

## Lattice Anharmonicity and Optical Absorption in Polar Crystals. II. Classical Treatment in the Linear Approximation

A. A. MARADUDIN

*Westinghouse Research Laboratories, Pittsburgh 35, Pennsylvania*

AND

R. F. WALLIS

*U. S. Naval Research Laboratory, Washington 25, D. C.*

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An expression for the elements of the dielectric susceptibility tensor for an ionic crystal has been derived in a manner analogous to that employed by Kubo in his treatment of magnetic susceptibility. In the high-temperature (classical) limit, this expression reduces to the Laplace transform of the autocorrelation function of the single normal coordinate which interacts directly with the external radiation field. We have applied this formalism to the calculation of the high-temperature linear optical absorption coefficient of an anharmonic ionic crystal for which we have retained only cubic anharmonic terms in the lattice Hamiltonian. We have solved directly for the Laplace transform of the autocorrelation function to lowest order in the anharmonic coupling constant by solving the equations of motion for the normal coordinates after they have been linearized. The linear absorption coefficient obtained from the susceptibility tensor is of Lorentzian form with a frequency-dependent damping constant which varies linearly with temperature. The absorption coefficient for a diatomic linear chain with nearest neighbor interactions has been evaluated.

### I. INTRODUCTION

IN a series of papers published in the 1930's, Born and Blackman presented a classical theory of anharmonic optical absorption in ionic crystals.<sup>1</sup> They started with the equations of motion of the individual normal coordinates which, due to the anharmonic interactions, form a set of nonlinear coupled equations. Treating the dispersion oscillator, i.e., the optical mode of infinite wavelength which couples directly to the external radiation field, separately from the other normal coordinates, they effectively linearized the equations of motion and solved them using ordinary time-dependent perturbation theory. Their results show a Lorentzian shape for the absorption curve as a function of the frequency of the external field which is peaked about the frequency of the dispersion oscillator ("dispersion frequency"), but in addition, the damping constant in the Lorentzian expression is itself a function of the frequency of the external field. This frequency dependence of the damping constant imparts additional, subsidiary, maxima to the absorption spectrum in qualitative agreement with experimental results.

Recently, notable advances have been made in the theory of transport properties and in methods of dealing with the statistical mechanics of systems of many interacting particles. These developments have prompted us to re-examine the theory of anharmonic optical absorption in ionic crystals with the objective of obtaining a systematic theory which not only can be extended to include higher-order contributions in the classical limit, but also can serve as the starting point for a satisfactory quantum mechanical theory. The necessity for a fresh approach is emphasized by certain

weaknesses in currently available quantum mechanical treatments.<sup>2</sup>

In this paper we develop the basic formalism which will be employed in these investigations.

We derive the equations of motion for the normal coordinates, and after linearizing them, solve them to obtain the absorption coefficient. The motivation for studying the linearized equations of motion is heuristic. If the equations are correct to lowest order in the anharmonic coupling constant, then we expect the solution to be correct to the same degree of approximation. We restrict ourselves to the classical case because its relative simplicity permits us to display our methods to best advantage. The more difficult quantum mechanical case will be treated in a subsequent paper.

The basic formulas required for the evaluation of the optical absorption coefficient are derived in Sec. II. In Sec. III, the equations of motion of the normal coordinates are obtained, and their solution, in the linear approximation, is carried out in Sec. IV. The resulting expression for the absorption coefficient is evaluated for a simple model in Sec. V.

### II. FORMULA FOR OPTICAL ABSORPTION COEFFICIENT

In deriving the formula for the optical absorption coefficient, we follow a procedure analogous to that employed by Kubo<sup>3</sup> in treating the magnetic susceptibility. We begin with the equation of motion of the density matrix for our crystal system in the absence of an external time-dependent perturbation:

$$\frac{\partial \rho}{\partial t} = \frac{-1}{i\hbar} [\rho H - H \rho] = \frac{-1}{i\hbar} [\rho, H]. \quad (2.1)$$

<sup>1</sup> M. Born and M. Blackman, *Z. Physik* **82**, 551 (1933); M. Blackman, *Z. Physik* **86**, 421 (1933); M. Blackman, *Phil. Trans. Roy. Soc. London* **A236**, 103 (1936).

<sup>2</sup> A. A. Maradudin and R. F. Wallis, *Phys. Rev.* **120**, 442 (1960).

<sup>3</sup> R. Kubo, *J. Phys. Soc. Japan* **12**, 570 (1957).

We now assume that, at time  $t = -\infty$ , an external electromagnetic field  $\mathbf{E}(t)$  is turned on. The interaction energy of our system with the external field has the form

$$H'(t) = -\mathbf{M} \cdot \mathbf{E}(t), \quad (2.2)$$

where  $\mathbf{M}$  is the dipole moment of the crystal. The equation of motion for the perturbed density matrix  $\rho + \Delta\rho$  becomes

$$\begin{aligned} \frac{\partial}{\partial t} [\rho + \Delta\rho] &= \frac{-1}{i\hbar} [\rho + \Delta\rho, H - \mathbf{M} \cdot \mathbf{E}(t)] \\ &\approx \frac{-1}{i\hbar} \{ [\rho, H] + [\Delta\rho, H] - [\rho, \mathbf{M} \cdot \mathbf{E}(t)] \}, \quad (2.3) \end{aligned}$$

where, since in all that follows we will be interested only in a linear relation between the dipole moment of the crystal and the external field  $\mathbf{E}(t)$ , we have neglected the commutator  $[\Delta\rho, \mathbf{M} \cdot \mathbf{E}(t)]$  as small of the second order in writing Eq. (2.3). With the aid of Eq. (2.1), we see that the equation of motion satisfied by  $\Delta\rho$  is

$$\frac{\partial \Delta\rho}{\partial t} = \frac{-1}{i\hbar} [\Delta\rho, H] + \frac{1}{i\hbar} [\rho, \mathbf{M} \cdot \mathbf{E}(t)]. \quad (2.4)$$

The solution to Eq. (2.4), subject to the condition  $\Delta\rho(-\infty) = 0$ , is

$$\begin{aligned} \Delta\rho(t) &= \frac{i}{\hbar} \sum_{\nu} \int_{-\infty}^t e^{-i(t-t')H/\hbar} \\ &\quad \times [M_{\nu, \rho}] e^{i(t-t')H/\hbar} E_{\nu}(t') dt', \quad (2.5) \end{aligned}$$

as can be verified by differentiation with respect to  $t$ .

The ensemble average of the expectation value of an operator  $B$  is given by

$$\langle B \rangle = \text{Trace}(\rho + \Delta\rho)B. \quad (2.6)$$

In the present case, we are interested in the expectation value of the  $\mu$  component of the dipole moment of our crystal  $M_{\mu}$ . Since in the absence of the external field the crystal has no permanent moment, we have that

$$\begin{aligned} \langle M_{\mu} \rangle &= \text{Trace} \Delta\rho M_{\mu} \\ &= \frac{i}{\hbar} \text{Trace} \sum_{\nu} \int_{-\infty}^t e^{-i(t-t')H/\hbar} \\ &\quad \times [M_{\nu, \rho}] e^{i(t-t')H/\hbar} E_{\nu}(t') M_{\mu} dt'. \quad (2.7) \end{aligned}$$

With the aid of the cyclic theorem for traces and the fact that  $E_{\nu}(t)$  is not an operator, this expression is rewritten as

$$\langle M_{\mu} \rangle = \frac{i}{\hbar} \text{Trace} \sum_{\nu} \int_{-\infty}^t [M_{\nu, \rho}] M_{\mu}(t-t') E_{\nu}(t') dt', \quad (2.8)$$

where we have put

$$\mathbf{M}(t) = e^{itH} \mathbf{M} e^{-itH}. \quad (2.9)$$

With a change of variable we obtain

$$\langle M_{\mu} \rangle = \frac{i}{\hbar} \text{Trace} \sum_{\nu} \int_0^{\infty} [M_{\nu, \rho}] M_{\mu}(\tau) E_{\nu}(t-\tau) d\tau. \quad (2.10)$$

If we describe our external field by the following relation,

$$\mathbf{E}(t) = e^{\epsilon t} \mathbf{E}_0 e^{i\omega t}, \quad (2.11)$$

where the factor  $e^{\epsilon t}$  is introduced to turn on the field adiabatically for  $t < 0$ , and  $\epsilon$  is eventually put equal to zero, we obtain finally that

$$\begin{aligned} \langle M_{\mu} \rangle &= \frac{i}{\hbar} \text{Trace} \sum_{\nu} E_{0\nu} e^{\epsilon t + i\omega t} \\ &\quad \times \int_0^{\infty} [M_{\nu, \rho}] M_{\mu}(\tau) e^{-\epsilon\tau - i\omega\tau} d\tau. \quad (2.12) \end{aligned}$$

The expression for the  $\mu\nu$  element of the dielectric susceptibility tensor thus becomes

$$\begin{aligned} \chi_{\mu\nu}(\omega) &= \frac{i}{\hbar V} \lim_{\epsilon \rightarrow 0^+} \text{Trace} \int_0^{\infty} e^{-i\omega\tau - \epsilon\tau} [M_{\nu, \rho}] M_{\mu}(\tau) d\tau, \quad (2.13) \end{aligned}$$

where  $V$  is the volume of the crystal.

If we assume that the unperturbed system is in a canonical distribution so that

$$\rho = e^{-\beta H} / Z, \quad (2.14)$$

where  $Z$  is the crystal's partition function; then, with the aid of Kubo's identity,

$$[A, e^{-\beta H}] = \frac{\hbar}{i} e^{-\beta H} \int_0^{\beta} e^{\lambda H} \dot{A} e^{-\lambda H} d\lambda, \quad (2.15)$$

we obtain

$$\begin{aligned} \chi_{\mu\nu}(\omega) &= \lim_{\epsilon \rightarrow 0^+} \frac{\text{Trace}}{ZV} \int_0^{\infty} e^{-i\omega\tau - \epsilon\tau} e^{-\beta H} \\ &\quad \times \int_0^{\beta} e^{\lambda H} \dot{M}_{\nu} e^{-\lambda H} d\lambda M_{\mu}(\tau) d\tau \\ &= \lim_{\epsilon \rightarrow 0^+} \frac{\text{Trace}}{ZV} \int_0^{\infty} d\tau e^{-i\omega\tau - \epsilon\tau} \\ &\quad \times \int_0^{\beta} e^{-\beta H} \dot{M}_{\nu}(-i\lambda\hbar) M_{\mu}(\tau) d\lambda. \quad (2.16a) \end{aligned}$$

In the classical limit,  $\hbar \rightarrow 0$  and we have

$$\chi_{\mu\nu}(\omega) = \lim_{\epsilon \rightarrow 0^+} \frac{\beta}{V} \int_0^{\infty} e^{-i\omega\tau - \epsilon\tau} \langle \dot{M}_{\nu}(0) M_{\mu}(\tau) \rangle d\tau, \quad (2.16b)$$

where  $\langle \dots \rangle$  means an average over the unperturbed canonical distribution.

