Mobility of Slow Electrons in a Polar Crystal

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We have obtained an approximate expression for the impedance function at all frequencies, temperatures, and coupling strengths of an electron coupled to a polar lattice (a system commonly called a polaron). The starting point for the calculation is the quantum mechanical expression for the expected current. The phonon coordinates are eliminated from this expression by well-known field-theory techniques. The resulting exact "influence functional" is then approximated by a corresponding quadratic "influence functional" which, it is hoped, imitates the real polaron. Correction terms are computed to account for the difference between the approximate impedance and the exact polaron impedance in a manner closely analogous to Feynman's treatment of the polaron self-energy. In fact, the analytic evaluation of the expression for the impedance obtained here is carried out using the approximate "influence functional" that was successfully employed in minimizing the binding (and free) energy of the polaron in earlier calculations. However, the accuracy obtained using this approximation, for the impedance calculation, is less satisfactory and its limitations are discussed. Nevertheless, beginning at intermediate coupling strengths, the approximate impedance produces a level structure of increasing complexity and narrowing resonances as the coupling strengthens. This suggests that further refinements may be fruitful. Methods for finding a better quadratic influence functional for use in our impedance expression as well as ways of improving the expression further are suggested. A comparison of our results with those of the Boltzmann equation points up interesting differences which arise from reversing the order of taking limits of zero frequency and coupling.

I. INTRODUCTION

AN electron in a polar crystal interacts with the surrounding crystal. The effect of this interaction is to surround the electron with a distorted lattice: a cloud of phonons. The nature of this system, "the polaron," has been extensively studied.[1–4] It is interesting as a phenomenon in solids, but it has an extended interest since it is one of the simplest examples of the interaction of a particle and a field. It is in many ways analogous to the problem of a nucleon interacting with a meson field. (The extra complications of spin and isotopic spin do not, however, permit direct use of the methods to be described here, without some extension of their power.) In cases of practical interest, the coupling between the electron and the longitudinal optical modes of vibration of the crystal is sufficiently strong that simple perturbation methods do not apply. It is the strong-coupling aspect of the problem which has aroused so much interest. For this reason, the "polaron problem" has generally been studied in a considerably idealized form.

It is assumed that in the undistorted lattice the electron would move as a free particle (with possibly an altered mass), that only the optical modes interact with the electron, that they do so in a very simple way, and that they all have the same frequency. These are quite drastic simplifications; however, sufficient data are not available to improve these assumptions so as to represent any actual crystal. The methods given here do not require these simplifications (except perhaps that the electron's kinetic energy is a quadratic function of its momentum); the same techniques can be readily applied to include variations of frequency and coupling of the optical modes with wave number, influences of other modes, etc., although some of the integrals done analytically here might have to be done numerically.

In discussing losses and mobility such idealization may alter completely the true behavior, because some essential loss mechanism such as lattice defects or interaction with acoustic phonons has been idealized away. It is important to appreciate, therefore, that in all the remaining analysis and discussion we shall be talking only about a strictly idealized problem.

One of us[1] has shown that the ground-state energy and effective mass of the polaron could be calculated with considerable accuracy from a variational principal obeyed by path integrals. Of more interest, experimentally, is the mobility of the polaron and, more generally, its response to weak, spatially uniform, time varying electric fields. This is a more complicated problem involving the rate at which a drifting electron loses momentum by phonon interactions, through emissions of phonons or collisions with phonons already present. In the practical situation at temperatures not too near the melting point of the crystal the density of

[1] R. P. Feynman, Phys. Rev. **97**, 660 (1955), hereafter to be called I.
[2] H. Frohlich, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 325.
[3] S. I. Pekar, Zhur. Eksp. i Teoret. Fiz. **19**, 796 (1949).
[4] T. D. Schultz, Phys. Rev. **116**, 526 (1960).

optical phonons is quite low as a result of the high energy required to excite them. In our idealized model losses can occur only through collisions with optical phonons, so that these collisions could be analyzed by first finding the collision cross section and then using the Boltzmann equation (or equivalently the usual formulas for transport cross section) to get the mobility.[5] This is the technique generally employed in transport problems. Yet there exists a class of transport problems in which this cannot be done. If many phonons are colliding simultaneously with an electron most of the time, and if there are possibly quantum interferences among these collisions (such that the cross section for scattering from one phonon depends on the presence and behavior of others), the collisions cannot be separated in time as required for the validity of the Boltzmann transport equation. What we need to calculate (the average position of an electron at time t, if at $t=0$ a pulsed electric field was applied) can be easily written formally, but little has been done with such a form unless the coupling is weak or the collisions are well separated.[6,7]

A secondary interest which we had in this problem was to see if we could compute transport problems in cases when not only the perturbation theory, but also the Boltzmann equation is inadequate. Therefore, in spite of its lack of reality, we have analyzed the problem of the impedance of a polaron of arbitrary coupling strength in an oscillating electric field, for arbitrary temperatures (temperatures so high perhaps that the Boltzmann factor $e^{-\hbar\omega/kT}$ for the energy $\hbar\omega$ of the optical modes is not necessarily small).

In any specific range of conditions, such as low temperature, high temperature, or high frequency of external electric field, etc., special approximations might be made to obtain a better answer than is given by our general formula. However, it was of interest to see how well one could do in a general way for arbitrary values of the parameters.

II. FORMULATION OF THE MOBILITY PROBLEM IN TERMS OF THE ELECTRON COORDINATES ALONE

If a weak alternating electric field $E=E_0e^{i\nu t}$ is applied to the crystal in the x direction, the current induced (by motion of the electron) may be written as

$$j(\nu)=[z(\nu)]^{-1}E_0e^{i\nu t}. \tag{1}$$

This defines the impedance function $z(\nu)$ which we wish to calculate. We will assume that the crystal is isotropic so that $j=\langle\dot{x}\rangle$, where $\langle x\rangle$ is the expectation of the electron displacement in the x direction (taking the electric charge as unity). The displacement $\langle x\rangle$ is $E/i\nu z(\nu)$. Transformed to time variables, this implies that

$$\langle x(\tau)\rangle=-\int_{-\infty}^{\infty} iG(\tau-\sigma)E(\sigma)d\sigma, \tag{2}$$

where $G(\tau)$, i times the electron displacement at time τ induced by a pulsed electric field at time zero, has the inverse transform

$$\int_{-\infty}^{\infty} G(\tau)e^{-i\nu\tau}d\tau=G(\nu)=[\nu z(\nu)]^{-1}. \tag{3}$$

We take $G(\tau)=0$ for $\tau<0$.[8]

The effect of a perturbing field $\mathbf{E}(t)$ in the x direction is to add to the complete Hamiltonian of the system H, the term $-xE(t)\equiv-\mathbf{E}\cdot\mathbf{X}$ (where x is the component of the vector position of the electron $\mathbf{X}$ in the direction of the field). If at some time (a), long before the field is turned on [i.e., $\mathbf{E}(t)=0$ for $t<a$] the state of the system is represented by the density matrix ρ_a, then the density matrix at time τ is $U(\tau,a)\rho_aU'^{-1}(\tau,a)$. Thus, the expected position at time τ is

$$\langle x(\tau)\rangle=\mathrm{Tr}[xU(\tau,a)\rho_aU'^{-1}(\tau,a)], \tag{4}$$

where

$$U(\tau,a)=\exp\left\{-i\int_a^\tau[H_s-\mathbf{X}_s\cdot\mathbf{E}(s)]ds\right\} \tag{5}$$

is the unitary operator for the development of a state in time with the complete Hamiltonian $H-\mathbf{X}\cdot\mathbf{E}$.

We use a time-ordered operator notation; all unprimed operators are placed to the left, latest times farthest to the left, then the matrix ρ at the right and finally all primed operators on the right of ρ, with latest times farthest to the right.[9] Thus, primed operators are ordered oppositely to unprimed. We can, therefore, write

$$U'^{-1}(\tau,a)=\exp\left\{i\int_a^\tau[H_s'-\mathbf{X}_s'\cdot\mathbf{E}'(s)]ds\right\}. \tag{6}$$

The quantity E is not an operator but simply a function of s so that in (4), $E'(s)=E(s)$. However, as we shall see in a moment, it is convenient to handle a more general case where E and E' are different arbitrary functions of s.

For weak fields we expand (4) to first order in E and find an expression for $x(\tau)$ of the form (2). Evidently, $-iG(\tau-\sigma)$ is the response to a δ function E, so we may set $E(s)=\epsilon\delta(s-\sigma)=E'(s)$, substitute into (4), and expand the exponential to first order in ϵ. However, we note that (4) itself may be considered to be $-i$ times the first functional derivative with respect to $E(\tau)-E'(\tau)$ of

$$g=\mathrm{Tr}[U(b,a)\rho_aU'^{-1}(b,a)], \tag{7}$$

[5] J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

[6] R. Kubo, J. Phys. Soc. Japan **12**, 570, 1203 (1957).

[7] M. Lax, Phys. Rev. **109**, 1921 (1958).

[8] In our idealized model $\mathbf{X}$ and $\mathbf{E}$ will be in the same direction, although in general (in the presence of magnetic field or anisotropic crystalline fields), G and z will be tensors.

