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Lattice Anharmonicity and Optical Absorption in Polar Crystals: I. The Linear Chain

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A calculation of the optical absorption spectrum of an anharmonic one-dimensional lattice of alternating positively and negatively charged particles of different masses is carried out using two different approaches: the recent theory of Born and Huang, and ordinary second-order time-dependent perturbation theory. Closed-form expressions for the absorption spectrum are obtained for both low and high temperatures. It is found that subsidiary absorption peaks may be expected at frequencies other than the dispersion frequency ω_d. At high temperatures the absorption at ω_d varies as T^{-2} or T^{-3} depending on how certain thermal averages are carried out. Predictions based on these results are made regarding which features of the present spectra can be expected to persist for three-dimensional lattices.

I. INTRODUCTION

It is well known[1] that in the harmonic approximation the absorption spectrum of a cubic crystal of the sodium chloride type consists of an infinitely sharp line (viz., a δ function) at the dispersion frequency, which is the frequency of the transverse mode of zero wave vector in the optical branch (the dispersion oscillator). These results are contradicted by experimental evidence which shows that strong absorption at the dispersion frequency is superimposed on a continuous background of absorption which shows subsidiary maxima. Since the calculations of Pauli[2] in 1925, this discrepancy has been attributed to the neglect of the anharmonic terms in the expansion of the lattice potential energy in powers of the displacements of the ions from their equilibrium positions [see, however, Rosenstock[3] and Lax and Burstein[4]]. Pauli studied a linear chain of alternating positively and negatively charged particles of equal mass. He obtained a dispersion formula of the form

$$\epsilon(\omega)=\epsilon_\infty+\frac{\epsilon_0-\epsilon_\infty}{1-(\omega/\omega_d)^2-i(\omega/\omega_d)\gamma/\omega_d}, \tag{1.1}$$

where $\epsilon(\omega)$ is the frequency-dependent dielectric constant, ϵ_0 and ϵ_∞ are the limiting values of the dielectric constant at low and high frequencies, respectively, ω_d is the dispersion frequency, and γ is a damping constant which is independent of the frequency. Although such a dispersion formula predicts a continuous absorption with a maximum at the dispersion frequency, it does not predict any subsidiary maxima.

Pauli's work was extended by Born and Blackman[5] who studied a linear chain of alternating positively and negatively charged particles of different masses. They showed that in this model the effect of these anharmonic terms is to damp the infinitely sharp absorption at the dispersion frequency, to provide a continuous absorption at frequencies different from the dispersion frequency, and to provide subsidiary or secondary maxima in the spectra. An analogous calculation was carried out for a three-dimensional lattice[1] and the results, though more complex, were qualitatively similar. More recently a calculation along the lines of Born and Blackman's treatment was carried out by Neuberger[6] for the case of sodium chloride. Using Kellermann's[7] model for the harmonic part of the crystal Hamiltonian and a simple expression for the anharmonic potential energy, he obtained the optical constants as functions of the frequency of the incident radiation, leaving the anharmonic force constant as an adjustable parameter. His results at a given temperature are in qualitative agreement with experiment.[8]

As opposed to these purely classical calculations an elaborate quantum mechanical treatment of infrared absorption in MgO was carried out by Barnes, Brattain, and Seitz.[9] Objecting to the use of a central force interaction potential in the work of Born and Blackman, they assumed a general potential of interaction whose properties were restricted only by symmetry conditions. Furthermore, rather than attempting to calculate the complete absorption spectrum, they restricted themselves to a determination of the frequencies at which strong absorption would be expected to occur. Their results showed that in addition to these sharp absorption lines there should exist a continuous absorption spectrum. Their method of calculation did not allow for the possibility of damping of absorption at the dispersion frequency and is unrealistic in this respect.

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Born and Huang[10] have recently presented a new treatment of anharmonic optical absorption in complex lattices. It is a quantum mechanical treatment which is based on a modification of time-dependent perturbation theory due to Weisskopf and Wigner.[11] The Born-Huang approach is applied in the present paper to the calculation of the absorption spectrum of one particular nontrivial model: a linear chain of alternating positively and negatively charged particles with different masses and nearest-neighbor interactions only. The choice of this model was based on the following considerations: The various calculations which enter into the determination of the absorption spectrum can all be carried out in closed form, which simplifies the discussion of which features of the present spectrum can be expected to persist for a three-dimensional lattice. Furthermore, this model has been studied extensively in the past, and our results can be compared directly with those of earlier investigations.

The Born-Huang treatment, however, is not free from objections. For example, if one carries out an ordinary second-order time-dependent perturbation calculation of the absorption one finds[12] that in second order certain intermediate states which enter into the calculation are ignored in the treatment of Born and Huang.[13] One can, however, develop the Born-Huang treatment in a systematic manner and show that their use of Wigner-Weisskopf time-dependent perturbation theory is equivalent to summing a selected subclass of diagrams to all orders in the perturbation parameter. Using such a treatment one can estimate the importance of the intermediate states neglected by Born and Huang. These remarks serve to illustrate the fact that at the present time no completely satisfactory theory of optical absorption in anharmonic lattices exists. The present calculations are presented as being illustrative of what is in most ways the most satisfactory theory to date, and a more fundamental approach to this entire problem will be presented in a paper now in preparation.

In order to make the foregoing arguments quantitative, and to make this paper self-contained, we present a brief resume of the Born-Huang theory in Appendix A. The result of their theory of primary importance to the present calculation is their expression for the partial dielectric susceptibility due to the jth optical mode of zero wave vector in the state with quantum number $v^0(0;j)$. The general expression for the elements of this tensor is quite lengthy [B-H(46.41)], but it simplifies in a number of special cases. It is these particular cases to which we restrict ourselves in the rest of this paper. The expressions for the dielectric susceptibility and their regions of applicability are given below:

(i) the low-temperature limit ($T=0$°K)

$$a^1(\omega)=-\frac{1}{v_a}\frac{[M(0;1)]^2}{2\omega_d}\left\{\frac{1}{\omega_d-\omega+i\gamma_{+1}(\omega_d-\omega)}+\frac{1}{\omega_d+\omega}\right\}; \tag{1.2a}$$

(ii) the wings of the absorption region[14] ($\omega>2\omega_d$ and $\omega-\omega_d\gg$damping constants γ)

$$a^1(\omega)=-\frac{1}{v_a}\frac{[M(0;1)]^2}{2\omega_d}\left\{\frac{2\omega_d}{\omega_d^2-\omega^2}+iv^0(0;1)\left[\frac{\gamma_{-1}(-\omega_d-\omega)-\gamma_{+1}(\omega_d+\omega)}{(\omega_d+\omega)^2}+\frac{\gamma_{+1}(\omega_d-\omega)-\gamma_{-1}(-\omega_d+\omega)}{(\omega_d-\omega)^2}\right]\right.$$
$$\left.+i\left[\frac{4\omega\omega_d\gamma_0(0)}{(\omega_d^2-\omega^2)^2}+\frac{\gamma_{+1}(\omega_d-\omega)}{(\omega_d-\omega)^2}-\frac{\gamma_{+1}(\omega_d+\omega)}{(\omega_d+\omega)^2}\right]\right\}; \tag{1.2b}$$

(iii) the center of the dispersion region ($\omega=\omega_d$)

$$a^1(\omega)=-\frac{1}{v_a}\frac{[M(0;1)]^2}{2\omega_d}\left\{\frac{1}{2\omega_d}+i\left[\frac{1}{\gamma_0(0)+\gamma_{+1}(0)}+\frac{v^0(0;1)(\gamma_{-1}(0)-\gamma_{+1}(0))}{(\gamma_0(0)+\gamma_{+1}(0))(\gamma_0(0)+\gamma_{-1}(0))}\right]\right\}. \tag{1.2c}$$

In these equations ω is the frequency of the incident radiation; the superscript 1 refers to the optical branch of the frequency spectrum of our one-dimensional lattice; ω_d is the dispersion frequency, in the present case the maximum frequency of the optical branch; v_a is the volume of a unit cell; $M(0;1)$ is a coefficient in the expansion of the electric moment of the lattice; and $v^0(0;1)$ is the harmonic oscillator quantum number of the dispersion oscillator in its initial state.

In order that the quantities $a^1(\omega)$ shall have the proper dimensions, we shall assume that our system consists of a collection of parallel independent linear chains arranged so that the atoms form a sodium chloride type cubic lattice. The unit cell volume v_a can then be taken to be $2a_0^3$ where a_0 is the spacing between nearest-neighbor particles in the lattice.

The quantities $\gamma_0(\omega)$, $\gamma_{\pm1}(\omega)$ appearing in Eq. (1.2)

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[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 341.

[11] V. Weisskopf and E. Wigner, Z. Physik **63**, 54 (1930); **65**, 18 (1930).

[12] W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed., p. 138 ff.

[13] We are indebted to M. Lax for this remark. It is gone into in more detail in Sec. VI of this paper.

[14] This expression corrects a misprint in B-H(47.10).

are damping constants of the type obtained by Pauli, Eq. (1.1), except that in the present case they are frequency dependent. They are defined in terms of matrix elements of the anharmonic part of the Hamiltonian, H_a, by

$$\gamma_0(\omega)=\frac{\pi}{\hbar^2}\lim_{\Delta\omega\rightarrow 0}\frac{1}{\Delta\omega}\sum_{(n')}^{\omega}|\langle n'|H_A|0\rangle|^2, \qquad (1.3\text{a})$$

where the symbol $\sum_{(n')}{}^{\omega}$ means that the summation is over all final states n' which have transition frequencies, $\omega=\omega_0-\omega_{n'}$, in the interval $(\omega, \omega+\Delta\omega)$. The subscript on the γ refers to the initial state with respect to which the transition frequency is defined. Similarly we have that

$$\gamma_{\pm 1}(\omega_\pm)=\frac{\pi}{\hbar^2}\lim_{\Delta\omega\pm\rightarrow 0}\frac{1}{\Delta\omega_\pm}\sum_{(s)}^{\omega\pm}|\langle s|H_A|\pm 1\rangle|^2, \qquad (1.3\text{b})$$

where the state ± 1 refers to the state obtained from the initial state 0 by changing the quantum number of the dispersion oscillator by ± 1. The states s are all states other than the states 0, ± 1, and the transition frequency $\omega_\pm$ is defined by $\omega_{\pm 1}-\omega_s$ where the energies of the states ± 1 and s are $\hbar\omega_{\pm 1}$ and $\hbar\omega_s$.

The dielectric susceptibility can be written as[15]

$$a^1(\omega)=a-i\sigma/\omega, \qquad (1.4)$$

where a is the real part and σ is the conductivity. The latter in turn is related to the absorption coefficient $\eta(\omega)$ by[15,16]

$$\eta(\omega)=(4\pi/nc)\sigma(\omega), \qquad (1.5)$$

where n is the refractive index of the crystal, and c is the speed of light. In Eq. (1.5) we have assumed that the refractive index is equal to the square root of the dielectric constant and that the effective electric field is equal to the average microscopic electric field. It is the calculation of $\eta(\omega)$ that will occupy us in the remainder of this paper.

It is our intention in this paper to give an example of the application of the Born-Huang theory to a particular model which can be discussed rather completely, and at the same time to present a critique of the theory itself. In Sec. II we carry out a normal coordinate transformation of the Hamiltonian of the anharmonic crystal interacting with an external electromagnetic field. The transformed Hamiltonian is then reduced according to a prescription of Born and Huang, and is made the basis of the calculation of the damping constants in Sec. III. The absorption coefficients at low and high temperatures are calculated in Secs. IV and V, respectively. In Sec. VI a second-order perturbation calculation of the absorption spectrum is carried out. Finally, in Sec. VII we discuss the results of these calculations with a view to making predictions for the three-dimensional case and comparing them with experiment.

II. THE PERTURBED HAMILTONIAN

We consider a linear chain of $2N$ ions in which the even-numbered lattice points are occupied by ions of mass M_2 while the odd-numbered lattice points are occupied by ions of mass M_1 where with no loss of generality we assume that $M_1>M_2$. The charge on the nth ion is given by $(-1)^{n+1}\epsilon$.

If we expand the potential energy of this lattice to cubic terms in the displacements of the ions from their equilibrium positions and assume only nearest-neighbor interactions, the total Hamiltonian for the lattice in the presence of an external electric field E is

$$\begin{aligned}H=\tfrac{1}{2}\sum_{n=1}^{N}&(M_1u_{2n+1}{}^2+M_2u_{2n}{}^2)\\&+\frac{\alpha}{2}\sum_{n=1}^{N}(u_{2n}-u_{2n-1})^2+(u_{2n}-u_{2n+1})^2\\&+\frac{\beta}{6}\sum_{n=1}^{N}(u_{2n}-u_{2n-1})^3-(u_{2n}-u_{2n+1})^3\\&-\epsilon E\sum_{n=1}^{N}(u_{2n}-u_{2n+1}). \qquad (2.1)\end{aligned}$$

In this expression the first two terms represent the kinetic and potential energy of the lattice in the usual harmonic approximation, the third term is the anharmonic energy, while the last term represents the electric energy, where ϵ is the magnitude of the electronic charge.

We impose the Born-von Kármán cyclic boundary condition on the displacements:

$$u_{2n+N}=u_{2n}, \quad u_{2n+1+N}=u_{2n+1}. \qquad (2.2)$$

We now introduce the following normal coordinate transformation:

$$\begin{aligned}u_{2n}&=\frac{1}{(NM_2)^{\frac{1}{2}}}\sum_{k=-N/2+1}^{N/2}\sum_{j=1}^{2}e^{\pi ik2n/N}e(2n|k;j)Q(k;j),\\u_{2n+1}&=\frac{1}{(NM_1)^{\frac{1}{2}}}\sum_{k=-N/2+1}^{N/2}\sum_{j=1}^{2}e^{\pi ik(2n+1)/N}e(2n+1|k;j)Q(k;j),\end{aligned} \qquad (2.3)$$

where

$$\begin{aligned}e(2n|k;1)&=\cos\alpha_k, & e(2n|k;2)&=\sin\alpha_k,\\e(2n+1|k;1)&=-\sin\alpha_k, & e(2n+1|k;2)&=\cos\alpha_k,\end{aligned} \qquad (2.4\text{a})$$

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[15] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 631.

