from the zero of ϵ_1 as much as it does at room temperature. Hence there is no net change in the energy location of the ELF peak for this alloy. For the remaining alloys there is a shift to lower energy of the zero of ϵ_1 as well as an increase in ϵ_2 near the plasma energy; both of these tend to shift the ELF peak to a lower energy.

APPENDIX

We attempt to assess the accuracy of our measurements. We estimate that the reflectance R can be measured to $2\frac{1}{2}\%$ at room temperature and $3\frac{1}{2}\%$ at 4.4°K, while transmittance T errors are $3\frac{1}{2}$ and 4%, respectively, over the central one-half of our wavelength range. These errors are expected to be systematic and should be nearly the same at all wavelengths for any one film. Calculations were made of the changes in R and T produced by changes in n and k. From these we conclude that the largest single error in k arises from the $2\frac{1}{2}\%$ error in d, the film thickness. This error is constant for any one film and may even be about the same for all films. The errors in d and T make k accurate to about $4\frac{1}{2}\%$. (The observed maximum deviation of a value of k at any wavelength from the average for 10 Ag films was 6%.) The calculations show that the relative error in n is approximately 10 times the relative error in R over the central half of our wavelength range. Thus n should be uncertain to about 25%, but the maximum single deviation from the average for nine Ag films was 10% for photon energies below 4.0 eV. The errors in n diminish upon alloying and for the 4.2%-In alloy, the relative errors in R and n are about equal. The actual systematic errors may not have been as large as predicted because our results agree well with those of Ref. 38, measured by quite a different technique. Above 4.0 eV the accuracy suffers greatly because of the form of the equations for n and k in terms of R and T. Of 10 Ag films, only one, that used for Fig. 1, gave data above 4.0 eV in agreement with those of Ref. 39. Hence the data on alloys can be trusted only below about 4 eV.

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A Quantum Dissipation Theory of Anharmonic Crystals

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A quantum-mechanical dissipation theory is applied to the problem of anharmonic vibrations of a crystal. Equations for the anharmonic phonon creation and annihilation operators are obtained, from which may be extracted damping-constant and frequency-shift expressions. These are compared with the results of other techniques.

I. INTRODUCTION

It is the purpose of this paper to demonstrate the application of a formal quantum-mechanical dissipation theory for the harmonic oscillator[1] to the problem of the anharmonic crystal. Anharmonicity has received direct attention from many authors[2–12] employing many different techniques. However, to approach it from a dissipation theory viewpoint utilizes the attractive concept of a phonon undergoing decay as it interacts with, and loses energy to, other phonons.

The final equation of motion, which is derived in Sec. II [Eq. (2.44)], shows that in addition to damping there also exists a driving force which restores energy to the mode. As suggested by Senitzky[1] the source of this compensating effect is quantum-mechanical fluctuations without which dissipation may not properly (quantum mechanically) be treated. Just as in classical dissipation problems, the driving forces are not considered when deducing damping properties of the system; and if the aim of this paper is to calculate only these, then concern for the fluctuations is pedantic. But in Sec. III it is shown that their inclusion leads to correct commutation relations for the phonon creation and annihilation operators. The derivations of Sec. II depend on such commutation relations and therefore consideration of fluctuations is essential for consistency.

The application Senitzky envisaged was a radiation field in a microwave cavity. Consequently, although

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its loss mechanism was unspecified, his theory when applied to the anharmonic crystal Hamiltonian requires certain modifications of them both. The alteration to the crystal Hamiltonian constitutes an approximation in that certain classes of terms are neglected, and this will be referred to in a later section. The basis of Senitzky's theory is the Hamiltonian

$$H=H_{\text{osc}}+H_{\text{loss}}+\alpha P\Gamma, \tag{1.1}$$

where the operators P and Γ refer to the oscillator and loss-mechanism, respectively. The self-adjointness of Γ is a property employed in the derivation of the equation [Ref. 1, Eq. (21)]. Use of the slightly different form,

$$H=H_{\text{osc}}+H_{\text{loss}}+aX+a^\dagger X^\dagger, \tag{1.2}$$

in this treatment introduces a complication because the X and $X^\dagger$, which incorporate coupling coefficients, are not self-adjoint.

As a further simplification of the crystal Hamiltonian normally used, the fourth-order anharmonic terms (four-operator products) will not be considered. Their inclusion only increases the bookkeeping and adds nothing to the underlying theme which is to apply the loss-mechanism concept to anharmonicity.

In Sec. II, equations of motion for operators of the anharmonic phonon are deduced and solved. The commutation properties of these operators are investigated in Sec. III, and Kramers-Kronig relations between damping-constant and frequency-shift expressions are presented in Sec. IV. Section V is an attempt to display the theory and results of this paper in perspective with the work of others in both anharmonic crystal and dissipation fields.

II. COMPLEX DAMPING CONSTANT

The Hamiltonian of the anharmonic crystal is

$$H=\sum_{\mathbf{k},j}\hbar\omega_{\mathbf{k}j}a_{\mathbf{k}j}{}^\dagger a_{\mathbf{k}j}+\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}V(\mathbf{k}_1j_1,\mathbf{k}_2j_2,\mathbf{k}_3j_3)$$
$$\times(a_{-\mathbf{k}_1j_1}{}^\dagger+a_{\mathbf{k}_1j_1})(a_{-\mathbf{k}_2j_2}{}^\dagger+a_{\mathbf{k}_2j_2})(a_{-\mathbf{k}_3j_3}{}^\dagger+a_{\mathbf{k}_3j_3}). \tag{2.1}$$

Anharmonic terms of order higher than third have been omitted as well as the zero-point energy.

Selecting those parts of H which represent (i) a given mode (oscillator), (ii) all other modes (loss mechanism reservoir of oscillators), and (iii) the interaction of (i) with (ii) (coupling), a reduced Hamiltonian may be defined as

$$H_{\text{red}}=H_{\text{osc}}+H_l+H_{\text{int}}=\hbar\omega_{\mathbf{k}j}a_{\mathbf{k}j}{}^\dagger a_{\mathbf{k}j}$$
$$+\sum_{\mathbf{k}_1,j_1}\hbar\omega_{\mathbf{k}_1j_1}a_{\mathbf{k}_1j_1}{}^\dagger a_{\mathbf{k}_1j_1}+a_{\mathbf{k}j}X_{\mathbf{k}j}+a_{\mathbf{k}j}{}^\dagger X_{\mathbf{k}j}{}^\dagger. \tag{2.2}$$

In this equation, $X_{\mathbf{k}j}$ is given by

$$X_{\mathbf{k}j}=3\sum_{\mathbf{k}_1\mathbf{k}_2}{}'\sum_{j_1j_2}{}'[V(\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)a_{\mathbf{k}_1j_1}a_{\mathbf{k}_2j_2}$$
$$+V(\mathbf{k}j,\mathbf{k}_1j_1,-\mathbf{k}_2j_2)a_{\mathbf{k}_1j_1}a_{\mathbf{k}_2j_2}{}^\dagger$$
$$+V(\mathbf{k}j,-\mathbf{k}_1j_1,\mathbf{k}_2j_2)a_{\mathbf{k}_1j_1}{}^\dagger a_{\mathbf{k}_2j_2}$$
$$+V(\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_2j_2)a_{\mathbf{k}_1j_1}{}^\dagger a_{\mathbf{k}_2j_2}{}^\dagger], \tag{2.3}$$

where the prime signifies the exclusion of $(\mathbf{k},j)$ from the summations over $(\mathbf{k}_ij_i)$. The anharmonic terms neglected are those (a) containing neither $a_{\mathbf{k}j}$ nor $a_{\mathbf{k}j}{}^\dagger$; (b) containing either $a_{\mathbf{k}j}$ and $a_{\mathbf{k}j}{}^\dagger$ together, or each more than once. A similar reduced Hamiltonian was used for the $\mathbf{k}=0$ transverse optic mode in the optical absorption theory of Born and Huang[2] and also of Maradudin and Wallis.[3] The latter pair of authors qualitatively justify the approximation but in a later paper[5] comment on its rather arbitrary nature and employ the full Hamiltonian.