[9] R. P. Feynman, Phys. Rev. **84**, 108 (1951).

as $b \to +\infty$, and $a \to -\infty$. That is to say, we calculate g from (5), (6), and (7) with

$$E(s)=\epsilon\delta(s-\sigma)+\eta\delta(s-\tau) \tag{8a}$$

and

$$E'(s)=\epsilon\delta(s-\sigma)-\eta\delta(s-\tau). \tag{8b}$$

The quantity we require is

$$G(\tau-\sigma)=\tfrac{1}{2}(\partial^2 g/\partial\eta\partial\epsilon)_{\eta=\epsilon=0}. \tag{9}$$

If the initial state is one of a definite temperature T, then

$$\rho_a=\exp(-\beta H)/Q, \tag{10}$$

where $\beta=1/kT$ and Q is a normalizing constant, which we eliminate by calculating $(1/2g)(\partial^2 g/\partial\eta\partial\epsilon)$ evaluated at $\epsilon=\eta=0$.

The Hamiltonian representing an electron in interaction with the vibrational modes of a crystal is

$$H=\mathbf{P}^2/2m+\sum_{\mathbf{K}}\omega_{\mathbf{K}}a_{\mathbf{K}}^{\dagger}a_{\mathbf{K}} + V^{-1/2}\sum_{\mathbf{K}}[C_{\mathbf{K}}^{*}a_{\mathbf{K}}^{\dagger}\exp(-i\mathbf{K}\cdot\mathbf{X}) + C_{\mathbf{K}}a_{\mathbf{K}}\exp(i\mathbf{K}\cdot\mathbf{X})]. \tag{11}$$

In this expression, $a_{\mathbf{K}}$, $a_{\mathbf{K}}^{\dagger}$ are the annihilation and creation operation of phonons of momentum $\mathbf{K}$, frequency $\omega_{\mathbf{K}}$, coupled to the electron via the coupling coefficient $C_{\mathbf{K}}$; $\mathbf{P}$ is the momentum of the electron; $\mathbf{X}$ is its coordinate; m is its effective mass calculateed in a fixed lattice; V is the crystal volume. We take $\hbar=1$, $m=1$.

As a specific example we shall take the simplified model of Fröhlich[2] in which $\omega_{\mathbf{K}}=1$ independent of $\mathbf{K}$, and $C_{\mathbf{K}}=i2^{3/4}\pi^{1/2}\alpha^{1/2}/|\mathbf{K}|$, where α is a constant related to the dielectric constant; intermediate coupling corresponds to $\alpha\approx 6$.

The quantity ρ_a, the initial distribution, should be $e^{-\beta H}$ for the full Hamiltonian H. If the time (a) is sufficiently far in the past we can just as well take $\rho_a=\text{const}\times\exp(-\beta\sum_{\mathbf{K}}\omega_{\mathbf{K}}a_{\mathbf{K}}^{\dagger}a_{\mathbf{K}})$. That is, we may assume that in the past only the oscillators were in thermal equilibrium at temperature β^{-1}. As a result of the coupling, the entire system will come very quickly to thermal equilibrium at the same temperature. The energy of the single electron and its coupling are infinitesimal (of the order $1/V$) relative to the heat bath of the system of phonon oscillators, so that the exchange of energy between the electron and the lattice will bring everything to thermal equilibrium at the original lattice temperature.

With this choice of ρ_a the dependence of U, U', and ρ_a in (7) on the phonon oscillator coordinates is sufficiently simple so that the oscillator coordinates may be eliminated and the entire expression reduced to a double path integral involving the electrons coordinates only. This reduction, explained in Appendix A, is carried out by methods analogous to those used before by one of the authors on problems in electrodynamics.[9]

The result is (taking $a \to -\infty$, $b \to +\infty$)

$$g=\int\int e^{i\Phi}\mathfrak{D}\mathbf{X}(t)D\mathbf{X}'(t), \tag{12}$$

where

$$\Phi=\int_{-\infty}^{+\infty}\left[\frac{1}{2}\left(\frac{d\mathbf{X}(t)}{dt}\right)^2-\frac{1}{2}\left(\frac{d\mathbf{X}'(t)}{dt}\right)^2\right]dt-\int_{-\infty}^{+\infty}[\mathbf{E}(t)\cdot\mathbf{X}(t)-\mathbf{E}'(t)\cdot\mathbf{X}'(t)]dt$$
$$+\frac{i}{2}\int\frac{d^3K}{(2\pi)^3}|C_{\mathbf{K}}|^2\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\{\exp[i\mathbf{K}\cdot\mathbf{X}(t)]-\exp[i\mathbf{K}\cdot\mathbf{X}'(t)]\}\times[y(\omega_{\mathbf{K}},t-s)$$
$$\times\{\exp[-i\mathbf{K}\cdot\mathbf{X}(s)]+\exp[-i\mathbf{K}\cdot\mathbf{X}'(s)\}+ia(\omega_{\mathbf{K}},t-s)\{\exp[-i\mathbf{K}\cdot\mathbf{X}(s)]-\exp[-i\mathbf{K}\cdot\mathbf{X}'(s)]\}]dsdt. \tag{13}$$

The functions $y(\omega,\tau)$ and $a(\omega,\tau)$ are given in Appendix A. In the special case of Fröhlich's Hamiltonian the integral on $\mathbf{K}$ can be performed to give

$$\Phi_F=\int_{-\infty}^{+\infty}\left[\frac{1}{2}\left(\frac{d\mathbf{X}(t)}{dt}\right)^2-\frac{1}{2}\left(\frac{d\mathbf{X}'(t)}{dt}\right)^2\right]dt+\int_{-\infty}^{+\infty}[\mathbf{E}(t)\cdot\mathbf{X}(t)-\mathbf{E}'(t)\cdot\mathbf{X}'(t)]dt$$
$$+i\alpha 2^{-3/2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\left[\frac{e^{-i|t-s|}+2P(\beta)\cos(t-s)}{|\mathbf{X}(t)-\mathbf{X}(s)|}+\frac{e^{+i|t-s|}+2P(\beta)\cos(t-s)}{|\mathbf{X}'(t)-\mathbf{X}'(s)|}\right.$$
$$\left.-\frac{2[e^{-i(t-s)}+2P(\beta)\cos(t-s)]}{|\mathbf{X}'(t)-\mathbf{X}(s)|}\right]dtds, \tag{14}$$

where $P(\beta)=[e^{\beta}-1]^{-1}$.

The double integral $\mathfrak{D}\mathbf{X}(t)\mathfrak{D}\mathbf{X}'(t)$ is only over those paths which satisfy the boundary condition $\mathbf{X}(t)-\mathbf{X}'(t)=0$ at times t approaching $\pm\infty$. The boundary conditions on the paths at large positive or negative times, reflects the arbitrariness of the initial electron state.

Thus, we have reduced the problem of find G via (7), (8), and (9) to that of finding the dependence of a path integral (12) on the forcing functions E and E'. This expression is exact [for the Hamiltonian (11)] but quite complicated. In the next section we discuss approximate methods of evaluation.

III. A METHOD OF APPROXIMATION

In I, a path integral, similar to (14), had to be evaluated. It was argued there that in some rough approximation the "interaction of the charge with itself" represented there by a term in the action function S, $2^{-3/2}\alpha e^{-|t-s|}|\mathbf{X}(t)-\mathbf{X}(s)|^{-1}$, might be imitated by a function S_0 in which this term is replaced by $1/2Ce^{-w|t-s|}[\mathbf{X}(t)-\mathbf{X}(s)]^2$. One may think of the interaction term in S as indicating that at time t the particle acts as though it were in a potential $2^{-1/2}\alpha\int_{-\infty}^{t}e^{-(t-s)}\times|\mathbf{X}(t)-\mathbf{X}(s)|^{-1}ds$ resulting from the electrostatic interaction of the electron with its mean charge density of its previous positions [the weight for different times being $e^{-(t-s)}$]. The assumption then is that such a potential may be roughly replaced by a parabolic potential centered at the mean position of the electron in the past [the weight for different times being $e^{-w(t-s)}$]. In fact, the extra parameter w can be adjusted to compensate partly for the error of using a parabolic potential in place of the true potential form. This argument strongly suggests that the dynamical behavior of the electron, (its motion under an applied electric field) might be described approximately if we replace Φ by a Φ_0, where

$$\Phi_0=\int_{-\infty}^{+\infty}\left[\frac{1}{2}\left(\frac{d\mathbf{X}(t)}{dt}\right)^2-\frac{1}{2}\left(\frac{d\mathbf{X}'(t)}{dt}\right)^2\right]dt-\int_{-\infty}^{+\infty}[\mathbf{E}(t)\cdot\mathbf{X}(t)-\mathbf{E}'(t)\cdot\mathbf{X}'(t)]dt$$
$$-\frac{iC}{2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\{[\mathbf{X}(t)-\mathbf{X}(s)]^2[e^{-iw|t-s|}+2P(\beta w)\cos w(t-s)]$$
$$+[\mathbf{X}'(t)-\mathbf{X}'(s)]^2[e^{+iw|t-s|}+2P(\beta w)\cos w(t-s)]$$
$$-2[\mathbf{X}'(t)-\mathbf{X}(s)]^2[e^{-iw(t-s)}+2P(\beta w)\cos w(t-s)]\}dtds. \quad (15)$$

The parameters C and w are to be determined so as to approximate Φ as closely as possible. At zero temperature ($P=0$), we shall fix C and w at the values given in I. The assumption that Φ_0 is a good approximation to Φ for computing the mobility at low temperatures is based on the supposition that the comparison Lagrangian, which gives a good fit to the ground-state energy at zero temperature, will also give the dynamical behavior of the system. In finding the ground-state energy, the parameters can be chosen by a variational principle but we know of no such principle for the mobility. At finite temperatures the parameters C and w can be determined from a variational principal for the free energy which is a direct extension of the method used in I for the ground-state energy, and reduces to it in the zero-temperature limit. Others[10,10a] have derived in detail the expressions from which the best C and w may be determined for finite β. Thus, C and w can be considered as known functions of α and β even though, unfortunately, no closed analytic form exists, and in any specific calculation they would have to be evaluated numerically.