[16] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

and

$$\tan 2\alpha_k=[2(M_1M_2)^{\frac{1}{2}}/(M_1-M_2)]\cos\frac{\pi k}{N}. \qquad (2.4b)$$

When we substitute Eq. (2.3) and Eq. (2.4) into Eq. (2.1), we obtain

$$H=\tfrac{1}{2}\sum_k\sum_j\{|\dot{Q}(k;j)|^2+\omega^2(k;j)|Q(k;j)|^2\}+\frac{1}{6\sqrt{N}}\sum_{kk'k''}\sum_{jj'j''}\Delta(k+k'+k'')\Phi(kk'k'';jj'j'')$$
$$\times Q(k;j)Q(k';j')Q(k'';j'')+E\sqrt{N}\sum_j M(0;j)Q(0;j), \qquad (2.5)$$

where

$$\omega^2(k;1)=\frac{\alpha}{M_1M_2}\left\{M_1+M_2+\left(M_1^2+M_2^2+2M_1M_2\cos\frac{2\pi k}{N}\right)^{\frac{1}{2}}\right\}, \qquad (2.6a)$$

$$\omega^2(k;2)=\frac{\alpha}{M_1M_2}\left\{M_1+M_2-\left(M_1^2+M_2^2+2M_1M_2\cos\frac{2\pi k}{N}\right)^{\frac{1}{2}}\right\}, \qquad (2.6b)$$

$$\Phi(kk'k'';jj'j'')=2i\beta\,\mathrm{Im}\prod_{(k;j)=(k;j)}^{(k'';j'')}\left[\frac{e(2n|k;j)}{(M_2)^{\frac{1}{2}}}-\frac{e(2n+1|k;j)}{(M_1)^{\frac{1}{2}}}e^{-\pi ik/N}\right], \qquad (2.7)$$

$$M(0;j)=-\epsilon\left\{\frac{e(2n|0;j)}{(M_2)^{\frac{1}{2}}}-\frac{e(2n+1|0;j)}{(M_1)^{\frac{1}{2}}}\right\}, \qquad (2.8)$$

and

$$\begin{aligned}\Delta(k+k'+k'')&=1 \quad \text{if} \quad k+k'+k''=0,\ \pm N,\\ &=0 \quad \text{otherwise.}\end{aligned} \qquad (2.9)$$

The normal mode frequencies $\omega^2(k;1)$ occupy the optical band while the frequencies $\omega^2(k;2)$ occupy the acoustic band. We note from Eq. (2.8) and Eq. (2.4) that

$$M(0;1)=-\epsilon(1/M_1+1/M_2)^{\frac{1}{2}}, \quad M(0;2)=0, \qquad (2.10)$$

so that the external electric field interacts only with that normal mode whose frequency is the largest in the optical band. This normal mode will be referred to in what follows as the dispersion oscillator. It is characterized by the indices (0; 1).

We now turn to a more careful discussion of the anharmonic term in the Hamiltonian. In their treatment of optical absorption in ionic lattices, Born and Huang replace the exact anharmonic Hamiltonian by a "reduced" Hamiltonian which contains only terms proportional to the dispersion oscillator normal coordinate:

$$H_A{}^{\mathrm{red}}=\frac{1}{2\sqrt{N}}Q(0;1)\sum_{k';j'j''}\Phi(0\,k'\,-k';1j'j'')$$
$$\times Q(k';j')Q(-k';j''). \qquad (2.11)$$

The physical motivation for this choice for the reduced anharmonic Hamiltonian is that since only the mode (0; 1) interacts directly with the external field, the other vibrational modes act as a viscous medium which dissipates the energy of the mode (0; 1) which is excited by the field. The effect of the terms not containing $Q(0;1)$ is to modify somewhat the nature of the dissipating oscillators, and for a first approximation they are neglected. Of the remaining terms only the terms linear in $Q(0;1)$ are retained since terms quadratic or cubic in $Q(0;1)$ give contributions of $O(N^{-1})$ and $O(N^{-2})$ compared with the linear terms. There is in addition a considerable mathematical simplification introduced by the adoption of the reduced anharmonic Hamiltonian, viz., the elimination of the "umklapp" processes [the terms in Eq. (2.9) for which $k+k'+k''=\pm N$].

Since for the calculation of the absorption coefficient we will need the matrix elements of $H_A{}^{\mathrm{red}}$ between harmonic oscillator wave functions belonging to the unperturbed Hamiltonian, we rewrite Eq. (2.11) in a more suitable form for this purpose. In Eq. (2.11) the summations over k', j', j'' are over only those values for which $(k';j')$ and $(-k';j'')$ do not equal (0; 1). This means that

$$H_A{}^{\mathrm{red}}=\frac{1}{2\sqrt{N}}Q(0;1)\Phi(000;122)Q^2(0;2)$$
$$+\frac{1}{2\sqrt{N}}Q(0;1)\sum_{k\neq 0}\{\Phi(0\,k\,-k;111)Q(k;1)Q(-k;1)$$
$$+\Phi(0\,k\,-k;112)Q(k;1)Q(-k;2)$$
$$+\Phi(0\,k\,-k;121)Q(k;2)Q(-k;1)$$
$$+\Phi(0\,k\,-k;122)Q(k;2)Q(-k;2)\}. \qquad (2.12)$$

However, as we will show below, for all k

$$\begin{aligned}\Phi(0\,k\,-k;111)&=\Phi(0\,k\,-k;122)=0,\\ \Phi(0\,k\,-k;121)&=-\Phi(0\,k\,-k;112).\end{aligned}\tag{2.13}$$

Hence we obtain

$$\begin{aligned}H_A{}^{\text{red}}&=\frac{1}{2\sqrt{N}}Q(0;1)\sum_{k\neq 0}\Phi(0\,k\,-k;112)\\ &\quad\times[Q(k;1)Q(-k;2)-Q(k;2)Q(-k;1)]\qquad(2.14)\\ &=\frac{1}{\sqrt{N}}Q(0;1)\sum_{k\neq 0}\Phi(0\,k\,-k;112)\\ &\quad\times Q(k;1)Q(-k;2),\qquad(2.15)\end{aligned}$$

where we have replaced the summation index k by $-k$ in the second term of Eq. (2.14) and have used the symmetry property $\Phi(kk'k'';jj'j'')=\Phi(kk''k';jj''j')$ in writing Eq. (2.15). In what follows we drop the restriction $k\neq 0$ on the sum, as retaining this term affects our final answer only by the addition of a term of $O(N^{-1})$.

The calculation of the matrix elements of $H_A{}^{\text{red}}$ is simplified by expressing $Q(k;j)$ in terms of real normal coordinates. Instead of this, however, we write $H_A{}^{\text{red}}$ in terms of auxiliary coordinates

$$Q(k;j)=a_+(-k;j)+a_-(k;j),\tag{2.16}$$

which are related to real normal coordinates $q(k;j)$

$$\begin{aligned}a_+(-k;j)&=\frac{1}{2}\left\{\frac{\dot{q}(-k;j)}{\omega(k;j)}+iq(-k;j)\right\},\\ a_-(k;j)&=\frac{1}{2}\left\{\frac{\dot{q}(k;j)}{\omega(k;j)}-iq(k;j)\right\}.\end{aligned}\tag{2.17}$$

The reason for making this transformation is that in view of Eq. (2.17) the matrix elements of a_+ and a_- between harmonic oscillator wave functions whose arguments are the $q(k;j)$ have the simple form

$$\begin{aligned}\langle v+1|a_+|v\rangle&=i(\hbar/2\omega)^{\frac{1}{2}}(v+1)^{\frac{1}{2}},\\ \langle v-1|a_-|v\rangle&=-i(\hbar/2\omega)^{\frac{1}{2}}v^{\frac{1}{2}},\end{aligned}\tag{2.18}$$

where $v(k;j)$ is the quantum number associated with the normal coordinate $q(k;j)$ of frequency $\omega(k;j)$.

Transforming $H_A{}^{\text{red}}$ by substituting Eq. (2.17) into Eq. (2.15), we obtain

$$\begin{aligned}H_A{}^{\text{red}}&=\frac{1}{\sqrt{N}}[a_+(0;1)+a_-(0;1)]\\ &\quad\times\sum_k\Phi(0\,k\,-k;112)[a_+(-k;1)+a_-(k;1)]\\ &\quad\times[a_+(k;2)+a_-(-k;2)].\end{aligned}\tag{2.19}$$

In this equation all terms are distinct. Each gives rise to a distinct transition involving three oscillators, one of which is the dispersion oscillator. We define the transition for a particular transition by

$$\omega_{\text{initial}}-\omega_{\text{final}},\tag{2.20}$$

where the ω's are defined in terms of the energies of the corresponding states. Thus we have that

$$\hbar\omega=\hbar\omega_{\text{initial}}-\hbar\omega_{\text{final}}\tag{2.21}$$

is the negative of the change in the energy of the system due to the transition.

The coefficients $\Phi(kk'k'';jj'j'')$ are given by Eq. (2.7). If we expand the product, retain only the imaginary part, set $k=0$ and $k''=-k'$, we obtain

$$\begin{aligned}\Phi(0\,k\,-k;jj'j'')&=2i\beta\left(\sin\frac{\pi k}{N}\right)\frac{e(2n|0;j)}{(M_1M_2)^{\frac{1}{2}}}\\ &\quad\times\left[\frac{e(2n-1|k;j')e(2n|-k;j'')}{(M_2)^{\frac{1}{2}}}\right.\\ &\quad\left.-\frac{e(2n|k;j')e(2n-1|-k;j'')}{(M_2)^{\frac{1}{2}}}\right]\\ &\quad+2i\beta\left(\sin\frac{\pi k}{N}\right)\frac{e(2n-1|0;j)}{(M_1M_2)^{\frac{1}{2}}}\\ &\quad\times\left[\frac{e(2n|k;j')e(2n-1|-k;j'')}{(M_1)^{\frac{1}{2}}}\right.\\ &\quad\left.-\frac{e(2n-1|k;j')e(2n|-k;j'')}{(M_1)^{\frac{1}{2}}}\right].\end{aligned}\tag{2.22}$$

From this expression and Eq. (2.4) we readily obtain

$$\begin{aligned}&\Phi(0\,k\,-k;111)=\Phi(0\,k\,-k;122)=0,\\ &\Phi(0\,k\,-k;112)=-\Phi(0\,k\,-k;121)\\ &\qquad=-2i\beta\frac{(M_1+M_2)^{\frac{1}{2}}}{M_1M_2}\sin\frac{\pi k}{N}.\end{aligned}\tag{2.23}$$

III. EVALUATION OF THE DAMPING CONSTANTS

The three damping constants which appear in the Born-Huang theory of optical absorption are defined by

$$\gamma_0(0)=\frac{\pi}{\hbar^2}\lim_{\Delta\omega\to 0}\frac{1}{\Delta\omega}\sum_{(n')}^{0}|\langle n'|H_A{}^{\text{red}}|0\rangle|^2,\tag{3.1a}$$

$$\gamma_{\pm j}(\omega_\pm)=\frac{\pi}{\hbar^2}\lim_{\Delta\omega_\pm\to 0}\frac{1}{\Delta\omega_\pm}\sum_{(s)}^{\omega_\pm}|\langle s|H_A{}^{\text{red}}|\pm j\rangle|^2,\tag{3.1b}$$

where the symbol $\sum_{(m)}{}^{\omega}$ means a summation over all final states m for which the transition frequency lies in the interval $(\omega,\omega+\Delta\omega)$. We can rewrite these functions in a more transparent form by introducing a function $F(\omega)$ which is defined in such a way that $F(\omega)\Delta\omega$ is the number of transition frequencies in the interval $(\omega, \omega+\Delta\omega)$. Then Eqs. (3.1) can be rewritten as

$$\gamma_0(0)=\frac{\pi}{\hbar^2}F(0)[|\langle n'|H_A{}^{\mathrm{red}}|0\rangle|^2]_{\omega=0}, \tag{3.2a}$$

$$\gamma_\pm(\omega_\pm)=\frac{\pi}{\hbar^2}F(\omega_\pm)[|\langle s|H_A{}^{\mathrm{red}}|\pm j\rangle|^2]_{\omega=\omega_\pm}. \tag{3.2b}$$

For our one-dimensional problem $F(\omega)$ can be found exactly in closed form. In the present case it is only necessary to know the distribution functions of

$$\omega(k;1)+\omega(k;2)$$

and

$$\omega(k;1)-\omega(k;2),$$

since these are the only combinations of $\omega(k;1)$ and $\omega(k;2)$ which occur in the expressions for the transition frequencies obtained from Eq. (2.21).