It is convenient at this stage to introduce the harmonic-oscillator counterparts to the operators already mentioned; that is, the operators characteristic of an uncoupled oscillator/loss mechanism system. They are

$$\begin{aligned} a_{\mathbf{k}j}{}^0(t)&=a_{\mathbf{k}j}{}^0(0)\exp(-i\omega_{\mathbf{k}j}t),\\ a_{\mathbf{k}j}{}^{0\dagger}(t)&=a_{\mathbf{k}j}{}^{0\dagger}(0)\exp(i\omega_{\mathbf{k}j}t),\end{aligned} \tag{2.4}$$

and their dependents are

$$X_l{}^0(t),\quad X_l{}^{0\dagger}(t),\quad H_l{}^0(t). \tag{2.5}$$

By specifying that the interaction commences at $t=0$, the following identities hold:

$$\begin{aligned} &a_{\mathbf{k}j}(0)\equiv a_{\mathbf{k}j}{}^0(0),\qquad a_{\mathbf{k}j}{}^\dagger(0)\equiv a_{\mathbf{k}j}{}^{0\dagger}(0),\\ &X_{\mathbf{k}j}(0)\equiv X_{\mathbf{k}j}{}^0(0),\quad X_{\mathbf{k}j}{}^\dagger(0)\equiv X_{\mathbf{k}j}{}^{0\dagger}(0),\\ &H_l(0)\equiv H_l{}^0(0)=H_l{}^0,\quad \text{say.}\end{aligned} \tag{2.6}$$

The reduced Hamiltonian provides the starting point for an analysis based on Senitzky's quantum dissipation formalism.

It may be deduced from Eq. (2.2) that

$$i\dot{a}_{\mathbf{k}j}=\omega_{\mathbf{k}j}a_{\mathbf{k}j}+X_{\mathbf{k}j}{}^\dagger, \tag{2.7}$$

$$i\dot{a}_{\mathbf{k}j}{}^\dagger=-\omega_{\mathbf{k}j}a_{\mathbf{k}j}{}^\dagger-X_{\mathbf{k}j}, \tag{2.8}$$

where the commutation relations used in their derivation are unitary transforms of analogous ones for the uncoupled operators. In order to show that such transforms exist it is only necessary to realize that the operators $a_{\mathbf{k}j}(t)$, $X_{\mathbf{k}j}(t)$ and their adjoints have no explicit time dependence. That is, the entire time dependence of these operators is transferred to the state vector under a unitary transformation from the Heisenberg picture (in terms of which this paper is written) to the Schrödinger picture. The explicit time derivatives of the Heisenberg operators then are zero, and hence unitary time-evolution operators may be used to express the time development of the noncoupled (harmonic) phonon operator as

$$a_{\mathbf{k}j}^0(t)=U(t,0)a_{\mathbf{k}j}^0(0)U^\dagger(t,0)\,,$$

and the coupled (anharmonic) phonon operator as

$$a_{\mathbf{k}j}(t)=V(t,0)a_{\mathbf{k}j}(0)V^\dagger(t,0)\,.$$

Thus, from Eq. (2.6), the uncoupled and coupled operators are connected by the equation

$$a_{\mathbf{k}j}(t)=W(t,0)a_{\mathbf{k}j}^0(t)W^\dagger(t,0)\,, \tag{2.9}$$

with the unitary operator $W(t,0)=V(t,0)U^\dagger(t,0)$.

The integral forms of Eqs. (2.7) and (2.8) are

$$a_{\mathbf{k}j}(t)=a_{\mathbf{k}j}^0(t)+(i\hbar)^{-1}\times\int_0^t dt_1\,X_{\mathbf{k}j}^\dagger(t_1)\exp[-i\omega_{\mathbf{k}j}(t-t_1)]\,, \tag{2.10}$$

$$a_{\mathbf{k}j}^\dagger(t)=a_{\mathbf{k}j}^{0\dagger}(t)-(i\hbar)^{-1}\times\int_0^t dt_1\,X_{\mathbf{k}j}(t_1)\exp[i\omega_{\mathbf{k}j}(t-t_1)]\,. \tag{2.11}$$

Continuing the analysis for $a_{\mathbf{k}j}(t)$ only, from Eq. (2.2) the loss Hamiltonian equation of motion is

$$\dot{H}_l(t)=(i\hbar)^{-1}[H_l,H_{\text{int}}]\,, \tag{2.12}$$

or in integral form

$$H_l(t)=H_l^0(t)+(i\hbar)^{-1}\int_0^t dt_1\times[H_l(t_1)\{a_{\mathbf{k}j}(t_1)X_{\mathbf{k}j}(t_1)+a_{\mathbf{k}j}^\dagger(t_1)X_{\mathbf{k}j}^\dagger(t_1)\}]\,. \tag{2.13}$$

Again, from Eq. (2.2) the loss operator equation of motion is

$$\dot{X}_{\mathbf{k}j}^\dagger(t)=(i\hbar)^{-1}[X_{\mathbf{k}j}^\dagger(t),H_l(t)]\,. \tag{2.14}$$

Substituting for H_l from Eq. (2.13) and rewriting in integral form, Eq. (2.14) becomes

$$X_{\mathbf{k}j}^\dagger(t)=X_{\mathbf{k}j}^{0\dagger}(t)+\hbar^{-2}\int_0^t dt_1\int_0^{t_1} dt_2\exp[(i/\hbar)(t-t_1)H_l^0]\times[X_{\mathbf{k}j}^\dagger(t_1),[\{a_{\mathbf{k}j}(t_2)X_{\mathbf{k}j}(t_2)+a_{\mathbf{k}j}^\dagger(t_2)X_{\mathbf{k}j}^\dagger(t_2)\}\times H_l(t_2)]]\exp[-(i/\hbar)(t-t_1)H_l^0]\,. \tag{2.15}$$

Using Eq. (2.15), Eq. (2.10) is then

$$a_{\mathbf{k}j}(t)=a_{\mathbf{k}j}^0(t)+(i\hbar)^{-1}\int_0^t dt_1\,X_{\mathbf{k}j}^{0\dagger}(t_1)\exp[-i\omega_{\mathbf{k}j}(t-t_1)]+(i\hbar^3)^{-1}\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\exp[-i\omega_{\mathbf{k}j}(t-t_1)]$$
$$\times\exp[(i/\hbar)(t_1-t_2)H_l^0][X_{\mathbf{k}j}^\dagger(t_2),[\{a_{\mathbf{k}j}(t_3)X_{\mathbf{k}j}(t_3)+a_{\mathbf{k}j}^\dagger(t_3)X_{\mathbf{k}j}^\dagger(t_3)\},H_l(t_3)]]\exp[-(i/\hbar)(t_1-t_2)H_l^0]\,. \tag{2.16}$$

The double commutator may be approximated by (i) assuming only slight disturbance of the loss mechanism so that $X_{\mathbf{k}j}$ and $X_{\mathbf{k}j}^\dagger$ are replaced by $X_{\mathbf{k}j}^0$ and $X_{\mathbf{k}j}^{0\dagger}$, respectively; and (ii) ignoring quantum-mechanical properties of the loss mechanism in terms above second order. This allows removal of $a_{\mathbf{k}j}$ and $a_{\mathbf{k}j}^\dagger$ from the commutators which are then replaced by their expectation values times the unit operator. Senitzky discusses these modifications in detail.

Then Eq. (2.16) may be written (approximately) as

$$a_{\mathbf{k}j}(t)=a_{\mathbf{k}j}^0(t)+(i\hbar)^{-1}\int_0^t dt_1\,X_{\mathbf{k}j}^{0\dagger}(t_1)\exp[-i\omega_{\mathbf{k}j}(t-t_1)]+(i\hbar^3)^{-1}\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\exp[-i\omega_{\mathbf{k}j}(t-t_1)]$$
$$\times\{\langle[X_{\mathbf{k}j}^{0\dagger}(t_2),[X_{\mathbf{k}j}^0(t_3),H_l^0(t_3)]]\rangle a_{\mathbf{k}j}(t_3)+\langle[X_{\mathbf{k}j}^{0\dagger}(t_2),[X_{\mathbf{k}j}^{0\dagger}(t_3),H_l^0(t_3)]]\rangle a_{\mathbf{k}j}^\dagger(t_3)\}\,. \tag{2.17}$$

Here

$$\langle\text{operator}\rangle=(Z)^{-1}\sum_r\langle r|\text{op.}|r\rangle\exp(-E_r/kT)\,, \tag{2.18}$$

where

$$Z=\sum_r\exp(-E_r/kT)\,,$$

and the expectation value is taken with respect to the loss mechanism. That is, r refers to a state of the reservoir of harmonic oscillators corresponding to the normal modes of the crystal other than the $(\mathbf{k}j)$ mode.