Actually, we shall not be satisfied merely to replace Φ by Φ_0, but we shall obtain a first correction to $z(v)$ by studying, in the next section, the first term in an expansion of $\exp[i(\Phi-\Phi_0)]$:

$$g=\int\int e^{i\Phi}\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'\approx\int\int e^{i\Phi_0}\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'$$
$$+\int e^{i\Phi_0}i(\Phi-\Phi_0)\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'. \quad (16)$$

In this section, however, we will consider only the first term,

$$g_0=\int e^{i\Phi_0}\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'. \quad (17)$$

We can expect to evaluate the integral (17) exactly, because the expression for Φ_0 is a quadratic form in $\mathbf{X}(t)\,\mathbf{X}'(t)$ and all such "Gaussian" path integrals can be evaluated exactly.[9] There are several ways to perform the integration in (17). One way is to observe that the expression (15) is obtained by eliminating the variable $\mathbf{Y}$ from a system in which an electron interacts with a single particle described by the Lagrangian

$$L_0=\tfrac{1}{2}(d\mathbf{X}/dt)^2+\tfrac{1}{2}(d\mathbf{Y}/dt)^2-\tfrac{1}{2}k(\mathbf{X}-\mathbf{Y})^2+\mathbf{E}\cdot\mathbf{X}. \quad (18)$$

If we calculate the g for such a system by integrating over all the $\mathbf{Y}$ variables first, then (17) results; provided we choose $k=(v^2-w^2)$ and $M=(v^2-w^2)/w^2$, where $v^2=w^2+4C/w$. However, L_0 can be re-analyzed as the

[10] Y. Osaka, Progr. Theoret. Phys. (Kyoto) **22**, 437 (1959).

[10a] M. A. Krivologz and S. I. Pekar, Bull. Acad. Sci. U.S.S.R. **21**, 1, 13, 29 (1957).

sum of two normal modes,

$$L_0=\tfrac{1}{2}(M+1)(d\mathbf{X}_2/dt)^2+\mathbf{E}\cdot\mathbf{X}_2+\frac{M}{2(M+1)}\times[(d\mathbf{X}_1/dt)^2-v^2\mathbf{X}_1^2]-\frac{M}{(M+1)}\mathbf{E}\cdot\mathbf{X}_1, \quad (19)$$

so that g_0 can be written as the product of two factors, one for each harmonic oscillator. For a single oscillator of mass m and frequency ω, coupled as $\mathbf{\Gamma}(t)\cdot\mathbf{X}$, the value of g is given in Appendix A. Here we have two oscillators, one of mass $m_1=M+1=v^2/w^2$ and frequency $\omega_1=0$ coupled with a $\mathbf{\Gamma}(t)=\mathbf{E}(t)$, and a second oscillator with $m_2=M/M+1$, $\omega_2=v$, and $\mathbf{\Gamma}(t)=-(M/M+1)\mathbf{E}(t)=-[(v^2-w^2)/v^2]\mathbf{E}(t)$. If the contributions of the two normal modes are combined, g_0 takes the form

$$g_0=\exp\left(\frac{i}{4\pi}\int_{-\infty}^{+\infty}[f(-\nu)-f'(-\nu)]\{[f(\nu)+f'(\nu)]Y_0(\nu)+i[f(\nu)-f'(\nu)]A_0(\nu)\}d\nu\right), \quad (20)$$

where[11]

$$Y_0(\nu)=-(\nu^2-w^2)/(\nu-i\varepsilon)^2[(\nu-i\varepsilon)^2-v^2] \quad (21)$$

and

$$A_0(\nu)=\frac{\pi}{2}\left\{\frac{2w^2}{v^2\beta\varepsilon^2}[\delta(\nu+\varepsilon)+\delta(\nu-\varepsilon)]+[1+2P(\beta v)]\times\frac{(v^2-w^2)}{v^3}[\delta(\nu+v)+\delta(\nu-v)]\right\}. \quad (22)$$

We have expressed $E(t)$ and $E'(t)$ by their Fourier transforms

$$f(\nu)=\int_{-\infty}^{+\infty}E(t)e^{-i\nu t}dt. \quad (23)$$

To obtain $G_0(\tau-\sigma)$ we must evaluate g_0 for E and E' given in (8), that is to say, we must substitute

$$f(\nu)=\epsilon e^{-i\nu\sigma}+\eta e^{i\nu\tau},\qquad f'(\nu)=\epsilon e^{-i\nu\sigma}-\eta e^{i\nu\tau}, \quad (24)$$

into (20), and find the term of order $\epsilon\eta$. Evidently

$$G_0(\tau-\sigma)=\frac{+i}{2\pi}\int_{-\infty}^{+\infty}Y_0(\nu)e^{+i\nu(\tau-\sigma)}d\nu, \quad (25)$$

where $G_0(\tau-\sigma)$ is the zeroth order approximation to $G(\tau-\sigma)$ [Eq. (2)]. Therefore,

$$G_0(\nu)=+iY_0(\nu). \quad (26)$$

Since Y_0 is the classical response function for the comparison system L_0, the result has the immediate interpretation that $G_0(\nu)$ is the response we would have predicted for the system L_0 had we treated it classically. In addition, there is no temperature dependence in G_0 (except through the variation of the parameters v, w with temperature). Both of these well-known results follow from the linearity of L_0.[12,13]

For a particle of mass m, for low frequencies, $G\approx -i/m\nu^2$ so that a comparison of this expression with (21) and (26) gives an effective electron mass $m=v^2/w^2$. This value for m is not the same as the more accurate value given in I, but as Shultz[4] has shown, it is numerically not very different over a wide range of α. Thus, the reactive part of G_0 may be satisfactory, but the dissipative (real part) appearing as it does all at the single frequency v, must be only a very crude approximation.

In the next section we shall compute the corrections implied by the additional expansion terms in (16). We shall find that the mass is now exactly that given in I, and that the dissipatiion has a much more realistic behavior.

IV. FIRST CORRECTION TERM

To evaluate the second term on the right-hand side of (16) we shall have to integrate $e^{i\Phi_0}(\Phi-\Phi_0)$. In order to see what is involved, consider only one of the terms arising from $\Phi e^{i\Phi_0}$:

$$T=\int e^{i\Phi_0}\left\{\int\frac{d^3K}{(2\pi)^3}|C_\mathbf{K}|^2\times\int_{-\infty}^{+\infty}\int_{-\infty}^{\infty}\exp\{i\mathbf{K}\cdot[\mathbf{X}(t)-\mathbf{X}(s)]\}\times[y(\omega_\mathbf{K},t-s)+ia(\omega_\mathbf{K},t-s)]dsdt\right\}\times\mathfrak{D}\mathbf{X}(t)\mathfrak{D}\mathbf{X}'(t). \quad (27)$$

Other terms from Φ are similar to (27) with some replacements of $\mathbf{X}$ by $\mathbf{X}'$, while the terms from Φ_0 we will consider later. Evaluation of (27) requires a knowledge of the path integral

$$R(K,t,s)=\int e^{i\Phi_0}\exp\{i\mathbf{K}\cdot[\mathbf{X}(t)-\mathbf{X}(s)]\}\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'. \quad (28)$$

Once $R(K,t,s)$ has been evaluated, (27) becomes an ordinary multiple integral:

$$T=\int\frac{d^3K}{(2\pi)^3}|C_\mathbf{K}|^2\int_{-\infty}^{+\infty}\int_{-\infty}^{\infty}R(K,t,s)\times[y(\omega_\mathbf{K},t-s)+ia(\omega_\mathbf{K},t-s)]dsdt. \quad (29)$$

[11] ε is a small positive quantity and the limit $\varepsilon\to 0$ is to be taken.

[12] F. L. Vernon, Jr., Ph.D. thesis, California Institute of Technology, 1959 (unpublished).

[13] R. W. Hellwarth, Hughes Research Laboratories, Fourth Quarterly Progress Report, September 15, 1958 (unpublished).

The function R is easily evaluated. It is clearly given by our general formula (20) with

$$\mathbf{f}(\nu)=(\epsilon e^{-i\nu\sigma}+\eta e^{-i\nu\tau})\hat{\imath}+\mathbf{K}(e^{-i\nu t}-e^{-i\nu s}) \tag{30}$$

and[14]

$$\mathbf{f}(\nu)=(\epsilon e^{-i\nu\sigma}-\eta e^{-i\nu\tau})\hat{\imath}. \tag{31}$$

Similarly, a term of the form (27) with $\mathbf{X}(t)$ replaced by $\mathbf{X}'(t)$ can be expressed in terms of our general path integral (20) by using the proper f's,

$$\mathbf{f}(\nu)=(\epsilon e^{-i\nu\sigma}+\eta e^{-i\nu\tau})\hat{\imath}-\mathbf{K}e^{-i\nu s} \tag{32}$$

and

$$\mathbf{f}'(\nu)=(\epsilon e^{-i\nu\sigma}-\eta e^{-i\nu\tau})\hat{\imath}-\mathbf{K}e^{-i\nu t}. \tag{33}$$

In this way, $\int e^{i\Phi_0}\Phi\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'$ can be evaluated. Similarly the term $\int e^{i\Phi_0}\Phi_0\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'$ may be obtained. To get $\int e^{i\Phi_0}[\mathbf{X}(t)-\mathbf{X}(s)]^2\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'$, one can differentiate R with respect to K twice and evaluate it at $K=0$. (Details are given in Appendix B.)