These distribution functions can be determined as follows. From Eq. (2.6a) and Eq. (2.6b) we have that

$$\omega^2(k;1)=\tfrac{1}{2}\omega_d{}^2+\tfrac{1}{2}\omega_d{}^2[1-(4\omega_a{}^2\omega_b{}^2/\omega_d{}^4) \times\sin^2(\pi k/N)]^{\frac{1}{2}}, \tag{3.3a}$$

$$\omega^2(k;2)=\tfrac{1}{2}\omega_d{}^2-\tfrac{1}{2}\omega_d{}^2[1-(4\omega_a{}^2\omega_b{}^2/\omega_d{}^4) \times\sin^2(\pi k/N)]^{\frac{1}{2}}, \tag{3.3b}$$

where we have introduced $\omega_a{}^2=2\gamma/M_1$ and $\omega_b{}^2=2\gamma/M_2$. Thus we obtain

$$[\omega(k;1)+\omega(k;2)]^2=\omega_d{}^2+2\omega_a\omega_b\sin(\pi k/N), \tag{3.4}$$

so that

$$\begin{gathered}\omega(k;1)+\omega(k;2)=[\omega_d{}^2+2\omega_a\omega_b\sin(\pi k/N)]^{\frac{1}{2}}\\ \omega_d\leq\omega(k;1)+\omega(k;2)\leq\omega_a+\omega_b.\end{gathered} \tag{3.5a}$$

In a similar fashion we find

$$\begin{gathered}\omega(k;1)-\omega(k;2)=[\omega_d{}^2-2\omega_a\omega_b\sin(\pi k/N)]^{\frac{1}{2}},\\ \omega_b-\omega_a\leq\omega(k;1)-\omega(k;2)\leq\omega_d.\end{gathered} \tag{3.5b}$$

We want to know how many normal modes there are, for example, with $\omega(k;1)+\omega(k;2)$ in the interval $(\omega, \omega+d\omega)$. This is given by

$$F_\alpha(\omega)d\omega=w(\varphi)(d\varphi/d\omega)d\omega, \quad \varphi=\pi k/N, \tag{3.6}$$

where $w(\varphi)$ is the number of frequencies per unit wave vector range. In the present case due to the two-fold degeneracy of the frequencies it becomes

$$w(\varphi)=2N/\pi. \tag{3.7}$$

From Eq. (3.5a) we find that

$$\sin\varphi=(\omega^2-\omega_d{}^2/)2\omega_a\omega_b, \tag{3.8}$$

so that

$$d\varphi/d\omega=2\omega[4\omega_a{}^2\omega_b{}^2-(\omega^2-\omega_d{}^2)^2]^{-\frac{1}{2}}, \tag{3.9}$$

and

$$\begin{gathered}F_\alpha(\omega)=(4N\omega/\pi)[4\omega_a{}^2\omega_b{}^2-(\omega^2-\omega_d{}^2)^2]^{-\frac{1}{2}},\\ \omega_d\leq\omega\leq\omega_a+\omega_b.\end{gathered} \tag{3.10}$$

Similarly we find

$$\begin{gathered}F_\beta(\omega)=(4N\omega/\pi)[4\omega_a{}^2\omega_b{}^2-(\omega_d{}^2-\omega^2)^2]^{-\frac{1}{2}},\\ \omega_b-\omega_a\leq\omega\leq\omega_d,\end{gathered} \tag{3.11}$$

where $F_\beta(\omega)d\omega$ is the number of normal modes with $\omega(k;1)-\omega(k;2)$ in the interval $(\omega, \omega+d\omega)$.

With these results and the results of the preceding section it is a straightforward calculation to obtain the damping constants. We begin by obtaining $\gamma_{+1}(\omega_d-\omega)$ at the absolute zero of temperature. This is a particularly simple case since here $v(0;1)=+1$, while all other $v(k;j)$ are zero. The squares of the moduli of the only nonvanishing matrix elements of $H_A{}^{\mathrm{red}}$ together with their transition frequencies are found from Eq. (2.19) to be

$$\begin{gathered}\frac{\hbar^3|\Phi(0\;k\;-k;112)|^2}{4N\omega_d\omega(-k;1)\omega(k;2)},\\ -\omega_d-[\omega(-k;1)+\omega(k;2)],\end{gathered} \tag{3.12a}$$

$$\begin{gathered}\frac{\hbar^3|\Phi(0\;k\;-k;112)|^2}{8N\omega_d\omega(-k;1)\omega(k;2)},\\ \omega_d-[\omega(-k;1)+\omega(k;2)].\end{gathered} \tag{3.12b}$$

Each of these terms must now be multiplied by $\pi/\hbar^2$ and summed over those values of k for which the corresponding transition frequency lies between $\omega_d-\omega$ and $\omega_d-\omega+\Delta\omega$. By Eq. (3.1b) and Eq. (3.2b) the result of these operations is

$$\begin{aligned}\gamma_{+1}(\omega_d-\omega)=&\frac{\pi\hbar}{4N\omega_d}\\ &\times\left\{\frac{|\Phi(0\;k\;-k;112)|^2}{\omega(k;1)\omega(k;2)}\right\}_{\varphi=\varphi_1}F_\alpha(\omega-2\omega_d)\\ &+\frac{\pi\hbar}{8N\omega_d}\left\{\frac{|\Phi(0\;k\;-k;112)|^2}{\omega(k;1)\omega(k;2)}\right\}_{\varphi=\varphi_2}F_\alpha(\omega),\end{aligned} \tag{3.13}$$

where

$$\begin{gathered}\varphi_1=\sin^{-1}\frac{(\omega-2\omega_d)^2-\omega_d{}^2}{2\omega_a\omega_b},\\ \varphi_2=\sin^{-1}\frac{\omega^2-\omega_d{}^2}{2\omega_a\omega_b}.\end{gathered} \tag{3.14}$$

If we substitute into Eq. (3.13) the expressions for $\Phi(0\;k\;-k;112)$ given in Eq. (2.23) and make use of

Eq. (3.14) we obtain finally

$$\begin{aligned}\gamma_{+1}(\omega_d-\omega)&=C\omega_d f_1(x), \quad 3\leq x\leq 2+y\\ &=C\omega_d f_2(x), \quad 1\leq x\leq y\\ &=0 \quad \text{otherwise,}\end{aligned}\tag{3.15}$$

where $\omega=x\omega_d$, $y\omega_d=\omega_a+\omega_b$,

$$C=2\beta^2(\hbar\omega_d/\omega_a{}^2\omega_b{}^2\omega_d{}^2)[(M_1+M_2)/M_1{}^2M_2{}^2],\tag{3.16}$$

$$f_1(x)=\frac{(x-1)(x-2)(x-3)}{[z-(x-1)^2(x-3)^2]^{\frac{1}{2}}},\tag{3.17}$$

$$f_2(x)=\frac{x(x^2-1)}{2[z-(x^2-1)^2]^{\frac{1}{2}}},\tag{3.18}$$

and $z=4\omega_a{}^2\omega_b{}^2/\omega_d{}^4$. A plot of $f_1(x)$ and $f_2(x)$ is given in Fig. 1. In this paper we assume the following values for the various physical quantities:

$$\begin{aligned}&\Theta_D=\hbar\omega_d/k=250°\text{K}, \quad M_1=2M_2,\\ &\beta=18\times10^{11}\ \text{erg/cm}^3, \quad \alpha=9\times10^3\ \text{erg/cm}^2.\end{aligned}\tag{3.19}$$

The values of C, y, and z are then 0.0383, 1.3939, and 8/9, respectively.

We turn now to the case of the "wings" of the absorption region. The derivation of Eq. (1.2b) is based on the assumption that $\omega>2\omega_d$. Therefore, in obtaining the damping constants $\gamma_{+1}(\omega_d+\omega)$, $\gamma_{+1}(\omega_d-\omega)$, $\gamma_{-1}(-\omega_d+\omega)$, $\gamma_{-1}(-\omega_d-\omega)$, and $\gamma_0(0)$, which appear in Eq. (1.2b), we can neglect all contributions which give rise to nonvanishing terms in the interval $0\leq\omega\leq2\omega_d$. We consider the nonvanishing contributions outside this interval separately.

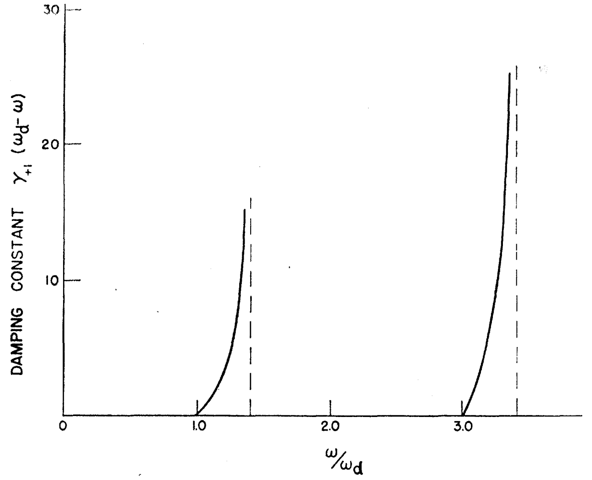

FIG. 1. The damping constant $\gamma_{+1}(\omega_d-\omega)$ in units of $C\omega_d$ plotted as a function of ω/ω_d at the absolute zero of temperature.

If we examine the nonvanishing matrix elements of $H_A{}^{\text{red}}$, Eq. (2.19), which contribute to $\gamma_{+1}(\omega_d-\omega)$ [these correspond to setting the dispersion oscillator quantum number $v(0;1)$ equal to $v^0(0;1)+1$, where $v^0(0;1)$ is its value in the initial state], we find only two whose transition frequencies are compatible with the condition $\omega>2\omega_0$:

$$\begin{aligned}\gamma_{+1}(\omega_d-\omega)&=\hbar|\Phi(0\,k\,-k;112)|^2f_0(\omega)\left.\frac{[v^0(0;1)+2][v^0(-k;1)+1][v^0(k;2)+1]}{2\omega_d\omega(-k;1)\omega(k;2)}\right|_{\varphi1}\\ &\qquad\qquad \text{for} \quad 3\omega_d\leq\omega\leq2\omega_d+\omega_a+\omega_b,\\ &=\hbar|\Phi(0\,k\,-k;112)|^2f_0(\omega)\left.\frac{[v^0(0;1)+2][v^0(-k;1)+1][v^0(-k;2)]}{2\omega_d\omega(-k;1)\omega(-k;2)}\right|_{\varphi2}\\ &\qquad\qquad \text{for} \quad 2\omega_d+\omega_b-\omega_a\leq\omega\leq3\omega_d,\\ &=0 \quad \text{otherwise,}\end{aligned}\tag{3.20}$$

where

$$\begin{aligned}\sin\phi_1&=(\omega-\omega_d)(\omega-3\omega_d)/2\omega_a\omega_b,\\ \sin\phi_2&=(3\omega_d-\omega)(\omega-\omega_d)/2\omega_a\omega_b,\end{aligned}\tag{3.21}$$

$$|\Phi(0\,k\,-k;112)|^2=4\beta^2[(M_1+M_2)/M_1{}^2M_2{}^2]\sin\varphi,\tag{3.22a}$$

$$f_0(\omega)=\frac{\omega-2\omega_d}{\{4\omega_a{}^2\omega_b{}^2-[(\omega-2\omega_d)^2-\omega_d{}^2]^2\}^{\frac{1}{2}}},\tag{3.22b}$$

In the limit of high temperatures we need the following thermal averages:

$$\begin{aligned}&\langle v^0(0;1)+2\rangle\langle v^0(-k;1)+1\rangle\langle v^0(k;2)+1\rangle\\ &\qquad\sim(kT)^3/\hbar^3\omega_d\omega(-k;1)\omega(k;2),\\ &\langle v^0(0;1)+2\rangle\langle v^0(-k;1)+1\rangle\langle v^0(-k;2)\rangle\\ &\qquad\sim(kT)^3/\hbar^3\omega_d\omega(-k;1)\omega(-k;2).\end{aligned}\tag{3.23}$$

In this limit we obtain finally

$$\begin{aligned}&\gamma_{+1}(\omega_d-\omega)=C\omega_d{}^2f_0(\omega)(kT/\hbar\omega_d)^3,\\ &2\omega_d+\omega_b-\omega_a\leq\omega\leq2\omega_d+\omega_b+\omega_a.\end{aligned}\tag{3.24}$$

Turning to $\gamma_{-1}(\omega-\omega_d)$ we find that the only nonvanishing matrix elements which contribute to $\gamma_{-1}(\omega-\omega_d)$ [these correspond to setting $v(0;1)$ equal to $v^0(0;1)-1$], and are compatible with the requirement that $\omega > 2\omega_d$, lead to

$$\begin{aligned}\gamma_{-1}(\omega-\omega_d) &= \hbar|\Phi(0\,k\,-k;112)|^2 f_0(\omega)\left.\frac{[v^0(0;1)-1][v^0(k;1)][v^0(k;2)+1]}{2\omega_d\omega(k;1)\omega(k;2)}\right|_{\phi 1} \quad \text{for} \quad 2\omega_d+\omega_b-\omega_a \le \omega \le 3\omega_d,\\ &= \hbar|\Phi(0\,k\,-k;112)|^2 f_0(\omega)\left.\frac{[v^0(0;1)-1][v^0(k;1)][v^0(-k;2)]}{2\omega_d\omega(k;1)\omega(k;2)}\right|_{\phi 2} \quad \text{for} \quad 3\omega_d \le \omega \le 2\omega_d+\omega_a+\omega_b,\\ &= 0 \quad \text{otherwise},\end{aligned} \tag{3.25}$$

where

$$\begin{aligned}\sin\phi_1 &= [\omega_d^2-(\omega-2\omega_d)^2]/2\omega_a\omega_b,\\ \sin\phi_2 &= [(\omega-2\omega_d)^2-\omega_d^2]/2\omega_a\omega_b.\end{aligned} \tag{3.26}$$

With the aid of the following high-temperature thermal averages

$$\begin{aligned}\langle v^0(0;1)-1\rangle\langle v^0(k;1)\rangle\langle v^0(k;2)+1\rangle &\sim (kT)^3/\hbar^3\omega_d\omega(k;1)\omega(k;2)\\ \langle v^0(0;1)-1\rangle\langle v^0(k;1)\rangle\langle v^0(-k;2)\rangle &\sim (kT)^3/\hbar^3\omega_d\omega(k;1)\omega(-k;2),\end{aligned} \tag{3.27}$$

we obtain in this limit

$$\begin{aligned}\gamma_{-1}(\omega-\omega_d) &= C\omega_d^2 f_0(\omega)(kT/\hbar\omega_d)^3,\\ &\qquad 2\omega_d+\omega_b-\omega_a \le \omega \le 2\omega_d+\omega_b+\omega_a\\ &= 0 \quad \text{otherwise.}\end{aligned} \tag{3.28}$$

In calculating the thermal averages in Eq. (3.27) the range of the dispersion oscillator $v^0(0;1)$ was restricted to $v^0(0;1) \ge 1$ in order that a state with a quantum number -1 not be included. Thus

$$\langle v^0(0;1)-1\rangle = \sum_{v=1}^{\infty}(v-1)e^{-v\hbar\omega_d/kT}\Big/\sum_{v=1}^{\infty}e^{-v\hbar\omega_d/kT}. \tag{3.29}$$

We see, comparing Eq. (3.24) and Eq. (3.28), that, to this approximation, in the high-temperature limit $\gamma_{+1}(\omega_d-\omega)$ equals $\gamma_{-1}(\omega-\omega_d)$.

Turning to the remaining damping constants we find that there are no nonvanishing contributions to $\gamma_{+1}(\omega_d+\omega)$, $\gamma_{-1}(-\omega_d-\omega)$, and $\gamma_0(0)$ in the region $\omega > 2\omega_d$.