The relation between the susceptibility tensor and the absorption coefficient is obtained as follows.<sup>4</sup> From the relation between the dielectric constant and the susceptibility

$$\epsilon_{\mu\nu}(\omega) = \delta_{\mu\nu} + 4\pi\chi_{\mu\nu}(\omega), \quad (2.17)$$

we find, in the plane-polarized case, that

$$\epsilon_{xx}(\omega) = 1 + 4\pi\chi_{xx}(\omega). \quad (2.18)$$

We now set  $\epsilon_{xx} = n^2$ , where  $n = \lambda + i\mu$  and break up  $\chi_{xx}$  into its real and imaginary parts

$$\chi_{xx}(\omega) = \chi_{xx}^{(1)} - i\chi_{xx}^{(2)}. \quad (2.19)$$

$\lambda$  is known as the ordinary index of refraction, while  $\mu$  is the extinction coefficient. If  $\chi_{xx}$  is so small that its square can be neglected relative to  $\chi_{xx}$  itself, then we find for  $\lambda$  and  $\mu$

$$\begin{aligned} \lambda &= 1 + 2\pi\chi_{xx}^{(1)}(\omega), \\ \mu &= -2\pi\chi_{xx}^{(2)}(\omega). \end{aligned} \quad (2.20)$$

The linear absorption coefficient  $\alpha_{xx}(\omega)$  is given by

$$\alpha_{xx}(\omega) = -2\frac{\omega}{c}\mu = +4\pi\chi_{xx}^{(2)}. \quad (2.21)$$

Since the absorption coefficient  $\alpha_{xx}(\omega)$  is just proportional to the imaginary part of  $\chi_{xx}(\omega)$ , Eqs. (2.16) formally solve the problem of determining the absorption coefficient of our crystal.

We will be concerned here with the classical limit, and Eq. (2.16b) is the basic equation of this paper.

In an ionic crystal, the dipole moment  $\mathbf{M}$  is given by

$$\mathbf{M} = \sum_{l\kappa} \epsilon_{\kappa} \mathbf{u}(l\kappa), \quad (2.22)$$

where  $\mathbf{u}(l\kappa)$  is the vector displacement of the  $\kappa$ th ion in the  $l$ th unit cell from its equilibrium position and  $\epsilon_{\kappa}$  is the charge on the  $\kappa$ th kind of ion in a unit cell. We now expand  $\mathbf{u}(l\kappa)$  in terms of normal coordinates,

$$\mathbf{u}(l\kappa) = \frac{1}{(NM_{\kappa})^{\frac{1}{2}}} \sum_{\mathbf{k}j} \mathbf{e}(\kappa|\mathbf{k}j) Q(\mathbf{k}j) e^{2\pi i \mathbf{k} \cdot \mathbf{x}(l)}, \quad (2.23a)$$

where  $\mathbf{e}(\kappa|\mathbf{k}j)$  is an eigenvector (normalized to unity) of the dynamical matrix for our crystal. The normal coordinates  $Q(\mathbf{k}j)$  satisfy the reality condition

$$Q(\mathbf{k}j) = Q^*(-\mathbf{k}j), \quad (2.23b)$$

where  $j$  labels the branches of the frequency spectrum, with the consequence that  $Q(0j)$  is a real quantity. The  $\mu$  component of  $\mathbf{M}$  can be written as

$$M_{\mu} = \sqrt{N} \sum_j M_{\mu}(0j) Q(0j), \quad (2.24)$$

<sup>4</sup> R. C. O'Rourke, U. S. Naval Research Laboratory Report No. 4975, 1957 (unpublished), p. 207.

where

$$M_{\mu}(0j) = \sum_{\kappa} \frac{\epsilon_{\kappa}}{\sqrt{M_{\kappa}}} e_{\mu}(\kappa|0j). \quad (2.25)$$

In fact, however,  $M_{\mu}(0j)$  vanishes for  $j$  corresponding to an acoustic branch, so that we can write

$$M_{\mu} = \sqrt{N} M_{\mu}(0j) Q(0j), \quad (2.26)$$

where it is now to be understood that  $j$  refers to an optical branch.

Thus, for the partial dielectric susceptibility associated with the  $j$ th dispersion oscillator, we find, on combining Eqs. (2.26) and (2.16b),

$$\begin{aligned} \chi_{\mu\nu}^{(j)}(\omega) &= \frac{NM_{\mu}(0j)M_{\nu}(0j)}{V\kappa T} \lim_{\epsilon \rightarrow 0^+} \int_0^{\infty} e^{-i\omega t - \epsilon t} \\ &\quad \times \langle \dot{Q}(0j; 0) Q(0j; t) \rangle dt, \end{aligned} \quad (2.27)$$

where by  $Q(0j; t)$  we mean the value of the normal coordinate  $Q(0j)$  at time  $t$ . If we can find a way of expressing  $Q(0j)$  at time  $t$  in terms of its value at time  $t=0$  in the form

$$Q(0j; t) = Q(0j; 0)F_{0j}(t) + \dot{Q}(0j; 0)G_{0j}(t), \quad (2.28)$$

then we can rewrite Eq. (2.27) as

$$\begin{aligned} \chi_{\mu\nu}^{(j)}(\omega) &= \frac{NM_{\mu}(0j)M_{\nu}(0j)}{V\kappa T} \langle \dot{Q}(0j; 0) Q(0j; 0) \rangle \\ &\quad \times \lim_{\epsilon \rightarrow 0^+} \int_0^{\infty} e^{-i\omega t - \epsilon t} G_{0j}(t) dt, \end{aligned} \quad (2.29)$$

since the thermal average of  $\dot{Q}(0j; 0)Q(0j; 0)$  will vanish. This is essentially what we will do in the present paper, although we will have to be somewhat more careful in evaluating the thermal averages than has been indicated in the derivation of Eq. (2.29).

As an illustration of the use of Eq. (2.27), we calculate the absorption in a purely harmonic lattice. In this case, we have that

$$Q(0j; t) = Q(0j; 0) \cos\omega_{0j}t + \dot{Q}(0j; 0) (\sin\omega_{0j}t/\omega_{0j}), \quad (2.30)$$

where  $\omega_{0j}$  is the frequency associated with the mode  $(\mathbf{k}j)$ . Equation (2.27) becomes

$$\begin{aligned} \chi_{\mu\nu}^{(j)}(\omega) &= \frac{NM_{\mu}(0j)M_{\nu}(0j)}{V\omega_{0j}} \lim_{\epsilon \rightarrow 0^+} \int_0^{\infty} e^{-i\omega t - \epsilon t} \sin\omega_{0j}t dt, \end{aligned} \quad (2.31)$$

since in the harmonic approximation  $\langle \dot{Q}(0j; 0) Q(0j; 0) \rangle = \kappa T$ , so that

$$\text{Im}\chi_{\mu\nu}^{(j)}(\omega) = -\frac{\pi NM_{\mu}(0j)M_{\nu}(0j)}{2V\omega_{0j}} \delta(\omega_{0j} - \omega). \quad (2.31)$$

Combining this result with Eq. (2.21), we find for the

linear absorption coefficient

$$\alpha_{xx}^{(j)} = + \frac{2\pi^2}{c} \frac{\omega}{\omega_{0j}} \frac{M_x(0j)M_x(0j)}{v_a} \delta(\omega - \omega_{0j}), \quad (2.32)$$

where  $v_a$  is the volume of a unit cell in the crystal. This is the expected result. A factor  $(1/n_0)$ , where  $n_0$  is the high-frequency refractive index, may be included on the right-hand side of Eq. (2.32) to take into account the electronic polarization.

The approach outlined in this section has at least two advantages over more conventional ways of calculating the optical absorption. Firstly, since all that is required is the time evolution of one particular normal coordinate, questions relating to the intensive or extensive nature of the damping constants which appear in the course of the calculations are absent; the required damping constants come out automatically as intensive quantities rather than as the differences of extensive quantities. Secondly, we note that the integral in the expression for the susceptibility tensor Eq. (2.29) is of the Laplace form with a complex parameter  $s = \epsilon + i\omega$ . This suggests that if we solve not for the primitive function  $G_{0j}(t)$  but instead for its Laplace transform  $g_{0j}(s)$ , we need only replace  $s$  by  $\epsilon + i\omega$  in the expression for  $g_{0j}(s)$  and pass to the limit as  $\epsilon \rightarrow 0+$  in order to obtain the susceptibility and hence the absorption coefficient. Not only does this procedure eliminate any need for ever returning to the time-dependent representation, but, more importantly, it introduces the frequency dependence into the damping constants in a very natural way, something which appears to be extremely difficult in the time-dependent formalism. Indeed, it is rather natural to solve the equations of motion by Laplace transform techniques, since the latter are particularly well suited for solving initial-value problems.

### III. EQUATIONS OF MOTION OF THE NORMAL COORDINATES

If we retain only cubic anharmonic terms in the expansion of the potential energy of the crystal, the Hamiltonian for our vibrating lattice becomes<sup>5</sup>

$$H = \frac{1}{2} \sum_{l\kappa\alpha} M_\kappa \dot{u}_\alpha^2(l\kappa) + \frac{1}{2} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa; l'\kappa') u_\alpha(l\kappa) u_\beta(l'\kappa') \\ + \frac{1}{6} \sum_{l\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l''\kappa''\gamma} \Phi_{\alpha\beta\gamma}(l\kappa; l'\kappa'; l''\kappa'') u_\alpha(l\kappa) \\ \times u_\beta(l'\kappa') u_\gamma(l''\kappa'') + \dots, \quad (3.1)$$

where  $u_\alpha(l\kappa)$  is the  $\alpha$ -Cartesian component of the displacement of the  $\kappa$ th atom in the  $l$ th unit cell from its equilibrium position,  $M_\kappa$  is the mass of the  $\kappa$ th kind of atom in a unit cell, and the indices  $l$  and  $\kappa$  range over  $N$  unit cells and two atoms per unit cell, respec-

tively. The  $\Phi$  coefficients are general force constants for our crystal.

If we apply the normal coordinate transformation given in Eq. (2.25) to the above Hamiltonian, we obtain the result that

$$H = \frac{1}{2} \sum_{\mathbf{k}j} \{ \dot{Q}(\mathbf{k}j) \dot{Q}(-\mathbf{k}j) + \omega_j^2(\mathbf{k}) Q(\mathbf{k}j) Q(-\mathbf{k}j) \} \\ + \frac{1}{6\sqrt{N}} \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} \sum_{j'j''} \Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}'') \Phi(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \\ \times Q(\mathbf{k}j) Q(\mathbf{k}'j') Q(\mathbf{k}''j''), \quad (3.2)$$

with

$$\Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}'') = 1, \quad \mathbf{k}+\mathbf{k}'+\mathbf{k}'' = \mathbf{K} \\ = 0 \quad \text{otherwise}, \quad (3.3)$$

where  $\mathbf{K}$  is a primitive translation vector of the reciprocal lattice. The  $\{\omega_j^2(\mathbf{k})\}$  are the eigen values of the dynamical matrix for our crystal, and are the squares of the normal-mode frequencies.

