q},\omega)=\hbar(\omega^2-\omega_{\beta\alpha}{}^2)\delta_{\alpha\alpha'}\delta_{\beta\beta'}-(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2} \times\langle\alpha\alpha'|V_{\mathbf{q}}|\beta\beta'\rangle(-\omega_{\beta'\alpha'}f_{\beta'\alpha'})^{1/2}, \quad (4.6)$$

where

$$\langle\alpha\alpha'|V_{\mathbf{q}}|\beta\beta'\rangle=\int d\mathbf{x}\,d\mathbf{x}'\, \varphi_\alpha(\mathbf{x})\varphi_{\alpha'}(\mathbf{x}') \times V_{\mathbf{q}}(\mathbf{x}-\mathbf{x}')\varphi_\beta(\mathbf{x})\varphi_{\beta'}(\mathbf{x}') \quad (4.7)$$

and

$$V_{\mathbf{q}}(\mathbf{x}-\mathbf{x}')=\sum_{\mathbf{R}\neq 0} e^{-i\mathbf{q}\cdot\mathbf{R}}V(\mathbf{R}+\mathbf{x}-\mathbf{x}'). \quad (4.8)$$

$M_{\alpha\beta,\alpha'\beta'}(\mathbf{q},\omega)$ is the same as that of GW [Eq. (24)], and Eq. (4.5) is the same as Eq. (29) of FW. The formal solution of Eq. (4.5) is then given by

$$\xi_{\alpha\beta}(\mathbf{q},\omega)=(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2} \times\sum_{\alpha',\beta'}[M^{-1}(\mathbf{q},\omega)]_{\alpha\beta,\alpha'\beta'}(-\omega_{\beta'\alpha'}f_{\beta'\alpha'})^{1/2} \times\int d\mathbf{x}_1\varphi_{\alpha'}(\mathbf{x}_1)\varphi_{\beta'}(\mathbf{x}_1)V^{\text{ext}}(\mathbf{x}_1;\mathbf{q}\omega). \quad (4.9)$$

Assuming the external disturbance to be of the form

$$V^{\text{ext}}(\mathbf{x}_1;\mathbf{q}\omega)=-\mathbf{x}_1\cdot\mathbf{J}^{\text{ext}}(\mathbf{q},\omega), \quad (4.10)$$

we can from Eq. (4.9) calculate the response of the mean displacement of an atom to an external force, following FW [Eqs. (32), (33), (35), and (36)]. We then obtain for the displacement response function

$$\mathbf{D}(\mathbf{q},\omega)=-\sum_{\alpha,\beta}\sum_{\alpha',\beta'}\langle\alpha|\mathbf{x}|\beta\rangle(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2} \times[M^{-1}(\mathbf{q},\omega)]_{\alpha\beta,\alpha'\beta'}(-\omega_{\beta'\alpha'}f_{\beta'\alpha'})^{1/2}\langle\alpha'|\mathbf{x}|\beta'\rangle. \quad (4.11)$$

Introducing the eigenvectors $U_{\alpha\beta,\nu}$ and the eigenfrequencies $\hbar(\omega^2-\zeta_{\mathbf{q}\nu}{}^2)$ of the Hermitian matrix $M_{\alpha\beta,\alpha'\beta'}$, we can write its inverse as

$$[M^{-1}(\mathbf{q},\omega)]_{\alpha\beta,\alpha'\beta'}=\sum_\nu \hbar^{-1}(\omega^2-\zeta_{\mathbf{q}\nu}{}^2)^{-1}U_{\alpha\beta,\nu}U_{\alpha'\beta',\nu}, \quad (4.12)$$

and hence

$$\mathbf{D}(\mathbf{q},\omega)=-\sum_\nu \hbar^{-1}(\omega^2-\zeta_{\mathbf{q}\nu}{}^2)^{-1} \times\{\sum_{\alpha,\beta}\langle\alpha|\mathbf{x}|\beta\rangle(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2}U_{\alpha\beta,\nu}\} \times\{\sum_{\alpha',\beta'}U_{\alpha'\beta',\nu}(-\omega_{\beta'\alpha'}f_{\beta'\alpha'})^{1/2}\langle\alpha'|\mathbf{x}|\beta'\rangle\}. \quad (4.13)$$

This agrees with Eq. (3.24) only if

$$\sum_{\alpha,\beta}\langle\alpha|\mathbf{x}|\beta\rangle(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2}U_{\alpha\beta,\nu}=\hbar^{1/2}M^{-1/2}\mathbf{e}_{\mathbf{q}\nu}, \quad \nu=1,2,3$$
$$=0, \quad \text{otherwise}. \quad (4.14)$$

It can be verified (see Appendix C) that this relation is satisfied by assuming

$$U_{\alpha\beta,\nu}=\hbar^{1/2}M^{1/2}(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2}\langle\alpha|\mathbf{e}_{\mathbf{q}\nu}\cdot\mathbf{x}|\beta\rangle, \quad \nu=1,2,3$$
$$=\text{some vectors orthogonal to the above}, \quad \nu>3. \quad (4.15)$$

The corresponding eigenfrequencies are for $\nu=1$, 2, 3 identical to those in Eq. (3.23), and they are unknown for $\nu>3$.

The above eigenvectors $U_{\alpha\beta,\nu}$ are precisely those assumed by GW [Eq. (39)]. We can therefore conclude that our assumption in Sec. III is indeed equivalent to theirs.

V. PHONON DAMPING

In this section we shall show how we can generalize the treatment of FW and GW by also taking into account the response of the second cumulant in Eq. (3.11). In this way we obtain damping of the collective modes.

In order to bring the rather heavy mathematical formalism into a tractable form, we shall first introduce a suitable matrix notation. By $\mathfrak{X}$ we mean a row matrix with the following 12 components:

$$\mathfrak{X}=(x_1,x_2,x_3,x_1x_1,x_1x_2,x_1x_3,x_2x_1,x_2x_2,x_2x_3, x_3x_1,x_3x_2,x_3x_3), \quad (5.1)$$

where here the subscripts 1, 2, 3 denote Cartesian components. The corresponding transposed column matrix is denoted by $\mathfrak{X}^T$. Similarly we introduce the 12×12 matrix

$$\mathfrak{D}(\mathbf{R}-\mathbf{R}',t-t')=-\int d\mathbf{x}\,d\mathbf{x}'\,\mathfrak{X}^T\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')\mathfrak{X}' \quad (5.2)$$

analogous to the 3×3 matrix in Eq. (3.7). $\mathfrak{X}^T\mathfrak{X}'$ is the 12×12 product matrix obtained by multiplying the components of $\mathfrak{X}^T$ and $\mathfrak{X}'$.

In its physical interpretation $\mathfrak{D}$ consists of four different submatrices, so that we shall write it in the form

$$\mathfrak{D}(\mathbf{R}-\mathbf{R}',t-t') =\begin{pmatrix}\mathbf{D}_{11}(\mathbf{R}-\mathbf{R}',t-t') & \mathbf{D}_{12}(\mathbf{R}-\mathbf{R}',t-t')\\ \mathbf{D}_{21}(\mathbf{R}-\mathbf{R}',t-t') & \mathbf{D}_{22}(\mathbf{R}-\mathbf{R}',t-t')\end{pmatrix}. \quad (5.3)$$

$\mathbf{D}_{11}$ is the 3×3 matrix introduced in Eq. (3.7) and written there without subscripts; thus

$$\mathbf{D}_{11}(\mathbf{R}-\mathbf{R}',t-t')=\mathbf{D}(\mathbf{R}-\mathbf{R}',t-t'). \quad (5.4)$$