Using the data of Eq. (3.19), a plot of

$$\gamma_{+1}(\omega_d-\omega)/C\omega_d = \gamma_{-1}(\omega-\omega_d)/C\omega_d$$

is given in Fig. 2 for $T = 250$°K.

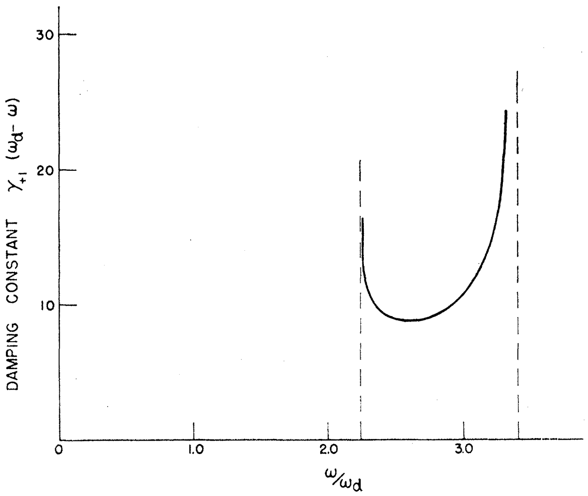

FIG. 2. The damping constant $\gamma_{+1}(\omega_d-\omega)$ in units of $C\omega_d$ plotted as a function of ω/ω_d for $\omega > 2\omega_d$ and a temperature of 250°K.

We turn finally to a consideration of the center of the dispersion region. From Eq. (1.2c) we see that only the damping constants $\gamma_0(0)$, $\gamma_{+1}(0)$, and $\gamma_{-1}(0)$ are required in this case. These three damping constants are given by

$$\begin{aligned}\gamma(0) &= \frac{\pi\hbar}{8N}\sum_k|\Phi(0\,k\,-k;112)|^2\frac{[v(0;1)+1]v(k;1)[v(k;2)+1]}{\omega_d\omega(k;1)\omega(k;2)}\\ &+\frac{\pi\hbar}{8N}\sum_k|\Phi(0\,k\,-k;112)|^2\frac{[v(0;1)+1]v(k;1)v(-k;2)}{\omega_d\omega(k;1)\omega(-k;2)}\\ &+\frac{\pi\hbar}{8N}\sum_k|\Phi(0\,k\,-k;112)|^2\frac{v(0;1)[v(-k;1)+1][v(k;2)+1]}{\omega_d\omega(-k;1)\omega(k;2)}\\ &+\frac{\pi\hbar}{8N}\sum_k|\Phi(0\,k\,-k;112)|^2\frac{v(0;1)[v(-k;1)+1]v(-k;2)}{\omega_d\omega(-k;1)\omega(-k;2)},\end{aligned} \tag{3.30}$$

where the first summation is over those values of k for which $\omega(k;1)-\omega(k;2)=\omega_d$; the second, $\omega(k;1)+\omega(-k;2)=\omega_d$; the third, $\omega(-k;1)+\omega(k;2)=\omega_d$; and the last, $\omega(-k;1)-\omega(-k;2)=\omega_d$; and where $v(0;1)$ equals

$v^0(0;1)+1$ for $\gamma_{+1}(0)$, $v^0(0;1)$ for $\gamma_0(0)$, and $v^0(0;1)-1$ for $\gamma_{-1}(0)$. They can be expressed more compactly as

$$\begin{aligned}\gamma_{+1}(0)&=[v^0(0;1)+2]A+[v^0(0;1)+1]B,\\ \gamma_0(0)&=[v^0(0;1)+1]A+[v^0(0;1)]B,\\ \gamma_{-1}(0)&=v^0(0;1)A+[v^0(0;1)-1]B,\end{aligned} \tag{3.31}$$

where

$$A=\frac{\pi\hbar}{8N\omega_d}\left\{\sum_k |\Phi(0\,k\,-k;112)|^2\frac{v(k;1)[v(k;2)+1]}{\omega(k;1)\omega(k;2)}+\sum_k |\Phi(0\,k\,-k;112)|^2\frac{v(k;1)v(-k;2)}{\omega(k;1)\omega(-k;2)}\right\}, \tag{3.32a}$$

the first summation being over those values of k for which $\omega(k;1)-\omega(k;2)=\omega_d$, the second over those for which $\omega(k;1)+\omega(-k;2)=\omega_d$;

$$\begin{aligned}B=\frac{\pi\hbar}{8N\omega_d}\Bigg\{&\sum_k |\Phi(0\,k\,-k;112)|^2\frac{[v(-k;1)+1][v(k;2)+1]}{\omega(-k;1)\omega(k;2)}\\ &+\sum_k |\Phi(0\,k\,-k;112)|^2\frac{[v(-k;1)+1]v(-k;2)}{\omega(-k;1)\omega(-k;2)}\Bigg\},\end{aligned} \tag{3.32b}$$

the first summation being over those values of k for which $\omega(-k;1)+\omega(k;2)=\omega_d$, the second over those for which $\omega(-k;1)-\omega(-k;2)=\omega_d$. Since $\omega(k;1)+\omega(k;2)$ and $\omega(k;1)-\omega(k;2)$ can equal ω_d only at $k=0$, we have since

$$\begin{aligned}F_\alpha(\omega_d)&=F_\beta(\omega_d)=4N\omega_d/\pi\omega_a\omega_b,\\ \omega(k;1)\omega(k;2)&=\omega_a\omega_b\sin(\pi k/N),\end{aligned} \tag{3.33}$$

that

$$A=\tfrac{1}{2}C\omega_d\lim_{k\to 0} v(0;1)[v(k;2)+1+v(-k;2)]\sin(\pi k/N), \tag{3.34a}$$

$$B=\tfrac{1}{2}C\omega_d\lim_{k\to 0} [v(0;1)+1][v(k;2)+1+v(-k;2)]\sin(\pi k/N). \tag{3.34b}$$

However, we find that

$$\langle v(k;2)+v(-k;2)+1\rangle=\langle 2v(k;2)+1\rangle=\coth[\hbar\omega(k;2)/2kT], \tag{3.35}$$

while as $k\to 0$

$$\omega^2(k;2)\to(\omega_a^2\omega_b^2/\omega_d^2)\sin^2/(\pi k/N), \tag{3.36}$$

so that

$$\lim_{k\to 0}\langle v(k;2)+1+v(-k;2)\rangle\sin(\pi k/N)=\lim_{k\to 0}\sin(\pi k/N)\coth[(\hbar/2kT)(\omega_a\omega_b/\omega_d)\sin(\pi k/N)]=2kT\omega_d/\hbar\omega_a\omega_b, \tag{3.37}$$

in the high-temperature limit. Thus we obtain the result that

$$A=v(0;1)(C\omega_d^2/\hbar\omega_a\omega_b)kT, \tag{3.38a}$$

$$B=[v(0;1)+1](C\omega_d^2/\hbar\omega_a\omega_b)kT, \tag{3.38b}$$

so that the expressions for the thermal averages of the damping constants become

$$\langle\gamma_{+1}(0)\rangle=2Cz^{-\frac{1}{2}}(kT/\hbar)\langle[v^0(0;1)+2]v^0(0;1)+[v^0(0;1)+1]^2\rangle, \tag{3.39a}$$

$$\langle\gamma_0(0)\rangle=2Cz^{-\frac{1}{2}}(kT/\hbar)\langle[v^0(0;1)+1]v^0(0;1)+[v^0(0;1)+1]v^0(0;1)\rangle, \tag{3.39b}$$

$$\langle\gamma_{-1}(0)\rangle=2Cz^{-\frac{1}{2}}(kT/\hbar)\langle[v^0(0;1)]^2+[v^0(0;1)+1][v^0(0;1)-1]\rangle. \tag{3.39c}$$

In the limit of high temperatures the thermal averages are found to be

$$\begin{aligned}&\langle[v^0(0;1)+2]v^0(0;1)+[v^0(0;1)+1]^2\rangle\sim 4(kT/\hbar\omega_d)^2\\ &\langle 2[v^0(0;1)+1]v^0(0;1)\rangle\sim 4(kT/\hbar\omega_d)^2\\ &\langle[v^0(0;1)]^2+[v^0(0;1)+1][v^0(0;1)-1]\rangle\sim 4(kT/\hbar\omega_d)^2,\end{aligned} \tag{3.40}$$

so that to this approximation

$$\langle\gamma_{+1}(0)\rangle=\langle\gamma_0(0)\rangle=\langle\gamma_{-1}(0)\rangle=8C\omega_d z^{-\frac{1}{2}}\left(\frac{kT}{\hbar\omega_d}\right)^3. \tag{3.41}$$

The explicit expressions for the damping constants in this region, however, are of less interest than the corresponding absorption coefficient, which we evaluate in Sec. V.

It is worth pointing out that in the evaluation of the high-temperature thermal average of the last term in Eq. (3.39c), the harmonic oscillator quantum number $v^0(0;1)$ can only assume the values $v^0(0;1)\geqslant 1$ in order that an initial state with a quantum number -1 not be included.

IV. ABSORPTION COEFFICIENT AT LOW TEMPERATURES

If we combine Eq. (1.2a), Eq. (1.4), and Eq. (1.5), we find that the absorption coefficient at the absolute zero of temperature is given as a function of the frequency of the incident radiation by

$$\eta(\omega)=\frac{4\pi}{nc}\frac{1}{v_a}\frac{[M(0;1)]^2}{2\omega_d}\frac{\omega\gamma_{+1}(\omega_d-\omega)}{(\omega_d-\omega)^2+\gamma_{+1}{}^2(\omega_d-\omega)}. \qquad (4.1)$$

If we use the definition $\omega=x\omega_d$ of Sec. III, together with Eq. (3.18), we can rewrite Eq. (4.1) in the form

$$\begin{aligned}\eta(\omega)&=\eta_0\frac{Cxf_1(x)}{(1-x)^2+C^2f_1{}^2(x)}, \quad 3\leqslant x\leqslant 3.3939;\\ &=\eta_0\frac{Cxf_2(x)}{(1-x)^2+C^2f_2{}^2(x)}, \quad 1\leqslant x\leqslant 1.3939; \qquad (4.2)\\ &=0 \quad \text{otherwise};\end{aligned}$$

where

$$\eta_0=(2\pi/nv_ac\omega_d)[M(0;1)]^2. \qquad (4.2\text{a})$$

The absorption coefficient in units of η_0 is plotted as a function of x in Fig. 3.

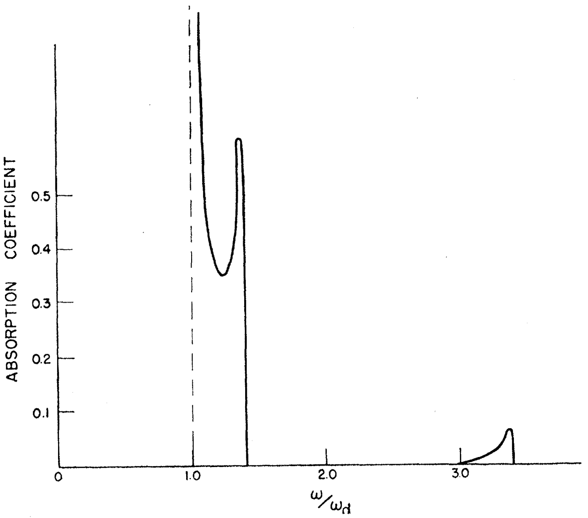

FIG. 3. The absorption coefficient η in units of η_0 plotted as a function of ω/ω_d at the absolute zero of temperature. The method of Born and Huang was used to calculate η.

V. ABSORPTION COEFFICIENTS AT HIGH TEMPERATURES

In this section we apply the results of Sec. III to the calculation of the high-temperature expressions for the absorption coefficient in the wings of the absorption region and at the center of the dispersion region. In the latter case we also present an alternative derivation of the high-temperature absorption coefficient which we feel is more justified than that of Born and Huang.

The expression for $a^1(\omega)$ in the wings of the absorption region is given by Eq. (1.2b). The only nonvanishing damping constants in this region were shown in Sec. III to be $\gamma_{+1}(\omega-\omega_d)$ and $\gamma_{-1}(\omega-\omega_d)$. Hence Eq. (1.2b) can be rewritten as

$$a^1(\omega)=-\frac{1}{v_a}\frac{[M(0;1)]^2}{2\omega_d}\left\{\frac{2\omega_d}{\omega_d{}^2-\omega^2}+iv^0(0;1)\left[\frac{\gamma_{+1}(\omega_d-\omega)-\gamma_{-1}(\omega-\omega_d)}{(\omega_d-\omega)^2}\right]+i\frac{\gamma_{+1}(\omega_d-\omega)}{(\omega_d-\omega)^2}\right\}, \quad \omega>2\omega_d, \qquad (5.1)$$

so that in this case

$$\eta(\omega)=\eta_0\frac{\omega}{(\omega_d-\omega)^2}\{v^0(0;1)[\gamma_{+1}(\omega_d-\omega)-\gamma_{-1}(\omega-\omega_d)]+\gamma_{+1}(\omega_d-\omega)\}, \quad \omega>2\omega_d. \qquad (5.2)$$

To obtain the high-temperature form for this expression we need the thermal average $\langle v^0(0;1)[\gamma_{+1}(\omega_d-\omega)-\gamma_{-1}(\omega-\omega_d)]\rangle$ which is given explicitly by [see Eq. (3.20) and Eq. (3.25)]

$$\begin{aligned}\langle v^0(0;1)[\gamma_{+1}(\omega_d-\omega)-\gamma_{-1}(\omega-\omega_d)]\rangle&=\frac{\hbar|\Phi(0\,k\,-k;112)|^2}{2\omega_d\omega(-k;1)\omega(k;2)}f_0(\omega)\\ &\times[\langle v^0(0;1)[v^0(0;1)+2][v^0(-k;1)+1][v^0(k;2)+1]-v^0(0;1)[v^0(0;1)-1][v^0(k;1)][v^0(-k;2)]\rangle]\Big|_{\phi_1},\\ &\qquad 3\omega_d\leq\omega\leq 2\omega_d+\omega_a+\omega_b, \qquad (5.3)\end{aligned}$$

with a corresponding expression for the frequency range $2\omega_d+\omega_b-\omega_a\leqslant\omega\leqslant 3\omega_d$. In Eq. (5.3), ϕ_1 is defined by

$$\sin\phi_1=(\omega-\omega_d)(\omega-3\omega_d)/2\omega_a\omega_b. \qquad (5.4)$$