The coefficient  $\Phi(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')$  is given explicitly by

$$\Phi(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \\ = \sum_{\kappa\alpha} \sum_{l'\kappa'\beta} \sum_{l''\kappa''\gamma} \frac{\Phi_{\alpha\beta\gamma}(0\kappa; l'\kappa'; l''\kappa'')}{(M_\kappa M_{\kappa'} M_{\kappa''})^{\frac{1}{2}}} \\ \times e_\alpha(\kappa | \mathbf{k}j) e_\beta(\kappa' | \mathbf{k}'j') e_\gamma(\kappa'' | \mathbf{k}''j'') \\ \times e^{2\pi i[\mathbf{k}' \cdot \mathbf{x}(l') + \mathbf{k}'' \cdot \mathbf{x}(l'')]}, \quad (3.4)$$

and is completely symmetric in the indices  $\mathbf{k}j$ ,  $\mathbf{k}'j'$ ,  $\mathbf{k}''j''$ .

For convenience we put

$$\frac{1}{2\sqrt{N}} \Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}'') \Phi(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \\ \equiv V(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j''), \quad (3.5a)$$

and we see that this function satisfies the relation

$$V(-\mathbf{k}j; -\mathbf{k}'j'; -\mathbf{k}''j'') = V^*(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j''). \quad (3.5b)$$

Hamilton's equations of motion for the lattice become

$$P(\mathbf{k}j) = \frac{\partial H}{\partial \dot{Q}(-\mathbf{k}j)} = \dot{Q}(\mathbf{k}j), \quad (3.6a)$$

$$\dot{P}(\mathbf{k}j) = - \frac{\partial H}{\partial Q(-\mathbf{k}j)} = -\omega_j^2(\mathbf{k}) \\ - \sum_{\mathbf{k}'\mathbf{k}''} \sum_{j'j''} V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \\ \times Q(\mathbf{k}'j') Q(\mathbf{k}''j''). \quad (3.6b)$$

Combining these two equations, we obtain

$$\ddot{Q}(\mathbf{k}j) + \omega_j^2(\mathbf{k}) Q(\mathbf{k}j) = - \sum_{\mathbf{k}'\mathbf{k}''} \sum_{j'j''} V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \\ \times Q(\mathbf{k}'j') Q(\mathbf{k}''j''). \quad (3.7)$$

In the harmonic approximation, the right-hand side

<sup>5</sup> See, for example, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 343.

of Eq. (3.7) vanishes, and the solution for the normal coordinates can be written as

$$Q(\mathbf{k}j; t) = \frac{1}{2} \left[ Q(\mathbf{k}j; 0) + \frac{\dot{Q}(\mathbf{k}j; 0)}{i\omega_j(\mathbf{k})} \right] e^{i\omega_j(\mathbf{k})t} + \frac{1}{2} \left[ Q(\mathbf{k}j; 0) - \frac{\dot{Q}(\mathbf{k}j; 0)}{i\omega_j(\mathbf{k})} \right] e^{-i\omega_j(\mathbf{k})t}. \quad (3.8)$$

In the anharmonic case, it is convenient to introduce new variables  $C(\mathbf{k}j; t)$  and  $C(\mathbf{k}-j; t)$  in place of  $Q(\mathbf{k}j; t)$  and  $\dot{Q}(\mathbf{k}j; t)$  by means of the relations

$$C(\mathbf{k}j; t) = \frac{1}{2} \left[ Q(\mathbf{k}j; t) + \frac{\dot{Q}(\mathbf{k}j; t)}{i\omega_j(\mathbf{k})} \right] e^{-i\omega_j(\mathbf{k})t}, \quad (3.9a)$$

$$C(\mathbf{k}-j; t) = \frac{1}{2} \left[ Q(\mathbf{k}j; t) - \frac{\dot{Q}(\mathbf{k}j; t)}{i\omega_j(\mathbf{k})} \right] e^{i\omega_j(\mathbf{k})t}. \quad (3.9b)$$

By using Eq. (3.7) one can verify that the quantities  $C(\mathbf{k}\pm j; t)$  satisfy the equation

$$\begin{aligned} \frac{d}{dt} C(\mathbf{k}\pm j; t) &= \mp \frac{e^{\mp i\omega_j(\mathbf{k})t}}{2i\omega_j(\mathbf{k})} \sum_{\mathbf{k}'\mathbf{k}''j'j''} V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \\ &\times [C(\mathbf{k}'j'; t)e^{i\omega_{j'}(\mathbf{k}')t} + C(\mathbf{k}'-j'; t)e^{-i\omega_{j'}(\mathbf{k}')t}] \\ &\times [C(\mathbf{k}''j''; t)e^{i\omega_{j''}(\mathbf{k}'')t} \\ &+ C(\mathbf{k}''-j''; t)e^{-i\omega_{j''}(\mathbf{k}'')t}]. \quad (3.10) \end{aligned}$$

$$\begin{aligned} \frac{d}{dt} C_{\mathbf{k}j}^{(1)} &= \frac{i}{2\omega_j(\mathbf{k})} \sum_{\mathbf{k}'\mathbf{k}''} \sum_{j'j''} V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') c_{\mathbf{k}'j'}^{(0)} c_{\mathbf{k}''j''}^{(0)} e^{i[\omega_{j'}(\mathbf{k}') + \omega_{j''}(\mathbf{k}'') - \omega_j(\mathbf{k})]t} \\ &+ \frac{i}{\omega_j(\mathbf{k})} \sum_{\mathbf{k}'\mathbf{k}''} \sum_{j'j''} V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') c_{\mathbf{k}'j'}^{(0)} c_{\mathbf{k}''j''}^{(1)} e^{i[\omega_{j'}(\mathbf{k}') + \omega_{j''}(\mathbf{k}'') - \omega_j(\mathbf{k})]t}. \quad (3.14) \end{aligned}$$

It is with the solution of this equation (in the special case  $\mathbf{k}=0$ ) that we will be concerned in this paper.

IV. SOLUTIONS OF EQUATIONS OF MOTION

In calculating the dielectric susceptibility tensor, we must evaluate the thermal average

$$\langle \dot{Q}^*(\mathbf{k}j; 0) Q(\mathbf{k}j; t) \rangle,$$

in the special case  $\mathbf{k}=0$ . In terms of the new normal

$$\begin{aligned} \chi_{\mu\nu}^{(j)}(\omega) &= \frac{\omega_{0j}}{i} \frac{NM_\mu(0j)M_\nu(0j)}{VkT} \lim_{\epsilon \rightarrow 0^+} \left\{ \int_0^\infty e^{-(\epsilon+i\omega-i\omega_{0j})t} \langle [C^*(0j; 0) - C^*(0-j; 0)] C(0j; t) \rangle dt \right. \\ &\quad \left. + \int_0^\infty e^{-(\epsilon+i\omega+i\omega_{0j})t} \langle [C^*(0j; 0) - C^*(0-j; 0)] C(0-j; t) \rangle dt \right\}. \quad (4.1) \end{aligned}$$

Thus, the problem of obtaining  $\chi_{\mu\nu}^{(j)}(\omega)$  reduces to finding the Laplace transforms of  $C(0j; t)$  and  $C(0-j; t)$  and evaluating the indicated thermal average. In view of Eq. (3.13), the Laplace transform of  $C(\mathbf{k}j; t)$  can be

By adopting the notation

$$\begin{aligned} \omega_j(\mathbf{k}) &= -\omega_{-j}(\mathbf{k}), \\ V(-\mathbf{k}\pm j; \mathbf{k}'\pm j'; \mathbf{k}''\pm j'') &= V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j''), \quad (3.11) \end{aligned}$$

we can rewrite Eq. (3.10) in the compact form

$$\begin{aligned} \frac{d}{dt} C(\mathbf{k}j; t) &= -\frac{1}{2i\omega_j(\mathbf{k})} \sum_{\mathbf{k}'\mathbf{k}''} \sum_{\pm j'\pm j''} V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'') \\ &\times C(\mathbf{k}'j'; t) C(\mathbf{k}''j''; t) \\ &\times e^{i[\omega_{j'}(\mathbf{k}') + \omega_{j''}(\mathbf{k}'') - \omega_j(\mathbf{k})]t}, \quad (3.12) \end{aligned}$$

where  $j'$  and  $j''$  are now summed over positive and negative values and  $j$  may be either positive or negative.

For the purposes of the present paper, we linearize the equation (3.12) in the following way. In the absence of the anharmonic interactions the  $C(\mathbf{k}j; t)$  are independent of time. We thus write

$$C(\mathbf{k}j; t) = c_{\mathbf{k}j}^{(0)} + c_{\mathbf{k}j}^{(1)}(t), \quad (3.13)$$

where  $c_{\mathbf{k}j}^{(0)}$  is the time-independent solution to the harmonic equation of motion, and  $c_{\mathbf{k}j}^{(1)}(t)$  represents the time-dependent correction due to anharmonicity. Substituting Eq. (3.13) into Eq. (3.12) and retaining only linear terms in  $c_{\mathbf{k}j}^{(1)}(t)$ , we obtain

coordinates  $C(\mathbf{k}j; t)$  and  $C(\mathbf{k}-j; t)$ , this average becomes

$$\begin{aligned} -i\omega_{\mathbf{k}j} \langle [C^*(\mathbf{k}j; 0) - C^*(\mathbf{k}-j; 0)] \\ \times [C(\mathbf{k}j; t)e^{i\omega_{\mathbf{k}j}t} + C(\mathbf{k}-j; t)e^{-i\omega_{\mathbf{k}j}t}] \rangle. \end{aligned}$$

In this expression and in what follows, for typographical convenience, we have expressed  $\omega_j(\mathbf{k})$  as  $\omega_{\mathbf{k}j}$ . If we substitute this expression back into Eq. (2.29), we obtain the result that

written as

$$\begin{aligned} \mathcal{L}\{C(\mathbf{k}j; t)\} &= \mathcal{L}\{c_{\mathbf{k}j}^{(0)} + c_{\mathbf{k}j}^{(1)}(t)\} \\ &= \frac{c_{\mathbf{k}j}^{(0)}}{s} + \gamma_{\mathbf{k}j}(s). \end{aligned} \tag{4.2}$$

We begin by taking the Laplace transform of Eq. (3.14). We obtain

$$\begin{aligned} \gamma_{\mathbf{k}j}(s) &= \frac{c_{\mathbf{k}j}^{(1)}(0)}{s} + \frac{i}{2s\omega_{\mathbf{k}j}} \sum_{\mathbf{k}'\mathbf{k}''\mathbf{j}'\mathbf{j}''} \frac{V(-\mathbf{k}j; \mathbf{k}'\mathbf{j}'; \mathbf{k}''\mathbf{j}'')c_{\mathbf{k}'\mathbf{j}'}^{(0)}c_{\mathbf{k}''\mathbf{j}''}^{(0)}}{s - i(\omega_{\mathbf{k}'\mathbf{j}'} + \omega_{\mathbf{k}''\mathbf{j}''} - \omega_{\mathbf{k}j})} \\ &\quad + \frac{i}{s\omega_{\mathbf{k}j}} \sum_{\mathbf{k}'\mathbf{k}''\mathbf{j}'\mathbf{j}''} V(-\mathbf{k}j; \mathbf{k}'\mathbf{j}'; \mathbf{k}''\mathbf{j}'')c_{\mathbf{k}'\mathbf{j}'}^{(0)}\gamma_{\mathbf{k}''\mathbf{j}''}(s) [s - i(\omega_{\mathbf{k}'\mathbf{j}'} + \omega_{\mathbf{k}''\mathbf{j}''} - \omega_{\mathbf{k}j})]. \end{aligned} \tag{4.3}$$

We assume that  $c_{\mathbf{k}j}^{(1)}(0) \equiv 0$ . This can be regarded as equivalent to incorporating it into the definition of  $c_{\mathbf{k}j}^{(0)}$ .