Matrix elements of the uncoupled loss mechanism are defined by

$$\langle r|X_{\mathbf{k}j}^0(t)|s\rangle=\langle r|X_{\mathbf{k}j}^0(0)|s\rangle\exp(-i\omega_{rs}t)=\bar{X}_{rs}\exp(-i\omega_{rs}t) \tag{2.19}$$

and

$$\langle r|X_{\mathbf{k}j}^{0\dagger}(t)|s\rangle=\bar{X}^\dagger{}_{rs}\exp(i\omega_{rs}t)\,, \tag{2.20}$$

where

$$\omega_{rs}=(E_r-E_s)/\hbar.$$

From Eqs. (2.19) and (2.20) may be derived the equations

$$\langle r|[X_{\mathbf{k}j}^{0\dagger}(t_2),[X_{\mathbf{k}j}^{0}(t_3),H_l^0(t_3)]]|r\rangle=\sum_s \hbar\omega_{rs}\{\exp[i\omega_{rs}(t_2-t_3)]|\bar{X}^\dagger{}_{rs}|^2+\exp[-i\omega_{rs}(t_2-t_3)]|\bar{X}_{rs}|^2\}, \quad (2.21)$$

where

$$|\bar{X}^\dagger{}_{rs}|^2=\bar{X}^\dagger{}_{rs}\bar{X}_{sr}, \quad |\bar{X}_{rs}|^2=\bar{X}_{rs}\bar{X}^\dagger{}_{sr}, \quad (2.22)$$

and

$$\langle r|[X_{\mathbf{k}j}^{0\dagger}(t_2),[X_{\mathbf{k}j}^{0\dagger}(t_3),H_l^0(t_3)]]|r\rangle=2\sum_s \hbar\omega_{rs}\bar{X}^\dagger{}_{rs}\bar{X}^\dagger{}_{sr}\cos\omega_{rs}(t_2-t_3). \quad (2.23)$$

It is shown in Appendix A that for general $(\mathbf{k}j)$,

$$\bar{X}^\dagger{}_{rs}\bar{X}^\dagger{}_{sr}\equiv 0. \quad (2.24)$$

Then Eq. (2.17) becomes

$$a_{\mathbf{k}j}(t)=a_{\mathbf{k}j}^0(t)+(i\hbar)^{-1}\int_0^t dt_1\, X_{\mathbf{k}j}^{0\dagger}(t_1)\exp[-i\omega_{\mathbf{k}j}(t-t_1)]+(i\hbar^2Z)^{-1}\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\, a_{\mathbf{k}j}(t_3)$$
$$\times\sum_{rs}\omega_{rs}\exp(-E_r/kT)\exp[-i\omega_{\mathbf{k}j}(t-t_1)]\{|\bar{X}^\dagger{}_{rs}|^2\exp[i\omega_{rs}(t_2-t_3)]+|\bar{X}_{rs}|^2\exp[-i\omega_{rs}(t_2-t_3)]\}. \quad (2.25)$$

By changing the order of integration and evaluating the time integrals over t_1 and t_2, the last term of Eq. (2.25) may be rewritten

$$L(\omega_{\mathbf{k}j},t)=-(i\hbar^2Z)^{-1}\int_0^t dt_3\, a_{\mathbf{k}j}(t_3)\sum_{rs}\exp(-E_r/kT)$$
$$\times\left(\left\{\frac{\exp[i\omega_{rs}(t-t_3)]-\exp[-i\omega_{\mathbf{k}j}(t-t_3)]}{\omega_{rs}+\omega_{\mathbf{k}j}}+\frac{1-\exp[-i\omega_{\mathbf{k}j}(t-t_3)]}{\omega_{\mathbf{k}j}}\right\}|\bar{X}^\dagger{}_{rs}|^2\right.$$
$$\left.+\left\{\frac{\exp[-i\omega_{rs}(t-t_3)]-\exp[-i\omega_{\mathbf{k}j}(t-t_3)]}{\omega_{rs}-\omega_{\mathbf{k}j}}+\frac{1-\exp[-i\omega_{\mathbf{k}j}(t-t_3)]}{\omega_{\mathbf{k}j}}\right\}|\bar{X}_{rs}|^2\right). \quad (2.26)$$

Assuming energy levels of the phonon reservoir to be closely spaced, the summations may be approximated by integrals

$$\sum_{rs}\rightarrow\int_0^\infty dE_r\,\eta(E_r)\int_0^\infty dE_s\,\eta(E_s), \quad (2.27)$$

where $\eta(E)$ is the density of reservoir (loss-mechanism) energy states. If $|\bar{X}^\dagger{}_{rs}|^2$ and $|\bar{X}_{rs}|^2$ are also replaced by the real functions $\bar{X}^{\dagger 2}(E_r,E_s)$ and $\bar{X}^2(E_r,E_s)$ obtained by averaging the former pair over all states r and s lying in small intervals about E_r and E_s, respectively, then it is shown in Appendix B(1) that

$$\bar{X}^{\dagger 2}(E_r,E_s)\equiv\bar{X}^2(E_r,E_s). \quad (2.28)$$

Hence Eq. (2.26) is now given by

$$L(\omega_{\mathbf{k}j},t)=(i\hbar^2Z)^{-1}\int_0^t dt_1\, a_{\mathbf{k}j}(t_1)F(\omega_{\mathbf{k}j},t-t_1), \quad (2.29)$$

where

$$F(\omega,\tau)=\int_0^\infty dE_r\,\eta(E_r)\int_0^\infty dE_s\,\eta(E_s)\exp(-E_r/kT)$$
$$\times\left\{\frac{\exp(-i\omega\tau)-\exp(i\omega_{rs}\tau)}{\omega+\omega_{rs}}-\frac{\exp(-i\omega\tau)-\exp(-i\omega_{rs}\tau)}{\omega-\omega_{rs}}\right\}\bar{X}^{\dagger 2}(E_r,E_s). \quad (2.30)$$

The double integral is redefined in the form

$$\int_0^\infty dE_r \int_0^\infty dE_s = \int_0^\infty \hbar d\omega' \int_{\frac{1}{2}\hbar\omega'}^\infty dE + \int_{-\infty}^0 \hbar d\omega' \int_{-\frac{1}{2}\hbar\omega'}^\infty dE = \int \hbar d\omega' \int dE, \quad (2.31)$$

in which

$$E = \tfrac{1}{2}(E_r + E_s) \quad \text{and} \quad \omega' = \omega_{rs} = \omega_r - \omega_s. \quad (2.32)$$

Thus Eq. (2.30) becomes

$$F(\omega,\tau) = \int \hbar d\omega' \int dE\ \eta(E+\tfrac{1}{2}\hbar\omega')\eta(E-\tfrac{1}{2}\hbar\omega') \times \exp[-(E+\tfrac{1}{2}\hbar\omega')/kT] \times \bar{X}^{\dagger 2}(E+\tfrac{1}{2}\hbar\omega', E-\tfrac{1}{2}\hbar\omega') f(\omega',\tau), \quad (2.33)$$

where

$$f(\omega',\tau) = \frac{\exp(-i\omega\tau) - \exp(i\omega'\tau)}{\omega+\omega'} - \frac{\exp(-i\omega\tau) - \exp(-i\omega'\tau)}{\omega-\omega'} = -f(-\omega',\tau). \quad (2.34)$$

Using Eqs. (2.30), (2.32), and the identity deduced in Appendix B(2) that

$$\bar{X}^{\dagger 2}(E, E-\hbar\omega') \equiv \bar{X}^{\dagger 2}(E-\hbar\omega', E), \quad (2.35)$$

Eq. (2.33) may be simplified to

$$F(\omega,\tau) = -\hbar \int_0^\infty d\omega' [1-\exp(-\hbar\omega'/kT)] \times B(\omega') f(\omega'\tau). \quad (2.36)$$

Here the real quantity $B(\omega')$ is given by

$$B(\omega') = \int_0^\infty dE\ \eta(E+\hbar\omega')\eta(E) \times \exp(-E/kT)\bar{X}^{\dagger 2}(E+\hbar\omega', E). \quad (2.37)$$

If Eq. (2.36) is rewritten in the form

$$F(\omega,\tau) = \hbar \exp(-i\omega\tau) \int_0^\infty d\omega' [1-\exp(-\hbar\omega'/kT)] B(\omega') \times \left\{ \frac{1-\exp[i(\omega-\omega')\tau]}{\omega-\omega'} - \frac{1-\exp[i(\omega+\omega')\tau]}{\omega+\omega'} \right\}, \quad (2.38)$$

then for $\tau(=t-t_1)$ large (or equivalently $\omega\tau \gg 1$), it is approximated by[13]

$$F(\omega,\tau) = \hbar \exp(-i\omega\tau) \int_0^\infty d\omega' [1-\exp(-\hbar\omega'/kT)] B(\omega') \times [\xi(\omega-\omega') - \xi(\omega+\omega')], \quad (2.39)$$

with

$$\xi(\omega\pm\omega') = 1/(\omega\pm\omega')_P - i\pi\delta(\omega\pm\omega'). \quad (2.40)$$

Both Senitzky and Lax[14] employ a similar approximation to this one, which here renders the frequency integral time-independent.