Evaluating the thermal averages in the high-temperature limit we obtain

$$\langle v^0(0;1)[v^0(0;1)+2][v^0(-k;1)+1][v^0(k;2)+1]\rangle$$
$$\sim\frac{2(kT)^4}{\hbar^4\omega_d^2\omega(-k;1)\omega(k;2)}\left\{1+\frac{\hbar[\omega_d+\omega(-k;1)+\omega(k;2)]}{2kT}+\cdots\right\}, \tag{5.5}$$
$$\langle v^0(0;1)[v^0(0;1)-1][v^0(k;1)][v^0(-k;2)]\rangle\sim\frac{2(kT)^4}{\hbar^4\omega_d^2\omega(k;1)\omega(-k;2)}\left[1-\frac{\hbar[\omega(k;1)+\omega(-k;2)]}{2kT}+\cdots\right].$$

With these results we find that

$$\langle v^0(0;1)[\gamma_{+1}(\omega_d-\omega)-\gamma_{-1}(\omega-\omega_d)]\rangle=\frac{\hbar}{2}|\Phi(0\;k\;-k;112)|^2f_0(\omega)\frac{[\omega_d+2\omega(k;1)+2\omega(k;2)]}{\hbar^3\omega_d^3\omega^2(k;1)\omega^2(k;2)}(kT)^3\bigg|_{\phi1}$$
$$=2\hbar\beta^2[(M_1+M_2)/(M_1^2M_2^2)]f_0(\omega)[(2\omega-3\omega_d)/\omega_a^2\omega_b^2](kT/\hbar\omega_d)^3. \tag{5.6}$$

Similarly we find that Eq. (5.6) also holds in the high-temperature limit in the frequency range $2\omega_d+\omega_b-\omega_a\leqslant\omega\leqslant 3\omega_d$. Combining these results with Eq. (5.2) and Eq. (3.24), we obtain finally

$$\eta(\omega)=2\eta_0C\frac{\omega\omega_d^2}{(\omega-\omega_d)}f_0(\omega)\left(\frac{kT}{\hbar\omega_d}\right)^3,\quad 2\omega_d+\omega_b-\omega_a\leq\omega\leq 2\omega_d+\omega_a+\omega_b. \tag{5.7}$$

The absorption coefficient in units of η_0 is plotted as a function of $x=\omega/\omega_d$ at three temperatures in Fig. 4.

Turning now to the center of the dispersion region we see from Eq. (1.2c) that the absorption coefficient is given by

$$\eta(\omega_d)=\eta_0\left\{\frac{\omega_d}{\gamma_0(0)+\gamma_{+1}(0)}+\frac{\omega_d v^0(0;1)[\gamma_{-1}(0)-\gamma_{+1}(0)]}{[\gamma_0(0)+\gamma_{+1}(0)][\gamma_0(0)+\gamma_{-1}(0)]}\right\}. \tag{5.8}$$

At high temperatures we find, with the aid of Eq. (3.39), that

$$\begin{aligned}&\langle v^0(0;1)[\gamma_{-1}(0)-\gamma_{+1}(0)]\rangle\sim 2C\omega_d z^{-\frac{1}{2}}(kT/\hbar\omega_d)\langle v^0(0;1)[v^0(0;1)+1][v^0(0;1)-1]-[v^0(0;1)]^3\\&\qquad\qquad -4[v^0(0;1)]^2-v^0(0;1)\rangle\\&\langle\gamma_0(0)+\gamma_{-1}(0)\rangle\sim 2C\omega_d z^{-\frac{1}{2}}(kT/\hbar\omega_d)\langle 3[v^0(0;1)]^2+2v^0(0;1)+[v^0(0;1)+1][v^0(0;1)-1]\rangle\\&\langle\gamma_0(0)+\gamma_{+1}(0)\rangle\sim 2C\omega_d z^{-\frac{1}{2}}(kT/\hbar\omega_d)\langle 4[v^0(0;1)]^2+6v^0(0;1)+1\rangle,\end{aligned} \tag{5.9}$$

so that the expression for the absorption coefficient becomes

$$\eta(\omega)=\eta_0(z^{\frac{1}{2}}/2C)\left(\frac{\hbar\omega_d}{kT}\right)\frac{1}{\langle 4v^2+6v+1\rangle}\left[1+\frac{\langle v(v+1)(v-1)-v^3-4v^2-v\rangle}{\langle 3v^2+2v+(v+1)(v-1)\rangle}\right]. \tag{5.10}$$

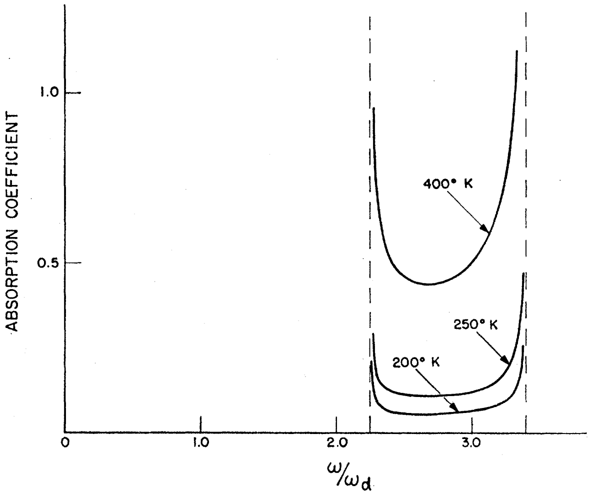

FIG. 4. The absorption coefficient η in units of η_0 plotted as a function of ω/ω_d for $\omega>2\omega_d$ at three temperatures. The method of Born and Huang was used to calculate η.

We have the following thermal averages

$$\begin{gathered}\langle 4v^2+6v+1\rangle \sim 8(kT/\hbar\omega_d)^2,\\ \langle v(v+1)(v-1)-v^3-4v^2-v\rangle \sim -2(kT/\hbar\omega_d)^2,\\ \langle 3v^2+2v+(v+1)(v-1)\rangle \sim 8(kT/\hbar\omega_d)^2,\end{gathered} \tag{5.11}$$

and we obtain finally

$$\eta(\omega)=\frac{3}{64}\eta_0\frac{z^{\frac{1}{2}}}{C}\left(\frac{\Theta_D}{T}\right)^3. \tag{5.12}$$

We conclude this section with an alternative calculation of the absorption coefficient at the center of the dispersion region which we feel is more correct than the one just presented. It proceeds from the point of view that experimentally one does not measure a damping constant directly, but instead measures the absorption coefficient and then introduces a damping constant through some theoretical expression, such as Eq. (1.1). We therefore proceed to calculate $\eta(\omega)$ directly without the need for an explicit subsidiary calculation of the damping constants.

To calculate the thermal average of $\eta(\omega)$ we need the following average:

$$\langle A\rangle=\left\langle\frac{1}{\gamma_0(0)+\gamma_{+1}(0)}\right\rangle+\left\langle\frac{v^0(0;1)[\gamma_{-1}(0)-\gamma_{+1}(0)]}{[\gamma_0(0)+\gamma_{+1}(0)][\gamma_0(0)+\gamma_{-1}(0)]}\right\rangle=\left\langle\frac{v^0(0;1)+1}{\gamma_0(0)+\gamma_{+1}(0)}\right\rangle-\left\langle\frac{v^0(0;1)}{\gamma_0(0)+\gamma_{-1}(0)}\right\rangle. \tag{5.13}$$

Recalling Eq. (3.31) and Eq. (3.34), and defining $D(k)$ by

$$D(k)=\frac{\hbar\beta^2}{\omega_a{}^2\omega_b{}^2}\frac{M_1+M_2}{M_1{}^2M_2{}^2}\sin\frac{\pi k}{N}, \tag{5.14}$$

we can rewrite Eq. (5.13) as

$$\begin{aligned}\langle A\rangle=\lim_{k\to 0}\frac{1}{D}\Big\{&\langle[v^0(0;1)+1]/[2v^0(0;1)+3]v^0(k;1)[v^0(k;2)+v^0(-k;2)+1]\\ &+[2v^0(0;1)+1][v^0(-k;1)+1][v^0(k;2)+v^0(-k;2)+1]\rangle\\ &-\langle v^0(0;1)/[2v^0(0;1)+1]v^0(k;1)[v^0(k;2)+v^0(-k;2)+1]\\ &+v^0(0;1)[v^0(-k;1)+1][v^0(k;2)+v^0(-k;2)+1]\\ &+(1-\delta_{v^0(0;1),0})[v^0(0;1)-1][v^0(-k;1)+1][v^0(k;2)+v^0(-k;2)+1]\rangle\Big\}\\ &=\lim_{k\to 0}\frac{1}{D}\{\langle A_1\rangle-\langle A_2\rangle\}.\end{aligned} \tag{5.15}$$

$\langle A_1\rangle$ can be factored into

$$\begin{aligned}\langle A_1\rangle&=\left\langle\frac{1}{v^0(k;2)+v^0(-k;2)+1}\right\rangle\left\langle\frac{v^0(0;1)+1}{4[v^0(0;1)]^2+6v^0(0;1)+1}\right\rangle\\ &=\langle A_{11}\rangle\langle A_{12}\rangle,\end{aligned} \tag{5.16}$$

while $\langle A_2\rangle$ becomes

$$\begin{aligned}\langle A_2\rangle&=\left\langle\frac{1}{v^0(k;2)+v^0(-k;2)+1}\right\rangle\left\langle\frac{v^0(0;1)}{4[v^0(0;1)]^2+2v^0(0;1)-1-\delta_{v^0(0;1),0}\{[v^0(0;1)]^2-1\}}\right\rangle.\\ &=\langle A_{21}\rangle\langle A_{22}\rangle\end{aligned} \tag{5.17}$$

We consider first the factor

$$\langle A_{12}\rangle=\left\langle\frac{v^0(0;1)+1}{4[v^0(0;1)]^2+6v^0(0;1)+1}\right\rangle=\frac{e^{-\frac{1}{2}x}}{Z(\omega_d)}\sum_{n=0}^{\infty}\frac{(n+1)e^{-nx}}{4n^2+6n+1}, \tag{5.18}$$

where $x=\hbar\omega_d/kT$, and

$$Z(\omega)=\sum_{n=0}^{\infty}e^{-(n+\frac{1}{2})\hbar\omega/kT}\sim e^{-\frac{1}{2}\hbar\omega/kT}\left\{\left[\frac{kT}{\hbar\omega}+\frac{1}{2}+O\left(\left|\frac{\hbar\omega}{kT}\right|^2\right)\right]\right\}\quad\text{as}\quad\left(\frac{\hbar\omega}{kT}\right)\to 0. \tag{5.19}$$

Now we can write

$$\sum_{n=0}^{\infty}\frac{(n+1)e^{-nx}}{4n^2+6n+1}=\frac{1}{2\sqrt{5}}\sum_{n=0}^{\infty}(n+1)e^{-nx}\left(\frac{1}{n+a}-\frac{1}{n+b}\right)=\frac{1}{2\sqrt{5}}(1-a)\sum_{n=0}^{\infty}\frac{e^{-nx}}{n+a}-\frac{1}{2\sqrt{5}}(1-b)\sum_{n=0}^{\infty}\frac{e^{-nx}}{(n+b)},\tag{5.20}$$

where

$$a=\tfrac{3}{4}-\tfrac{1}{4}\sqrt{5},\quad b=\tfrac{3}{4}+\tfrac{1}{4}\sqrt{5}.\tag{5.21}$$

The value of the sum

$$S(x)=\sum_{n=0}^{\infty}\frac{e^{-nx}}{n+a},\quad 0<a,\tag{5.22}$$

in the limit as $x\rightarrow 0$ is obtained in Appendix B and is given by

$$S(x)\sim-\ln x+[c(a)-\ln a-\epsilon]+O(x\ln x),\tag{5.23}$$

where $\epsilon=0.5772$ is Euler's constant, while $c(a)$ is defined by

$$c(a)=\int_0^{\infty}e^{-au}\left(\frac{1}{1-e^{-u}}-\frac{1}{u}\right)du.\tag{5.24}$$

With the aid of this result we find that

$$\begin{aligned}\langle A_{12}\rangle=&\frac{1}{(kT/\hbar\omega_d+\frac{1}{2}+\cdots)}\frac{1}{2\sqrt{5}}\left\{(1-a)\left[-\ln\frac{\hbar\omega_d}{kT}+(c(a)-\ln a-\epsilon)+\cdots\right]\right.\\&\left.-(1-b)\left[-\ln\frac{\hbar\omega_d}{kT}+(c(b)-\ln b-\epsilon)+\cdots\right]\right\}\\=&\frac{1}{2\sqrt{5}}\left[\frac{\hbar\omega_d}{kT}-\frac{1}{2}\left(\frac{\hbar\omega_d}{kT}\right)^2+\cdots\right]\left[(a-b)\ln\frac{\hbar\omega_d}{kT}+(1-a)(c(a)-\ln a-\epsilon)-(1-b)(c(b)-\ln b-\epsilon)+\cdots\right].\end{aligned}\tag{5.25}$$

Turning now to the average

$$\langle A_{22}\rangle=\left\langle\frac{v^0(0;1)}{4[v^0(0;1)]^2+2v^0(0;1)-1-\delta_{v^0(0;1),0}\{[v^0(0;1)]^2-1\}}\right\rangle=\frac{e^{-\frac{1}{2}x}}{Z(\omega_d)}\left[\frac{1}{2}+\sum_{n=1}^{\infty}\frac{ne^{-nx}}{4n^2+2n-1}\right],\tag{5.26}$$

we reduce it to

$$\langle A_{22}\rangle=\frac{e^{-\frac{1}{2}x}}{Z(\omega_d)}\left[\frac{1}{2}+\frac{1}{2\sqrt{5}}\sum_{n=1}^{\infty}ne^{-nx}\left(\frac{1}{n+c}-\frac{1}{n+d}\right)\right],\tag{5.27}$$

where

$$c=\tfrac{1}{4}-\tfrac{1}{4}\sqrt{5},\quad d=\tfrac{1}{4}+\tfrac{1}{4}\sqrt{5}.\tag{5.28}$$