The final result for the first-order change in G is

$$G_1=-iY_0^2(\nu)[\chi(\nu)+(4C/w)\nu^2/(\nu^2-w^2)], \tag{34}$$

where

$$\chi(\nu)=\int_0^\infty[1-e^{i\nu u}]\,\mathrm{Im}S(u)du, \tag{35a}$$

and

$$S(u)=\int\frac{d^3K}{(2\pi)^3}|C_{\mathbf{K}}|^2\frac{2K^2}{3}e^{-K^2D(u)/2}$$
$$[\exp(i\omega_{\mathbf{K}}u)+2P(\beta\omega_{\mathbf{K}})\cos(\omega_{\mathbf{K}}u)]. \tag{35b}$$

"Im" means the imaginary part and the function $D(u)$ is defined as

$$D(u)=\frac{w^2}{v^2}\left[\frac{v^2-w^2}{w^2v}[1-e^{+iv u}\right.$$
$$\left.+4P(\beta v)\sin^2(vu/2)]-iu+u^2/\beta\right]. \tag{35c}$$

For Fröhlich's Hamiltonian, the integration over $\mathbf{K}$ may be done to give

$$S(u)=2\alpha/3\sqrt{\pi}\{[D(u)]^{-3/2}[e^{iu}+2P(\beta)\cos u]\}. \tag{36}$$

We have found an approximate form for $G(\nu)$:

$$G(\nu)=G_0(\nu)+G_1(\nu). \tag{37}$$

From it we may find the impedance to first order in $G_1(\nu)$:

$$\nu z(\nu)=1/G(\nu)\sim 1/G_0(\nu)-[1/G_0(\nu)^2]G_1(\nu). \tag{38}$$

The question arises as to whether it is more accurate to expand in this way or to leave the formula as $\nu z(\nu)=(G_0+G_1)^{-1}$. Of course, if G_1 were truly small it would not matter. However, there are excellent reasons to believe that the expanded form is far more accurate. This is best explained by considering a simple example of a free particle to which we add a harmonic binding as a perturbation. The resulting G's are [Φ_0 arising from $\frac{1}{2}m(d\mathbf{X}/dt)^2$ only],

$$G_0(\nu)=+iY_0(\nu)=-i/m\nu^2 \tag{39a}$$

and

$$G_1(\nu)=-i\omega_0^2/m\nu^4, \tag{39b}$$

where ω_0 is the natural frequency of the oscillator. In this case the expanded form of $z(\nu)$ is

$$i\nu z(\nu)=m(\omega_0^2-\nu^2). \tag{40}$$

The true $G(\nu)$ shows a structure (resonance at $\nu=\omega_0$) which is not reflected in an expanded form of G, but which is precisely duplicated (for this linear system) if one expands $z(\nu)$. Therefore, we substitute (34) into (38) to obtain the simple result,

$$-i\nu z(\nu)=\nu^2-\chi(\nu). \tag{41}$$

With $\chi(\nu)$ given by (35), this is our final expression for the impedance of the polaron. It is Eqs. (41) and (35) which we will evaluate in various limits and discuss in the following sections.

The first term on the right-hand side of (41) is a pure free-particle term, while $\chi(\nu)$ contains all of the corrections due to the interaction with phonons. The entire dependence of our results (41) on the trial action Φ_0 is in $D(u)$, Eq. (35c). $D(u)$ in turn appears only in the exponential term in Eq. (35b). This exponential is an effect due to recoil as can be seen by expanding the $\exp(i\mathbf{K}\cdot\mathbf{X})$ term in the Hamiltonian as $1+i\mathbf{K}\cdot\mathbf{X}$ (which we may call a dipole, or linear coupling approximation). If the expansion is made, then the exponential term $e^{-K^2D(u)/2}$ in (35b) will not appear. In other words, if we had any problem in which the field oscillators were coupled linearly to the electron's coordinate $\mathbf{X}$, then our method would give us the exact formula for the impedance irrespective of the choice made for the trial functional Φ_0.[15] This is fact in the best argument for treating the perturbation expansion (16) as an expansion for $z(\nu)$ in the manner of Eq. (38).

Therefore, insofar as the system of phonons behaves as though they were linearly coupled, so there were no recoil effects, (41) is exact. However, recoil effects *are* included in (41); it is only that they are not included precisely. They are approximated by finding their effect for the imitative functional Φ_0 rather than the true functional Φ. For this reason we expect (41) to be an excellent approximation to the true impedance of the polaron.

[14] Equation (20) is a one-dimensional formula. For the case of vector forces the product of two f's is to be interpreted as a dot product.

[15] Assuming that Φ_0 also implies a linear coupling and is a quadratic functional of $\mathbf{X}(t)$, $\mathbf{X}'(t)$.

V. BEHAVIOR OF THE IMPEDANCE

For purposes of further analysis in which we shall change the contour of integration on the variable u, we list some properties of $S(u)$. For real u, $S^*(u)=S(-u)$ and $S(iu)$ is purely real. In addition $S(u)=S(i\beta-u)$ for complex u. The real part of $D(u)$ must be positive in order for the K integral to converge. Therefore, the region of u where this happens, namely the strip parallel to the real axis between the lines $u=$real and $u=$real$+i\beta$, is the region free of singularities for $S(u)$. In the limit of zero temperatures ($\beta\to\infty$) this strip, over which $S(u)$ is analytic, widens to include the entire upper half-plane.

1. Zero Temperature, $\nu<1$; Effective Mass

For Fröhlich's case we consider first the case $\nu<1$, $\beta=\infty$. Then the path of integration [in the integral for $\chi(\nu)$] along the real axis may be rotated to the path along the positive or negative imaginary axis $u\approx 0$ to $\pm i\infty$ (depending on the sign of e^{iu}). The resulting expression is

$$-i\nu z(\nu)=\nu^2-\frac{2\alpha}{3\sqrt{\pi}}\int_0^\infty e^{-\tau}(1-\cosh\nu\tau)\times\left[\frac{v^2-w^2}{v^3}(1-e^{-v\tau})+\frac{w^2}{v^2}\tau\right]^{-3/2}d\tau. \quad (42)$$

Therefore, z is purely imaginary for $\nu<1$ and there is no dissipation at the absolute zero of temperature (a dc field will continue to accelerate the electrons indefinitely). The reason for this behavior is simply that there are no existing phonons for the electrons to scatter off and none can be created by the electrons until the frequency ν of the applied field is high enough to excite the electrons to a state of energy $\hbar\nu$ higher than the energy $\hbar\omega$ needed to create a phonon. If there is a range of frequencies ω down to zero (as for acoustic modes) then a resistance exists at any frequency of the applied field and at zero temperature. In the Fröhlich model it begins at $\nu=1$. Of course, a dc field will eventually speed the electrons up until they can radiate phonons and dissipate energy. However, this is a nonlinear effect in the applied field strength and is not described by a theory of the impedance. For extremely low frequencies ν we can put $(1-\cosh\nu\tau)=-\nu^2\tau^2/2$. The result is that

$$-i\nu z(\nu)=\nu^2\left\{1+\frac{\alpha}{3\sqrt{\pi}}\int_0^\infty u^2e^{-u}\times\left[\left(\frac{v^2-w^2}{v^3}\right)(1-e^{-vu})+\frac{w^2}{v^2}u\right]^{-3/2}du\right\}. \quad (43)$$

The polaron behaves like a free particle with an effective mass. This mass is the same as the one derived in I, by a modification of the variational ground-state energy calculation.

2. General Expression for Dissipation

The analytic properties of $S(u)$ outlined at the beginning of this section allows one to rewrite the expression for the Im$\chi(\nu)$ in a form more convenient for computation. We may write (35a) as

$$\mathrm{Im}\chi(\nu)=\mathrm{Im}\int_0^\infty \sin(\nu u)S(u)du. \quad (44)$$

Using the fact that $S(u)$ is analytic between $u=$real and $u=$real$+i\beta$, we may change the contour of integration in (44) from along the real axis to one which goes first from 0 to $i\beta/2$ up the imaginary axis and then from $i\beta/2$ to $i\beta/2+\infty$ parallel to the real axis. (The closing piece of the contour required at infinity does not contribute.) Because $S(iu)$ and $\sin(i\nu u)d(iu)$ are real, the leg of the contour up the imaginary axis contributes nothing to (44), which requires the imaginary part. The contribution from the remaining part of the contour (from $i\beta/2$ to $i\beta/2+\infty$) gives

$$\mathrm{Im}\chi(\nu)=\sinh(\beta\nu/2)\int_0^\infty \cos(\nu u)\Sigma(u)du, \quad (45a)$$

where $\Sigma(u)=S(u+i\beta/2)$ is given by

$$\Sigma(u)=\int\frac{d^3K}{(2\pi)^3}|C_{\mathbf{K}}|^2\times\tfrac{2}{3}K^2\frac{\cos(\omega_{\mathbf{K}}u)\exp[-\frac{1}{2}K^2\Delta(u)]}{\sinh(\beta\omega_{\mathbf{K}}/2)} \quad (45b)$$

and $\Delta(u)\equiv D(u+i\beta/2)$.