Hence, Eq. (2.29) is simply

$$L(\omega_{\mathbf{k}j},t) = -\beta_{\mathbf{k}j} \int_0^t dt_1\ a_{\mathbf{k}j}(t_1) \exp[-i\omega_{\mathbf{k}j}(t-t_1)], \quad (2.41)$$

where

$$\beta_{\mathbf{k}j} = -(i\hbar Z)^{-1} \int_0^\infty d\omega' [1-\exp(-\hbar\omega'/kT)B(\omega')] \times [\xi(\omega_{\mathbf{k}j}-\omega') - \xi(\omega_{\mathbf{k}j}+\omega')]. \quad (2.42)$$

Substituting for $L(\omega_{\mathbf{k}j})$ in Eq. (2.25), the final form of the integral equation is

$$a_{\mathbf{k}j}(t) = a_{\mathbf{k}j}{}^0(t) + (i\hbar)^{-1} \int_0^t dt_1\ X_{\mathbf{k}j}{}^{0\dagger}(t_1) \exp[-i\omega_{\mathbf{k}j}(t-t_1)] - \beta_{\mathbf{k}j} \int_0^t dt_1\ a_{\mathbf{k}j}(t_1) \exp[-i\omega_{\mathbf{k}j}(t-t_1)]. \quad (2.43)$$

Expressed as a differential equation this becomes

$$\dot{a}_{\mathbf{k}j} + i(\omega_{\mathbf{k}j} - i\beta_{\mathbf{k}j})a_{\mathbf{k}j} = (i\hbar)^{-1} X_{\mathbf{k}j}{}^{0\dagger}(t). \quad (2.44)$$

The exact solution is then

$$a_{\mathbf{k}j}(t) = a_{\mathbf{k}j}{}^0(0) \exp[-i(\omega_{\mathbf{k}j} - i\beta_{\mathbf{k}j})t] + (i\hbar)^{-1} \int_0^t dt_1\ X_{\mathbf{k}j}{}^{0\dagger}(t_1) \times \exp[-i(\omega_{\mathbf{k}j} - i\beta_{\mathbf{k}j})(t-t_1)]. \quad (2.45)$$

The analogous creation operator equation is, taking the adjoint of Eq. (2.45),

$$a_{\mathbf{k}j}{}^\dagger(t) = a_{\mathbf{k}j}{}^{0\dagger}(0) \exp[i(\omega_{\mathbf{k}j} + i\beta_{\mathbf{k}j}{}^*)t] - (i\hbar)^{-1} \int_0^t dt_1\ X_{\mathbf{k}j}{}^0(t_1) \times \exp[i(\omega_{\mathbf{k}j} + i\beta_{\mathbf{k}j}{}^*)(t-t_1)]. \quad (2.46)$$

By inspection, the damping constant $\Gamma_{\mathbf{k}j}$ and frequency shift $\Delta_{\mathbf{k}j}$ of the $(\mathbf{k}j)$th mode may be immediately deduced as

$$\Gamma_{\mathbf{k}j} = \mathrm{Re}\beta_{\mathbf{k}j} = \pi(\hbar Z)^{-1} \times \int_0^\infty d\omega' [1-\exp(-\hbar\omega'/kT)] B(\omega') \times [\delta(\omega_{\mathbf{k}j}-\omega') - \delta(\omega_{\mathbf{k}j}+\omega')] \quad (2.47)$$

[13] See, for instance, W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed.

[14] M. Lax, Phys. Rev. **160**, 290 (1967), paper V.

and

$$\Delta_{\mathbf{k}j}=\mathrm{Im}\beta_{\mathbf{k}j}=(\hbar Z)^{-1}\times\int_0^\infty d\omega'\,[1-\exp(-\hbar\omega'/kT)]B(\omega')\times\left[\frac{1}{(\omega_{\mathbf{k}j}-\omega')_P}-\frac{1}{(\omega_{\mathbf{k}j}+\omega')_P}\right]. \quad (2.48)$$

Note that if approximations consistent with those of Senitzky are employed, then, since the main contribution comes from the region $\omega'\approx\omega_{\mathbf{k}j}$, the above equations simplify:

$$\Gamma_{\mathbf{k}j}\approx\pi(\hbar Z)^{-1}\int_0^\infty d\omega'\,[1-\exp(-\hbar\omega'/kT)]\times B(\omega')\delta(\omega_{\mathbf{k}j}-\omega')$$
$$\approx\pi(\hbar Z)^{-1}\int_{-\infty}^\infty d\omega'\,[1-\exp(-\hbar\omega'/kT)]\times B(\omega')\delta(\omega_{\mathbf{k}j}-\omega'), \quad (2.49)$$

or

$$\Gamma_{\mathbf{k}j}\approx\pi(\hbar Z)^{-1}[1-\exp(-\hbar\omega_{\mathbf{k}j}/kT)]B(\omega_{\mathbf{k}j}),$$

and similarly

$$\Delta_{\mathbf{k}j}\approx(\hbar Z)^{-1}\int_{-\infty}^\infty d\omega'\frac{[1-\exp(-\hbar\omega'/kT)]}{(\omega_{\mathbf{k}j}-\omega')_P}B(\omega').$$

III. COMMUTATION PROPERTIES

In Sec. II, the anharmonic phonon operators have been assumed to satisfy the commutation relation

$$[a_{\mathbf{k}j}(t),a_{\mathbf{k}j}^\dagger(t)]=1. \quad (3.1)$$

As originally stated its validity may be established by considering a unitary transformation of the corresponding one for harmonic phonons. However, as a check of the internal consistency of the theory and approximations used in this paper, the commutation relation is also derived from the operator expressions given by Eqs. (2.45) and (2.46). The technique used is similar to that of Senitzky.

Substituting Eqs. (2.45) and (2.46), the commutator is

$$[a_{\mathbf{k}j}(t),a_{\mathbf{k}j}^\dagger(t)]=\exp(-2\Gamma_{\mathbf{k}j}t)+S, \quad (3.2)$$

where

$$S=\hbar^{-2}\exp(-2\Gamma_{\mathbf{k}j}t)\times\int_0^t dt_1\int_0^{t_1}dt_2\,[X_{\mathbf{k}j}^{0\dagger}(t_1),X_{\mathbf{k}j}^0(t_2)]\times\exp[-(\Gamma_{\mathbf{k}j}+i\bar{\omega}_{\mathbf{k}j})(t-t_1)]\times\exp[-(\Gamma_{\mathbf{k}j}-i\bar{\omega}_{\mathbf{k}j})(t-t_2)] \quad (3.3)$$

and

$$\bar{\omega}_{\mathbf{k}j}=\omega_{\mathbf{k}j}+\Delta_{\mathbf{k}j}. \quad (3.4)$$

In Appendix C, the quantity S is evaluated using approximations consistent with those of Sec. II:

$$S=[1-\exp(-2\Gamma_{\mathbf{k}j}t)]. \quad (3.5)$$

Hence Eq. (3.1) follows.