Since $c<0$ we rewrite this expression in the form

$$\langle A_{22}\rangle=\left[\frac{\hbar\omega_d}{kT}-\frac{1}{2}\left(\frac{\hbar\omega_d}{kT}\right)^2+\cdots\right]\left[\frac{1}{2}+\frac{1}{2\sqrt{5}}\sum_{n=0}^{\infty}e^{-nx}\left(\frac{d}{n+d}+\frac{|c|}{n-|c|}\right)\right].\tag{5.29}$$

The value of the sum

$$S'(x)=\sum_{n=0}^{\infty}\frac{e^{-nx}}{n-a},\quad 1>a>0,\tag{5.30}$$

in the limit as $x\rightarrow 0$ is obtained in Appendix B and is given by

$$S'(x)=-\ln x+\left[c(a')-\ln a'-\epsilon-\frac{1}{1-a'}\right]+O(x\ln x),\tag{5.31}$$

where $a' = 1-a$. With the aid of this result, Eq. (5.29) becomes

$$\langle A_{22}\rangle = \left[\frac{\hbar\omega_d}{kT} - \frac{1}{2}\left(\frac{\hbar\omega_d}{kT}\right)^2 + \cdots\right]\left\{\frac{1}{2} + \frac{1}{2\sqrt{5}}\left[-(d+|c|)\ln x + d(c(d) - \ln d - \epsilon) + |c|\left(c(1-|c|) - \ln(1-|c|) - \epsilon - \frac{1}{|c|} + \cdots\right)\right]\right\}. \tag{5.32}$$

The last average we consider is

$$\langle A_{11}\rangle = \langle A_{21}\rangle = \left\langle\frac{1}{v^0(k;2)+v^0(-k;2)+1}\right\rangle = \frac{e^{-\hbar\omega(k;2)/kT}}{Z[\omega(k;2)]Z[\omega(-k;2)]}\sum_{m,n=0}^{\infty}\frac{e^{-(m+n)\hbar\omega(k;2)/kT}}{m+n+1}, \tag{5.33}$$

where we have used the fact that $\omega(k;2) = \omega(-k;2)$. The double sum

$$\sum_{m,n=0}^{\infty}\frac{e^{-(m+n)x}}{m+n+1} = \sum_{m,n=0}^{\infty} e^{-(m+n)x}\int_0^{\infty} e^{-t-(m+n)t}dt = \int_0^{\infty} e^{-t}\frac{1}{[1-e^{-(t+x)}]^2}dt \tag{5.34}$$

is evaluated in the limit as $x \to 0$ in Appendix B with the result that

$$\langle A_{11}\rangle = \langle A_{21}\rangle = \frac{e^{-\hbar\omega(k;2)/kT}}{[Z(\omega(k;2))]^2}\left[\frac{kT}{\hbar\omega(k;2)} + p + \left(p - \frac{5}{12}\right)\frac{\hbar\omega(k;2)}{kT} + \cdots\right], \tag{5.35}$$

where the constant p is defined by

$$p = \int_0^{\infty} e^{-u}\left[\frac{1}{(1-e^{-u})^2} - \frac{1}{u} - \frac{1}{u^2}\right]du. \tag{5.36}$$

Recalling Eq. (5.19) we obtain finally

$$\langle A_{11}\rangle = \langle A_{21}\rangle \sim \frac{\hbar\omega(k;2)}{kT} + O\left(\left|\frac{\hbar\omega(k;2)}{kT}\right|^2\right). \tag{5.37}$$

Combining the results of Eq. (5.25), Eq. (5.32), and Eq. (5.37), we find that in the high-temperature limit

$$\langle A_1\rangle - \langle A_2\rangle = \langle A_{11}\rangle(\langle A_{12}\rangle - \langle A_{22}\rangle) \simeq \frac{\hbar^2\omega(k;2)\omega_d}{(kT)^2}B, \tag{5.38}$$

where the constant B is given by

$$B = -\frac{1}{2} + \frac{1}{2\sqrt{5}}\left\{(1-a)[c(a) - \ln a - \epsilon] - (1-b)[c(b) - \ln b - \epsilon] - d[c(d) - \ln d - \epsilon] - |c|\left[c(1-|c|) - \ln(1-|c|) - \epsilon - \frac{1}{c}\right]\right\}. \tag{5.39}$$

Combining Eq. (5.15) and Eq. (5.38) we obtain

$$\langle A\rangle \sim \lim_{k\to 0}\frac{\omega_a{}^2\omega_b{}^2}{\hbar\beta^2}\frac{M_1{}^2M_2{}^2}{M_1+M_2}\frac{\omega(k;2)}{\sin(\pi k/N)}\frac{\hbar^2\omega_d}{(kT)^2}B = 2\frac{B}{C}\frac{\hbar^2\omega_a\omega_b}{\omega_d(kT)^2}. \tag{5.40}$$

Since

$$\eta(\omega_d) = \tfrac{1}{2}\eta_0\omega_d\langle A\rangle, \tag{5.41}$$

we see that this method of evaluating $\eta(\omega_d)$ leads to an absorption coefficient at ω_d which has a T^{-2} dependence on temperature in the high-temperature limit as contrasted with the T^{-3} dependence predicted by Eq. (5.12).

To evaluate the constant B we need the values of $c(a)$, $c(b)$, etc. These quantities are evaluated by using the result in Appendix B, and substituting the values into Eq. (5.39) we obtain $B = 0.4790$. Finally we can write

$$\eta(\omega_d) = 0.2395\frac{\eta_0}{C}z^{\frac{1}{2}}\left(\frac{\Theta_D}{T}\right)^2. \tag{5.42}$$

VI. ORDINARY SECOND ORDER TIME DEPENDENT PERTURBATION THEORY OF THE ABSORPTION COEFFICIENT

In this section we give a calculation of the absorption coefficient following the second-order time-dependent perturbation theory described in Heitler.[12] The unperturbed states consist of the normal mode oscillators

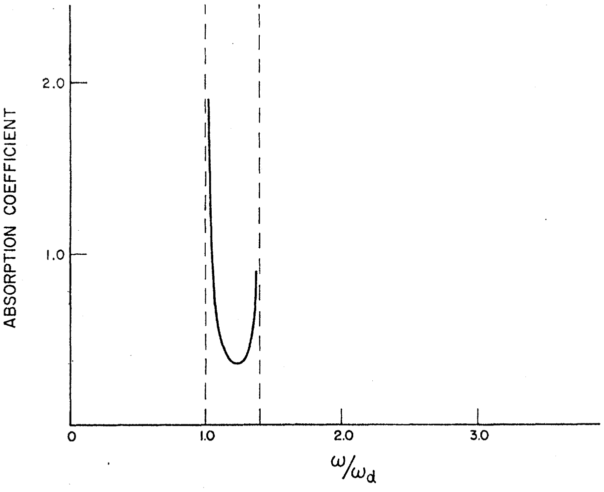

FIG. 5. The absorption coefficient η in units of η_0 plotted as a function of ω/ω_d at the absolute zero of temperature. The method of Barnes, Brattain, and Seitz was used to calculate η.

in the harmonic approximation together with the radiation field. They are characterized by the quantum numbers of the normal mode oscillators and the number of photons present.

The perturbing term in the Hamiltonian is the sum of H_A, the anharmonic contribution, and H_E, the interaction term between the radiation and the lattice. As in the preceding work with the Weisskopf-Wigner method we consider only cubic anharmonic terms in the Hamiltonian, and we further assume that these terms are linear in the dispersion oscillator coordinate $Q(0;1)$. The anharmonic terms in the Hamiltonian are then given by Eq. (2.11) or by Eq. (2.19) after the transformation to creation and annihilation operators. The radiation-lattice interaction term H_E is given by

$$H_E=\sum_i \frac{e_i}{M_ic}\mathbf{p}_i\cdot\mathbf{A}, \tag{6.1}$$

where $\mathbf{A}$ is the vector potential for the radiation and $\mathbf{p}_i$, e_i, and M_i are the momentum, charge and mass of the ith ion.

The second order transitions proceed from initial state 0 to final state s via certain intermediate states which consist of two classes. The first class, labeled by j, contains states coupled to the initial state by the radiation interaction and to the final state by the anharmonic interaction. The second class, labeled t, contains states coupled to the initial state by the anharmonic interaction and to the final state by the radiation interaction. The intermediate states t are ignored by Born and Huang except in calculating the damping of the initial state 0.

The appropriate matrix elements for second-order transitions can be written in the form

$$C_{s0}^{\pm}=\frac{1}{\hbar\omega}\sum_j\frac{(\omega_0-\omega_j)}{(\omega_0-\omega_j\pm\omega)}\int\psi_s^*H_A\psi_jd\tau\int\psi_j^*(\sum_i e_iu_i)\psi_0d\tau+\frac{1}{\hbar\omega}\sum_t\frac{(\omega_t-\omega_s)}{(\omega_0-\omega_t)}\int\psi_s^*(\sum_i e_iu_i)\psi_td\tau\int\psi_t^*H_A\psi_0d\tau, \tag{6.2}$$

where the quantities ψ are zero order lattice wave functions consisting of products of $2N$ harmonic oscillator wave functions of the $2N$ normal coordinates $q(k;\,j)$. The energies of the states 0, s, j, and t are $\hbar\omega_0$, $\hbar\omega_s$, $\hbar\omega_j$, and $\hbar\omega_t$, and the photon energy is $\hbar\omega$. The plus sign in Eq. (6.2) is used for absorption and the minus sign for induced emission.

For a given initial state 0 the absorption coefficient corrected for induced emission can be written as

$$\eta=\frac{4\pi^2\omega}{Nv_a n\hbar c}\{\sum_s |C_{s0}^+|^2\delta(\omega_0-\omega_s+\omega) -\sum_s |C_{s0}^-|^2\delta(\omega_0-\omega_s-\omega)\} \tag{6.3}$$

where the sums are over all final states s. By carrying out a thermal average of Eq. (6.3) over the initial states 0 one obtains an expression for the net absorption coefficient at a given temperature. It may be pointed out that first-order transitions of the harmonic lattice contribute a δ-function absorption at the dispersion frequency ω_d which is not included in Eq. (6.3).

We consider first the case of absorption at the absolute zero of temperature. One finds, after evaluating the matrix elements $C_{s0}^{\pm}$ for our model, that there is no induced emission correction and that the absorption coefficient can be written as

$$\eta=\tfrac{1}{2}\eta_0C[(x+1)/(x-1)][z-(x^2-1)^2]^{-\frac{1}{2}} \quad \text{for} \quad 1\leqslant x\leqslant y, \tag{6.4}$$
$$=0 \quad \text{otherwise.}$$

The quantities C, x, y, and z are defined in Sec. III and η_0 in Sec. IV.

The absorption coefficient at the absolute zero of temperature is plotted in units of η_0 as a function of circular frequency in Fig. 5. There is a singularity at $\omega=\omega_d$ with a frequency dependence $(\omega-\omega_d)^{-1}$. In addition there is a singularity at $\omega=\omega_a+\omega_b$ with a frequency dependence $(\omega_a+\omega_b-\omega)^{-\frac{1}{2}}$. It may be noted that there is no absorption at frequencies higher than $\omega_a+\omega_b$.

Turning now to the absorption at high temperatures we find after evaluating the matrix elements $C_{s0}^{\pm}$ and carrying out the thermal averages that the net absorption coefficient corrected for induced emission can be written as

$$\eta=\eta_0C(kT/\hbar\omega_d)[x/(x-1)^2][z-(x^2-1)^2]^{-\frac{1}{2}} \quad \text{for} \quad y'\leqslant x\leqslant y, \tag{6.5}$$
$$=0 \quad \text{otherwise.}$$

The quantity y' is defined by $y'\omega_d=\omega_b-\omega_a$, and it has been assumed that $kT\gg\hbar\omega_d$.

One notes from Eq. (6.5) that at high temperatures there is a singularity in the absorption coefficient at ω_d with frequency dependence $(\omega-\omega_d)^{-2}$. There are additional singularities at $\omega_a+\omega_b$ and $\omega_b-\omega_a$ with frequency dependences $(\omega_a+\omega_b-\omega)^{-\frac{1}{2}}$ and $(\omega-\omega_b+\omega_a)^{-\frac{1}{2}}$, respectively. The absorption coefficient increases as the first power of the absolute temperature T at all frequencies. This dependence is not valid, however, at the dispersion frequency ω_d because damping is neglected.

VII. DISCUSSION

The calculations of the optical absorption spectrum at low temperatures provide an interesting comparison between the Born-Huang theory and the ordinary second-order perturbation theory of anharmonic effects. Both procedures lead to strong absorption near the dispersion frequency ω_d and subsidiary absorption near $\omega_a+\omega_b$. The small absorption near $3\omega_d$ obtained with the Born-Huang theory is not found with ordinary perturbation theory. In the latter procedure, transitions leading to absorption near $3\omega_d$ involve second-order matrix elements which vanish identically due to exact cancellation of terms corresponding to intermediate states j with those corresponding to intermediate states t and consequently the absorption near $3\omega_d$ is spurious.

The inclusion of damping in the Born-Huang method eliminates the singularity in the absorption at $\omega_a+\omega_b$ found in the ordinary perturbation calculations. However, at low temperatures the frequency dependence of the Born-Huang damping constants produces a singularity in absorption at ω_d having the same frequency dependence as that found by ordinary perturbation theory. The persistence of a singularity at ω_d may be a consequence of the one-dimensional character of our model. Nevertheless, it points up the fact that the use of Weisskopf-Wigner perturbation theory does not guarantee the elimination of singularities in the absorption spectrum. The $(\omega-\omega_d)^{-1}$ singularity appears to arise from the k dependence of the anharmonic coefficient $\Phi(0\,k\,-k;112)$ rather than from the frequency distribution function $F\alpha(\omega)$ or the normal mode frequencies $\omega(k;1)$ and $\omega(k;2)$.