$$\Delta(u)=\frac{w^2}{v^2}\left[\left(\frac{v^2-w^2}{w^2v}\right)\frac{\cosh(\beta v/2)-\cos(vu)}{\sinh(\beta v/2)}+\frac{u^2}{\beta}+\frac{\beta}{4}\right]. \quad (45c)$$

The dc mobility μ for the polaron is given by

$$\mu^{-1}=\lim_{\nu\to 0}\mathrm{Im}\chi(\nu)/\nu.$$

Our results (44), therefore, gives

$$\mu^{-1}=\tfrac{1}{2}\beta\int_0^\infty\Sigma(u)du. \quad (46)$$

For the case of Fröhlich's Hamiltonian, we find that

$$\mathrm{Im}\chi(\nu)=\frac{2\alpha}{3\sqrt{\pi}}\frac{\beta^{3/2}\sinh(\beta\nu/2)}{\sinh(\beta/2)}\left(\frac{v}{w}\right)^3\times\int_0^\infty\frac{\cos(\nu u)\cos(u)du}{[u^2+a^2-b\cos(\nu u)]^{3/2}}, \quad (47a)$$

where

$$a^2\equiv\beta^2/4+R\beta\coth(\beta v/2),\qquad b\equiv R\beta/\sinh(\beta v/2), \quad (47b)$$

and

$$R\equiv(v^2-w^2)/w^2v. \tag{47c}$$

3. Dissipation at Low Temperatures

For low temperatures $e^{-\beta}$ and, therefore, $e^{-\beta v}$ are very much less than one, so that (47a) may be expanded as a power series in b.

$$\mathrm{Im}\chi(\nu)=\frac{2\alpha}{3\sqrt{\pi}}\frac{\sinh(\beta\nu/2)}{\sinh(\beta/2)}\left(\frac{v}{w}\right)^3\int_0^\infty\frac{\cos(\nu u)\cos u}{(u^2+a^2)^{3/2}}\times\left\{1+\frac{3\beta Re^{-\beta v/2}\cos(vu)}{(u^2+a^2)}+\frac{15}{4}\frac{\beta^2R^2e^{-\beta v}}{(u^2+a^2)^2}[1+\cos(2vu)]+\cdots\right\}du. \tag{48}$$

Now an integral like $\int\cos(\lambda u)du/(u^2+a^2)^{3/2}$ falls off exponentially like $(2\pi|\lambda|)^{1/2}(a)^{-3/2}e^{-|\lambda|a}$ as λ increases. Thus, the smallest values of λ count, and these count with the smallest power $e^{-\beta}$ in front. This permits us to select the important terms for each ν. For example, the last term in brackets contributes when $\nu\approx 2v+1$ for there is a contribution from $\cos(\nu u)\cos(u)\cos(2vu)$. The $e^{-\beta v}$ is compensated for by the $e^{\beta(\nu-1)/2}$ in front.

For $\nu<1+v$, and $|1-\nu|>\beta^{-1}$, only the first term in the expansion contributes and we obtain

$$\mathrm{Im}\chi(\nu)\approx\tfrac{2}{3}\alpha\left(\frac{v}{w}\right)^3(1-e^{-\beta\nu})e^{\beta(\nu-1)/2}\times[(|\nu-1|)^{1/2}e^{-\beta|\nu-1|/2}e^{-R|\nu-1|}+(\nu+1)^{1/2}e^{-\beta(\nu+1)/2}e^{-R(\nu+1)}]. \tag{49}$$

As $\beta\to\infty$ this shows a threshold at $\nu=1$. Below $\nu=1$ the result is nearly zero; above, it is $\sim\frac{2}{3}\alpha(v/w)^3(\nu-1)^{1/2}\times\exp[-R(\nu-1)]$. This is the threshold to create one optical phonon from the energy quantum $\hbar\nu$ supplied by the external field. If we have an excess energy $\nu-1$, the final electron has momentum proportional to $(\nu-1)^{1/2}$ and this appears as a factor because of the phase space available. The cross section depends in some way on the frequency above threshold; the factor $\exp[-R(\nu-1)]$ is a rough approximation to this, generated by our model Φ_0.

To study the dependence on β in a little more detail, in case $\nu<1$, (49) can be rewritten as

$$\mathrm{Im}\chi(\nu)\approx\tfrac{2}{3}\alpha(v/w)^3[(1-\nu)^{1/2}e^{-\beta(1-\nu)}e^{-R(1-\nu)}+(1+\nu)^{1/2}e^{-R(1+\nu)}e^{-\beta}-(1-\nu)^{1/2}e^{-R(1-\nu)}e^{-\beta}-(1+\nu)^{1/2}e^{-R(1+\nu)}e^{-\beta(1+\nu)}]. \tag{50}$$

The terms are easily understood. In the first, an electron absorbs a quantum of energy ν to emit a phonon with energy one. The chance that the electron has enough energy, $1-\nu$, to do this is $e^{-\beta(1-\nu)}$. In the second, the electron absorbs a quantum ν and also absorbs a phonon (they are present in number $e^{-\beta}$) so the outgoing electron momentum is $(1+\nu)^{1/2}$. The third corresponds to the electron absorbing a phonon and emitting a quantum $\hbar\nu$ to the electric field. This emission contributes negatively to the energy loss of the electric field. The fourth term results from a particularly energetic electron of energy exceeding $1+\nu$ radiating a phonon and emitting a quantum to the field.

Since the dc mobility is given by the $\mathrm{Im}\chi(\nu)/\nu$ as $\nu\to 0$ (50) gives an expression at low temperatures for the dc mobility of the Fröhlich model. Using our trial functional Φ_0, we find that

$$\mu=\left(\frac{w}{v}\right)^3(3/4\alpha\beta)e^{\beta}\,e^{(v^2-w^2)/w^2v}. \tag{51}$$

The dependence of (51) on the coupling strength α is as α^{-1} for small α (and high β) because the "best" $w\approx v$ for small α (see I). This dependence on α is of course the same as is derived by perturbation theory. As α becomes large ($\alpha\gg 1$) the best parameters satisfy the relation $v/w\sim\alpha^2$. Therefore, the mobility μ becomes proportional to $\alpha^{-7}e^{\alpha^2}$ at high coupling strengths. The result (51) *can not* be compared directly with the results of previous calculations[4,5,16,17] because its temperature dependence is e^{β}/β rather than the e^{β} dependence found in the other approaches. At high β (where these previous calculations are valid), the different dependence on temperature would be experimentally unobservable. However, the origin and significance of this (incorrect) temperature dependence is interesting and will be discussed at some length in a later section.

Returning to our general expression for the $\mathrm{Im}\chi(\nu)$ (48), we see that there are other thresholds at higher frequencies coming from higher terms in the sum (48). For $\beta=\infty$ the next threshold is at $\nu=v+1$, the contribution above threshold being $(2\alpha/3)(v/w)^3(\nu-v-1)^{3/2}\times\exp[-R(\nu-v-1)]$. These higher thresholds correspond to exciting the electron to an excited state of energy v and emitting a phonon. The position of this excited state (at v) and the higher ones along with the selection rule that says these cannot be excited without the emission of a p-state phonon is a fiction supplied by our imitating action Φ_0.

Of course, for strong couplings, there will be such complicated excited states, with partial selection rules leading to a complex curve for $\mathrm{Im}\chi(\nu)$. For strong electron-phonon coupling, the electron is in effect bound in a potential which it makes by distorting the lattice in its neighborhood. If the lattice were held fixed in this distorted state, we would expect the electron to have various excited states in this potential. In fact, the lattice moves so that "states" are unstable, but for large α the excitation energies are of order α^2 larger than the lattice frequency so it cannot follow quickly enough.

[16] F. Low and D. Pines, Phys. Rev. **98**, 414 (1955).
[17] Y. Osaka, Progr. Theoret. Phys. (Kyoto) **25**, 4, 517 (1961).

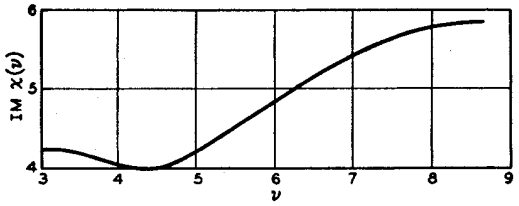

FIG. 1. Plot of Im $\chi(\nu)$ for $\alpha=3$, $w=2.5$, $v=3.4$ and $\beta=100$. ν is plotted in units of the optical mode frequency ω and Im $\chi(\nu)$ is plotted in units of (m/ω).

The Im$\chi(\nu)$ should have a maximum when ν is equal to a frequency which can be absorbed in going to such an excited "state." The widths of these maxima reflect the lifetimes of these "states" for phonon emission. Naturally, we cannot expect our approximate formula (35a) to give such detailed results correctly.[18] It is reassuring, however, that our method gives such a realistic looking behavior, and strongly suggests that it represents a long step forward toward the correct Im$\chi(\nu)$. In the last section we outline some ways of improving the Im$\chi(\nu)$. When the coupling is not too strong ($\alpha\approx 3$), these thresholds are weak and hard to see, and the curves will have a "washed out" appearance. In Figs. 1–3 are given curves of Im$\chi(\nu)$ vs ν for $\alpha=3$, $\alpha=5$, $\alpha=7$ and for low temperatures ($\beta=100$). These figures show the resonance effects very nicely. As a functon of frequency each curve consists of maxima of increasing width. As a function of α the curves show more maxima of decreasing width as α increases. All of the curves were computed numerically on an IBM 7090 computer, using an infinite power series expansion of (47a) in terms of K functions (Bessel functions of imaginary argument). The values of the parameters used were $w=2.5$, $v=3.4$ for $\alpha=3$, $w=2.1$, $v=4.0$ for $\alpha=5$, and $w=1.6$, $v=5.8$ for $\alpha=7$.