IV. KRAMERS-KRONIG RELATIONS

The complex damping constant $\beta_{\mathbf{k}j}^*$ is related to the retarded Green's function for the loss mechanism operators, $G_r(\tau)$, according to (Appendix D)

$$\beta_{\mathbf{k}j}^*=\Gamma(\omega_{\mathbf{k}j})-i\Delta(\omega_{\mathbf{k}j})$$
$$=-\hbar^{-2}\int_0^\infty d\tau\,\exp(-i\omega_{\mathbf{k}j}\tau)\times\langle[X_{\mathbf{k}j}^{0\dagger}(\tau),X_{\mathbf{k}j}^0(0)]\rangle$$
$$=-i\hbar^{-2}\int_{-\infty}^\infty d\tau\,\exp(-i\omega_{\mathbf{k}j}\tau)G_r^*(\tau), \quad (4.1)$$

where

$$G_r^*(\tau)=-i\theta(\tau)\langle[X_{\mathbf{k}j}^{0\dagger}(\tau),X_{\mathbf{k}j}^0(0)]\rangle \quad (4.2)$$

and

$$\theta(\tau)=1,\quad \tau>0$$
$$=0,\quad \tau<0. \quad (4.3)$$

The real and imaginary parts of the Fourier transform of the retarded Green's function are related by the Kramers-Kronig relations

$$\Delta(\omega_{\mathbf{k}j})=-\frac{1}{\pi}\int_{-\infty}^\infty d\omega'\frac{\Gamma(\omega')}{(\omega'-\omega_{\mathbf{k}j})_P}, \quad (4.4)$$

$$\Gamma(\omega_{\mathbf{k}j})=\frac{1}{\pi}\int_{-\infty}^\infty d\omega'\frac{\Delta(\omega')}{(\omega'-\omega_{\mathbf{k}j})_P}. \quad (4.5)$$

Zubarev,[15] for example, deduces this property from the analyticity of the retarded Green's function in the upper-half complex plane.

V. COMPARISON WITH OTHER METHODS

In a treatment of optical absorption in polar crystals Wallis and Maradudin[5] (to be referred to as WM III) derive expressions for the damping constant and frequency shift for the $\mathbf{k}=0$ phonon mode. Employing the definition

$$V(\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)=(2N)^{-1/2}\Delta(\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\times\Phi(\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2), \quad (5.1)$$

their equations [WM III Eqs. (31a) and (31b)], may

[15] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

be rewritten

$$\Gamma_{0j}=\frac{\pi\hbar}{8N}\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2}\Delta(\mathbf{k}_1+\mathbf{k}_2)\frac{|\Phi(0j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)|^2}{\omega(0j)|\omega(\mathbf{k}_1j_1)|\omega(\mathbf{k}_2j_2)}(n_1+\tfrac{1}{2})\delta[\omega-\omega_1-\omega_2], \tag{5.2}$$

$$\Delta_{0j}=\frac{\hbar}{8N}\sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{j_1j_2}\Delta(\mathbf{k}_1+\mathbf{k}_2)\frac{|\Phi(0j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)|^2}{\omega(0j)|\omega(\mathbf{k}_1j_1)|\omega(\mathbf{k}_2j_2)}\frac{(n_1+\tfrac{1}{2})}{(\omega-\omega_1-\omega_2)_P}. \tag{5.3}$$

In obtaining this result, the full Hamiltonian [Eq. (2.1)] was used to generate an equation of motion for the phonon creation and annihilation operators [WM III, Eqs. (11a) and (11b)]. These operator equations are virtually identical to Eqs. (2.7) and (2.8) (above) which were generated by the reduced Hamiltonian, Eq. (2.2). The Eqs. (2.7) and (2.8) differ only in that terms with operators of the same $(\mathbf{k}j)$ as that for which the equation of motion is written, are excluded from the summation [i.e., as described after Eq. (2.3)].

It is not surprising, then, that direct evaluation of Eq. (2.17) should yield (after a great amount of tedious manipulation involving the use of Wick's theorem to evaluate thermal averages of six-operator products)

$$\Gamma_{\mathbf{k}j}=\frac{\pi\hbar}{16N}\sum_{\mathbf{k}_1\mathbf{k}_2}{}'\sum_{j_1j_2}{}'\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{|\Phi(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)|^2}{\omega(\mathbf{k}j)\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}\{-(n_1+n_2+1)\delta(\omega+\omega_1+\omega_2)+(n_1+n_2+1)\delta(\omega+\omega_1-\omega_2)$$
$$-(n_1-n_2)\delta(\omega-\omega_1+\omega_2)+(n_1-n_2)\delta(\omega+\omega_1-\omega_2)\}, \tag{5.4}$$

$$\Delta_{\mathbf{k}j}=\frac{\hbar}{16N}\sum_{\mathbf{k}_1\mathbf{k}_2}{}'\sum_{j_1j_2}{}'\Delta(-\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\frac{|\Phi(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)|^2}{\omega(\mathbf{k}j)\omega(\mathbf{k}_1j_1)\omega(\mathbf{k}_2j_2)}$$
$$\times\left\{-\frac{n_1+n_2+1}{(\omega+\omega_1+\omega_2)_P}+\frac{n_1+n_2+1}{(\omega-\omega_1-\omega_2)_P}-\frac{n_1-n_2}{(\omega-\omega_1+\omega_2)_P}+\frac{n_1-n_2}{(\omega+\omega_1-\omega_2)_P}\right\}. \tag{5.5}$$

This result immediately degenerates into the WM III Eq. (31) by setting $\mathbf{k}\equiv 0$ and restricting $\omega>0$, the conditions for optical absorption processes. Maradudin and Fein,[6] when considering the scattering of neutrons by anharmonic crystals, also obtain Eqs. (5.4) and (5.5) but with the addition to Eq. (5.4) of a fourth-order term of magnitude comparable to the third-order contribution.

Wallis and Maradudin,[5] employ an equation-of-motion technique in which terms generated by iteration are classified according to diagrams of successively higher order. The complex dielectric susceptibility tensor deduced by Kubo formalism then gives damping-constant and frequency-shift expressions.

On the other hand Maradudin and Fein (and Cowley[7]), use a diagrammatic Green's-function approach to evaluate the Fourier transform of a time-relaxed displacement-displacement correlation function. A Dyson equation for the phonon propagator is obtained and approximate solution to lowest order yields the damping constant and frequency shift [M. and F., Eqs. (5.5)].

Thompson[8] and Pathak[9] use a truncated equation of motion for the same Green's function as Maradudin and Fein; Viswanathan and Watanabe[10] use temperature-dependent perturbation theory and Van-Hove's discussion of inner displacements; Ishikawa[11] uses a canonical transformation; and Wallace[12] uses an iterated equation of motion (renormalization) for the phonon operators. All obtain, effectively, the expressions of Maradudin and Fein [M. and F., Eqs. (5.5)].

The one-particle Green's function of all the above methods has the general retarded form

$$G_r(\tau,0)=-i\theta(\tau)\langle[A(\tau),B(0)]\rangle. \tag{5.6}$$

When the operators are defined as

$$A(\tau)\equiv a_{\mathbf{k}j}(\tau) \quad\text{and}\quad B(0)\equiv a_{\mathbf{k}j}{}^{\dagger}(0),$$

the equations for the annihilation and creation operators [Eqs. (2.45) and (2.46)] allow Eq. (5.6) to be rewritten

$$G_r(\tau,0)=-i\theta(\tau)\exp(-i\bar{\omega}_{\mathbf{k}j}\tau)\exp(-\Gamma_{\mathbf{k}j}\tau), \tag{5.6'}$$

with

$$\bar{\omega}_{\mathbf{k}j}=\omega_{\mathbf{k}j}+\Delta_{\mathbf{k}j}.$$

Comparison with the Green's-function work previously cited and with the general results of, for example, Galitskii and Migdal[16] illustrates the equivalence of their interpretation to that presented here. Damping constants and frequency shifts apparent in the operator equations are just those arising from the Green's function.

The formalism of Sec. II, based as it is on that of Senitzky, bears close resemblance to the noise theory of

[16] V. M. Galitskii and A. B. Migdal, Zh. Eksperim. i Teor. Fiz. 34, 139 (1958) [English transl.: Soviet Phys.—JETP 34, 96 (1958).