This is the part of $\mathfrak{D}$ whose Fourier transform has poles corresponding to phonon modes. $\mathbf{D}_{12}(\mathbf{R}-\mathbf{R}',t-t')$ is a 3×9 matrix with the elements

$$[\mathbf{D}_{12}(\mathbf{R}-\mathbf{R}',\,t-t')]_{i,jm}=-(i\hbar)^{-1}\theta(t-t')\times\langle[u_i(\mathbf{R},t),u_j(\mathbf{R}',t')u_m(\mathbf{R}',t')]\rangle\,,\quad(5.5)$$

the subscripts denoting the Cartesian components and $\theta(t)$ being the same step function as in Eq. (2.6). Similarly, $\mathbf{D}_{21}(\mathbf{R}-\mathbf{R}',\,t-t')$ is a 9×3 matrix where

$$[\mathbf{D}_{21}(\mathbf{R}-\mathbf{R}',\,t-t')]_{jm,i}=-(i\hbar)^{-1}\theta(t-t')\times\langle[u_j(\mathbf{R},t)u_m(\mathbf{R},t),u_i(\mathbf{R}',t')]\rangle\,.\quad(5.6)$$

$\mathbf{D}_{22}(\mathbf{R}-\mathbf{R}',\,t-t')$ is a 9×9 matrix whose elements are

$$[\mathbf{D}_{22}(\mathbf{R}-\mathbf{R}',\,t-t')]_{ij,mn}=-(i\hbar)^{-1}\theta(t-t')\times\langle[u_i(\mathbf{R},t)u_j(\mathbf{R},t),u_m(\mathbf{R}',t')u_n(\mathbf{R}',t')]\rangle\,.\quad(5.7)$$

Analogous to the matrix $\mathbf{D}^{(0)}(t-t')$ in Eq. (3.9) we introduce

$$\mathfrak{D}^{(0)}(t-t')=-\int d\mathbf{x}\,d\mathbf{x}'\,\mathfrak{X}^T\chi^{(0)}(\mathbf{x}t;\mathbf{x}'t')\mathfrak{X}'\,,\quad(5.8)$$

which has a structure similar to that shown in Eqs. (5.3)–(5.7).

Multiplying Eq. (3.5) for the function $\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')$ with the product matrix $\mathfrak{X}^T\mathfrak{X}'$ and integrating over $\mathbf{x}$ and $\mathbf{x}'$, we obtain the following equation for $\mathfrak{D}(\mathbf{R}-\mathbf{R}',\,t-t')$:

$$\mathfrak{D}(\mathbf{R}-\mathbf{R}',\,t-t')+\sum_{\mathbf{R}_1}{}'\int_{-\infty}^{\infty}dt_1\int d\mathbf{x}_1\,d\mathbf{x}''\times\left\{\int d\mathbf{x}\,\mathfrak{X}^T\chi^{(0)}(\mathbf{x}t;\mathbf{x}''t_1)\right\}V(\mathbf{R}-\mathbf{R}_1+\mathbf{x}''-\mathbf{x}_1)\times\left\{\int d\mathbf{x}'\,\chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1t_1;\mathbf{x}'t')\mathfrak{X}'\right\}=\delta_{\mathbf{R}\mathbf{R}'}\mathfrak{D}^{(0)}(t-t')\,.\quad(5.9)$$

This equation is a generalization of Eq. (3.10). We shall use the same procedure to solve it as was used in Sec. III.

The integral within the second curly bracket in Eq. (5.9) is a row matrix, whose elements are actually of two different types. The first three elements are the components of the following vector quantity:

$$\text{(I)}\quad\int d\mathbf{x}'\,\chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1t_1;\mathbf{x}'t')\mathbf{x}'=(i\hbar)^{-1}\theta(t_1-t')\times\langle[\rho_{\mathbf{R}_1}(\mathbf{x}_1,t_1),\mathbf{u}(\mathbf{R}',t')]\rangle\,.\quad(5.10)$$

The remaining nine elements form a tensor

$$\text{(II)}\quad\int d\mathbf{x}'\,\chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1t_1;\mathbf{x}'t')\mathbf{x}'\mathbf{x}'=(i\hbar)^{-1}\theta(t_1-t')\times\langle[\rho_{\mathbf{R}_1}(\mathbf{x}_1,t_1),\mathbf{u}(\mathbf{R}',t')\mathbf{u}(\mathbf{R}',t')]\rangle\,.\quad(5.11)$$

The vector function is precisely the same as that appearing in Eq. (3.10). As shown in Appendix A, it gives the linear response of the density of the $\mathbf{R}$th atom to an applied weak external disturbance, represented in the Hamiltonian by a term of the form

$$H_I=-\sum_{\mathbf{R}}\mathbf{u}(\mathbf{R},t)\cdot\mathbf{J}(\mathbf{R},t)\,,\quad(5.12)$$

where $\mathbf{J}(\mathbf{R},t)$ is an external force on the $\mathbf{R}$th atom. Thus, from Eq. (A7) we have

$$\int d\mathbf{x}'\,\chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1t_1;\mathbf{x}'t')x_i'=-\delta\langle\rho_{\mathbf{R}_1}(\mathbf{x}_1,t_1)\rangle/\delta J_i(\mathbf{R}',t')\,,\quad(5.13)$$

where the functional derivative is assumed to be evaluated for the external disturbance tending to zero.

Similarly, the tensor function in Eq. (5.11) gives the linear response of the mean density a of particular atom to a weak external disturbance represented by

$$H_{II}=-\sum_{\mathbf{R}}\mathbf{u}(\mathbf{R},t)\cdot\mathbf{J}(\mathbf{R},t)\cdot\mathbf{u}(\mathbf{R},t)\,.\quad(5.14)$$

We can, therefore, write

$$\int d\mathbf{x}'\,\chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1t_1;\mathbf{x}'t')x_i'x_j'=-\delta\langle\rho_{\mathbf{R}_1}(\mathbf{x}_1,t_1)\rangle/\delta J_{ij}(\mathbf{R}',t')\,,\quad(5.15)$$

where the functional derivative is again evaluated for zero external disturbance. The term in Eq. (5.14) couples the width of the mean density profile to $\mathbf{J}(\mathbf{R},t)$.

In precisely the same way as was done in Eq. (3.11), we write

$$\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle=(2\pi)^{-3}\int d\mathbf{q}\,e^{i\mathbf{q}\cdot\mathbf{x}}\exp\{-i\mathbf{q}\cdot\langle\mathbf{u}(\mathbf{R},t)\rangle-\tfrac{1}{2}\mathbf{q}\cdot\langle\mathbf{u}(\mathbf{R},t)\mathbf{u}(\mathbf{R},t)\rangle_c\cdot\mathbf{q}+\cdots\}\,,\quad(5.16)$$

and we shall here assume that only the mean displacement $\langle\mathbf{u}(\mathbf{R},t)\rangle$ and the width tensor $\langle\mathbf{u}(\mathbf{R},t)\mathbf{u}(\mathbf{R},t)\rangle_c$ change as a result of the external disturbances. The higher cumulants keep their equilibrium values. We have then, as a generalization of Eq. (3.12),

$$\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle_{\text{ind}}=-\nabla_{\mathbf{x}}\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle_0\cdot\langle\mathbf{u}(\mathbf{R},t)\rangle+\tfrac{1}{2}\nabla_{\mathbf{x}}\nabla_{\mathbf{x}}\langle\rho_{\mathbf{R}}(\mathbf{x})\rangle_0:\langle\mathbf{u}(\mathbf{R},t)\mathbf{u}(\mathbf{R},t)\rangle_c{}^{\text{ind}}\,,\quad(5.17)$$

noting that the external disturbances are assumed infinitesimal. From Eq. (5.17) and using Eqs. (5.13) and (5.15), it follows that

$$\int d\mathbf{x}'\,\chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1t_1;\mathbf{x}'t')x_i'=\nabla_m\langle\rho_{\mathbf{R}_1}(\mathbf{x}_1)\rangle_0\frac{\delta\langle u_m(\mathbf{R}_1,t_1)\rangle}{\delta J_i(\mathbf{R}',t')}-\tfrac{1}{2}\nabla_{mn}{}^2\langle\rho_{\mathbf{R}_1}(\mathbf{x}_1)\rangle_0\frac{\delta\langle u_m(\mathbf{R}_1,t_1)u_n(\mathbf{R}_1,t_1)\rangle_c}{\delta J_i(\mathbf{R}',t')}\quad(5.18)$$

and

$$\int d\mathbf{x}'\, \chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1 t_1;\mathbf{x}'t')x_i'x_j' = \nabla_m \langle \rho_{\mathbf{R}_1}(\mathbf{x}_1)\rangle_0 \frac{\delta\langle u_m(\mathbf{R}_1,t_1)\rangle}{\delta J_{ij}(\mathbf{R}',t')} - \tfrac{1}{2}\nabla_{mn}{}^2 \langle \rho_{\mathbf{R}_1}(\mathbf{x}_1)\rangle_0 \frac{\delta\langle u_m(\mathbf{R}_1,t_1)u_n(\mathbf{R}_1,t_1)\rangle_c}{\delta J_{ij}(\mathbf{R}',t')}. \quad (5.19)$$