For the purpose of calculating optical absorption we need  $\gamma_{0j}(s)$ . However, it is just as easy to solve for a general  $\gamma_{\mathbf{k}j}(s)$ , and we solve for this variable by iteration:

$$\begin{aligned} \gamma_{\mathbf{k}j}(s) &= \frac{i}{2s} \sum_{\mathbf{k}'\mathbf{k}''\mathbf{j}'\mathbf{j}''} \frac{V(-\mathbf{k}j; \mathbf{k}'\mathbf{j}'; \mathbf{k}''\mathbf{j}'')c_{\mathbf{k}'\mathbf{j}'}^{(0)}c_{\mathbf{k}''\mathbf{j}''}^{(0)}}{\omega_{\mathbf{k}j}[s - i(\omega_{\mathbf{k}'\mathbf{j}'} + \omega_{\mathbf{k}''\mathbf{j}''} - \omega_{\mathbf{k}j})]} \\ &\quad + \frac{(i)^2}{2s} \sum_{\mathbf{k}'\mathbf{k}''\mathbf{k}_1'\mathbf{k}_1''\mathbf{j}'\mathbf{j}''\mathbf{j}_1'\mathbf{j}_1''} \frac{V(-\mathbf{k}j; \mathbf{k}'\mathbf{j}'; \mathbf{k}''\mathbf{j}'')V(-\mathbf{k}''\mathbf{j}''; \mathbf{k}_1'\mathbf{j}_1'; \mathbf{k}_1''\mathbf{j}_1'')c_{\mathbf{k}'\mathbf{j}'}^{(0)}c_{\mathbf{k}_1'\mathbf{j}_1'}^{(0)}c_{\mathbf{k}_1''\mathbf{j}_1''}^{(0)}}{\omega_{\mathbf{k}j}\omega_{\mathbf{k}''\mathbf{j}''}[s - i(\omega_{\mathbf{k}'\mathbf{j}'} + \omega_{\mathbf{k}''\mathbf{j}''} - \omega_{\mathbf{k}j})]} \\ &\quad \times \frac{1}{s - i(\omega_{\mathbf{k}'\mathbf{j}'} + \omega_{\mathbf{k}''\mathbf{j}''} - \omega_{\mathbf{k}j}) - i(\omega_{\mathbf{k}_1'\mathbf{j}_1'} + \omega_{\mathbf{k}_1''\mathbf{j}_1''} - \omega_{\mathbf{k}''\mathbf{j}''})} + \dots \end{aligned} \tag{4.4}$$

At this point, we can effect an immediate simplification in this expansion if we remember that, for the calculation of optical absorption, we require the thermal average of the product of  $\gamma_{\mathbf{k}j}(s)$  and  $\gamma_{\mathbf{k}-j}(s)$  with  $C^*(\mathbf{k}-j; 0)$  and  $C^*(\mathbf{k}j; 0)$  in the special case  $\mathbf{k}=0$ . From Eqs. (3.10) and the relations

$$\begin{aligned} \langle Q^*(\mathbf{k}j)Q(\mathbf{k}'\mathbf{j}') \rangle &= \frac{kT}{\omega_{\mathbf{k}j}^2} \Delta(\mathbf{k}' - \mathbf{k}) \delta_{jj'}, \\ \langle \dot{Q}^*(\mathbf{k}j)\dot{Q}(\mathbf{k}'\mathbf{j}') \rangle &= kT\Delta(\mathbf{k}' - \mathbf{k}) \delta_{jj'}, \end{aligned} \tag{4.5}$$

we obtain the results that

$$\begin{aligned} \langle C^*(\mathbf{k}j; 0)C(\mathbf{k}'\mathbf{j}'; 0) \rangle &= \frac{kT}{2\omega_{\mathbf{k}j}^2} \Delta(\mathbf{k}' - \mathbf{k}) \delta_{jj'}, \\ \langle C^*(\mathbf{k}-j; 0)C(\mathbf{k}'\mathbf{j}'; 0) \rangle &= \langle C^*(\mathbf{k}j; 0)C(\mathbf{k}'-j'; 0) \rangle \\ &= 0, \end{aligned} \tag{4.6}$$

$$\langle C^*(\mathbf{k}-j; 0)C(\mathbf{k}'-j'; 0) \rangle = \frac{kT}{2\omega_{\mathbf{k}j}^2} \Delta(\mathbf{k}' - \mathbf{k}) \delta_{jj'}.$$

The thermal averages, Eq. (4.5), have been evaluated in the harmonic approximation. They suffice, however, to give us final results which are correct to the lowest order in the anharmonic coupling constant.

These results imply that only the even-order terms in this expansion give a nonvanishing contribution after averaging since the thermal average of the product of an odd number of normal coordinates vanishes. Furthermore, in the even-order terms, certain pairings of indices on the  $c_{\mathbf{k}j}^{(0)}$  are required in order that the thermal averages do not vanish. As an example, we work out explicitly the second-order contribution. We compute first  $\langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}j}(s) \rangle$ . This quantity is given by

$$\begin{aligned} \langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}j}(s) \rangle &= \frac{(i)^2}{2s} \sum_{\mathbf{k}'\mathbf{k}''\mathbf{k}_1'\mathbf{k}_1''\mathbf{j}'\mathbf{j}''\mathbf{j}_1'\mathbf{j}_1''} \frac{V(-\mathbf{k}j; \mathbf{k}'\mathbf{j}'; \mathbf{k}''\mathbf{j}'')V(-\mathbf{k}''\mathbf{j}''; \mathbf{k}_1'\mathbf{j}_1'; \mathbf{k}_1''\mathbf{j}_1'')}{\omega_{\mathbf{k}j}\omega_{\mathbf{k}''\mathbf{j}''}[s - i(\omega_{\mathbf{k}'\mathbf{j}'} + \omega_{\mathbf{k}''\mathbf{j}''} - \omega_{\mathbf{k}j})]} \\ &\quad \times \frac{\langle c_{\mathbf{k}j}^{*(0)}c_{\mathbf{k}'\mathbf{j}'}^{(0)}c_{\mathbf{k}_1'\mathbf{j}_1'}^{(0)}c_{\mathbf{k}_1''\mathbf{j}_1''}^{(0)} \rangle}{[s - i(\omega_{\mathbf{k}'\mathbf{j}'} + \omega_{\mathbf{k}''\mathbf{j}''} - \omega_{\mathbf{k}j}) - i(\omega_{\mathbf{k}_1'\mathbf{j}_1'} + \omega_{\mathbf{k}_1''\mathbf{j}_1''} - \omega_{\mathbf{k}''\mathbf{j}''})]}. \end{aligned} \tag{4.7}$$

The thermal average vanishes unless the normal coordinates are grouped in pairs. We neglect here the cases in which all four normal coordinates are equal since neglect of such terms leads to an error of only  $O(N^{-1})$ . In view

of Eqs. (4.6) and (3.9) there are three possible pairings, and these are given by

$$\begin{aligned}
 (a) \quad & \mathbf{k}_1'' = \mathbf{k}, \quad j_1'' = j; \quad \mathbf{k}_1' = -\mathbf{k}', \quad j_1' = -j' \\
 (b) \quad & \mathbf{k}_1' = \mathbf{k}, \quad j_1' = j; \quad \mathbf{k}_1'' = -\mathbf{k}', \quad j_1'' = -j' \\
 (c) \quad & \mathbf{k}' = \mathbf{k}, \quad j' = j; \quad \mathbf{k}_1'' = -\mathbf{k}_1', \quad j_1'' = -j_1'.
 \end{aligned}
 \tag{4.8}$$

However, of these three possible pairings, only the first two give nonvanishing contributions since it is a general result that<sup>6</sup>

$$V(-\mathbf{k}j; \mathbf{k}j; \mathbf{k}''j'') \equiv 0. \tag{4.9}$$

The contributions from the first and second sets of pairings are equal to each other and are given by

$$\begin{aligned}
 \frac{(i)^2}{2s} \sum_{\mathbf{k}'\mathbf{k}''j_1'j_1''} \frac{V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')V(-\mathbf{k}''j''; \mathbf{k}j; -\mathbf{k}'-j')}{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}[s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}-\omega_{\mathbf{k}j})]} \left(\frac{kT}{2}\right)^2 \frac{1}{\omega_{\mathbf{k}j}^2\omega_{\mathbf{k}'j'}^2[s-i(\omega_{\mathbf{k}'j'}-\omega_{\mathbf{k}j})-i(\omega_{\mathbf{k}j}-\omega_{\mathbf{k}'j'})]} \\
 = \frac{(i)^2 (kT)^2}{2s^2 2^2\omega_{\mathbf{k}j}^2} \sum_{\mathbf{k}'\mathbf{k}''j_1'j_1''} \frac{|V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')|^2}{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}^2\omega_{\mathbf{k}''j''}} \frac{1}{s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}-\omega_{\mathbf{k}j})}.
 \end{aligned}
 \tag{4.10}$$

In a similar fashion, the thermal average  $\langle C^*(\mathbf{k}-j; 0)\gamma_{\mathbf{k}j}(s) \rangle$  is found to be the sum of two terms, each of which is equal to

$$\frac{(i)^2 (kT)^2}{2s 2^2\omega_{\mathbf{k}j}^2} \sum_{\mathbf{k}'\mathbf{k}''j_1'j_1''} \frac{|V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')|^2}{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}^2\omega_{\mathbf{k}''j''}} \frac{1}{[s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}-\omega_{\mathbf{k}j})][s+2i\omega_{\mathbf{k}j}]}. \tag{4.11}$$

Similarly, the thermal averages  $\langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}-j}(s) \rangle$  and  $\langle C^*(\mathbf{k}-j; 0)\gamma_{\mathbf{k}-j}(s) \rangle$  are given by

$$\langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}-j}(s) \rangle = -2 \frac{(i)^2 (kT)^2}{2s 2^2\omega_{\mathbf{k}j}^2} \sum_{\mathbf{k}'\mathbf{k}''j_1'j_1''} \frac{|V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')|^2}{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}^2\omega_{\mathbf{k}''j''}} \frac{1}{[s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}+\omega_{\mathbf{k}j})][s-2i\omega_{\mathbf{k}j}]}, \tag{4.12}$$

$$\langle C^*(\mathbf{k}-j; 0)\gamma_{\mathbf{k}-j}(s) \rangle = -2 \frac{(i)^2 (kT)^2}{2s^2 2^2\omega_{\mathbf{k}j}^2} \sum_{\mathbf{k}'\mathbf{k}''j_1'j_1''} \frac{|V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')|^2}{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}^2\omega_{\mathbf{k}''j''}} \frac{1}{s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}-\omega_{\mathbf{k}j})}, \tag{4.13}$$

respectively.