Callen and Welton,[17] and Bernard and Callen.[18] Mori[19] and Tani[20] continue the extension of noise theory and Brownian motion into the domain of anharmonic crystal vibrations. Equation (2.44) is identical to the Langevin equation [Mori, Eq. (1.2)]. Mori's later equation [Mori, Eq. (3.10)],

$$\frac{d}{dt}A(t)-i\hat{\omega}A(t)+\int_0^t \phi(t-s)A(s)ds=f(t)\,, \quad (5.7)$$

may be compared with a generalized form of Eq. (2.44) in which the time approximation referred to above Eq. (2.39) has not been utilized. Thus, without the time approximation, Eq. (2.43) has the form

$$a(t)=a^0(t)+(i\hbar)^{-1}\int_0^t dt_1\, X^{0\dagger}(t_1)\exp[-i\omega(t-t_1)]+(i\hbar Z)^{-1}\int_0^t dt_1\, a(t_1)\exp[-i\omega(t-t_1)]$$
$$\times\int_0^\infty d\omega'\,[1-\exp(-\hbar\omega'/kT]B(\omega')\left\{\frac{1-\exp[i(\omega-\omega')(t-t_1)]}{\omega-\omega'}-\frac{1-\exp[i(\omega+\omega')(t-t_1)]}{\omega+\omega'}\right\}. \quad (5.8)$$

Therefore Eq. (2.44) becomes

$$\frac{d}{dt}a(t)+i\omega a(t)-(i\hbar)^{-1}\times\int_0^t dt_1\,\phi(t-t_1)a(t_1)=(i\hbar)^{-1}X^{0\dagger}(t)\,, \quad (5.9)$$

where

$$\phi(t-t_1)=-2Z^{-1}\int_0^\infty d\omega'[1-\exp(-\hbar\omega'/kT)]\times B(\omega')\sin\omega'(t-t_1)$$
$$=(i\hbar)^{-1}\langle[X^{0\dagger}(t),X^0(t_1)]\rangle\,, \quad (5.10)$$

by Appendix C. Since it is shown in Appendix C that

$$\langle[a(t),a^\dagger(t)]\rangle=1\,, \quad (5.11)$$

then, by inspection, the equation [Mori, Eq. (3.12)] is similar to the above equation for $\phi(t-t_1)$. To within definitions of scalar products, then, Eq. (5.9) and Mori's Eq. (3.10) are equivalent.

Tani employs Mori's results (leaving out the operator's randomly fluctuating part) to deduce the temperature dependence of lifetime expressions for soft, ferroelectric modes.

Probably the analysis closest to that presented here is given by Lax.[21,22] In the first paper[21] particularly, the concept of one lattice vibration interacting with a reservoir of all other lattice vibrations through the anharmonic coupling is developed along equation of motion lines. Thermal averaging is made with respect to the reservoir and, although providing an iteration procedure, the theory given considers the reservoir as a set of noninteracting modes. His second paper of interest[22] is more general. An impedance-plus-noise-source "black box" is substituted for the reservoir and the moments of noise-source operators [the operators $X_{\mathbf{k}j}(t)$ used in this paper] are determined in terms of experimental damping coefficients. That Lax's expressions for the damping and frequency shift are equivalent to the corresponding equations, Eqs. (2.47) and (2.48), is readily shown.

Lax derives the equation[20] [Lax, QIII, Eq. (5.23)],

$$b_{s,-\mathbf{q};\,t,\mathbf{q}}(\omega)=\int_0^\infty dt\exp(-i\omega t)\times\langle\langle(F_s(-\mathbf{q},t),F_t(\mathbf{q},0))\rangle\rangle\,, \quad (5.12)$$

where

$$F_s(\mathbf{k},t)\equiv[2\omega_s(\mathbf{k})/\hbar]^{1/2}X_{\mathbf{k}s}{}^0(t) \quad (5.13)$$

and

$$F_s(-\mathbf{k},t)\equiv[2\omega_s(\mathbf{k})/\hbar]^{1/2}X_{\mathbf{k}s}{}^{0\dagger}(t)\,. \quad (5.14)$$

Then Appendix D provides the equation

$$b_{t,-\mathbf{q};\,t,\mathbf{q}}(\omega)=2\omega_t(\mathbf{q})(\Delta_{\mathbf{q}t}+i\Gamma_{\mathbf{q}t})\,. \quad (5.15)$$

Substitution in Lax, QIII, Eq. (5.27) yields

$$\omega_t'^2(\mathbf{q})=\omega_t^2(\mathbf{q})-2\omega_t(\mathbf{q})(\Delta_{\mathbf{q}t}+i\Gamma_{\mathbf{q}t})\,, \quad (5.16)$$

where $\omega_t'(\mathbf{q})$ is the complex-shifted frequency for the $(\mathbf{q},t)$ mode. Setting

$$\omega_t'(\mathbf{q})=\omega_t(\mathbf{q})+\delta+i\gamma\,, \quad (5.17)$$

then for small damping and frequency shift these quantities are given by

$$\gamma\cong-\Gamma_{\mathbf{q}t}\,, \quad (5.18)$$

$$\delta\cong-\Delta_{\mathbf{q}t}\,, \quad (5.19)$$

and the results of both methods are equivalent.

VI. CONCLUSION

It has been shown that vibrations of the anharmonic crystal may, under certain approximations, be treated from a dissipation-theory viewpoint. The normal mode phonons of harmonic theory were each thought of as a

[17] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).
[18] W. Bernard and H. B. Callen, Rev. Mod. Phys. **31**, 1017 (1959).
[19] H. Mori, Progr. Theoret. Phys. (Kyoto) **33**, 423 (1965).
[20] K. Tani, Phys. Letters **25A**, 400 (1967).
[21] M. Lax, J. Phys. Chem. Solids **25**, 487 (1964), referred to as QIII.
[22] M. Lax, Phys. Rev. **145**, 110 (1966), referred to as QIV.

system undergoing dissipative coupling to another system, or reservoir, comprising all other phonons. The major approximation was to neglect (a) those interactions of the other phonons which specifically excluded the one considered, and (b) interactions of identical phonons.

By comparison with other theories, the results of which identify closely with those presented here, it appears that such a treatment is a valid one. However, the complexity of the loss-mechanism system prevents damping-constant and frequency-shift expressions deduced by this paper from being calculated numerically. The difficulty is that the density of total-energy states for the reservoir of harmonic oscillators is not known even approximately. A model more amenable to Senitzky's analysis should have clearly defined energy-level densities whereby the energy integrals, which here must remain unsolved, would be immediately evaluated.

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APPENDIX A

Here we prove the identity

$$\bar{X}^\dagger{}_{rs}\bar{X}^\dagger{}_{sr}\equiv 0.$$

From Eq. (2.20), it follows that

$$\bar{X}^\dagger{}_{rs}\bar{X}^\dagger{}_{sr}=\langle r|X_{\mathbf{k}j}{}^{0\dagger}(0)|s\rangle\langle s|X_{\mathbf{k}j}{}^{0\dagger}(0)|r\rangle, \quad \text{(A1)}$$

where, by Eq. (2.3),

$$\begin{aligned}X_{\mathbf{k}j}{}^{0\dagger}=3\sum_{\mathbf{k}_1\mathbf{k}_2}{}'\sum_{j_1j_2}{}'\big[&V(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)a_{\mathbf{k}_1j_1}{}^0a_{\mathbf{k}_2j_2}{}^0+V(-\mathbf{k}j,\mathbf{k}_1j_1,-\mathbf{k}_2j_2)a_{\mathbf{k}_1j_1}{}^0a_{\mathbf{k}_2j_2}{}^{0\dagger}\\&+V(-\mathbf{k}j,-\mathbf{k}_1j_1,\mathbf{k}_2j_2)a_{\mathbf{k}_1j_1}{}^{0\dagger}a_{\mathbf{k}_2j_2}{}^0+V(-\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_2j_2)a_{\mathbf{k}_1j_1}{}^{0\dagger}a_{\mathbf{k}_2j_2}{}^{0\dagger}\big]\\=X_{-\mathbf{k}j}{}^0.&\end{aligned} \quad \text{(A2)}$$