Repeated Cartesian indices are summed over in the conventional way, and the functional derivatives are evaluated for zero external distrubances. Finally we can identify these derivatives with the submatrices in Eq. (5.3) as follows:

$$\delta\langle \mathbf{u}(\mathbf{R}_1,t_1)\rangle/\delta \mathbf{J}(\mathbf{R}',t') = \mathbf{D}_{11}(\mathbf{R}_1-\mathbf{R}',\, t_1-t'), \quad (5.20)$$

$$\delta\langle \mathbf{u}(\mathbf{R}_1,t_1)\mathbf{u}(\mathbf{R}_1,t_1)\rangle_c/\delta \mathbf{J}(\mathbf{R}',t') = \mathbf{D}_{21}(\mathbf{R}_1-\mathbf{R}',\, t_1-t'), \quad (5.21)$$

$$\delta\langle \mathbf{u}(\mathbf{R}_1,t_1)\rangle/\delta \mathbf{J}(\mathbf{R}',t') = \mathbf{D}_{12}(\mathbf{R}_1-\mathbf{R}',\, t_1-t'), \quad (5.22)$$

$$\delta\langle \mathbf{u}(\mathbf{R}_1,t_1)\mathbf{u}(\mathbf{R}_1,t_1)\rangle_c/\delta \mathbf{J}(\mathbf{R}',t') = \mathbf{D}_{22}(\mathbf{R}_1-\mathbf{R}',\, t_1-t'). \quad (5.23)$$

Let us here for convenience introduce a row matrix operator which has the following 12 elements:

$$\boldsymbol{\nabla} = (\nabla_1,\, \nabla_2,\, \nabla_3,\, -\tfrac{1}{2}\nabla_{11}{}^2,\, -\tfrac{1}{2}\nabla_{12}{}^2,\, -\tfrac{1}{2}\nabla_{13}{}^2,\, -\tfrac{1}{2}\nabla_{21}{}^2,\, -\tfrac{1}{2}\nabla_{22}{}^2,\, -\tfrac{1}{2}\nabla_{23}{}^2,\, -\tfrac{1}{2}\nabla_{31}{}^2,\, -\tfrac{1}{2}\nabla_{32}{}^2,\, -\tfrac{1}{2}\nabla_{33}{}^2), \quad (5.24)$$

and also the corresponding transposed column matrix $\boldsymbol{\nabla}^T$. We can then write Eqs. (5.18) and (5.19), with Eqs. (5.20)–(5.23) inserted, in the following very concise form:

$$\int d\mathbf{x}'\, \chi_{\mathbf{R}_1-\mathbf{R}'}(\mathbf{x}_1 t_1;\, \mathbf{x}'t')\mathfrak{X}' = \boldsymbol{\nabla}\langle \rho_{\mathbf{R}_1}(\mathbf{x}_1)\rangle_0 \cdot \mathfrak{D}(\mathbf{R}_1-\mathbf{R}',\, t_1-t'). \quad (5.25)$$

The same kind of relation is obtained for $\chi^{(0)}(\mathbf{x}t;\,\mathbf{x}'t')$ and $\mathfrak{D}^{(0)}(t-t')$, and with the same arguments as we used to obtain Eq. (3.14), we get

$$\int d\mathbf{x}\, \mathfrak{X}^T \chi^{(0)}(\mathbf{x}t;\, \mathbf{x}''t_1) = \mathfrak{D}^{(0)}(t-t_1)\cdot \boldsymbol{\nabla}^T \langle \rho_{\mathbf{R}}(\mathbf{x}'')\rangle_0. \quad (5.26)$$

Inserting Eqs. (5.25) and (5.26) into Eq. (5.9) leads to

$$\mathfrak{D}(\mathbf{R}-\mathbf{R}',\, t-t') + \sum_{\mathbf{R}_1}{}' \int_{-\infty}^{\infty} dt_1\, \mathfrak{D}^{(0)}(t-t_1) \cdot \left\{ \int\!\!\int d\mathbf{x}''\, d\mathbf{x}_1\, \boldsymbol{\nabla}^T \langle \rho_{\mathbf{R}}(\mathbf{x}'')\rangle_0 V(\mathbf{R}-\mathbf{R}_1+\mathbf{x}''-\mathbf{x}_1) \times \boldsymbol{\nabla}\langle \rho_{\mathbf{R}_1}(\mathbf{x}_1)\rangle_0 \right\} \cdot \mathfrak{D}(\mathbf{R}_1-\mathbf{R}',\, t_1-t') = \delta_{\mathbf{R}\mathbf{R}'}\mathfrak{D}^{(0)}(t-t'). \quad (5.27)$$

We denote the negative of the quantity appearing in the curly bracket by $\mathfrak{T}(\mathbf{R}-\mathbf{R}')$. Performing some partial integrations to make $\boldsymbol{\nabla}$ and $\boldsymbol{\nabla}^T$ operate on the potential, we can bring the matrix $\mathfrak{T}(\mathbf{R}-\mathbf{R}')$ into the form

$$\mathfrak{T}(\mathbf{R}) = \begin{pmatrix} \mathbf{T}_{11}(\mathbf{R}) & \mathbf{T}_{12}(\mathbf{R}) \\ \mathbf{T}_{21}(\mathbf{R}) & \mathbf{T}_{22}(\mathbf{R}) \end{pmatrix}, \quad (5.28)$$

where the four submatrices are given below.

$\mathbf{T}_{11}$ is the 3×3 matrix introduced before in Eq. (3.16):

$$\mathbf{T}_{11}(\mathbf{R}) = \langle \nabla_{\mathbf{R}}\nabla_{\mathbf{R}} V(\mathbf{R})\rangle_0. \quad (5.29)$$

$\mathbf{T}_{12}$ is a 3×9 matrix with the elements

$$[\mathbf{T}_{12}(\mathbf{R})]_{i,jm} = -\tfrac{1}{2}\langle \nabla^3{}_{ijm} V(\mathbf{R})\rangle_0, \quad (5.30)$$

and similarly $\mathbf{T}_{21}$ is a 9×3 matrix with

$$[\mathbf{T}_{21}(\mathbf{R})]_{jm,i} = \tfrac{1}{2}\langle \nabla^3{}_{jmi} V(\mathbf{R})\rangle_0. \quad (5.31)$$

Finally $\mathbf{T}_{22}$ is a 9×9 matrix, where

$$[\mathbf{T}_{22}(\mathbf{R})]_{ij,mn} = -\tfrac{1}{4}\langle \nabla^4{}_{ijmn} V(\mathbf{R})\rangle_0. \quad (5.32)$$

Here the bracket $\langle\cdots\rangle_0$ indicates the same averaging procedure as used before in Eq. (3.16).