Rather diverse results have been obtained for the temperature dependence of the absorption coefficient at high temperatures. The classical calculations of Born and Blackman and of Neuberger can be expressed in terms of a Lorentz line shape with a damping constant that varies linearly with absolute temperature. This result is in agreement with the quantum mechanical second-order perturbation calculation given in the present paper for frequencies away from ω_d. The regions of absorption predicted by these two approaches are also in agreement, namely, between ω_d and $\omega_a+\omega_b$ at low temperatures and between $\omega_b-\omega_a$ and $\omega_a+\omega_b$ at high temperatures.

The Weisskopf-Wigner calculations given in this paper lead to a different temperature dependence of the absorption coefficient from that discussed in the preceding paragraph. At the dispersion frequency ω_d the absorption coefficient according to the Weisskopf-Wigner method varies with absolute temperature as T^{-3}, if the Born-Huang procedure for carrying out thermal averages is followed, or as T^{-2} if the absorption coefficient is averaged over initial states. The discrepancy arises from the fact that Born and Huang take the thermal average of a quotient to be the quotient of the thermal averages. This leads to a fortuitious cancelling of the T^{-2} terms. We feel that it is preferable to carry out thermal averages directly over the absorption coefficient and that the T^{-2} dependence is the more reliable result.

For frequencies $\omega>2\omega_d$ both our calculations using the Weisskopf-Wigner theory and those of Born and Huang give absorption proportional to T^{-3}. One is forced to be rather suspicious of this result because the intermediate states t are omitted in these calculations, and their inclusion leads to zero absorption for $\omega>2\omega_d$ as shown by the ordinary second-order perturbation theory results. The omission of the states t also casts doubt on the Weisskopf-Wigner temperature dependence of absorption at ω_d, especially since this dependence disagrees with the result from classical theory which should be valid at high temperatures.

Only quite recently have experimental data become available concerning the temperature dependence of the lattice vibration absorption of crystals. Heilmann[17] has studied the infrared reflectivity of lithium fluoride at various elevated temperatures and has analyzed his results in terms of a damped Lorentz oscillator. At the higher temperatures the damping constant varied as T^2. However, the highest temperature used by Heilmann corresponds only to a value of $kT/\hbar\omega_d$ of about two, so that he was not really in the high-temperature range in the sense of this paper.

A study of the infrared reflectivity of sodium chloride in the lattice vibration region has recently been made by Hass[18] in this laboratory. A range of temperatures up to 1000°K was employed corresponding to values of $kT/\hbar\omega_d$ up to about four. The reflectivity at the dispersion frequency ω_d was fitted using a damped Lorentz oscillator. The temperature dependence of the damping constant is most closely fitted by a T^2 law.

The experimental data presently available appear to be consistent with the theoretical result that the absorption coefficient at the dispersion frequency should vary as T^{-2}. It is, however, too early to draw any firm conclusions about agreement of theory and experiment. The theoretical treatment given in this paper has considered only cubic anharmonic terms and has neglected the higher-order terms. At high temperatures, especially, one might expect the high-order terms to

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[17] G. Heilmann, Z. Physik **152**, 368 (1958).

[18] M. Hass (to be published).

make important contributions to the absorption. This point remains to be investigated. In addition the role of charge deformation[4] has not been entirely clarified.

Although the model considered in this paper is one-dimensional, most of the gross features of the results, such as the temperature dependence of absorption, should persist in a three-dimensional model. A more realistic frequency dependence of absorption near the dispersion frequency at low temperatures may be expected from a three-dimensional calculation. The existence of additional branches of vibrational frequencies may lead to new absorption. For further discussion of one- and three-dimensional models see the papers of Blackman.[1,5]

The assumption that the important anharmonic terms are linear in the dispersion oscillator coordinate $Q(0;1)$ has been discussed by Born and Huang. Rather peculiar results are obtained if all cubic anharmonic terms are retained. In the ordinary second-order perturbation theory the absorption coefficient turns out to be proportional to N, the number of unit cells in the crystal, while in the Weisskopf-Wigner approach the damping constants are proportional to N. Both results are physically unacceptable and bear some resemblance to the difficulties in calculating extensive and intensive properties mentioned by Van Hove.[19] For a discussion of this problem see the recent paper of Brout.[20]

VIII. ACKNOWLEDGMENTS

We wish to thank Elias Burstein for many stimulating discussions concerning the origin of the subsidiary maxima in lattice vibration absorption. Thanks are also due S. O. Lundqvist and H. B. Rosenstock for helpful discussions. Finally, we thank M. Hass for many discussions concerning both the experimental and theoretical aspects of lattice vibration spectra.

APPENDIX A

We present here a brief discussion of the Born-Huang theory from a standpoint somewhat different from theirs, in order to clarify the approximations made in their theory. The problem we must solve is the following one. We first require the solutions of the perturbed Schrödinger equation for our system

$$(H_0+H_1)\Phi=i\hbar\partial\Phi/\partial t, \tag{A.1}$$

where H_0 is the harmonic part of the total Hamiltonian

$$H_0=\tfrac{1}{2}\sum_k\sum_j\{\dot{Q}^*(k;j)\dot{Q}(k;j)+\omega^2(k;j)Q^*(k;j)Q(k;j)\}, \tag{A.2}$$

while H_1 is the sum of the anharmonic potential energy and the term describing the interaction of the lattice with the external radiation:

$$H_1=\frac{1}{6\sqrt{N}}\sum_{kk'k''}\sum_{jj'j''}\Phi(kk'k'';jj'j'')Q(k;j)Q(k';j')Q(k'';j'')+\sqrt{N}\sum_j Q(0;j)\mathbf{M}(0;j)\cdot\{\mathbf{E}e^{-i\omega t}+\mathbf{E}^*e^{i\omega t}\} \tag{A.3}$$

$$=\lambda_1H_A+\lambda_2(H_Ee^{-i\omega t}+H_E^*e^{i\omega t}), \tag{A.4}$$

where λ_1 and λ_2 are perturbation expansion parameters which can be set equal to unity at the end of the calculation.

The induced electric moment due to the dispersion oscillator $(0;j)$ is the expectation value of the electric moment operator

$$\sqrt{N}\mathbf{M}(0;j)Q(0;j).$$

If we form the expectation value of this operator using the perturbed wave function Φ and divide this result by the total volume of the crystal, Nv_a, we obtain the dielectric polarization

$$\mathbf{P}^j(t)=(1/N^{\frac{1}{2}}v_a)\mathbf{M}(0;j)\langle\Phi|Q(0;j)|\Phi\rangle. \tag{A.5}$$

[Born and Huang actually average this expression over all initial times to obtain the dielectric polarization $\mathbf{P}^j(t)$ due to the oscillator $(0;j)$.] The coefficients of the terms linear in the external field in the expression for $\mathbf{P}^j(t)$ give $a_{\alpha\beta}{}^j$, the partial dielectric susceptibility due to the dispersion oscillator $(0;j)$.

It is well known that the solution to Eq. (A.1) can be expressed in terms of the solutions $\psi_n(t)$ of the unperturbed problem

$$H_0\psi_n(t)=i\hbar\partial\psi_n(t)/\partial t, \tag{A.6}$$

as

$$\Phi=\sum\nolimits_n a_n(t)\psi_n(t). \tag{A.7}$$

The coefficients $a_n(t)$ satisfy the equations

$$\frac{da_n(t)}{dt}=\frac{1}{i\hbar}\sum_{n'}\langle n|H_1|n'\rangle a_{n'}(t)e^{i(\omega_n-\omega_{n'})t}, \tag{A.8}$$

where the matrix elements of the perturbation Hamiltonian are evaluated between the time-independent solutions to Eq. (A.6), ϕ_n, defined by

$$H_0\phi_n=E_n\phi_n, \tag{A.9}$$

so that

$$\psi_n(t)=e^{-i\omega_nt}\phi_n,\quad \hbar\omega_n=E_n. \tag{A.10}$$

As long as we retain only cubic anharmonic terms and neglect the quartic and higher-order terms, the perturbation Hamiltonian has no diagonal matrix elements. It is furthermore clear from Eq. (A.3) that the matrix elements of the separate contributions to H_1

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[19] L. Van Hove, Massachusetts Institute of Technology Technical Report No. 11, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, 1959 (unpublished).

[20] R. Brout, Phys. Rev. **107**, 664 (1957).

are completely independent of each other. That is, no two states n and n' coupled by H_E or H_E^* are coupled by H_A, and vice versa. We further make the assumption that at time $t=0$ our system is in a definite unperturbed state which we denote by $n=0$, so that we have

$$a_0(0)=1, \tag{A.11a}$$

$$a_n(0)=0,\quad n\neq 0. \tag{A.11b}$$

With these conditions it is possible to solve for $a_0(t)$ in the following way. Following Born and Huang we assume that we can regard the electric field as infinitesimal in determining $a_0(t)$, at least to lowest order. Then we find on integrating both sides of Eq. (A.8) from 0 to t, and recalling the initial conditions (A.11), that

$$a_n(t)=\delta_{n0}+\frac{\lambda_1}{i\hbar}\sum_{n'}\langle n|H_A|n'\rangle \times\int_0^t a_{n'}(t_1)e^{i(\omega_n-\omega_{n'})t_1}dt_1. \tag{A.12}$$

We now proceed to solve this integral equation for $a_0(t)$ by iteration, remembering that

$$\langle n|H_A|n\rangle\equiv 0. \tag{A.13}$$

We obtain

$$a_0(t)=1+\left(\frac{\lambda_1}{i\hbar}\right)^2\sum_{n'}\langle 0|H_A|n'\rangle\langle n'|H_A|0\rangle \times\int_0^t dt_1\int_0^{t_1} dt_2 e^{i(\omega_0-\omega_{n'})t_1+i(\omega_{n'}-\omega_0)t_2}+\cdots, \tag{A.14}$$

where the first-order term vanishes as a consequence of Eq. (A.13). Following Van Hove[21] and Brout and Prigogine,[22] we retain in lowest order only those terms in the expansion, Eq. (A.14), which are of $O((\lambda_1^2t)^n)$. It is not too difficult to show that only those terms in the iteration expansion contribute to this approximation for which every second intermediate state is the same as the initial and final states. The nonvanishing terms form an exponential series which is summed to yield

$$a_0(t)=e^{-i\Delta\omega_0 t-\gamma_0 t}, \tag{A.15}$$

where

$$\gamma_0=\lambda_1^2\frac{\pi}{\hbar^2}\sum_{n'}|\langle n'|H_A|0\rangle|^2\delta(\omega_0-\omega_{n'}), \tag{A.16a}$$

$$\Delta\omega_0=\lambda_1^2\frac{1}{\hbar^2}\sum_{n'}|\langle n'|H_A|0\rangle|^2 P\left(\frac{1}{\omega_0-\omega_{n'}}\right), \tag{A.16b}$$

where $P(1/x)$ means the principal part of $1/x$. If, as Born and Huang do, we neglect the frequency shift $\Delta\omega_0$, the expression (A.15) for $a_0(t)$ is identical with theirs [B-H(46.24)]. We notice that $a_0(t)$ is of $O(\lambda_1^0)$.

To obtain the coefficients $a_n(t)$, $n\neq 0$, we proceed as follows. We rewrite Eq. (A.8) as

$$\frac{da_n(t)}{dt}=\frac{1}{i\hbar}\langle n|H_1|0\rangle a_0(t)e^{i(\omega_n-\omega_0)t} +\frac{1}{i\hbar}\sum_{\substack{n'\\ n'\neq 0}}\langle n|H_1|n'\rangle a_{n'}(t)e^{i(\omega_n-\omega_{n'})t}, \tag{A.17}$$

and we see immediately that $a_n(t)$ is of $O(\lambda)$. The states which are coupled to the initial state through H_E and H_E^* are called by Born and Huang "the states $\pm j$." The states which are coupled to the initial state through H_A we have called "the states t." All other states we call "the states s." This terminology differs from that of Born and Huang who label all states other than the states 0, $\pm j$ as "the states s." Integrating both sides of Eq. (A.17) from 0 to t, using Eq. (A.15), we obtain

$$\begin{aligned}a_n(t)=&\frac{\lambda_1}{i\hbar}\langle n|H_A|0\rangle\frac{e^{i(\omega_n-\omega_0)t-\gamma_0 t}-1}{i(\omega_n-\omega_0)-\gamma_0}\\ &+\frac{\lambda_2}{i\hbar}\langle n|H_E|0\rangle\frac{e^{i(\omega_n-\omega_0-\omega)t-\gamma_0 t}-1}{i(\omega_n-\omega_0-\omega)-\gamma_0}\\ &+\frac{\lambda_2}{i\hbar}\langle n|H_E^*|0\rangle\frac{e^{i(\omega_n-\omega_0+\omega)t-\gamma_0 t}-1}{i(\omega_n-\omega_0+\omega)-\gamma_0}\\ &+\frac{\lambda_1}{i\hbar}\sum_{\substack{n'\\ n'\neq 0}}\langle n|H_A|n'\rangle\int_0^t a_{n'}(t_1)e^{i(\omega_n-\omega_{n'})t_1}dt_1\\ &+\frac{\lambda_2}{i\hbar}\sum_{\substack{n'\\ n'\neq 0}}\langle n|H_E|n'\rangle\int_0^t a_{n'}(t_1)e^{i(\omega_n-\omega_{n'}-\omega)t_1}dt_1\\ &+\frac{\lambda_2}{i\hbar}\sum_{\substack{n'\\ n'\neq 0}}\langle n|H_E^*|n'\rangle\int_0^t a_{n'}(t_1)e^{i(\omega_n-\omega_{n'}+\omega)t_1}dt_1.\end{aligned} \tag{A.18}$$

We now solve these equations by iteration. In solving for $a_{\pm j}(t)$ we retain only terms of the type $\lambda_2(\lambda_1^2t)^n$. This choice is dictated both by the fact that in forming the expectation value $\langle\Phi|Q(0;j)|\Phi\rangle$ we wish to retain only terms linear in the external field, and $a_0(t)$ is of $O(\lambda^0)$, and by the fact that in these calculations we consistently ignore radiation damping. The result of this calculation is that for states $\pm j$ which couple to the state 0 through H_E and H_E^*,

$$a_{\pm j}(t)=-\frac{\lambda_2}{\hbar}\frac{\langle\pm j|H_E|0\rangle}{(\omega_{\pm j}-\omega_0-\omega)+i\gamma_0}\left[e^{i(\omega_{\pm j}-\omega_0-\omega)t-\gamma_0 t}-e^{-\gamma_{\pm j}t-i\Delta\omega_{\pm j}t}\right] -\frac{\lambda_2}{\hbar}\frac{\langle\pm j|H_E^*|0\rangle}{(\omega_{\pm j}-\omega_0+\omega)+i\gamma_0}\left[e^{i(\omega_{\pm j}-\omega_0+\omega)t-\gamma_0 t}-e^{-\gamma_{\pm j}t-i\Delta\omega_{\pm j}t}\right], \tag{A.19}$$

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[21] L. Van Hove, Physica **21**, 517 (1955).