Before proceeding to a general discussion of the contribution from the 2nth term in the expansion (4.4), we have one more point to bring out, and this is illustrated by the contribution from the fourth-order terms. Explicitly, we have that

$$\begin{aligned}
 \gamma_{\mathbf{k}j}^{(4)}(s) &= \frac{(i)^4}{2s} \sum_{\mathbf{k}'\mathbf{k}''\mathbf{k}_1'\mathbf{k}_1''} \sum_{j_1'j_1''j_2'j_2''} \sum_{\mathbf{k}_2'\mathbf{k}_2''\mathbf{k}_3'\mathbf{k}_3''} \sum_{j_2'j_2''j_3'j_3''} \sum_{\substack{\mathbf{k}_2'j_2'' \\ \mathbf{k}_3'j_3''}} \frac{V(-\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')V(-\mathbf{k}''j''; \mathbf{k}_1'j_1'; \mathbf{k}_1''j_1'')}{\omega_{\mathbf{k}j}\omega_{\mathbf{k}'j'}\omega_{\mathbf{k}''j''}\omega_{\mathbf{k}_1'j_1'}\omega_{\mathbf{k}_1''j_1''}} \\
 &\times \frac{V(-\mathbf{k}_1''j_1''; \mathbf{k}_2'j_2'; \mathbf{k}_2''j_2'')V(-\mathbf{k}_2''j_2''; \mathbf{k}_3'j_3'; \mathbf{k}_3''j_3'')c_{\mathbf{k}j'}^{(0)}c_{\mathbf{k}_1'j_1'}^{(0)}c_{\mathbf{k}_2'j_2'}^{(0)}c_{\mathbf{k}_3'j_3'}^{(0)}c_{\mathbf{k}_3''j_3''}^{(0)}}{[s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}-\omega_{\mathbf{k}j})][s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}-\omega_{\mathbf{k}j})-i(\omega_{\mathbf{k}_1'j_1'}+\omega_{\mathbf{k}_1''j_1''}-\omega_{\mathbf{k}''j''})]} \\
 &\times \frac{1}{[s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}-\omega_{\mathbf{k}j})-i(\omega_{\mathbf{k}_1'j_1'}+\omega_{\mathbf{k}_1''j_1''}-\omega_{\mathbf{k}''j''})-i(\omega_{\mathbf{k}_2'j_2'}+\omega_{\mathbf{k}_2''j_2''}-\omega_{\mathbf{k}_1'j_1'})]} \\
 &\times \frac{1}{[s-i(\omega_{\mathbf{k}'j'}+\omega_{\mathbf{k}''j''}-\omega_{\mathbf{k}j})-i(\omega_{\mathbf{k}_1'j_1'}+\omega_{\mathbf{k}_1''j_1''}-\omega_{\mathbf{k}''j''})-i(\omega_{\mathbf{k}_2'j_2'}+\omega_{\mathbf{k}_2''j_2''}-\omega_{\mathbf{k}_1'j_1'})-i(\omega_{\mathbf{k}_3'j_3'}+\omega_{\mathbf{k}_3''j_3''}-\omega_{\mathbf{k}_2'j_2'})]}.
 \end{aligned}
 \tag{4.14}$$

The law of formation of all higher-order terms should be clear from the results of Eqs. (4.4) and (4.14).

Now, for each of the four kinds of thermal averages, which arise from pairing either of  $C^*(\mathbf{k}j; 0)$  or  $C^*(\mathbf{k}-j; 0)$  with either of  $\gamma_{\mathbf{k}j}^{(4)}(s)$  or  $\gamma_{\mathbf{k}-j}^{(4)}(s)$ , there are 12 possible groupings of the six normal coordinates

$\{c_{\mathbf{k}j}^{(0)}\}$  into three groups of two each, if Eq. (4.9) is kept in mind. However, not all of these 12 groupings are equivalent for our purposes. We are primarily interested in those terms which dominate at large values of time, and we neglect all other terms. This choice follows from the fact that the dielectric susceptibility is associated with the long-time forced motion of the system produced by the external radiation. Ordinarily, short-time

<sup>6</sup> R. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), p. 37, second footnote.

transient terms will also occur, but these are of no importance in determining the susceptibility and should be neglected.

What criterion can we use to eliminate all terms in each order except those which give the dominant contribution? We are working with Laplace transforms which are of the form

$$f(s) = - \prod_{j=1}^{2n} \frac{1}{(s+ia_j)}, \quad (4.15)$$

in  $2n$ th order. Here some of the  $\{a_j\}$  can be equal to each other, and can also be zero. We know, for instance, that

$$F_1(t) = \mathcal{L}^{-1} \left\{ \frac{1}{(s+ia)^2} \right\} = t e^{-iat},$$

while

$$F_2(t) = \mathcal{L}^{-1} \left\{ \frac{1}{(s+ia)(s+ib)} \right\} = \frac{1}{i(b-a)} (e^{-iat} - e^{-ibt}), \quad a \neq b,$$

so that  $F_1(t)$  will dominate  $F_2(t)$  for large values of the

$$\begin{aligned} & \frac{c_{\mathbf{k}j'}^{(0)} c_{\mathbf{k}_1'j_1'}^{(0)} c_{\mathbf{k}_2'j_2'}^{(0)} \cdots c_{\mathbf{k}_{2n-1}'j_{2n-1}'}^{(0)} c_{\mathbf{k}_{2n-1}''j_{2n-1}''}^{(0)}}{[s - i(\omega_{\mathbf{k}j'} + \omega_{\mathbf{k}'j''} - \omega_{\mathbf{k}j}) - i(\omega_{\mathbf{k}_1'j_1'} + \omega_{\mathbf{k}_1''j_1''} - \omega_{\mathbf{k}_1'j_1'}) - \cdots \\ & \quad - i(\omega_{\mathbf{k}_{2n-1}'j_{2n-1}'} + \omega_{\mathbf{k}_{2n-1}''j_{2n-1}''} - \omega_{\mathbf{k}_{2n-2}''j_{2n-2}''})]} \\ & = \frac{c_{\mathbf{k}j'}^{(0)} c_{\mathbf{k}_1'j_1'}^{(0)} c_{\mathbf{k}_2'j_2'}^{(0)} \cdots c_{\mathbf{k}_{2n-1}'j_{2n-1}'}^{(0)} c_{\mathbf{k}_{2n-1}''j_{2n-1}''}^{(0)}}{s - i[\omega_{\mathbf{k}j'} - \omega_{\mathbf{k}j} + \omega_{\mathbf{k}_1'j_1'} + \omega_{\mathbf{k}_2'j_2'} + \cdots + \omega_{\mathbf{k}_{2n-1}'j_{2n-1}'} + \omega_{\mathbf{k}_{2n-1}''j_{2n-1}''}]}. \end{aligned} \quad (4.17)$$

When the numerator of this expression is multiplied either by  $c_{\mathbf{k}j}^{(0)*}$  or  $c_{\mathbf{k}-j}^{(0)*}$ , as is required in taking the thermal averages indicated in Eq. (4.1), then there is a one-to-one correspondence between the  $2n+2$  factors in the numerator and the  $2n+2$  frequencies in the denominator. Thus, when the  $\{c_{\mathbf{k}j}^{(0)}\}$  in the numerator are paired two-by-two in order to yield nonvanishing thermal averages, the frequencies in the denominator are paired in the same way. However, since in pairing the  $\{c_{\mathbf{k}j}^{(0)}\}$  we must form the product of  $c_{\mathbf{k}\alpha j\alpha}^{(0)}$  with  $c_{-\mathbf{k}\alpha-j\alpha}^{(0)} = c_{\mathbf{k}\alpha j\alpha}^{(0)*}$ , and since  $\omega_{\mathbf{k}j}$  changes its sign on reversing the sign of  $j$  regardless of the sign of  $\mathbf{k}$ , we see that, for every permissible pairing, the frequencies in the denominator cancel in pairs. This is the case for all sets  $\mathbf{k}_\alpha, j_\alpha$  except for the one which pairs with  $\mathbf{k}j$ . In this case, we have two different results depending on whether it is  $c_{\mathbf{k}j}^{(0)*}$  or  $c_{\mathbf{k}-j}^{(0)*}$  we have multiplied  $\gamma_{\mathbf{k}j}$  by. In the former case, it is clear from (4.17) that  $\omega_{\mathbf{k}j}$  in the denominator is cancelled also, and the entire factor collapses to  $s$ . In the latter case, it is seen that  $\omega_{\mathbf{k}j}$  is not cancelled and that, in fact, the factor in the denominator reduces to  $s - 2i\omega_{\mathbf{k}j}$ . Since in our present discussion,  $j$  always refers to an optical branch,  $\omega_{0j}$  is nonvanishing. An analogous set of results holds for the thermal averages of the products of  $c_{\mathbf{k}j}^{(0)*}$  and  $c_{\mathbf{k}-j}^{(0)*}$

time. This is a special case of a more general result, which can be stated in the following way: Of all Laplace transforms of the form of (4.15), the ones which contribute the highest power of  $t$  to the primitive function  $F(t) = \mathcal{L}^{-1}\{f(s)\}$  are those which contain the largest number of equal parameters  $\{a_j\}$ . The truth of this statement follows from a partial fractions expansion of the right-hand side of Eq. (4.15) and the fact that

$$\mathcal{L}^{-1} \left( \frac{1}{s^{n+1}} \right) = \frac{t^n}{n!}. \quad (4.16)$$

This result tells us, for example, that as long as we are interested in only those terms which dominate the long-time behavior of the integrand of Eq. (4.1), we can neglect the contribution from Eq. (4.11) in comparison with that from Eq. (4.10) and the contribution from Eq. (4.12) in comparison with that from Eq. (4.13). We now show that these results are contained in a more general result. Consider that part of the general  $2n$ th order term in the expansion of  $\gamma_{\mathbf{k}j}(s)$  which contains the product of the  $\{c_{\mathbf{k}j}^{(0)}\}$  coefficients and the last frequency denominator:

with  $\gamma_{\mathbf{k}-j}$ , as can be seen explicitly in the second-order results.