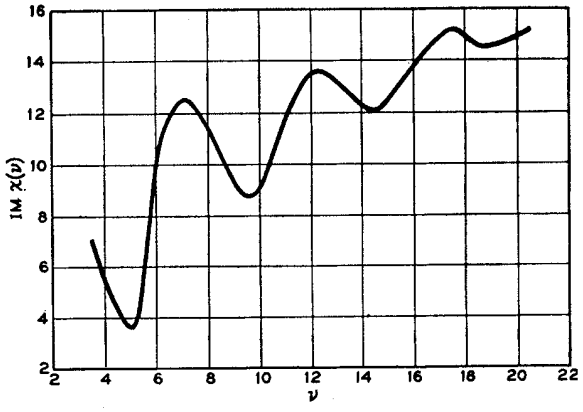

FIG. 2. Plot of Im $\chi(\nu)$ for $\alpha=5$, $w=2.1$, $v=4.0$, and $\beta=100$. ν is plotted in units of the optical mode frequency ω and Im $\chi(\nu)$ is plotted in units of (m/ω).

[18] Pekar, in the strong-coupling limit, using Gaussian trial wave functions for the electron, finds an excited state at precisely v.

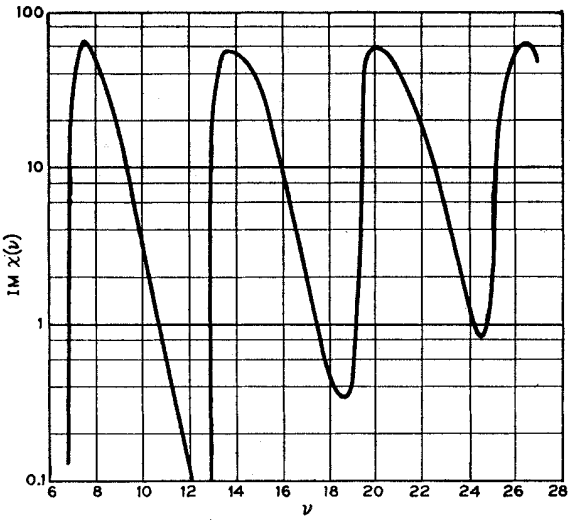

FIG. 3. Plot of Im $\chi(\nu)$ for $\alpha=7$, $w=1.6$, $v=5.8$, and $\beta=100$. ν is plotted in units of the optical mode frequency ω and Im $\chi(\nu)$ is plotted in units of (m/ω).

4. Behavior at High Temperatures

For high temperatures, β is small and (disregard for a moment the variation of w/v with temperature) $\Delta(u)$ varies like u^2/β. Therefore, only small u will be of importance in the exponent, and we can expand $\Delta(u)$ (45c) as

$$\Delta(u)=1/\beta[(u^2+\beta^2/4) -(v^2-w^2/12)(u^2+\beta^2/4)^2+\cdots]. \quad (52)$$

The leading term is, therefore, that of perturbation theory, and our formula is insensitive to the trial functional Φ_0. Actually this is even more accurate than it appears, because as T rises the parameters v and w change in just such a way that v^2-w^2 falls making the approximation (52) still better.[10,10a]

At very high temperatures the perturbation theory works because the electron has on the average, an energy high compared to the lattice frequency. In this case the effective polarization should fall to zero in the limit of infinite temperature. We, therefore, expect that the accuracy of our formula will increase as the temperature rises.

VI. WEAK-COUPLING LIMIT; THE BOLTZMANN EQUATION

In the limit of weak coupling (C_K small or α small) the "best" model parameters are $v\approx w$ or $C\approx 0$. That is, the model of (15) becomes the bare free electron. Perturbation theory is also simply the expansion (16) but with Φ_0 just the free-electron influence functional [i.e., $D(u)=-iu+u^2/\beta$]. Therefore, our series $G_0+G_1+\cdots$ for the admittance agrees with perturbation theory in the weak-coupling limit.

One would expect then, that in the limit of weak coupling the mobility in constant fields obtained here

would be exactly that obtained from the Boltzmann equation using perturbation theory for the electron-phonon scattering cross sections. This turns out to be not true; the question being whether the limit $\nu \to 0$ is taken before or after the limit of weak coupling $|C_{\mathbf{K}}|^2 \to 0$ is taken. A detailed comparison of our result to that of the Boltzmann equation for weak coupling is instructive.

The Boltzmann equation for a particle with momentum distribution $f(\mathbf{P})$ in an electric field $\mathbf{E}(t)$ in the x direction is

$$\partial f/\partial t + E\partial f/\partial P_x = -\int [\gamma(\mathbf{P}\to\mathbf{P}')f(\mathbf{P}) - \gamma(\mathbf{P}'\to\mathbf{P})f(\mathbf{P}')]d^3P'/(2\pi)^3. \quad (53)$$

In (53), $\gamma(\mathbf{P}\to\mathbf{P}')$ is the probability per second that an electron of momentum $\mathbf{P}$ is scattered to momentum $\mathbf{P}'$ by collisions with the phonon gas. This rate, using the usual perturbation theory, is

$$\gamma(\mathbf{P}\to\mathbf{P}') = 2\pi|C_{\mathbf{K}}|^2[(1-e^{-\beta\omega_{\mathbf{K}}})^{-1}\delta(\tfrac{1}{2}P'^2-\tfrac{1}{2}P^2+\omega_{\mathbf{K}}) + (e^{\beta\omega_{\mathbf{K}}}-1)^{-1}\delta(\tfrac{1}{2}P'^2-\tfrac{1}{2}P^2-\omega_{\mathbf{K}})]. \quad (54)$$

The first term in (54) is just the probability to emit a phonon of momentum $\mathbf{K}=\mathbf{P}'-\mathbf{P}$. The second term is the probability to absorb a phonon of momentum $\mathbf{K}$.

The Maxwell distribution, $f_0(P)=(2\pi/\beta)^{-3/2}e^{-\beta P^2/2}$, is a solution of (54) with no electric field since

$$\gamma(\mathbf{P}\to\mathbf{P}')f_0(P) = \gamma(\mathbf{P}'\to\mathbf{P})f_0(P'). \quad (55)$$

If E is a very weak, spatially uniform field varying as $E=E_0e^{i\nu t}$, the deviation of f from equilibrium can be written as $f=f_0[1+E_0e^{i\nu t}P_xh(\mathbf{P})]$, where $h(\mathbf{P})$ is a function of P^2 satisfying [using (54)]

$$(i\nu h+\beta)P_x = -\int \gamma(\mathbf{P}\to\mathbf{P}') \times [P_xh(\mathbf{P})-P_x'h(\mathbf{P}')]d^3P'/(2\pi)^3. \quad (56)$$

The current j is $-E_0e^{i\nu t}\int P_x^2h(\mathbf{P})f_0(P)d^3P$, so the impedance is given by $1/z(\nu)=-\int P_x^2h(\mathbf{P})f_0(P)d^3P$. Multiplying (56) by $P_xh(\mathbf{P})f_0(P)$ and integrating over all $\mathbf{P}$, we find another expression for the impedance:

$$z(\nu)=\frac{\frac{1}{2}\int\int f_0(P)\gamma(\mathbf{P}\to\mathbf{P}')[P_xh(\mathbf{P})-P_x'h(\mathbf{P}')]^2d^3P'd^3P+i\nu\int P_x^2h^2(\mathbf{P})f_0(P)d^3P\,(2\pi)^3}{(2\pi)^3\beta\left[\int P_x^2h(\mathbf{P})f_0(P)d^3P\right]^2}. \quad (57)$$

The integral equation is quite difficult to solve in general. We will content ourselves with an approximate analysis. The expression (57) has been written so that it is stationary[19] for variation of h about the true solution (56). That is, errors in h will appear only in second order in $z(\nu)$.

The simplest approximate solution to (56) is that $h(\mathbf{P})$ is a constant. Then (57) gives

$$z(\nu)-i\nu=\Gamma, \quad (58)$$

where

$$\Gamma=\frac{\beta}{2}\int\int f_0(P)\gamma(\mathbf{P}\to\mathbf{P}') \times(P_x-P_x')^2d^3Pd^3P'/(2\pi)^3. \quad (59)$$

This represents a frequency-independent pure resistance Γ. Thus, $i\nu\Gamma$ should be compared to the $\chi(\nu)$ of (35a). To do so we substitute (54) into (59). One sees that the first term in brackets in (54) gives the same contribution as the second, so calling $\mathbf{P}'=\mathbf{P}\approx\mathbf{K}$ we get (replacing K_x^2 by $K^2/3$)

$$\Gamma=\frac{\beta}{3(2\pi)^2}\int\int K^2|C_{\mathbf{K}}|^2P(\omega_{\mathbf{K}})f_0(P) \times\delta[\tfrac{1}{2}(\mathbf{P}-\mathbf{K})^2-\tfrac{1}{2}P^2-\omega_{\mathbf{K}}]d^3Pd^3K. \quad (60)$$

Next we replace the δ function by $\delta(x)=\int_{-\infty}^{\infty}e^{iux}du/2\pi$. The $\mathbf{P}$ integral is then readily evaluated to give

$$\Gamma=\beta\int d^3K\,(2\pi)^{-3}|C_{\mathbf{K}}|^2\tfrac{2}{3}K^2\int_{-\infty}^{\infty}du\,P(\omega_{\mathbf{K}}) \times\exp[-iu\omega_{\mathbf{K}}-\tfrac{1}{2}K^2(-iu+u^2/\beta)]. \quad (61)$$

Replacement here of u by $u+i\beta/2$ shows that $\Gamma=\mu^{-1}$ from (45a) if $\Delta(u)$ takes on its free-particle value, $u^2/\beta+\beta/4$.