[22] R. Brout and I. Prigogine, Physica **22**, 621 (1956).

where[23]

$$\gamma_{\pm j}=\lambda_1^2\frac{\pi}{\hbar^2}\sum_{\substack{n'\\ n'\neq 0}}|\langle\pm j|H_A|n'\rangle|^2\delta(\omega_{\pm j}-\omega_{n'}),\tag{A.20a}$$

$$\Delta\omega_{\pm j}=\lambda_1^2\frac{1}{\hbar^2}\sum_{\substack{n'\\ n'\neq 0}}|\langle\pm j|H_A|n'\rangle|^2P\left(\frac{1}{\omega_{\pm j}-\omega_{n'}}\right).\tag{A.20b}$$

We can solve Eq. (A.18) for the coefficient $a_t(t)$ in the same way, only in this case we retain terms of the type $\lambda_1(\lambda_1^2t)^n$. The result is

$$a_t(t)=\frac{\lambda_1}{i\hbar}\frac{\langle t|H_A|0\rangle}{i(\omega_t-\omega_0)-\gamma_0}\left[e^{i(\omega_t-\omega_0)t-\gamma_0t}-e^{-\gamma_tt-i\Delta\omega_tt}\right],\tag{A.21}$$

where

$$\gamma_t=\frac{\pi}{\hbar^2}\sum_{\substack{n'\\ n'\neq 0}}|\langle t|H_A|n'\rangle|^2\delta(\omega_t-\omega_{n'}),\tag{A.22a}$$

$$\Delta\omega_t=\frac{1}{\hbar^2}\sum_{\substack{n'\\ n'\neq 0}}|\langle t|H_A|n'\rangle|^2P\left(\frac{1}{\omega_t-\omega_{n'}}\right).\tag{A.22b}$$

Finally, the equations for the coefficients $a_s(t)$ are obtained from Eq. (A.18) by suppressing the first three terms on the right-hand side of this equation, and it is seen that $a_s(t)$ is of $O(\lambda^2)$. Since $Q(0;j)$ has nonvanishing matrix elements between the states s and t, and since $a_t(t)$ is of $O(\lambda_1)$, we keep only terms of $O(\lambda_1\lambda_2(\lambda_1^2t)^n)$. The result for $a_s(t)$ is cumbersome and will not be given here.

However, the result of this calculation shows that a typical term in the product $a_t^*(t)a_s(t)$ has the following schematic form:

$$a_t^*(t)a_s(t)\sim\frac{\lambda_1^2\lambda_2\langle 0|H_A|t\rangle\langle s|H_A|+j\rangle\langle +j|H_E|0\rangle}{[(\omega_t-\omega_0)-i\gamma_0][(\omega_{\pm j}-\omega_0-\omega)+i\gamma_0][(\omega_s-\omega_0-\omega)+i\gamma_0]},\tag{A.23}$$

apart from factors which involve products of differences of complex exponential functions of time. The imaginary part of this product (retaining only terms linear in the damping constants) is the sum of terms of the form

$$a_t^*(t)a_s(t)\sim\frac{\lambda_1^2\lambda_2\langle 0|H_A|t\rangle\langle s|H_A|+j\rangle\langle +j|H_E|0\rangle\gamma_0}{[(\omega_t-\omega_0)^2+\gamma_0^2][(\omega_{\pm j}-\omega_0-\omega)^2+\gamma_0^2][(\omega_s-\omega_0-\omega)^2+\gamma_0^2]}.\tag{A.24}$$

If all frequency differences appearing in the denominators are large compared with the damping constants, the order of such a term is

$$a_t^*(t)a_s(t)=O(\lambda_1^2\lambda_2\gamma_0)=O(\lambda_1^4\lambda_2),\tag{A.25}$$

in view of Eq. (A.16a). However, if one of the frequency differences is small or vanishes, the order of this term is

$$a_t^*(t)a_s(t)=O(\lambda_1^2\lambda_2/\gamma_0)=O(\lambda_2).\tag{A.26}$$

We now compare these qualitative results with those for the product $a_0^*(t)a_{\pm j}(t)$. A typical term in this product has the schematic form

$$a_0^*(t)a_{\pm j}(t)\sim\frac{\lambda_2\langle\pm j|H_E|0\rangle}{(\omega_{\pm j}-\omega_0-\omega)+i\gamma_0},\tag{A.27}$$

so that the imaginary part of this expression is of the form

$$a_0^*(t)a_{\pm j}(t)\sim\frac{\lambda_2\langle\pm j|H_E|0\rangle\gamma_0}{(\omega_{\pm j}-\omega_0-\omega)^2+\gamma_0^2}.\tag{A.28}$$

In the case that the frequency difference in the denominator becomes small or vanishes, the order of this term is

$$a_0^*(t)a_{\pm j}(t)=O(\lambda_2/\gamma_0)=O(\lambda_2/\lambda_1^2).\tag{A.29}$$

On the other hand, when the frequency difference in the denominator is large compared to the damping constant, the order of this term is

$$a_0^*(t)a_{\pm j}(t)=O(\lambda_2\gamma_0)=O(\lambda_2\lambda_1^2).\tag{A.30}$$

Comparing the results expressed by Eqs. (A.26) and (A.30), we see that in the frequency range where one of the frequency differences in the denominator of Eq. (A.24) vanishes, but the frequency difference in Eq. (A.28) does not, the term $a_t^*(t)a_s(t)$ contributes more importantly than the term $a_0^*(t)a_{\pm j}(t)$.

The treatment of Born and Huang neglects all contributions of the form $a_t^*(t)a_s(t)$. From the foregoing discussion one sees that under certain conditions such an approximation may lead to some error.

APPENDIX B

In this Appendix we obtain the leading terms in the asymptotic expansions of the sum

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[23] Approximations have been made in obtaining Eqs. (A.19) and (A.20) which eliminate the dependence of $\gamma_{\pm j}$ on ω but which do not affect the argument presented in this appendix.

$$S(x)=\sum_{n=0}^{\infty}\frac{e^{-nx}}{n+a},\quad a>0, \tag{B.1}$$

and of the integral

$$I(x)=\int_0^{\infty}e^{-t}\frac{dt}{[1+e^{-(x+t)}]^2}, \tag{B.2}$$

in the limit as $x\rightarrow 0+$.

I. We rewrite the sum (B.1) as

$$\begin{aligned}S(x)&=\sum_{n=0}^{\infty}e^{-nx}\int_0^{\infty}e^{-(n+a)t}dt\\&=\int_0^{\infty}e^{-at}\frac{dt}{1-e^{-(x+t)}}.\end{aligned} \tag{B.3}$$

With a change of variable $x+t=u$ we are led to

$$e^{-ax}S(x)=F(a;x)=\int_x^{\infty}e^{-au}\frac{du}{1-e^{-u}}. \tag{B.4}$$

We see that for $x\sim 0$ the main contribution to the integral comes from the neighborhood of $u=0$. We thus expand the denominator of the integrand in a power series in u to obtain

$$\begin{aligned}F(a;x)&=\int_x^{\infty}\frac{e^{-au}}{u}(1+\tfrac{1}{2}u+\tfrac{1}{12}u^2+\cdots)du\\&=-Ei(-ax)+\int_0^{\infty}e^{-au}(\tfrac{1}{2}+\tfrac{1}{12}u+\cdots)du\\&\quad-\int_0^{x}e^{-au}(\tfrac{1}{2}+\tfrac{1}{12}u+\cdots)du,\end{aligned} \tag{B.5}$$

where $-Ei(-z)$ is the exponential integral. Denoting by $c(a)$ the integral

$$\begin{aligned}c(a)&=\int_0^{\infty}e^{-au}(\tfrac{1}{2}+\tfrac{1}{12}u+\cdots)du\\&=\int_0^{\infty}e^{-au}\left(\frac{u}{1-e^{-u}}-1\right)\frac{du}{u},\end{aligned} \tag{B.6}$$

expanding the exponential in the second integral of Eq. (B.4) and integrating term by term, we find

$$\begin{aligned}F(a;x)=-Ei(-ax)+c(a)-\tfrac{1}{2}x\\+\tfrac{1}{2}(\tfrac{1}{2}a-\tfrac{1}{12})x^2+\cdots.\end{aligned} \tag{B.7}$$

The exponential integral $-Ei(-z)$ has the following asymptotic expansion for $z\rightarrow 0$ [24]:

$$-Ei(-z)=-\ln z-\epsilon+z-\tfrac{1}{4}z^2+\cdots,$$

where $\epsilon=\ln\gamma$ is Euler's constant $0.5772\cdots$. With this result and Eq. (B.4) we obtain finally

$$\begin{aligned}S(x)&=e^{ax}[-\ln ax-\epsilon+c(a)+(a-\tfrac{1}{2})x\\&\quad-(\tfrac{1}{4}a^2-\tfrac{1}{4}a+1/24)x^2+\cdots]\\&=-\ln x+[c(a)-\epsilon-\ln a]-ax\ln x+O(x).\end{aligned} \tag{B.8}$$

This result can be used to obtain the asymptotic form of the sum

$$S'(x)=\sum_{n=0}^{\infty}\frac{e^{-nx}}{n-a}\quad 0<a<1, \tag{B.9}$$

in the limit as $x\rightarrow 0$. Rewriting this sum as

$$S'(x)=-\frac{1}{a}+\sum_{n=1}^{\infty}\frac{e^{-nx}}{n-a}=-\frac{1}{a}+e^{-x}\sum_{n=0}^{\infty}\frac{e^{-nx}}{n+a'}, \tag{B.10}$$

where

$$0<a'=1-a,$$

and applying Eq. (B.8) we obtain finally

$$\begin{aligned}S'(x)=-\ln x+\left[c(a')-\ln a'-\epsilon-\frac{1}{1-a'}\right]\\+O(x\ln x).\end{aligned} \tag{B.11}$$

The integral for the constant $c(a)$ defined by Eq. (B.6) is evaluated in the following way. We make a change of variable $e^{-u}=x$ to rewrite Eq. (B.6) as[25]

$$\begin{aligned}c(a)&=\int_0^{1}x^{a-1}\left(\frac{1}{1-x}+\frac{1}{\ln x}\right)dx\\&=\ln a-\Psi(a)+\frac{1}{a},\end{aligned} \tag{B.12}$$

where $\Psi(x)=d/dx\ln(x!)$. The function $\Psi(x)$ is tabulated by Jahnke and Emde.

II. The derivation of the asymptotic expansion for $I(x)$ proceeds in a somewhat similar fashion. With a change of variable we find that

$$e^{-x}I(x)=G(x)=\int_x^{\infty}e^{-u}\frac{du}{(1-e^{-u})^2}. \tag{B.13}$$

Again it is the small-u region of the integrand which contributes dominantly to the integral for $x\sim 0$ so that expanding the denominator in powers of u we obtain

$$\begin{aligned}G(x)&=\int_x^{\infty}\frac{e^{-u}}{u^2}\left(1+u+\frac{5}{12}u^2+\cdots\right)du\\&=\int_x^{\infty}\frac{e^{-u}}{u^2}du+\int_x^{\infty}\frac{e^{-u}}{u}du\\&\quad+\int_0^{\infty}e^{-u}\left(\frac{5}{12}+\frac{u}{12}+\cdots\right)du\\&\quad-\int_0^{x}e^{-u}\left(\frac{5}{12}+\frac{1}{12}u+\cdots\right)du.\end{aligned} \tag{B.14}$$

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[24] Erdelyi, Magnus, Oberhettinger, and Tricomi, *Higher Transcendental Functions* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. II, p. 143.

[25] W. Grobner and N. Hofreiter, *Integraltafel* (Springer-Verlag, Wien and Innsbruch, 1958), Vol. II, p. 90.

If we introduce the well-known auxiliary integrals[26]

$$\phi_n(z)=\int_1^\infty t^n e^{-zt}dt \tag{B.15a}$$

$$=\frac{e^{-z}}{z}+\frac{n}{z}\phi_{n-1}(z), \tag{B.15b}$$

and denote the constant defined by the third integral in Eq. (B.14) by p,

$$p=\int_0^\infty e^{-u}\left(\frac{5}{12}+\frac{1}{12}u+\cdots\right)du$$

$$=\int_0^\infty e^{-u}\left(\frac{u^2}{(1-e^{-u})^2}-1-u\right)\frac{du}{u^2}, \tag{B.16}$$

we obtain

$$G(x)=\frac{1}{x}\phi_{-2}(x)+\phi_{-1}(x)+p$$
$$-\int_0^x\left(\frac{5}{12}-\frac{1}{3}u+\cdots\right)du. \tag{B.17}$$

Since it is readily verified that

$$\phi_{-1}(x)=-Ei(-x)=-\ln x-\epsilon+x-\tfrac{1}{4}x^2+O(x^3),$$

as $x\longrightarrow 0$, in view of Eq. (B.15b) we see that

$$\phi_{-2}(x)=1+x\ln x-(1-\epsilon)x-\tfrac{1}{2}x^2+O(x^3), \tag{B.18}$$

as $x\longrightarrow 0$. With these results the small-x expansion for $G(x)$ becomes

$$G(x)=1/x+(p-1)+\tfrac{1}{12}x+O(x^2), \tag{B.19}$$

so that finally

$$I(x)=1/x+p+(p-5/12)x+O(x^2). \tag{B.20}$$

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[26] M. Born and K. Huang, see reference 10, p. 389.