This fact has the consequence that we can neglect the thermal averages of the form  $\langle C^*(0-j; 0)C(0j; t) \rangle$  and  $\langle C^*(0j; 0)C(0-j; t) \rangle$  in determining the susceptibility tensor by means of Eq. (4.1). This is due to the following reasons. In determining the thermal averages  $\langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}j}(s) \rangle$  and  $\langle C^*(\mathbf{k}-j; 0)\gamma_{\mathbf{k}j}(s) \rangle$  there is clearly a one-to-one correspondence between the pairings of the  $\{c_{\mathbf{k}j}^{(0)}\}$  in the two cases. What is more, these pairings are identical in the two cases except in the case of the  $c_{\mathbf{k}\alpha j\alpha}^{(0)}$  which pairs with  $c_{\mathbf{k}j}^{(0)*}$  or with  $c_{\mathbf{k}-j}^{(0)*}$ , respectively. In the former case,  $j_\alpha = j$ ; in the latter case  $j_\alpha = -j$ . We have just seen that in the former case the last frequency factor in the denominator collapses down to  $s$ , while in the latter case it reduces to  $s - 2i\omega_{\mathbf{k}j}$ . There are thus two cases to consider.

(a)  $c_{\mathbf{k}, \pm j}^{(0)*}$  pairs with either  $c_{\mathbf{k}_{2n-1}'j_{2n-1}'}^{(0)}$  or  $c_{\mathbf{k}_{2n-1}''j_{2n-1}''}^{(0)}$ . In this case only the last frequency factor in the denominator is different in the expressions for the two thermal averages, the remaining factors are identical. Thus ignoring the frequency factors arising from the pairing of the remaining  $\{c_{\mathbf{k}j}^{(0)}\}$  among themselves which will be the same in the two cases the average  $\langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}j}(s) \rangle$  will contain a factor  $s^{-2}$



while the average  $\langle C^*(\mathbf{k}-j; 0)\gamma_{\mathbf{k}j}(s) \rangle$  will contain a factor  $s^{-1}(s-2i\omega_{\mathbf{k}j})^{-1}$ . The former average will thus contain at least one more power of  $t$  in the long-time behavior of its primitive function.

(b)  $c_{\mathbf{k}\pm j}^{(0)*}$  pairs with  $c_{\mathbf{k}\alpha j}^{(0)}$ , where  $\alpha \neq 2n-1$ . Equation (4.15) takes the following forms in the two cases:

$$\langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}j}(s) \rangle = \frac{1}{s} \left\{ \prod_{l=1}^{2n-1} \frac{1}{s-i\alpha_l} \right\} \frac{1}{s}, \quad (4.18a)$$

$$\langle C^*(\mathbf{k}-j; 0)\gamma_{\mathbf{k}j}(s) \rangle = \frac{1}{s} \left\{ \prod_{l=1}^{2n-1} \frac{1}{s-i\beta_l} \right\} \frac{1}{s-i\omega_{\mathbf{k}j}}, \quad (4.18b)$$

where the only difference between  $\alpha_l$  and  $\beta_l$  is that, if  $\omega_{\mathbf{k}j}$  appearing in  $\alpha_l$  is cancelled due to the pairing of the  $\{c_{\mathbf{k}j}^{(0)}\}$ , it appears as  $-2\omega_{\mathbf{k}j}$  in  $\beta_l$ . To obtain the highest power of  $t$  in the primitive function, we must have as many of the factors  $(s-i\alpha_l)^{-1}$  in Eq. (4.18a) equal to each other and/or to  $s^{-1}$  as possible, while for Eq. (4.18b) the condition is that as many of the factors  $(s-i\beta_l)^{-1}$  must be equal to each other and/or to  $s^{-1}$  or  $(s-2i\omega_{\mathbf{k}j})^{-1}$  as possible. It is clear that, however many equal factors  $(s-i\alpha_l)^{-1}$  we have in Eq. (4.18a), we have the same number of equal factors  $(s-i\beta_l)^{-1}$  in Eq. (4.18b), and the factors are in one-to-one correspondence between the two expressions. Equally clearly, we obtain the largest terms in  $t$  from Eq. (4.18a) if the factors  $(s-i\alpha_l)$  which are equal to each other in the product can also be made to equal  $s$ . Assuming,

provisionally, that this can always be done, the truth of our original assertion follows directly, since whatever pairing scheme is used to reduce any of the  $\{\alpha_l\}$  to zero, it requires the cancellation of the  $\omega_{\mathbf{k}j}$  appearing in it. This means that the corresponding  $\beta_l$  reduces to  $s-2i\omega_{\mathbf{k}j}$ . However, there is one more factor of  $s^{-1}$  in (4.18a) than there are factors of  $(s-2i\omega_{\mathbf{k}j})^{-1}$  in (4.18b), hence the latter, in the most favorable case, contributes one power of  $t$  less than the former. It follows by the same arguments that the thermal average  $\langle C^*(\mathbf{k}j; 0)C(\mathbf{k}-j; t) \rangle$  can be neglected compared with the thermal average  $\langle C^*(\mathbf{k}-j; 0)C(\mathbf{k}-j; t) \rangle$ .

It now remains to show that it is always possible to pair indices in the expression for the  $2n$ th order term in the expansion for  $\langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}j}(s) \rangle$  in such a way that the value of  $\alpha_l$  which maximizes the number of equal factors  $(s-i\alpha_l)^{-1}$  in the product in Eq. (4.18a) is zero. We will see that the solution of this problem in the form of a systematic scheme for classifying these dominant terms in each even order will lead immediately to the complete solution for  $\gamma_{\mathbf{k}j}(s)$  and for  $\gamma_{\mathbf{k}-j}(s)$ .

At this point it is advantageous to go over to a slightly more compact notation in which we replace the pair  $(\mathbf{k}j)$  by a single index  $k$ . The index  $-k$  means  $(-\mathbf{k}-j)$ . Since  $V(\mathbf{k}j; \mathbf{k}'j'; \mathbf{k}''j'')$  is independent of the signs of the  $j$ 's, we can write it in the new notation as  $V(k; k'; k'')$ . Furthermore, since  $\omega_{\mathbf{k}j} = \omega_{-\mathbf{k}j}$ , but  $\omega_{\mathbf{k}-j} = -\omega_{\mathbf{k}j}$ , we have in the new notation  $\omega_{-k} = -\omega_k$ .

In this notation the fourth-order contribution to  $\langle C^*(\mathbf{k}j; 0)\gamma_{\mathbf{k}j}(s) \rangle$ , Eq. (4.14), becomes

$$\begin{aligned} \langle C^*(k; 0)\gamma_k^{(4)}(s) \rangle &= \frac{(i)^4}{2s} \sum_{k'k''k_1'k_1''k_2'k_2''k_3'k_3''} \frac{V_{-kk'k''}V_{-k''k_1'k_1''}V_{-k_1''k_2'k_2''}V_{-k_2''k_3'k_3''}}{\omega_k\omega_{k''}\omega_{k_1'}\omega_{k_1''}\omega_{k_2'}\omega_{k_2''}} \\ &\times \frac{\langle c_k^{(0)*}c_{k'}^{(0)}c_{k_1'}^{(0)}c_{k_2'}^{(0)}c_{k_3'}^{(0)}c_{k_3''}^{(0)} \rangle}{[s-i(\omega_{k'}+\omega_{k''}-\omega_k)][s-i(\omega_{k'}+\omega_{k''}-\omega_k)-i(\omega_{k_1'}+\omega_{k_1''}-\omega_{k'})]} \\ &\times \frac{1}{[s-i(\omega_{k'}+\omega_{k''}-\omega_k)-i(\omega_{k_1'}+\omega_{k_1''}-\omega_{k'})-i(\omega_{k_2'}+\omega_{k_2''}-\omega_{k_1'})]} \\ &\times \frac{1}{[s-i(\omega_{k'}+\omega_{k''}-\omega_k)-i(\omega_{k_1'}+\omega_{k_1''}-\omega_{k'})-i(\omega_{k_2'}+\omega_{k_2''}-\omega_{k_1'})-i(\omega_{k_3'}+\omega_{k_3''}-\omega_{k_2'})]}. \end{aligned} \quad (4.19)$$

We have written out the last frequency factor in full, although we know that every pairing of the  $\{c_{\mathbf{k}}^{(0)}\}$  two-by-two consistent with the nonvanishing of the thermal average causes it to collapse down to  $s^{-1}$ . A combinatorial argument familiar from the theory of the imperfect gas<sup>7</sup> tells us that in  $2n$ th order there are

$$(2n+2)!/[n+1)!2^{n+1}], \quad (4.20)$$

possible pairings of the  $\{c_{\mathbf{k}}^{(0)}\}$  two-by-two. Of these,

however,

$$\frac{(2n-2)!}{(n-1)!2^{n-1}}(4n-3), \quad (4.21)$$

vanish because of Eq. (4.9). Hence, there are 15 possible pairings in fourth order, or which five can be ignored in view of Eq. (4.9). Direct enumeration shows us, with the aid of Eq. (4.16), that of the remaining ten pairings, four give rise to contributions which are proportional to  $t^2$  while the remainder are of lower order in  $t$ .

However, as a general method for studying the contributions from the  $2n$ th order, direct enumeration is completely impractical, and it becomes convenient

<sup>7</sup> The number of ways of arranging  $r$  distinguishable objects into  $k_1$  groups of one object,  $k_2$  groups of two objects, etc., is  $r!/[k_1!k_2!\dots k_r!(1!)^{k_1}(2!)^{k_2}\dots (r!)^{k_r}]$ .