With the above notations Eq. (5.27) is written

$$\mathfrak{D}(\mathbf{R}-\mathbf{R}',\, t-t') - \sum_{\mathbf{R}_1}{}' \int_{-\infty}^{\infty} dt_1\, \mathfrak{D}^{(0)}(t-t_1)\cdot \mathfrak{T}(\mathbf{R}-\mathbf{R}_1) \cdot \mathfrak{D}(\mathbf{R}_1-\mathbf{R}',\, t_1-t') = \delta_{\mathbf{R}\mathbf{R}'}\mathfrak{D}^{(0)}(t-t'), \quad (5.33)$$

which is a generalization of Eq. (3.15), Introducing the corresponding Fourier transforms as in Eqs. (3.17)–(3.19), we have

$$\mathfrak{D}(\mathbf{q},\omega) - \mathfrak{D}^{(0)}(\omega)\cdot \mathfrak{T}(\mathbf{q})\cdot \mathfrak{D}(\mathbf{q},\omega) = \mathfrak{D}^{(0)}(\omega), \quad (5.34)$$

and thus

$$\mathfrak{D}(\mathbf{q},\omega) = \{[\mathfrak{D}^{(0)}(\omega)]^{-1} - \mathfrak{T}(\mathbf{q})\}^{-1}. \quad (5.35)$$

We are actually not interested in the full matrix $\mathfrak{D}(\mathbf{q},\omega)$ but only in the submatrix $\mathbf{D}_{11}(\mathbf{q},\omega)$. The position of the poles of $\mathbf{D}_{11}(\mathbf{q},\omega)$ gives the frequencies and the damping of the phonon modes. We have, therefore, to extract this submatrix from $\mathfrak{D}(\mathbf{q},\omega)$. The mathematical procedure for doing this is given in Appendix E, where we use the relation

$$\mathbf{D}_{21}(\mathbf{q},\omega) = [\mathbf{D}_{12}(\mathbf{q},\omega)]^T, \quad (5.36)$$

which is proved separately in Appendix D.

We shall make certain approximations as we proceed. Partly, this is because we wish to get contact with familiar results for phonon damping, obtained from conventional perturbation procedure. If the coupling is weak between the displacement $\langle \mathbf{u}(\mathbf{R},t)\rangle$ of the particle mean density and the variation of its width, represented by $\langle \mathbf{u}(\mathbf{R},t)\mathbf{u}(\mathbf{R},t)\rangle_c$, the quantities $\mathbf{T}_{12}$ and $\mathbf{T}_{21}$ are small. We need then to include these only to lowest order, which actually means including quadratic terms in $\mathbf{T}_{12}$ and $\mathbf{T}_{21}$.

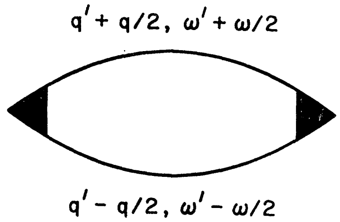

FIG. 1. Third-order diagram to the phonon self-energy in the conventional perturbation treatment. The filled triangles indicate three-phonon vertices.

Furthermore, we shall neglect $\mathbf{T}_{22}(\mathbf{q})$, containing the fourth spatial derivative of the interaction potential. We notice that the conventional fourth-order anharmonic correction to the phonon self-energy, obtained in lowest-order perturbation theory, is already included in the approximation in Sec. III. The term $\mathbf{T}_{22}(\mathbf{q})$ above contains those higher-order effects which were discussed by Enz[17] and more recently by Götze and Michel.[18] For solid helium these terms are probably not negligible. However, for the reason we intend to discuss this point in a separate paper, based on a treatment which goes beyond the SCF approximation, we shall here proceed as if $\mathbf{T}_{22}(\mathbf{q})$ can be neglected.

The equation obtained in Appendix E for the displacement response function is

$$\{[\mathbf{D}_{11}^{(0)}]^{-1}-\mathbf{T}_{11}-[\mathbf{D}_{11}^{(0)}]^{-1}\mathbf{D}_{12}^{(0)}\mathbf{T}_{21} -\mathbf{T}_{12}\mathbf{D}_{22}\mathbf{T}_{21}[\mathbf{I}+\mathbf{D}_{12}\mathbf{T}_{21}]^{-1}-\mathbf{T}_{12}\mathbf{D}_{21}^{(0)}[\mathbf{D}_{11}^{(0)}]^{-1} \times[\mathbf{I}+\mathbf{D}_{12}\mathbf{T}_{21}]^{-1}\}\,\mathbf{D}_{11}=\mathbf{I}. \quad (5.37)$$

For brevity the arguments $\mathbf{q}$ and ω have been dropped. In obtaining Eq. (5.37) the matrix $\mathbf{T}_{22}$ has been set to zero but so far no assumption on the magnitude of $\mathbf{T}_{12}$ and $\mathbf{T}_{21}$ has been made.

Because of the assumption that $\mathbf{T}_{12}$ and $\mathbf{T}_{21}$ are small quantities, to lowest order we can evaluate the response functions appearing in the curly bracket in Eq. (5.37) within the approximation in Sec. III. This implies

$$[\mathbf{D}_{11}^{(0)}(\omega)]^{-1}=-M\omega^2\mathbf{I}+\mathbf{T}_{11}(0) \quad (5.38)$$

and

$$\mathbf{D}_{12}^{(0)}(\omega)=\mathbf{D}_{21}^{(0)}(\omega)=0. \quad (5.39)$$

It also implies a certain relation between $\mathbf{D}_{22}(\mathbf{q},\omega)$ and the displacement response function which is discussed in the following.

To lowest order in $\mathbf{T}_{12}$ and $\mathbf{T}_{21}$, Eq. (5.37) then goes over to

$$\{-M\omega^2\mathbf{I}+\mathbf{T}_{11}(0)-\mathbf{T}_{11}(\mathbf{q})-\mathbf{T}_{12}(\mathbf{q}) \cdot\mathbf{D}_{22}(\mathbf{q},\omega)\cdot\mathbf{T}_{21}(\mathbf{q})\}\cdot\mathbf{D}_{11}(\mathbf{q},\omega)=\mathbf{I}. \quad (5.40)$$

[17] C. P. Enz, in *Mathematical Methods in Solid State and Superfluid Theory*, edited by R. C. Clark and G. H. Derrick (Plenum Press, Inc., New York, 1968), p. 339.
[18] W. Götze and K. H. Michel, Z. Physik **223**, 199 (1969).

From this the phonon self-energy is seen to be [cf. Eq. (3.21)]

$$\mathbf{M}(\mathbf{q},\omega)=M^{-1}[\mathbf{T}_{11}(0)-\mathbf{T}_{11}(\mathbf{q})]-M^{-1}\mathbf{T}_{12}(\mathbf{q}) \cdot\mathbf{D}_{22}(\mathbf{q},\omega)\cdot\mathbf{T}_{21}(\mathbf{q}). \quad (5.41)$$

The first part of Eq. (5.41) is the same as that found in Sec. III, whereas the second part is a result of the coupling between the displacement and the change of the width in the mean density $\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle$.

As shown in Appendix F, we can for the second contribution above [denoted by superscript (2)] write in space and time variables

$$M_{kl}^{(2)}(\mathbf{R}-\mathbf{R}',\,t-t') =(-i\hbar/2M)\sum_{\mathbf{R}_1,\mathbf{R}_2}\langle\nabla^3{}_{kmm'}V(\mathbf{R}-\mathbf{R}_1)\rangle_0 \times\{D_{mn}{}^{\mathcal{T}}(\mathbf{R}_1-\mathbf{R}_2,\,t-t')D_{n'm'}{}^{\mathcal{T}}(\mathbf{R}_2-\mathbf{R}_1,\,t'-t) -D_{mn}{}^{<}(\mathbf{R}_1-\mathbf{R}_2,\,t-t')D_{n'm'}{}^{>}(\mathbf{R}_2-\mathbf{R}_1,\,t'-t)\} \times\langle\nabla^3{}_{n'nl}V(\mathbf{R}_2-\mathbf{R}')\rangle_0, \quad (5.42)$$

where summation over repeated subscripts is made. Here $\mathbf{T}_{12}$ and $\mathbf{T}_{21}$ have been replaced by the expressions in Eqs. (5.30) and (5.31). The new quantities introduced here are

$$D_{mn}{}^{>}(\mathbf{R}-\mathbf{R}',\,t-t')=(-i\hbar)^{-1}\langle u_m(\mathbf{R},t)u_n(\mathbf{R}',t')\rangle, \quad (5.43)$$

$$D_{mn}{}^{<}(\mathbf{R}-\mathbf{R}',\,t-t')=(-i\hbar)^{-1}\langle u_n(\mathbf{R}',t')u_m(\mathbf{R},t)\rangle, \quad (5.44)$$

and the time-ordered phonon Green's function

$$\mathbf{D}^{\mathcal{T}}(\mathbf{R}-\mathbf{R}',\,t-t')=\mathbf{D}^{>}(\mathbf{R}-\mathbf{R}',\,t-t'),\quad t>t' \\ =\mathbf{D}^{<}(\mathbf{R}-\mathbf{R}',\,t-t'),\quad t<t'. \quad (5.45)$$

These quantities should be evaluated within the approximation in Sec. III.