Thus, the matrix element may be evaluated as

$$\begin{aligned}\bar{X}^\dagger{}_{rs}=3\sum_{\mathbf{k}_1\mathbf{k}_2}{}'\sum_{j_1j_2}{}'\Big[\prod_{\mathbf{k}_3j_3}{}''\Delta(n_{3,s}-n_{3,r})\Big]\{&[\delta_{1,2}\Delta(n_{1,s}-2-n_{1,r})\Delta(\omega_{rs}+2\omega_1)n_{1,s}{}^{1/2}(n_{1,s}-1)^{1/2}V(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_1j_1)\\&+(1-\delta_{1,2})\Delta(n_{1,s}-1-n_{1,r})\Delta(n_{2,s}-1-n_{2,r})\Delta(\omega_{rs}+\omega_1+\omega_2)n_{1,s}{}^{1/2}n_{2,s}{}^{1/2}V(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)]\\&+[\delta_{1,2}\Delta(n_{1,s}-n_{1,r})\Delta(\omega_{rs})(n_{1,s}+1)V(-\mathbf{k}j,\mathbf{k}_1j_1,-\mathbf{k}_1j_1)\\&+(1-\delta_{1,2})\Delta(n_{1,s}-1-n_{1,r})\Delta(n_{2,s}+1-n_{2,r})\Delta(\omega_{rs}+\omega_1-\omega_2)n_{1,s}{}^{1/2}(n_{2,s}+1)^{1/2}V(-\mathbf{k}j,\mathbf{k}_1j_1,-\mathbf{k}_2j_2)]\\&+[\delta_{1,2}\Delta(n_{1,s}-n_{1,r})\Delta(\omega_{rs})n_{1,s}V(-\mathbf{k}j,-\mathbf{k}_1j_1,\mathbf{k}_1j_1)\\&+(1-\delta_{1,2})\Delta(n_{1,s}+1-n_{1,r})\Delta(n_{2,s}-1-n_{2,r})\Delta(\omega_{rs}-\omega_1+\omega_2)(n_{1,s}+1)^{1/2}n_{2,s}{}^{1/2}V(-\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_2j_2)]\\&+[\delta_{1,2}\Delta(n_{1,s}+n_{1,r})\Delta(\omega_{rs}-2\omega_1)(n_{1,s}+1)^{1/2}(n_{1,s}+2)^{1/2}V(-\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_1j_1)\\&+(1-\delta_{1,2})\Delta(n_{1,s}+1-n_{1,r})\Delta(n_{2,s}+1-n_{2,r})\Delta(\omega_{rs}-\omega_1-\omega_2)(n_{1,s}+1)^{1/2}(n_{2,s}+1)^{1/2}V(-\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_2j_2)]\}.\end{aligned} \quad \text{(A3)}$$

In the above expression use is made of the identity

$$\delta_{1,2}\equiv\Delta(\mathbf{k}_1-\mathbf{k}_2)\Delta(j_1-j_2),$$

and $n_{\pm1,s}$ represents the quantum-mechanical expectation value for the number of phonons in the $(\pm\mathbf{k}_1,j_1)$ mode when the reservoir is in the state s with energy E_s.

Interchanging r and s a similar expression may be deduced for $\bar{X}^\dagger{}_{sr}$.

By inspection, the δ-functions enable the product expression to be evaulated:

$$\begin{aligned}\bar{X}^\dagger{}_{rs}\bar{X}^\dagger{}_{sr}=9\sum_{\mathbf{k}_1\mathbf{k}_2}{}'\sum_{j_1j_2}{}'\{&[\delta_{1,2}\Delta(\omega_{rs}+2\omega_1)n_{1,s}(n_{1,s}-1)V(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_1j_1)V(-\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_1j_1)\\&+2(1-\delta_{1,2})\Delta(\omega_{rs}+\omega_1+\omega_2)n_{1,s}n_{2,s}V(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)V(-\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_2j_2)]\\&+[\delta_{1,2}\Delta(\omega_{rs})(2n_{1,s}+1)^2V(-\mathbf{k}j,-\mathbf{k}_1j_1,\mathbf{k}_1j_1)V-\mathbf{k}j,\mathbf{k}_1j_1,-\mathbf{k}_1j_1)\\&+2(1-\delta_{1,2})\Delta(\omega_{rs}+\omega_1-\omega_2)(n_{1,s})V(-\mathbf{k}j,\mathbf{k}_1j_1,-\mathbf{k}_2j_2)V(-\mathbf{k}j,-\mathbf{k}_1j_1,\mathbf{k}_2j_2)\\&+2(1-\delta_{1,2})\Delta(\omega_{rs}-\omega_1+\omega_2)(n_{1,s}+1)n_{2,s}V(-\mathbf{k}j,-\mathbf{k}_1j_1,\mathbf{k}_2j_2)V(-\mathbf{k}j,\mathbf{k}_1j_1,-\mathbf{k}_2j_2)]\\&+[\delta_{1,2}\Delta(\omega_{rs}-2\omega_1)(n_{1,s}+1)(n_{1,s}+2)V(-\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_1j_1)V(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_1j_1)\\&+2(1-\delta_{1,2})\Delta(\omega_{rs}-\omega_1-\omega_2)(n_{1,s}+1)(n_{2,s}+1)V(-\mathbf{k}j,-\mathbf{k}_1j_1,-\mathbf{k}_2j_2)V(-\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)]\}.\end{aligned} \quad \text{(A4)}$$

The anharmonic coefficients are given by [Eq. (5.1)]

$$V(\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)=(2N)^{-1/2}\Delta(\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\Phi(\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2),$$

where Φ is a general force constant for the crystal. Since each term in Eq. (A4) contains a product of two δ functions which has the form

$$\Delta(\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2)\Delta(\mathbf{k}-\mathbf{k}_1-\mathbf{k}_2),$$

it then follows that

$$\bar{X}^\dagger{}_{rs}\bar{X}^\dagger{}_{sr}=0$$

for general $(\mathbf{k},j)$.

APPENDIX B

(1) Here we prove the identity [Eq. (2.35)]

$$\bar{X}^{\dagger 2}(E_r,E_s)\equiv\bar{X}^2(E_r,E_s).$$

It is defined in Eq. (2.22) that

$$|\bar{X}^\dagger{}_{rs}|^2=\bar{X}^\dagger{}_{rs}(\bar{X}^\dagger{}_{rs})^*=\bar{X}^\dagger{}_{rs}\bar{X}_{sr}.$$

$\bar{X}^\dagger{}_{rs}$ is evaluated in Appendix A;

$\bar{X}_{sr}$ may be evaluated similarly; and their product is obtained in a form analogous to Eq. (A4).

$$\begin{aligned}|\bar{X}^\dagger{}_{rs}|^2=9\sum_{\mathbf{k}_1\mathbf{k}_2}{}'\sum_{j_1j_2}{}'\{&[\delta_{1,2}\Delta(\omega_{rs}+2\omega_1)n_{1,s}(n_{1,s}-1)V(-\mathbf{k}j,\,\mathbf{k}_1j_1,\,\mathbf{k}_1j_1)V(\mathbf{k}j,\,-\mathbf{k}_1j_1,\,-\mathbf{k}_1j_1)\\&+2(1-\delta_{1,2})\Delta(\omega_{rs}+\omega_1+\omega_2)n_{1,s}n_{2,s}V(-\mathbf{k}j,\,\mathbf{k}_1j_1,\,\mathbf{k}_2j_2)V(\mathbf{k}j,\,-\mathbf{k}_1j_1,\,-\mathbf{k}_2j_2)]\\&+[\delta_{1,2}\Delta(\omega_{rs})(2n_{1,s}+1)^2V(-\mathbf{k}j,\,-\mathbf{k}_1j_1,\,\mathbf{k}_1j_1)V(\mathbf{k}j,\,\mathbf{k}_1j_1,\,-\mathbf{k}_1j_1)\\&+2(1-\delta_{1,2})\Delta(\omega_{rs}+\omega_1-\omega_2)n_{1,s}(n_{2,s}+1)V(-\mathbf{k}j,\,\mathbf{k}_1j_1,\,-\mathbf{k}_2j_2)V(\mathbf{k}j,\,-\mathbf{k}_1j_1,\,\mathbf{k}_2j_2)\\&+2(1-\delta_{1,2})\Delta(\omega_{rs}-\omega_1+\omega_2)(n_{1,s}+1)n_{2,s}V(-\mathbf{k}j,\,-\mathbf{k}_1j_1,\,\mathbf{k}_2j_2)V(\mathbf{k}j,\,\mathbf{k}_1j_1,\,-\mathbf{k}_2j_2)]\\&+[\delta_{1,2}\Delta(\omega-2\omega_1)(n_{1,s}+1)(n_{1,s}+2)V(-\mathbf{k}j,\,-\mathbf{k}_1j_1,\,-\mathbf{k}_1j_1)V(\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_1j_1)\\&+2(1-\delta_{1,2})\Delta(\omega-\omega_1-\omega_2)(n_{1,s}+1)(n_{2,s}+1)V(-\mathbf{k}j,\,-\mathbf{k}_1j_1,\,-\mathbf{k}_2j_2)V(\mathbf{k}j,\mathbf{k}_1j_1,\mathbf{k}_2j_2)]\}.\end{aligned}\quad\text{(A5)}$$