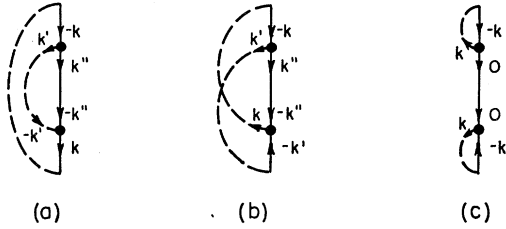


FIG. 1. Diagrams which represent the three possible pairings of normal coordinates to give a nonvanishing thermal average for the second-order term in Eq. (4.4).

to introduce diagrams to classify the various contributions. The diagrams corresponding to the three second-order pairings given by Eq. (4.8) are shown in Fig. 1. In these diagrams, the sequence of events described by the product of matrix elements  $V_{-kk'k''}V_{-k''k_1'k_1''}$  reading from left to right corresponds to reading the diagrams from top to bottom. Each dot corresponds to a matrix element  $V_{-k_\alpha''k_{\alpha+1}'k_{\alpha+1}''}$ . The solid line corresponds to the transfer of "momentum"  $k_\alpha''$  which is implied by the repetition of the last subscript in each matrix element as the first subscript in the succeeding element. At each vertex (dot) "momentum" is quasi-conserved in view of the  $\Delta$  function which is included in the definition of  $V_{-kk'k''}$ , Eq. (3.5). The dashed lines describe the pairings of the various subscripts as required for the nonvanishing of the thermal averages, supplemented by the  $\Delta$ -function restrictions. We have used the convention that a line (solid or dashed) carrying momentum  $-k$  to a vertex is described by a line directed toward the vertex, while a line carrying momentum  $k$  to a vertex is represented by a line directed away from the vertex.

We see clearly the difference between terms in the expansion which vanish due to Eq. (4.9), Fig. 1(c), and terms which do not vanish. The former are char-

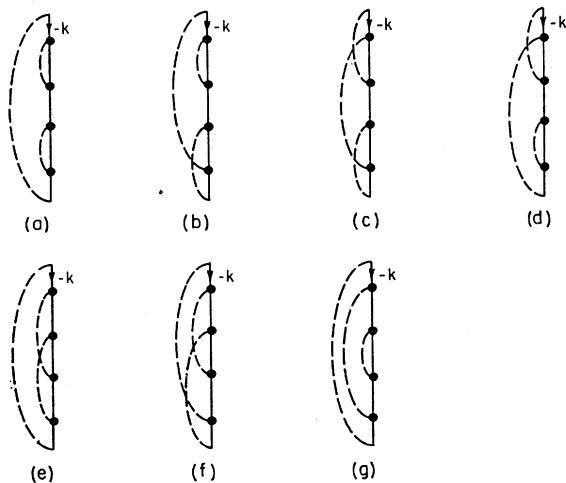


FIG. 2. Typical fourth-order diagrams associated with Eq. (4.19). Only the first four correspond to the sequential pairing of vertices.

acterized by a vanishing momentum transfer between two consecutive vertices.

The diagrams for some typical fourth-order and sixth-order terms are shown in Figs. 2 and 3, respectively.

We now ask, of the

$$\frac{(2n+2)!}{(n+1)!2^{n+1}} \frac{(2n-2)!}{(n-1)!2^{n-1}} (4n-3)$$

possible diagrams which are consistent with the requirements of nonvanishing thermal averages and Eq. (4.9), which ones correspond to terms contributing the highest power of  $t$  to the primitive function of the Laplace transform? This question was answered by Brout and Prigogine<sup>8</sup> in connection with the study of an expansion similar to Eq. (4.4) but in the time representation. They pointed out that the most effective pairing scheme in  $2n$ th order was the sequential pairing of the matrix elements in the product  $V_{-kk'k''} \times V_{-k''k_1'k_1''} V_{-k_1''k_2'k_2''} V_{-k_2''k_3'k_3''} \dots$ . By this we mean pairing  $V_{-kk'k''}$  with  $V_{-k''k_1'k_1''}$  so that  $k_1'=k$ ,  $k_1''=-k'$  or  $k_1'=-k'$ ,  $k_1''=k$ ; pairing  $V_{-k_1''k_2'k_2''}$  with  $V_{-k_2''k_3'k_3''}$  so that  $k_3'=-k_1''$ ,  $k_3''=-k_2'$ , or  $k_3'=-k_2'$ ,  $k_3''=k_1''$ , etc. In  $2n$ th order there are clearly  $2^n$  such diagrams. That such a pairing should give rise to the highest power of  $t$  in each order may be seen from the following remarks. Firstly, we see that each of the  $2^n$  sequential pairing of the  $V$ 's corresponds to a pairing of the  $(2n+2) \{c_k^{(0)}\}$  two-by-two, and hence is of the form required for nonvanishing thermal averages. Secondly, each such sequential pairing of the  $V$ 's causes every second frequency factor in the denominator to collapse to  $s$ , while the remaining factors reduce to the form  $[s-i(\omega_1+\omega_2+\omega_3)]$ . This result is what was required to justify the neglect of the thermal averages  $\langle C^*(\mathbf{k}-j; 0)\gamma_{kj}(s) \rangle$  and  $\langle C^*(\mathbf{k}j; 0)\gamma_{k-j}(s) \rangle$ . Finally, nonsequential pairing leads to the loss of at least one power of  $t$  in the primitive function. The pairing of additional subscripts to collapse any of the remaining factors of the form  $[s-i(\omega_1+\omega_2+\omega_3)]$  would lead to the loss of at least two summation indices and hence to two powers of  $N$ .

The  $2^n$  diagrams in  $2n$ th order which correspond to the sequential pairing of the  $V$  matrix elements can be constructed without difficulty by starting at the top and drawing a different diagram for each of the alternative pairings at every second vertex. These diagrams have the property that if they are cut by a horizontal line between two consecutive vertices belonging to the same pair only one pairing line is cut, while if they are cut by a horizontal line between two consecutive vertices belonging to two different pairs, two pairing lines are cut. Thus, in Fig. 2 only the first four diagrams correspond to sequentially paired vertices, and these in fact exhaust the possibilities in fourth order. In Fig. 3 only the first two diagrams correspond to sequen-

<sup>8</sup> R. Brout and I. Prigogine, *Physica* 22, 35 (1956).

tially paired vertices. The remaining six can be drawn with the aid of the rules given above.

Of the  $2^n$  dominant diagrams in  $2n$ th order, two play a particularly important role if we restrict ourselves to a solution for  $\langle C^*(k; 0)\gamma_k(s) \rangle$  which is exact to lowest order in the anharmonic force constants. These are the diagrams which correspond to those given by Figs. 2(a), 2(b) and Figs. 3(a) and 3(b), for fourth- and sixth-order terms, respectively. Since  $V_{kk'k''}$  is completely symmetric in the indices, the contributions from these two diagrams in each order are the same, and we need study only the contribution from the first kind of diagrams, i.e., those given by Figs. 2(a) and 3(a). The importance of this kind of diagram is that it represents a situation in which the same momentum  $k$  is transferred between every second pair of vertices. These diagrams are thus somewhat analogous to the so-called "ring" diagrams which describe the dominant contributions to the thermodynamic functions of the

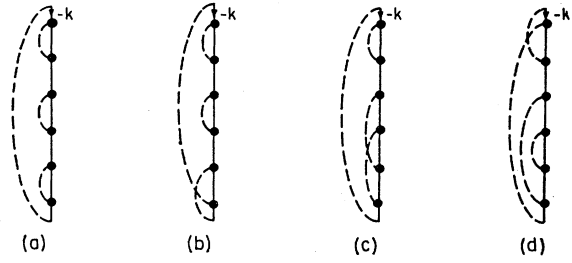


FIG. 3. Typical sixth-order diagram. The first two correspond to sequential pairing of vertices.

interacting electron gas in the high-density limit.<sup>9</sup> The consequence of this is that the contribution from such a diagram in  $2n$ th order is just the  $n$ th power of the contribution of the second-order term given by Fig. 1(a) or equivalently by Fig. 1(b). This is shown explicitly by writing out the contributions to  $\langle C^*(k; 0)\gamma_k(s) \rangle$  from the diagrams of Figs. 1(a), 2(a), and 3(a):

$$\text{2nd order: } \frac{(i)^2 (kT)^2}{2s^2 2^2 \omega_k^2} \sum_{k'k''} \frac{V_{-kk'k''} V_{-k''-k'k}}{\omega_k \omega_{k'}^2 \omega_{k''} [s - i(\omega_{k'} + \omega_{k''} - \omega_k)]} = \frac{kT}{4s\omega_k^2} G_2, \quad (4.22a)$$

$$\text{4th order: } \frac{(i)^4 (kT)^3}{2s^3 2^3 \omega_k^2} \sum_{k'k''} \sum_{k_2'k_2''} \frac{V_{-kk'k''} V_{-k''-k'k} V_{-kk_2'k_2''} V_{-k_2''-k_2'k}}{(\omega_k \omega_{k'}^2 \omega_{k''}) (\omega_k \omega_{k_2'}^2 \omega_{k_2''}) [s - i(\omega_{k'} + \omega_{k''} - \omega_k)]} \\ \times \frac{1}{[s - i(\omega_{k_2'} + \omega_{k_2''} - \omega_k)]} = \frac{kT}{4s\omega_k^2} (G_2)^2, \quad (4.22b)$$

$$\text{6th order: } \frac{(i)^6 (kT)^4}{2s^4 2^4 \omega_k^2} \sum_{k'k''} \sum_{k_2'k_2''} \sum_{k_4'k_4''} \frac{V_{-kk'k''} V_{-k''-k'k} V_{-kk_2'k_2''} V_{-k_2''-k_2'k} V_{-kk_4'k_4''} V_{-k_4''-k_4'k}}{(\omega_k \omega_{k'}^2 \omega_{k''}) (\omega_k \omega_{k_2'}^2 \omega_{k_2''}) (\omega_k \omega_{k_4'}^2 \omega_{k_4''})} \\ \times \frac{1}{[s - i(\omega_{k'} + \omega_{k''} - \omega_k)] [s - i(\omega_{k_2'} + \omega_{k_2''} - \omega_k)] [s - i(\omega_{k_4'} + \omega_{k_4''} - \omega_k)]} = \frac{kT}{4s\omega_k^2} (G_2)^3. \quad (4.22c)$$

In these expressions, we have put

$$G_2 = \frac{(i)^2 kT}{s 2} \sum_{k'k''} \frac{|V_{-kk'k''}|^2}{\omega_k \omega_{k'}^2 \omega_{k''} [s - i(\omega_{k'} + \omega_{k''} - \omega_k)]}. \quad (4.23)$$

If we sum the contributions from all orders in the expansion, we obtain

$$\langle C^*(k; 0)\gamma_k(s) \rangle = \frac{kT}{4s\omega_k^2} \frac{G_2}{1 - G_2}. \quad (4.24)$$

This result must be doubled to give the total contribution from the "ring" diagrams.