Going back to the Fourier transforms, we finally have

$$M_{kl}^{(2)}(\mathbf{q},\omega)=\frac{i\hbar}{2M}\tilde{T}_{kmm'}(\mathbf{q})\int\frac{d\mathbf{q}'}{v}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi} \times\{D_{mn}{}^{\mathcal{T}}(\mathbf{q}'+\tfrac{1}{2}\mathbf{q},\,\omega'+\tfrac{1}{2}\omega)D_{n'm'}{}^{\mathcal{T}}(\mathbf{q}'-\tfrac{1}{2}\mathbf{q},\,\omega'-\tfrac{1}{2}\omega) -D_{mn}{}^{<}(\mathbf{q}'+\tfrac{1}{2}\mathbf{q},\,\omega'+\tfrac{1}{2}\omega)D_{n'm'}{}^{>}(\mathbf{q}'-\tfrac{1}{2}\mathbf{q},\,\omega'-\tfrac{1}{2}\omega)\} \times[\tilde{T}_{n'nl}(\mathbf{q})]^*, \quad (5.46)$$

where

$$\tilde{T}_{kmm'}(\mathbf{q})=\sum_{\mathbf{R}\neq 0}e^{-i\mathbf{q}\cdot\mathbf{R}}\langle\nabla^3{}_{kmm'}V(\mathbf{R})\rangle_0, \quad (5.47)$$

are the components of $\mathbf{T}_{21}(\mathbf{q})$ multiplied by 2. We note that $\tilde{T}_{kmm'}(\mathbf{q})$ is an odd function of $\mathbf{q}$ and that $\tilde{T}_{kmm'}(-\mathbf{q})=\tilde{T}_{kmm'}{}^*(\mathbf{q})$. The $\mathbf{q}'$ integration in Eq. (5.46) goes over the first Brillouin zone, v being its volume in reciprocal space [$v=(2\pi)^3$/volume of unit cell]. The self-energy above gives a damping as well as a frequency shift of the phonons.

The expression in Eq. (5.46) for the self-energy is similar to that found in conventional perturbation treatment. There one finds that a phonon, to lowest anharmonic order, decays into two other phonons, giving both a damping and a frequency shift. The corresponding contribution to the self-energy is conventionally represented by the diagram in Fig. 1. The explicit expression for it is

$$M_{kl}^{(2)}(\mathbf{q},\omega)=\frac{i\hbar}{2M}\int\frac{d\mathbf{q}'}{v}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}$$
$$\times\Phi_{kmm'}(\tfrac{1}{2}\mathbf{q}-\mathbf{q}',\,-\mathbf{q},\,\tfrac{1}{2}\mathbf{q}+\mathbf{q}')$$
$$\times\{D_{mn}{}^{\mathcal{T}}(\mathbf{q}'+\tfrac{1}{2}\mathbf{q},\,\omega'+\tfrac{1}{2}\omega)D_{n'm'}{}^{\mathcal{T}}(\mathbf{q}'-\tfrac{1}{2}\mathbf{q},\,\omega'-\tfrac{1}{2}\omega)$$
$$-D_{mn}{}^{<}(\mathbf{q}'+\tfrac{1}{2}\mathbf{q},\,\omega'+\tfrac{1}{2}\omega)D_{n'm'}{}^{>}(\mathbf{q}'-\tfrac{1}{2}\mathbf{q},\,\omega'-\tfrac{1}{2}\omega)\}$$
$$\times[\Phi_{n'nl}(\tfrac{1}{2}\mathbf{q}-\mathbf{q}',\,-\mathbf{q},\,\tfrac{1}{2}\mathbf{q}+\mathbf{q}')]^{*},\quad(5.48)$$

where

$$\Phi_{kmm'}(\tfrac{1}{2}\mathbf{q}-\mathbf{q}',\,-\mathbf{q},\,\tfrac{1}{2}\mathbf{q}+\mathbf{q}')=-\{V_{kmm'}(\tfrac{1}{2}\mathbf{q}-\mathbf{q}')+V_{kmm'}(-\mathbf{q})+V_{kmm'}(\tfrac{1}{2}\mathbf{q}+\mathbf{q}')\}\quad(5.49)$$

with

$$V_{kmm'}(\mathbf{q})=\sum_{\mathbf{R}\neq 0}e^{-i\mathbf{q}\cdot\mathbf{R}}\nabla^{3}{}_{kmm'}V(\mathbf{R}).\quad(5.50)$$

If we omit the second term within the curly bracket in Eq. (5.48), then we have the time-ordered self-energy, and this expression agrees with that obtained by Maradudin and Fein.[15] The result in the form given in Eq. (5.48) can be found in a paper by Niklasson.[19]

For the purpose of comparison we also write Eq. (5.48) in space and time variables as follows:

$$M_{kl}^{(2)}(\mathbf{R}-\mathbf{R}',\,t-t')$$
$$=(-i\hbar/2M)\sum_{\mathbf{R}_1,\mathbf{R}_2}\sum_{\mathbf{R}_1',\mathbf{R}_2'}\Phi_{kmm'}(\mathbf{R},\mathbf{R}_1,\mathbf{R}_1')$$
$$\times\{D_{mn}{}^{\mathcal{T}}(\mathbf{R}_1-\mathbf{R}_2,\,t-t')D_{n'm'}{}^{\mathcal{T}}(\mathbf{R}_2'-\mathbf{R}_1',\,t'-t)$$
$$-D_{mn}{}^{<}(\mathbf{R}_1-\mathbf{R}_2,\,t-t')D_{n'm'}{}^{>}(\mathbf{R}_2'-\mathbf{R}_1',\,t'-t)\}$$
$$\times\Phi_{n'nl}(\mathbf{R}_2',\mathbf{R}_1',\mathbf{R}'),\quad(5.51)$$

where

$$\Phi_{kmm'}(\mathbf{R},\mathbf{R}_1,\mathbf{R}_1')=\sum_{\mathbf{R}'}\nabla^{3}{}_{kmm'}V(\mathbf{R}-\mathbf{R}')\times[\delta_{\mathbf{R}\mathbf{R}_1}-\delta_{\mathbf{R}'\mathbf{R}_1}][\delta_{\mathbf{R}\mathbf{R}_1'}-\delta_{\mathbf{R}'\mathbf{R}_1'}].\quad(5.52)$$

Comparing Eqs. (5.46) and (5.48), we see that both expressions have the same structure and they both represent a process where one phonon splits into two phonons, conserving the frequency and the wave vector (modulo a reciprocal-lattice vector). In the SCF approximation the third-order anharmonic force constants $\tilde{T}_{kmm'}(\mathbf{q})$ contain an averaging over the atomic displacements, and, therefore, they include certain anharmonic corrections which are neglected in the lowest-order perturbation results. On the other hand, the SCF approximation leaves out certain terms which certainly are of importance in an actual quantitative calculation. This is obvious from comparing Eqs. (5.42) and (5.51). If in the latter equation we omit terms with $\mathbf{R}_1\neq\mathbf{R}_1'$, $\mathbf{R}_2\neq\mathbf{R}_2'$, we recover Eq. (5.42) with the renormalized third-order force constants replaced by the bare ones. In the diagrammatic language, it means that we are in the SCF approximation replacing the three-point vertices in Fig. 1 by two-point vertices, depending only on the lattice positions of two atoms. In $(\mathbf{q}\omega)$ variables it implies omitting the first and the third terms in Eq. (5.49).

We notice that the third-order force constants in Eqs. (5.47) and (5.49) both vanish linearly with $\mathbf{q}$ as $\mathbf{q}\to 0$, but those in Eq. (5.47) have an incorrect coefficient of this linear term due to the neglect of the terms mentioned above. We believe that the SCF approximation gives qualitatively and also semiquantitatively the correct damping and frequency shift for most of the phonons. We stress again that the ordinary fourth-order frequency shift is included in the renormalized harmonic-force constants.

VI. CONCLUDING REMARKS

We wish here to make some general remarks on the SCF method.