It is defined in Eq. (2.22) that

$$|\bar{X}_{rs}|^2=\bar{X}_{rs}(\bar{X}_{rs})^*=\bar{X}_{rs}\bar{X}^\dagger{}_{sr},$$

and a treatment similar to the above yields an equation differing only from Eq. (A5) in that $n_{-1,s}$ and $n_{-2,s}$ replace $n_{1,s}$ and $n_{2,s}$, respectively. In the discussion following Eq. (2.27), $\bar{X}^{\dagger 2}(E_r,E_s)$ and $\bar{X}^2(E_r,E_s)$ are defined as averages of $|\bar{X}^\dagger{}_{rs}|^2$ and $|\bar{X}_{rs}|^2$ over all states r and s lying in small intervals about E_r and E_s, respectively. This averaging allows the quantum-mechanical, number-operator expectation values to be replaced by their thermal averages

$$n_{-1,s}\rightarrow\bar{n}_{-1,s},\quad n_{+1,s}\rightarrow\bar{n}_{+1,s}.$$

From the property of thermal averages that

$$\bar{n}_{-\mathbf{k}}\equiv\bar{n}_{\mathbf{K}},$$

one immediately obtains

$$\bar{X}^{\dagger 2}(E_r,E_s)=\bar{X}^2(E_r,E_s).$$

(2) Here we prove the identity

$$\bar{X}^{\dagger 2}(E_r,E_s)\equiv\bar{X}^{\dagger 2}(E_s,E_r).$$

Since

$$|\bar{X}^\dagger{}_{sr}|^2=|\bar{X}_{rs}|^2$$

by definition, substitution in Eq. (2.28) yields Eq. (2.35).

APPENDIX C

Here we prove the commutator [Eq. (3.1)],

$$[a_{\mathbf{k}j}(t),a_{\mathbf{k}j}{}^\dagger(t)]=1.$$

It is defined in Eq. (3.3) that

$$S=\hbar^{-2}\exp(-2\Gamma_{\mathbf{k}j}t)\int_0^t dt_1\int_0^t dt_2\,[X_{\mathbf{k}j}{}^{0\dagger}(t_1),X_{\mathbf{k}j}{}^0(t_2)]$$
$$\times\exp[-(\Gamma_{\mathbf{k}j}+i\bar{\omega}_{\mathbf{k}j})(t-t_1)]\exp[-(\Gamma_{\mathbf{k}j}-i\bar{\omega}_{\mathbf{k}j})(t-t_2)].$$

As is consistent with the steps following Eq. (2.16) in the analysis, the commutator may be replaced by its expectation value which may then be evaluated:

$$\begin{aligned}[X_{\mathbf{k}j}{}^{0\dagger}(t_1),X_{\mathbf{k}j}{}^0(t_2)]&\rightarrow\langle[X_{\mathbf{k}j}{}^{0\dagger}(t_1),X_{\mathbf{k}j}{}^0(t_2)]\rangle\\&=-2i\hbar Z^{-1}\int_0^\infty d\omega'[1-\exp(-\hbar\omega'/kT)]\\&\qquad\times B(\omega')\sin\omega'(t_1-t_2).\end{aligned}\quad\text{(A6)}$$

Defining

$$\xi=t_1+t_2,\quad\eta=t_1-t_2,\quad\text{(A7)}$$

and

$$\int_0^t dt_1 \int_0^t dt_2 = \frac{1}{2}\left[\int_0^t d\xi \int_{-\xi}^{\xi} d\eta + \int_t^{2t} d\xi \int_{-(2t-\xi)}^{2t-\xi} d\eta\right] = \frac{1}{2}\int d\xi \int d\eta, \quad \text{(A8)}$$

then Eq. (3.3) may be rewritten as

$$S = (i\hbar Z)^{-1} \exp(-2\Gamma_{\mathbf{k}j}t) \int d\xi \int d\eta \int_0^\infty d\omega' \times [1-\exp(-\hbar\omega'/kT)]B(\omega') \times \exp(\Gamma_{\mathbf{k}j}\xi) \exp(i\bar{\omega}_{\mathbf{k}j}\eta) \sin\omega'\eta. \quad \text{(A9)}$$

The η integrations have the form

$$\int_{-x}^{+x} d\eta \exp(i\bar{\omega}_{\mathbf{k}j}\eta) \sin\omega'\eta = i\left[\frac{\sin(\bar{\omega}_{\mathbf{k}j}-\omega')x}{\bar{\omega}_{\mathbf{k}j}-\omega'} - \frac{\sin(\bar{\omega}_{\mathbf{k}j}+\omega')x}{\bar{\omega}_{\mathbf{k}j}+\omega'}\right] \approx i\pi[\delta(\bar{\omega}_{\mathbf{k}j}-\omega') - \delta(\bar{\omega}_{\mathbf{k}j}+\omega')], \quad \text{(A10)}$$

for x large. That is, when

$$\xi(=t_1+t_2) \text{ and } 2t-\xi(=2t-t_1-t_2)$$

are both large, Eq. (A9) becomes [see the approximation preceding Eq. (2.39)]

$$S = \pi(\hbar Z)^{-1} \exp(-2\Gamma_{\mathbf{k}j}t) \int_0^{2t} d\xi \exp(\Gamma_{\mathbf{k}j}\xi) \times \int_0^\infty d\omega' [1-\exp(-\hbar\omega'/kT)] \times B(\omega')[\delta(\bar{\omega}_{\mathbf{k}j}-\omega') - \delta(\bar{\omega}_{\mathbf{k}j}+\omega')]. \quad \text{(A11)}$$

If it is assumed that $\bar{\omega}_{\mathbf{k}j} \approx \omega_{\mathbf{k}j}$, use of Eq. (2.47) enables Eq. (A11) to be rewritten as

$$S = \Gamma_{\mathbf{k}j} \exp(-2\Gamma_{\mathbf{k}j}t) \int_0^{2t} d\xi \exp(\Gamma_{\mathbf{k}j}\xi) = 1 - \exp(-2\Gamma_{\mathbf{k}j}t). \quad \text{(A12)}$$

Then, by Eq. (3.2), it is immediately seen that

$$[a_{\mathbf{k}j}(t), a_{\mathbf{k}j}^\dagger(t)] = 1.$$

APPENDIX D

Here we prove the equation [Eq. (4.1)]

$$\beta_{\mathbf{k}j}^* = \Gamma_{\mathbf{k}j} - i\Delta_{\mathbf{k}j} = -\hbar^{-2} \int_0^\infty d\tau \exp(-i\omega_{\mathbf{k}j}\tau) \times \langle [X_{\mathbf{k}j}^{0\dagger}(\tau), X_{\mathbf{k}j}^0(0)] \rangle.$$

Commencing with Eq. (A6), the following steps yield Eq. (4.1):

$$\int_0^\infty d\tau \exp(-i\omega_{\mathbf{k}j}\tau) \langle [X_{\mathbf{k}j}^{0\dagger}(\tau), X_{\mathbf{k}j}^0(0)] \rangle$$
$$= -2i\hbar Z^{-1} \int_0^\infty d\omega' [1-\exp(-\hbar\omega'/kT)]B(\omega') \int_0^\infty d\tau \exp(-i\omega_{\mathbf{k}j}\tau) \sin\omega'\tau$$
$$= i\hbar Z^{-1} \int_0^\infty d\omega' [1-\exp(-\hbar\omega'/kT)]B(\omega')[\xi^*(\omega_{\mathbf{k}j}-\omega') - \xi^*(\omega_{\mathbf{k}j}+\omega')]$$
$$= -\hbar^2 \beta_{j\mathbf{k}}^*.$$