In similar fashion, we find that the analogous contribution to  $\langle C^*(-k; 0)\gamma_{-k}(s) \rangle$  is given by

$$\langle C^*(-k; 0)\gamma_{-k}(s) \rangle = \frac{kT}{2s\omega_k^2} \frac{F_2}{1 - F_2}, \quad (4.25)$$

where

$$F_2 = -\frac{(i)^2 kT}{s 2} \sum_{k'k''} \frac{|V_{-kk'k''}|^2}{\omega_k \omega_{k'}^2 \omega_{k''} [s - i(\omega_{k'} + \omega_{k''} + \omega_k)]}. \quad (4.26)$$

Recalling Eqs. (4.2) and (4.6), we obtain finally that, to lowest order in the perturbation,

$$\langle C^*(\mathbf{k}j; 0)\mathcal{L}\{C(\mathbf{k}j; t)\} \rangle = \frac{kT}{2s\omega_k^2} + \frac{kT}{2s\omega_k^2} \frac{G_2}{1 - G_2} \\ = \frac{kT}{2\omega_k^2} \frac{1}{s - sG_2}, \quad (4.27a)$$

$$\langle C^*(\mathbf{k}-j; 0)\mathcal{L}\{C(\mathbf{k}-j; t)\} \rangle = \frac{kT}{2s\omega_k^2} + \frac{kT}{2s\omega_k^2} \frac{F_2}{1 - F_2} \\ = \frac{kT}{2\omega_k^2} \frac{1}{s - sF_2}. \quad (4.27b)$$

Equations (4.27) constitute a formal solution to our problem.

<sup>9</sup> See, for example, E. W. Montroll and J. C. Ward, Phys. Fluids **1**, 55 (1958).

Before proceeding to write down the expression for the absorption coefficient, we must discuss briefly the contributions from the terms in  $2n$ th order which we have neglected. We have pointed out earlier that there are  $2^n$  terms in  $2n$ th order which arise from the sequential pairing of the  $V$ 's and which give the same  $t$  dependence to the primitive function. Of these  $2^n$  terms, we have used only two.

We have neglected the remaining  $2^n - 2$  terms primarily for two reasons. Firstly, they are at least of fourth order in the anharmonic force constants, compared with the terms of second order which we have retained. Since we have omitted the quartic anharmonic terms in the Hamiltonian which in general give a contribution of the same order in temperature as the cubic anharmonic terms we have neglected here, it would be inconsistent to retain higher-order cubic anharmonic terms without

at the same time introducing quartic, quintic,  $\dots$  terms into the Hamiltonian. Secondly, the linearization of the equations of motion of the normal coordinates has the effect of making all terms past second order in the expression for  $G_2$  of doubtful validity. Furthermore, in evaluating the thermal average of a product of two normal coordinates we have used the harmonic approximation. This is sufficient to the order we have worked. The retention of terms of fourth and higher orders in  $G_2$  would require a more accurate evaluation of these averages, including anharmonic corrections.

## V. THE ABSORPTION COEFFICIENT

In view of the remarks made in the preceding section, we can rewrite Eq. (4.1) for the dielectric susceptibility associated with the  $j$ th dispersion oscillator as

$$\chi_{\mu\nu}^{(j)}(\omega) = \frac{\omega_{0j} NM_\mu(0j)M_\nu(0j)}{i V kT} \lim_{\epsilon \rightarrow 0+} \left\{ \int_0^\infty e^{-(\epsilon+i\omega-i\omega_{0j})t} \langle C^*(0j; 0)C(0j; t) \rangle dt - \int_0^\infty e^{-(\epsilon+i\omega+i\omega_{0j})t} \langle C^*(0-j; 0)C(0-j; t) \rangle dt \right\} \quad (5.1)$$

$$= \frac{\omega_{0j} NM_\mu(0j)M_\nu(0j)}{i V kT} \lim_{\epsilon \rightarrow 0+} \left\{ \langle C^*(0j; 0) \mathcal{L}\{C(0j; t)\} \rangle_{s=\epsilon+i\omega-i\omega_{0j}} - \langle C^*(0-j; 0) \mathcal{L}\{C(0-j; t)\} \rangle_{s=\epsilon+i\omega+i\omega_{0j}} \right\}. \quad (5.2)$$

If we substitute Eq. (4.27) into Eq. (5.2) we find

$$\chi_{\mu\nu}^{(j)}(\omega) = \frac{\omega_{0j} NM_\mu(0j)M_\nu(0j)}{i V kT} \lim_{\epsilon \rightarrow 0+} \frac{kT}{2\omega_{0j}^2} \left\{ \left[ \epsilon+i\omega-i\omega_{0j} + \frac{kT}{2} \sum_{k'k''} \frac{|V_{0k'k''}|^2}{\omega_0\omega_{k'}^2\omega_{k''}(\epsilon+i\omega-i\omega_{k'}-i\omega_{k''})} \right]^{-1} - \left[ \epsilon+i\omega+i\omega_{0j} - \frac{kT}{2} \sum_{k'k''} \frac{|V_{0k'k''}|^2}{\omega_0\omega_{k'}^2\omega_{k''}(\epsilon+i\omega-i\omega_{k'}-i\omega_{k''})} \right]^{-1} \right\}. \quad (5.3)$$

We pass to the limit as  $\epsilon \rightarrow 0+$  with the aid of the relation

$$\lim_{\epsilon \rightarrow 0+} \frac{1}{x-i\epsilon} = \left( \frac{1}{x} \right)_P + i\pi\delta(x) \quad (5.4)$$

and obtain, finally, for the susceptibility

$$\chi_{\mu\nu}^{(j)}(\omega) = -\frac{NM_\mu(0j)M_\nu(0j)}{2\omega_{0j}V} \times \left\{ \frac{1}{\omega-\omega_0-\Delta\omega-i\gamma} - \frac{1}{\omega+\omega_0+\Delta\omega+i\gamma} \right\}, \quad (5.5)$$

where

$$\Delta\omega = \frac{kT}{2} \sum_{k'k''} \frac{|V_{0k'k''}|^2}{\omega_0\omega_{k'}^2\omega_{k''}(\omega-\omega_{k'}-\omega_{k''})_P}, \quad (5.6a)$$

$$\gamma = -\frac{\pi}{2} kT \sum_{k'k''} \frac{|V_{0k'k''}|^2}{\omega_0\omega_{k'}^2\omega_{k''}} \delta(\omega-\omega_{k'}-\omega_{k''}). \quad (5.6b)$$

Comparing Eqs. (5.5) and (2.21) we find that

$$\text{Im}\chi_{\mu\nu}^{(j)}(\omega) = -\frac{NM_\mu(0j)M_\nu(0j)}{2\omega_{0j}V} \times \left\{ \frac{\gamma}{(\omega-\omega_{0j}-\Delta\omega)^2+\gamma^2} + \frac{\gamma}{(\omega+\omega_{0j}+\Delta\omega)^2+\gamma^2} \right\}, \quad (5.7)$$

so that, finally, the linear absorption coefficient becomes

$$\alpha_{xx}^{(j)}(\omega) = \frac{4\pi}{c} \frac{\omega}{\omega_{0j}} \frac{[M_x(0j)]^2}{2v_a} \times \left\{ \frac{\gamma}{(\omega-\omega_{0j}-\Delta\omega)^2+\gamma^2} + \frac{\gamma}{(\omega+\omega_{0j}+\Delta\omega)^2+\gamma^2} \right\}, \quad (5.8)$$

where  $v_a$  is the volume of a unit cell in our crystal.

We now evaluate the damping constant  $\gamma$  and the absorption coefficient  $\alpha$  for the linear diatomic chain with nearest-neighbor interactions. The values of the various quantities required have been obtained pre-

viously.<sup>2</sup> The result for the damping constant is

$$\gamma = C \frac{kT}{\hbar} \omega^2 [(\omega_a + \omega_b)^2 - \omega^2]^{-\frac{1}{2}} [\omega^2 - (\omega_a - \omega_b)^2]^{-\frac{1}{2}},$$

$$\omega_a - \omega_b < \omega < \omega_a + \omega_b \quad (5.9)$$

= 0, otherwise,

where

$$\begin{aligned} \omega_a^2 &= 2\sigma_h/M_1, \\ \omega_b^2 &= 2\sigma_h/M_2, \\ C &= 2\sigma_A^2(\hbar\omega_0/\omega_a^2\omega_b^2\omega_0^2)[(M_1+M_2)/M_1^2M_2^2], \end{aligned} \quad (5.10)$$

$\sigma_h$  is the harmonic force constant,  $\sigma_a$  the anharmonic force constant, and  $M_1$  and  $M_2$  are the lighter and heavier masses, respectively. The absorption coefficient is obtained by substituting Eq. (5.9) in Eq. (5.8), taking  $j=1$  and using the relations

$$\begin{aligned} \omega_{01}^2 &= \omega_0^2 = \omega_a^2 + \omega_b^2, \\ M_x(01) &= -\epsilon[(M_1+M_2)/M_1M_2]^{\frac{1}{2}}, \end{aligned} \quad (5.11)$$

where  $\epsilon$  is the magnitude of the electronic charge.

## VI. DISCUSSIONS AND CONCLUSIONS

In the preceding sections, a systematic classical theory has been developed for the optical absorption coefficient associated with the lattice vibrations of an anharmonic ionic crystal. The various terms which arise in the solutions of the equations of motion can be classified in accordance with a natural measure of their importance in the long-time approximation. The solutions are obtained in a straightforward manner without the use of an artificial device such as an ansatz.

The earlier treatment of Blackman, like the present one, is based on perturbation theory and makes use of the long-time approximation. For the case of the diatomic linear chain, the damping constant obtained

by Blackman has the same qualitative dependence on frequency as that given by Eq. (5.9) although there are minor quantitative differences. Both theories lead to a damping constant which is proportional to the first power of the absolute temperature  $T$ . Recently, Neuberger<sup>10</sup> has used a procedure similar to that of Blackman to calculate the optical constants for a generalized Kellerman model of an ionic crystal. His results can be described in terms of a damping constant proportional to  $T$  as in the other classical calculations.

Experimental measurements of the high-temperature lattice vibration reflectivity have been carried out by Heilmann<sup>11</sup> for lithium fluoride and by Hass<sup>12</sup> for sodium chloride. Their results are reasonably well described by a damping constant proportional to  $T^2$ . Since the classical theories should be valid at high temperatures, it appears probable that quartic, and possibly higher-order anharmonic contributions, should be included in the theory. A theoretical investigation of the influence of quartic terms is being pursued by D. W. Jepsen.

As pointed out in a recent paper,<sup>2</sup> quantum-mechanical calculations of anharmonic lattice-vibration absorption based on the Born-Huang theory lead to a different high-temperature dependence from that given by the classical theories. Work is in progress on an improved quantum-mechanical theory which would overcome certain weaknesses in the Born-Huang approach and would make possible a more meaningful comparison with the classical case.

## ACKNOWLEDGMENT

This work was begun while the first named author (A.A.M.) was a consultant to the U. S. Naval Research Laboratory.

<sup>10</sup> J. Neuberger, Air Force Cambridge Research Center Report AFCRC-TR-57-353, New York University, 1957 (unpublished), p. 189.

<sup>11</sup> G. Heilmann, Z. Physik **152**, 368 (1958).

<sup>12</sup> M. Hass, Phys. Rev. **117**, 1497 (1960).