We have shown in this paper that by treating the basic equation of motion in space and time variables and by limiting ourselves to certain types of fluctuations, it is possible to give a straightforward discussion of lattice dynamics including anharmonic effects. It seems to us that the SCF method possesses sufficient simplicity and flexibility to allow other kinds of fluctuations to be included, e.g., diffusion of particles and presence of vacancies and interstitials. We stress, however, that the approximations going into the SCF equations prohibit obtaining quantitatively accurate results. An example of this limitation was pointed out at the end of Sec. V.

As it is presently formulated, the SCF method is also incapable of handling interparticle potentials which have a very singular short-range repulsive part. Therefore in order to apply the method to systems of actual interest, the interparticle potential must be replaced with some effective interaction. This has been done in numerical calculations,[20,21] but so far this problem has not been thoroughly investigated.

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APPENDIX A

From the definition of $\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')$ in Eq. (3.3) and from Eq. (3.6) we find that

$$\int d\mathbf{x}'\,\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')\mathbf{x}'=(i\hbar)^{-1}\theta(t-t')\times\langle[\rho_{\mathbf{R}}(\mathbf{x},t),\mathbf{u}(\mathbf{R}',t')]\rangle,\quad \text{(A1)}$$

and similarly

$$\int d\mathbf{x}\,\mathbf{x}\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')=(i\hbar)^{-1}\theta(t-t')\times\langle[\mathbf{u}(\mathbf{R},t),\rho_{\mathbf{R}'}(\mathbf{x}',t')]\rangle.\quad \text{(A2)}$$

In order to clarify the physical meaning of these response functions we consider a weak time-dependent external disturbance acting on the system. We introduce formally this disturbance through a term $H_1=BF(t)$ in the Hamiltonian of the system. $F(t)$ is an external force in a generalized sense, and B is a dynamical variable which can depend on the positions and velocities of all the particles. Linear-response theory[22] then tells us that the change of the mean value of any dynamical variable A is given by the expression

$$\delta\langle A(t)\rangle=(i\hbar)^{-1}\int_{-\infty}^{\infty}dt'\,\theta(t-t')\times\langle[A(t),B(t')]\rangle_0F(t').\quad \text{(A3)}$$

The averaged commutator is evaluated with no external disturbance present, indicated by the subscript zero. Then, by definition,

$$\delta\langle A(t)\rangle/\delta F(t')=(i\hbar)^{-1}\theta(t-t')\langle[A(t),B(t')]\rangle_0,\quad \text{(A4)}$$

implying here that the functional derivative is evaluated for zero disturbance.

As a special case, we consider

$$H_1=-\mathbf{u}(\mathbf{R}')\cdot\mathbf{J}(\mathbf{R}',t'),\quad \text{(A5)}$$

where $\mathbf{J}(\mathbf{R}',t')$ is an external force acting on the $\mathbf{R}'$th atom, and

$$A=\rho_{\mathbf{R}}(\mathbf{x}).\quad \text{(A6)}$$

Then, applying Eq. (A4) in Eq. (A1), we have

$$\int d\mathbf{x}'\,\chi_{\mathbf{R}-\mathbf{R}'}(\mathbf{x}t;\mathbf{x}'t')\mathbf{x}'=-\delta\langle\rho_{\mathbf{R}}(\mathbf{x},t)\rangle/\delta\mathbf{J}(\mathbf{R}',t').\quad \text{(A7)}$$

Similarly, if we choose

$$A=\mathbf{u}(\mathbf{R}),\quad \text{(A8)}$$

we have

$$\mathbf{D}(\mathbf{R}-\mathbf{R}',t-t')=\delta\langle\mathbf{u}(\mathbf{R},t)\rangle/\delta\mathbf{J}(\mathbf{R}',t')\quad \text{(A9)}$$

[cf. definition in Eq. (3.8)]. Equation (3.13) in the main text is now easily obtained, using Eqs. (A7) and (A9) together with Eq. (3.12).

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The response function in Eq. (A2) is in a similar way shown to give the response of $\langle\mathbf{u}(\mathbf{R},t)\rangle$ to an external potential $V_{\mathbf{R}'}{}^{\text{ext}}(\mathbf{x}',t')$.

APPENDIX B

We shall here employ the well-known relation between the time Fourier transform of an equilibrium retarded response function and the Fourier transform of the corresponding averaged commutator,

$$\mathfrak{F}\{\theta(t-t')\langle[\rho_{\mathbf{R}}(\mathbf{x},t),\mathbf{u}(\mathbf{R},t')]\rangle\}_\omega=\frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega-i0^+}\times\mathfrak{F}\{\langle[\rho_{\mathbf{R}}(\mathbf{x},t),\mathbf{u}(\mathbf{R},t')]\rangle\}_{\omega},\quad \text{(B1)}$$

and similarly

$$\mathfrak{F}\{\theta(t-t')\langle[\mathbf{u}(\mathbf{R},t),\rho_{\mathbf{R}}(\mathbf{x},t')]\rangle\}_\omega=\frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega-i0^+}\times\mathfrak{F}\{\langle[\mathbf{u}(\mathbf{R},t),\rho_{\mathbf{R}}(\mathbf{x},t')]\rangle\}_{\omega}.\quad \text{(B2)}$$

$\mathfrak{F}\{\cdots\}_\omega$ denotes the time Fourier transform of the function within the curly bracket. The averaged commutators above are odd functions of $(t-t')$. This is easily shown by writing the explicit expressions for these averages in terms of the eigenfunctions of the Hamiltonian, and using the fact that these eigenfunctions can be chosen real. It then follows that the two integrals in Eqs. (B1) and (B2) are equal. Hence we conclude from Eqs. (A1) and (A2) in Appendix A, replacing there $\chi_{\mathbf{R}-\mathbf{R}'}$ by $\chi^{(0)}$, that

$$\int d\mathbf{x}''\,\mathbf{x}''\chi^{(0)}(\mathbf{x}''t;\mathbf{x}'t')=\int d\mathbf{x}''\,\chi^{(0)}(\mathbf{x}'t;\mathbf{x}''t')\mathbf{x}''.\quad \text{(B3)}$$

APPENDIX C

To verify the statement in Eq. (4.15) we first show that

$$\hbar^{-1}M\sum_{\alpha,\beta}\langle\alpha|\mathbf{x}|\beta\rangle(-\omega_{\beta\alpha}f_{\beta\alpha})\langle\alpha|\mathbf{x}|\beta\rangle=\mathbf{I}.\quad \text{(C1)}$$

Introducing $(f_\beta-f_\alpha)$ for $f_{\beta\alpha}$ and using the real-valuedness of the Hartree wave functions, the left-hand side of (C1) can be written

$$-\hbar^{-1}M\sum_{\alpha,\beta}f_\alpha[\omega_{\alpha\beta}\langle\alpha|\mathbf{x}|\beta\rangle\langle\beta|\mathbf{x}|\alpha\rangle-\langle\alpha|\mathbf{x}|\beta\rangle\omega_{\beta\alpha}\langle\beta|\mathbf{x}|\alpha\rangle].\quad \text{(C2)}$$

Using the relation [see Eq. (38) of FW]

$$\omega_{\alpha\beta}\langle\alpha|\mathbf{x}|\beta\rangle=-\hbar M^{-1}\langle\alpha|\nabla|\beta\rangle\quad \text{(C3)}$$

and the identity $\sum_\beta|\beta\rangle\langle\beta|=1$ to perform the summation over the β states, Eq. (C2) becomes

$$\sum_\alpha f_\alpha\langle\alpha|[\nabla,\mathbf{x}]|\alpha\rangle=\mathbf{I}.\quad \text{(C4)}$$

Going back to Eq. (4.14) and using Eq. (4.15) for $U_{\alpha\beta,\nu}$, $\nu=1, 2, 3$, we now have

$$\sum_{\alpha,\beta} \langle\alpha|\mathbf{x}|\beta\rangle(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2}U_{\alpha\beta,\nu}=\hbar^{-1/2}M^{1/2}\sum_{\alpha,\beta}\langle\alpha|\mathbf{x}|\beta\rangle \times(-\omega_{\beta\alpha}f_{\beta\alpha})\langle\alpha|\mathbf{x}|\beta\rangle\cdot\mathbf{e}_{\mathbf{q}\nu}=\hbar^{1/2}M^{-1/2}\mathbf{e}_{\mathbf{q}\nu}. \quad \text{(C5)}$$

This verifies the statement after Eq. (4.14) for $\nu=1, 2, 3$.