This result is what we expected but there are two points to be made. Firstly, we made no assumption that ν was small in solving the Boltzmann equation. Why then do we not find that $\Gamma=\mathrm{Im}\chi(\nu)/\nu$ as a function of frequency instead of a constant, the limit as $\nu\to 0$ of $\mathrm{Im}\chi(\nu)/\nu$? The answer does not lie in trying to solve (56) more exactly, for if we take a high-frequency case so

[19] If $\nu=0$ (57) is a minimum, giving the useful variational principle for μ^{-1} discussed by Wilson [A. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1959), p. 300].

that the collision term in (56) is negligible compared to the $i\nu$ term, in first approximation $h=(\beta/i\nu)$ and is indeed constant as we assumed. That is, (58) is a *closer* approximation to the prediction of (56) the *higher* the value of ν relative to Γ. The answer is that the original formulation of the Boltzmann equation is faulty at high frequencies. It is assumed that the collisions are made and that between collisions the particle drifts in the electric field. But at higher frequencies new processes are possible in which, for example, the electron absorbs a quantum $\hbar\nu$ from the field and radiates a phonon. In the quantum theory for higher ν this cannot be analyzed as the succession of two independent events. Therefore, at the higher frequencies we may use our formulas (35). If the results deviate from that of the Boltzmann equation we must conclude the latter is inaccurate.

The second point to discuss is this. We did not solve the Boltzmann equation exactly; presumably, therefore, Γ is not exact. Why then is our result μ^{-1} from (51) not asymptotically exact as $\alpha\rightarrow 0$, in spite of our argument that our formulas should be correct in perturbation theory? The reason is easy to see from (57). For *finite* ν, as the coupling gets weaker the collision term falls below ν and Γ is in fact exact. Thus, for any ν *other than zero* in the limit of infinitesimal coupling our result (45) is *exact*. However, for $\nu=0$, to get the exact answer no matter how small the coupling, the full Boltzmann equation must be solved and our result for μ, (45), is only an approximation. [Mathematically, the lack of uniform convergence arises when we invert G and expand, because the resistive part of $\chi(\nu)$ exceeds the leading (reactive) term ν^2 no matter how small the coupling is if $\nu=0$.]

Although not exact, our result (45) for μ^{-1} is still a good approximation to the solution of the Boltzmann equation. The value of μ^{-1} obtained for Fröhlich's model at low temperature from (51) varies as $\beta^{-1}e^{-\beta}$, while from the Boltzmann equation we know that it should vary as a constant times $e^{-\beta}$.[5] But because of the rapid variation of the exponent these two are hard to distinguish (for example, the temperature at which the mobility reaches a given value is imperceptibly different in the two cases). At higher temperatures our results for μ^{-1} (46) no longer behaves as $e^{-\beta}/\beta$. In this case the values obtained from (46) and the Boltzamnn equation would come closer together. (At extremely low temperatures Fröhlich's model, of course, fails. Although acoustic phonons are not very effective, they cannot be disregarded for there are virtually no optical phonons excited.) As a test of our approximate solution of the Boltzmann equation we have also analyzed a system interacting at high temperature with acoustic phonons with $|C_{\mathbf{K}}|^2$ proportional to K^2, $\omega_{\mathbf{K}}=Kv_0$, and $\beta^{-1}>mv_0^2$. Such a coupling leads to a relaxation time for the electrons which varies inversely with their velocity. In this case μ is proportional to β in either theory, but Eq. (46) gives a result $32/9\pi$ or 13% higher than the more accurate solution of (56) given by (59).

VII. SUGGESTIONS FOR IMPROVING ACCURACY

The entire dependence of our result (35) for the polaron impedance on the imitating quadratic influence functional Φ_0 is contained in $D(u)$ which is expressed in terms of the model's response function, $Y_0(\nu)$. If in the expansion we used a more elaborate (but still quadratic) Φ_0, then all results would be the same but with a $D(u)$ coming from a different $Y_0(\nu)$ in (35). What is the best $Y_0(\nu)$ to take? We note that $Y_0(\nu)$ was also the first approximation to the desired function $Y(\nu)=[i\nu z(\nu)]^{-1}$. A natural suggestion, therefore, is that the best $Y_0(\nu)$ is the "true admittance function of the real polaron". Since the true $Y(\nu)$ is unknown, perhaps the next best alternative would be to use a $Y_0(\nu)$ in (35) such that the $z(\nu)$ itself equals $[i\nu Y_0(\nu)]^{-1}$; that is to use a $Y_0(\nu)$ which satisfies (35) self-consistently.

To find a self-consistent $Y_0(\nu)$ is not, in general, easy. However, one might use the results calculated here, for example, and re-insert them as a new $Y_0(\nu)$ in (35) and recalculate $z(\nu)$ to find a second iteration, which might provide an even better impedance with which to recalculate again if necessary. Aside from the great amount of work involved and questions of convergence of the procedure, we cannot even be sure if a substantial improvement would result; however, the following observations do suggest that a self-consistent solution of (35) could result in a considerable increase in accuracy.

In the variational principle of I, one can try a trial action functional S_0 which is more general than the two parameters one employed there and which describes an electron coupled to a general linear system,

$$S_0=\frac{1}{2}\int\left(\frac{d\mathbf{X}(t)}{dt}\right)^2dt+\frac{1}{2}\int h(t-s)x(t)x(s)dtds. \quad (62)$$

Then, putting $h(t)=\int\mathbf{h}(\nu)e^{i\nu t}d\nu/2\pi$, one finds that the function $\mathbf{h}(\nu)$ which gives the lowest energy in the variational principal at zero temperature, satisfies the integral equation

$$\mathbf{h}(\mu)=\frac{2}{3(2\pi)^3}\int\int K^2|C_{\mathbf{K}}|^2d^3K(1-\cos\mu\tau)\times e^{-\omega_{\mathbf{K}}\tau}e^{-\frac{1}{2}K^2\varphi(\tau)}d\tau, \quad (63)$$

where

$$\varphi(\tau)=\int^{\infty}2(1-\cos\mu\tau)\frac{1}{-\mu^2+\mathbf{h}(\mu)}\frac{d\mu}{(2\pi)}. \quad (64)$$

The Eqs. (35) treated as a self-consistent set with $D(u)$ generated from $Y(\nu)=[\nu^2+\chi(\nu)]^{-1}$ can be transformed for $\beta=0$ at least, to exactly this same pair of Eqs. (63) and (64). In this case $\chi(-i\mu)$ replaces $\mathbf{h}(\mu)$. We therefore, can conclude (for $\beta=0$) that if one tries as a trial action functional that for an electron coupled to a general linear system, no such system will produce a better result than one which has an impedance which is

the self-consistent solution of (35).[20] (Possibly the same is true for arbitrary β, but we have not checked this point.) These considerations substantiate further the interpretation of the expansion (38) in terms of an impedance rather than an admittance.

The above point, and the existence of a minimum principle for the Boltzmann equation, suggest that some minimum principle exists for the mobility $\chi(-i\mu)$ in quantum mechanics at arbitrary β.

Another way to improve accuracy is to try to include the next term $(\Phi-\Phi_0)^2$ in the expansion. The integrals to be performed still are of the form required for the evaluation of the $(\Phi-\Phi_0)$ term but with more complicated driving forces E and E'. Although the calculation would proceed straightforwardly it would, in general, be very laborious. However, for certain values of ν and β, one could do what amounts to the same thing in a somewhat easier way, For example, for $\beta^{-1}<\nu<1$ the various terms in (50) could be improved by calculating the appropriate cross sections more accurately. The cross section to absorb a quantum from the electric field and emit a single phonon requires matrix elements of quantities like $x_t \exp(i\mathbf{K}\cdot\mathbf{X}_s)$. Equation (50) corresponds to calculating these with the propagator $\exp(i\Phi_0)$, but an improvement can be made by calculating them with the propagator

$$[1+i(\Phi-\Phi_0)]\exp(i\Phi_0).$$

For zero frequency the Boltzmann equation can be used with the rates $\gamma(\mathbf{P}'\to\mathbf{P})$ calculated with the propagator $\exp(i\Phi_0)$; further improvement would again result by adding a correction for the difference of Φ and Φ_0.

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APPENDIX A

In this appendix we discuss a fundamental path integral (or trace) such as (7) for a single one-dimensional oscillator, in terms of which all other path integrals can be immediately evaluated.

The oscillator Hamiltonian $H=p^2/2+\omega^2q^2/2$. Let

$$U=\exp\left\{-i\int_{-\infty}^{+\infty}[H_t+\gamma(t)q_t]dt\right\},$$

$$U'=\exp\left\{i\int_{-\infty}^{+\infty}[H_t'+\gamma'(t)q'_t]dt\right\},$$

and $\rho_a=e^{-\beta H}/Q$. The $\mathrm{Tr}(U\rho_aU'^{-1})\equiv g$ may be done in several ways, for example by writing it in terms of path integrals and performing the resulting Gaussian integrals.[12] As an alternative method we choose to represent the trace in free oscillator eigenfunctions. In this representation $(\rho_a)_{n,n}=e^{-n\beta\omega}(1-e^{-\beta\omega})$ and

$$g\equiv\sum_{m,n}G_{m,n}G_{m,n}{}^{*\prime}e^{-\beta\omega n}(1-e^{-\beta\omega}), \tag{A1}$$

where $G_{m,n}$ is given in reference (9), Eq. (38) and $G_{m,n}{}'$ is the same expression with γ' replaced by γ.