To prove the statement for $\nu>3$, we write

$$\mathbf{x}=\sum_{\lambda=1}^{3}(\mathbf{e}_{\mathbf{q}\lambda}\cdot\mathbf{x})\mathbf{e}_{\mathbf{q}\lambda},$$

and then

$$\sum_{\alpha,\beta}(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2}\langle\alpha|\mathbf{x}|\beta\rangle U_{\alpha\beta,\nu} =\sum_{\lambda=1}^{3}\mathbf{e}_{\mathbf{q}\lambda}\{\sum_{\alpha,\beta}(-\omega_{\beta\alpha}f_{\beta\alpha})^{1/2}\langle\alpha|\mathbf{e}_{\mathbf{q}\lambda}\cdot\mathbf{x}|\beta\rangle U_{\alpha\beta,\nu}\} =\hbar^{1/2}\sum_{\lambda=1}^{3}\mathbf{e}_{\mathbf{q}\lambda}M^{-1/2}\{\sum_{\alpha,\beta}U_{\alpha\beta,\lambda}U_{\alpha\beta,\nu}\}=0. \quad \text{(C6)}$$

The last equality follows from the orthogonality of the vectors $U_{\alpha\beta,\nu}$. This concludes the proof of the statement in Eq. (4.15).

APPENDIX D

Using the same procedure as in Appendix B, we can write

$$[\mathbf{D}_{12}(\mathbf{q},\omega)]_{i,jm} =\mathfrak{F}\{\theta(t-t')\langle[u_i(\mathbf{R},t),u_j(\mathbf{R}',t')u_m(\mathbf{R}',t')]\rangle\}_{\mathbf{q}\omega} =\frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega-i0^+} \times\mathfrak{F}\{\langle[u_i(\mathbf{R},t),u_j(\mathbf{R}',t')u_m(\mathbf{R}',t')]\rangle\}_{\mathbf{q}\omega}, \quad \text{(D1)}$$

and similarly

$$[\mathbf{D}_{21}(\mathbf{q},\omega)]_{jm,i} =\mathfrak{F}\{\theta(t-t')\langle[u_j(\mathbf{R},t)u_m(\mathbf{R},t),u_i(\mathbf{R}',t')]\rangle\}_{\mathbf{q}\omega} =\frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega-i0^+} \times\mathfrak{F}\{\langle[u_j(\mathbf{R},t)u_m(\mathbf{R},t),u_i(\mathbf{R}',t')]\rangle\}_{\mathbf{q}\omega}, \quad \text{(D2)}$$

where $\mathfrak{F}\{\cdots\}_{\mathbf{q}\omega}$ denotes the Fourier transform with respect to $\mathbf{R}-\mathbf{R}'$ and $t-t'$ of the function within the curly bracket.

Since the averaged commutator is an even function of $\mathbf{R}-\mathbf{R}'$ and an odd function of $t-t'$, it follows that the two integrals are equal (see Appendix B). Hence Eq. (5.36) follows.

APPENDIX E

In this appendix we give the detailed derivation of Eq. (5.37) of the main text. We start from Eq. (5.34) and split it into its four matrix components and write these in terms of the submatrices in Eqs. (5.3) and (5.28). As explained in Sec. V, we set here $\mathbf{T}_{22}(\mathbf{q})=0$. The two equations coming from the upper row of Eq. (5.34) are then

$$\mathbf{D}_{11}-\mathbf{D}_{11}^{(0)}[\mathbf{T}_{11}\mathbf{D}_{11}+\mathbf{T}_{12}\mathbf{D}_{21}]-\mathbf{D}_{12}^{(0)}\mathbf{T}_{21}\mathbf{D}_{11}=\mathbf{D}_{11}^{(0)} \quad \text{(E1)}$$

and

$$\mathbf{D}_{12}-\mathbf{D}_{11}^{(0)}[\mathbf{T}_{11}\mathbf{D}_{12}+\mathbf{T}_{12}\mathbf{D}_{22}]-\mathbf{D}_{12}^{(0)}\mathbf{T}_{21}\mathbf{D}_{12}=\mathbf{D}_{12}^{(0)}, \quad \text{(E2)}$$

where the arguments $\mathbf{q}$ and ω have been omitted for brevity.

We multiply the above equations by the inverse of $\mathbf{D}_{11}^{(0)}$ and write the resultant equations as

$$\{[\mathbf{D}_{11}^{(0)}]^{-1}-\mathbf{T}_{11}-[\mathbf{D}_{11}^{(0)}]^{-1}\mathbf{D}_{12}^{(0)}\mathbf{T}_{21}\}\mathbf{D}_{11}-\mathbf{T}_{12}\mathbf{D}_{21}=\mathbf{I}, \quad \text{(E3)}$$

$$\{[\mathbf{D}_{11}^{(0)}]^{-1}-\mathbf{T}_{11}-[\mathbf{D}_{11}^{(0)}]^{-1}\mathbf{D}_{12}^{(0)}\mathbf{T}_{21}\}\mathbf{D}_{12}=\mathbf{T}_{12}\mathbf{D}_{22}+[\mathbf{D}_{11}^{(0)}]^{-1}\mathbf{D}_{12}^{(0)}. \quad \text{(E4)}$$

We notice that the quantities inside the curly brackets are the same in both equations, and we can use Eq. (E3) to eliminate the curly bracket in Eq. (E4). This gives

$$[\mathbf{I}+\mathbf{T}_{12}\mathbf{D}_{21}][\mathbf{D}_{11}]^{-1}\mathbf{D}_{12}=\mathbf{T}_{12}\mathbf{D}_{22}+[\mathbf{D}_{11}^{(0)}]^{-1}\mathbf{D}_{12}^{(0)} \quad \text{(E5)}$$

and

$$\mathbf{D}_{12}=\mathbf{D}_{11}[\mathbf{I}+\mathbf{T}_{12}\mathbf{D}_{21}]^{-1}\times\{\mathbf{T}_{12}\mathbf{D}_{22}+[\mathbf{D}_{11}^{(0)}]^{-1}\mathbf{D}_{12}^{(0)}\}. \quad \text{(E6)}$$

Further noting that $\mathbf{D}_{21}$ is the transpose of $\mathbf{D}_{12}$ (see Appendix D) we have

$$\mathbf{D}_{21}=\{\mathbf{D}_{22}\mathbf{T}_{21}+\mathbf{D}_{21}^{(0)}[\mathbf{D}_{11}^{(0)}]^{-1}\}\times[\mathbf{I}+\mathbf{D}_{12}\mathbf{T}_{21}]^{-1}\mathbf{D}_{11}. \quad \text{(E7)}$$

We now substitute this for $\mathbf{D}_{21}$ in Eq. (E3), and we obtain then the final equation for the matrix $\mathbf{D}_{11}$:

$$\{[\mathbf{D}_{11}^{(0)}]^{-1}-\mathbf{T}_{11}-[\mathbf{D}_{11}^{(0)}]^{-1}\mathbf{D}_{12}^{(0)}\mathbf{T}_{21}-\mathbf{T}_{12}\mathbf{D}_{22}\mathbf{T}_{21}[\mathbf{I}+\mathbf{D}_{12}\mathbf{T}_{21}]^{-1}-\mathbf{T}_{12}\mathbf{D}_{21}^{(0)}[\mathbf{D}_{11}^{(0)}]^{-1}\times[\mathbf{I}+\mathbf{D}_{12}\mathbf{T}_{21}]^{-1}\}\mathbf{D}_{11}=\mathbf{I}. \quad \text{(E8)}$$

APPENDIX F

From the definition in Eq. (5.7) we have

$$[\mathbf{D}_{22}(\mathbf{R}-\mathbf{R}', t-t')]_{mm',nn'}=-(i\hbar)^{-1}\theta(t-t')\times\langle[u_m(\mathbf{R},t)u_{m'}(\mathbf{R},t),u_n(\mathbf{R}',t')u_{n'}(\mathbf{R}',t')]\rangle. \quad \text{(F1)}$$

Within the approximation in Sec. III the individual phonon modes are statistically uncorrelated to each other, and we can express $\mathbf{u}(\mathbf{R},t)$ as a superposition of individual phonon contributions, writing concisely

$$\mathbf{u}(\mathbf{R},t)=N^{-1/2}\sum_{s} \boldsymbol{\xi}^s(\mathbf{R},t)\,, \tag{F2}$$

where the index s refers to a particular phonon mode. N is the total number of atoms in the crystal, and by the way of writing we indicate that each phonon contribution is of order $N^{-1/2}$.

We insert Eq. (F2) into Eq. (F1) and make use of the fact that $\langle\boldsymbol{\xi}^s(\mathbf{R},t)\boldsymbol{\xi}^{s'}(\mathbf{R}',t')\rangle=0$ for $s\neq s'$ and that N is essentially infinite. This leads to

$$\begin{aligned}[\mathbf{D}_{22}(\mathbf{R}-\mathbf{R}',\, t-t')]_{mm',nn'} =& -(i\hbar)^{-1}\theta(t-t')N^{-2}\sum_{s,s'}\{\langle\xi_m{}^s(\mathbf{R},t)\xi_n{}^s(\mathbf{R}',t')\rangle\\
&\times\langle\xi_{m'}{}^{s'}(\mathbf{R},t)\xi_{n'}{}^{s'}(\mathbf{R}',t')\rangle+\langle\xi_m{}^s(\mathbf{R},t)\xi_{n'}{}^s(\mathbf{R}',t')\rangle\langle\xi_{m'}{}^{s'}(\mathbf{R},t)\xi_n{}^{s'}(\mathbf{R}',t')\rangle-\langle\xi_n{}^s(\mathbf{R}',t')\xi_m{}^s(\mathbf{R},t)\rangle\\
&\times\langle\xi_{n'}{}^{s'}(\mathbf{R}',t')\xi_{m'}{}^{s'}(\mathbf{R},t)\rangle-\langle\xi_{n'}{}^s(\mathbf{R}',t')\xi_m{}^s(\mathbf{R},t)\rangle\langle\xi_n{}^{s'}(\mathbf{R}',t')\xi_{m'}{}^{s'}(\mathbf{R},t)\rangle\} = -(i\hbar)^{-1}\theta(t-t')\{\langle u_m(\mathbf{R},t)u_n(\mathbf{R}',t')\rangle\\
&\times\langle u_{m'}(\mathbf{R},t)u_{n'}(\mathbf{R}',t')\rangle+\langle u_m(\mathbf{R},t)u_{n'}(\mathbf{R}',t')\rangle\langle u_{m'}(\mathbf{R},t)u_n(\mathbf{R}',t')\rangle-\langle u_n(\mathbf{R}',t')u_m(\mathbf{R},t)\rangle\langle u_{n'}(\mathbf{R}',t')u_{m'}(\mathbf{R},t)\rangle\\
&-\langle u_{n'}(\mathbf{R}',t')u_m(\mathbf{R},t)\rangle\langle u_n(\mathbf{R}',t')u_{m'}(\mathbf{R},t)\rangle\}\,.\end{aligned} \tag{F3}$$

Here we have neglected higher-order terms in $1/N$.

Before we insert this into Eq. (5.41), we write the second part of the self-energy in space and time variables:

$$\begin{aligned}M_{kl}{}^{(2)}(\mathbf{R}-\mathbf{R}',\, t-t')=&(4M)^{-1}\sum_{\mathbf{R}_1,\mathbf{R}_2}\langle\nabla^3{}_{kmm'}V(\mathbf{R}-\mathbf{R}_1)\rangle_0\\
&\times[\mathbf{D}_{22}(\mathbf{R}_1-\mathbf{R}_2,\, t-t')]_{mm',nn'}\\
&\times\langle\nabla^3{}_{n'nl}V(\mathbf{R}_2-\mathbf{R}')\rangle_0\,.\end{aligned} \tag{F4}$$

Here we have used the expressions in Eqs. (5.30) and (5.31) for $\mathbf{T}_{12}$ and $\mathbf{T}_{21}$. Repeated subscripts are to be summed over. The first and second terms of Eq. (F3) give equal contributions when inserted in Eq. (F4) and similarly for the third and fourth terms. Thus we get

$$\begin{aligned}M_{kl}{}^{(2)}&(\mathbf{R}-\mathbf{R}',\, t-t')\\
&=-(2i\hbar M)^{-1}\theta(t-t')\sum_{\mathbf{R}_1,\mathbf{R}_2}\langle\nabla^3{}_{kmm'}V(\mathbf{R}-\mathbf{R}_1)\rangle_0\\
&\times\{\langle u_m(\mathbf{R}_1,t)u_n(\mathbf{R}_2,t')\rangle\langle u_{m'}(\mathbf{R}_1,t)u_{n'}(\mathbf{R}_2,t')\rangle\\
&-\langle u_n(\mathbf{R}_2,t')u_m(\mathbf{R}_1,t)\rangle\langle u_{n'}(\mathbf{R}_2,t')u_{m'}(\mathbf{R}_1,t)\rangle\}\\
&\times\langle\nabla^3{}_{n'nl}V(\mathbf{R}_2-\mathbf{R}')\rangle_0\,.\end{aligned} \tag{F5}$$

In order to bring this expression into a more familiar form, we introduce the quantities defined in Eqs. (5.43)–(5.45) of the main text. We first consider the terms inside the curly bracket in Eq. (F5), and we see that for $t>t'$

$$\begin{aligned}\{\cdots\}=&(-i\hbar)^2[D_{mn}{}^{>}(\mathbf{R}_1-\mathbf{R}_2,\, t-t')\\
&\times D_{n'm'}{}^{<}(\mathbf{R}_2-\mathbf{R}_1,\, t'-t)-D_{mn}{}^{<}(\mathbf{R}_1-\mathbf{R}_2,\, t-t')\\
&\times D_{n'm'}{}^{>}(\mathbf{R}_2-\mathbf{R}_1,\, t'-t)]\,.\end{aligned} \tag{F6}$$

We notice that the retarded self-energy in Eq. (F5) vanishes for $t<t'$. By writing the curly bracket as

$$\begin{aligned}\{\cdots\}=&(-i\hbar)^2[D_{mn}{}^{\mathcal{T}}(\mathbf{R}_1-\mathbf{R}_2,\, t-t')\\
&\times D_{n'm'}{}^{\mathcal{T}}(\mathbf{R}_2-\mathbf{R}_1,\, t'-t)-D_{mn}{}^{<}(\mathbf{R}_1-\mathbf{R}_2,\, t-t')\\
&\times D_{n'm'}{}^{>}(\mathbf{R}_2-\mathbf{R}_1,\, t'-t)]\,,\end{aligned} \tag{F7}$$

it agrees with Eq. (F6) for $t>t'$. The quantity on the right-hand side vanishes for $t<t'$, so that we can actually replace $\theta(t-t')\{\cdots\}$ in Eq. (F5) by the expression in Eq. (F7). We then have

$$\begin{aligned}M_{kl}{}^{(2)}&(\mathbf{R}-\mathbf{R}',\, t-t')\\
&=(-i\hbar/2M)\sum_{\mathbf{R}_1,\mathbf{R}_2}\langle\nabla^3{}_{kmm'}V(\mathbf{R}-\mathbf{R}_1)\rangle_0\\
&\times\{D_{mn}{}^{\mathcal{T}}(\mathbf{R}_1-\mathbf{R}_2,\, t-t')D_{n'm'}{}^{\mathcal{T}}(\mathbf{R}_2-\mathbf{R}_1,\, t'-t)\\
&-D_{mn}{}^{<}(\mathbf{R}_1-\mathbf{R}_2,\, t-t')D_{n'm'}{}^{>}(\mathbf{R}_2-\mathbf{R}_1,\, t'-t)\}\\
&\times\langle\nabla^3{}_{n'nl}V(\mathbf{R}_2-\mathbf{R}')\rangle_0\,.\end{aligned} \tag{F8}$$