By expanding

$$\exp[(x+i\xi)(y+i\xi^*)]=\sum_t(x+i\xi)^t(y+i\xi^*)^t/t!$$

in powers of x and y, one can show that $G_{m,n}$ may also be written as

$$G_{m,n}=G_{0,0}(m!n!)^{-1/2}e^{\xi\xi^*}\sum_t\frac{t!(i\xi)^{t-m}(i\xi^*)^{t-n}}{(t-m)!(t-n)!}, \tag{A2}$$

where

$$\xi=i(2\omega)^{-1/2}\int_{-\infty}^{+\infty}e^{i\omega t}\gamma(t)dt. \tag{A3}$$

The summation over m and n in our expression for g can be done by the binomial theorem if one uses this expression for $G_{m,n}$; but the one in reference (4), Eq. (38), for $G_{m,n}{}'$, calling $t=r+v$, where r is the free index in $G_{m,n}{}'$, permits summing first over r then over v. The final result is

$$g=G_{00}G_{00}{}'e^{\xi\xi^*}\times\exp[(1-e^{-\beta\omega})^{-1}(i\xi-i\xi')(i\xi^*-i\xi'^*e^{-\beta\omega})]. \tag{A4}$$

Substituting in for G_{00} and $G_{00}{}'$, we find that

$$g=\exp\left(\tfrac{1}{2}i\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}[\gamma(t)-\gamma'(t)]\{[\gamma(s)+\gamma'(s)]\times y(\omega,t-s)+i[\gamma(s)-\gamma'(s)]a(\omega,t-s)\}dtds\right), \tag{A5}$$

where

$$\begin{aligned} y(\omega,t-s)&=(1/\omega)\sin\omega(t-s), && t>s\\ &=0, && t<s \end{aligned} \tag{A6}$$

and

$$a(\omega,t-s)=(1/2\omega)\cos\omega(t-s)[1+2P(\beta\omega)]. \tag{A7}$$

If $\gamma(\nu)$, $\gamma'(\nu)$, $y(\nu)$, $a(\nu)$ are the Fourier transforms of $\gamma(t)$, $\gamma'(t)$, etc., so that, for example,

$$\gamma(t)=\int\gamma(\nu)e^{i\nu t}d\nu/2\pi, \tag{A8}$$

then the expression for g can be written in Fourier space as

$$g=\exp\left(\frac{i}{4\pi}\int_{-\infty}^{+\infty}[\gamma(-\nu)-\gamma'(-\nu)]\{[\gamma(\nu)+\gamma'(\nu)]\times y(\omega,\nu)+i[\gamma(\nu)-\gamma'(\nu)]a(\omega,\nu)\}d\nu\right). \tag{A9}$$

[20] One probably cannot get $\chi(\nu)$ from (63) and (64) by iteration for one finds $\chi(-i\mu)$ only approximately this way and one *cannot* pass to an accurate value on the real line from an imperfect knowledge on the negative imaginary axis alone.

Here,[11]

$$y(\omega,\nu)=1/(\nu-i\varepsilon)^2-\omega^2 \tag{A10}$$

and

$$a(\omega,\nu)=(\pi/2\omega)[1+2P(\beta\omega)][\delta(\nu+\omega)+\delta(\nu-\omega)]. \tag{A11}$$

For the case of the Hamiltonian (11), we can represent the particle motion by a path integral on $\mathbf{X}(t)$. Then we have in fact a large number of independent oscillators, each coupled to the particle. The $\mathbf{K}$ mode of frequency $\omega_{\mathbf{K}}$ is coupled by a $\gamma(t)=C_{\mathbf{K}}\exp[i\mathbf{K}\cdot\mathbf{X}(t)]$. Each of these modes contributes a factor like (A9) to g so that the final exponent is a sum of contributions from each oscillator mode.

We shall need the functions (A10), (A11) and superpositions of them (sums for various frequencies) which we call $Y(\nu)$, $A(\nu)$. We shall also need another function $D(u)$ defined as

$$D(u)=\pi^{-1}\int_{-\infty}^{+\infty}\{\sin(\nu u)Y(\nu)+[1-\cos(\nu u)]A(\nu)\}d\nu, \tag{A12}$$

and $\Delta(u)$ defined as $D(u+i\beta/2)$. All these functions are related to $Y(\nu)$, in fact to its imaginary part $\mathrm{Im}Y(\nu)$. We need it only for $\nu>0$, since $\mathrm{Im}Y(-\nu)=-\mathrm{Im}Y(\nu)$. For a single oscillator, from (A5) as we have $\mathrm{Im}y(\nu)=-(\pi/2\omega)[\delta(\nu-\omega)-\delta(\nu+\omega)]$. But $a(\nu)$ can also be written as

$$\frac{\pi}{2\omega}\left(\frac{e^{\beta\nu}+1}{e^{\beta\nu}-1}\delta(\nu-\omega)+\frac{e^{-\beta\nu}+1}{e^{-\beta\nu}-1}\delta(\nu+\omega)\right);$$

hence, $a(\nu)=-\coth(\beta\nu/2)\,\mathrm{Im}y(\nu)$. Further, since the poles of a general $Y(\nu)$ lie above the real axis, the real part of $Y(\nu)$ can be obtained from the imaginary part. Proceeding in this way, we find the following expressions for all the functions in terms of $\mathrm{Im}Y(\nu)$:

$$Y(\nu)=\frac{2}{\pi}\int_0^\infty\frac{\mathrm{Im}Y(\mu)\mu d\mu}{(\nu-i\varepsilon)^2-\mu^2} \tag{A13}$$

$$\mathrm{A}(\nu)=-\left(\frac{e^{\beta\nu}-1}{e^{\beta\nu}+1}\right)\mathrm{Im}Y(\nu), \tag{A41}$$

$$D(u)=-\frac{2}{\pi}\int_0^\infty\left(1-e^{i\nu u}+\frac{2(1-\cos\nu u)}{e^{\beta\nu}-1}\right)\mathrm{Im}Y(\nu)d\nu, \tag{A15}$$

and

$$\Delta(u)=-\frac{2}{\pi}\int\frac{[\cosh(\beta\nu/2)-\cos(\nu u)]}{\sinh(\beta\nu/2)}\mathrm{Im}Y(\nu)d\nu. \tag{A16}$$

Although derived for a single oscillator, these relations are linear and hold for any superposition of oscillators.

APPENDIX B

We give here the details of the calculation of the first order correction to G_1. As explained in the text, we can calculate an expression like (28) by substituting (30) and (31) into (20). If we write

$$g^0=\exp\left[\frac{i}{\pi}\int\eta e^{i\nu\tau}(\epsilon e^{-i\nu\sigma}Y_0+i\eta A_0e^{-i\nu\tau})d\nu\right]$$

for the expression (20) calculated for $K=0$, the result (20) with K included as in (30) and (31) is

$$\begin{aligned}R(K,t,s)&=g^0\exp\left\{\frac{iK^2}{4\pi}\int|e^{i\nu t}-e^{i\nu s}|^2(Y_0+iA_0)d\nu\right.\\&\quad+\frac{iK_x}{2\pi}\int(e^{i\nu t}-e^{i\nu s})(\epsilon e^{-i\nu\sigma}Y_0+i\eta A_0e^{-i\nu\tau})d\nu\\&\quad\left.+\frac{iK_x}{2\pi}\int(e^{-i\nu t}-e^{-i\nu s})\eta e^{i\nu\tau}(Y_0+iA_0)d\nu\right\}.\end{aligned} \tag{B1}$$

We shall ultimately only need the result to the first order in $\epsilon\eta$ [see (9)], so differentiating R with respect to η and ϵ, putting $\epsilon=\eta=0$ and calling the result $2r(K,t,s)$, we get (there is a 1/3 for averaging over directions of $\mathbf{K}$)[14]

$$\begin{aligned}r(K,t,s)=\left\{\right.&\frac{i}{2\pi}\int Y_0e^{i\nu(\tau-\sigma)}d\nu\\&-\frac{K^2}{3(8\pi^2)}\int(e^{i\nu t}-e^{i\nu s})e^{-i\nu\sigma}Y_0d\nu\\&\times\int(e^{i\mu t}-e^{i\mu s})iA_0(\mu)e^{-i\mu\tau}\\&\left.+(e^{i\mu t}-e^{-i\mu s})e^{i\mu\tau}[Y_0(\mu)+iA_0(\mu)]d\mu\right\}\\&\times\exp\left[\frac{iK^2}{4\pi}\int|e^{i\nu t}-e^{i\nu s}|^2(Y_0+iA_0)d\nu\right].\end{aligned} \tag{B2}$$

The first term is $G_0(\tau-\sigma)$ times the path integral with $\epsilon=\eta=0$. Such a term arises no matter what we integrate, so in total it gives $G_0(\tau-\sigma)\int e^{i\Phi_0}(\Phi-\Phi_0)\mathfrak{D}\mathbf{X}\mathfrak{D}\mathbf{X}'$. This term just cancels when we remember that we must divide $(\partial^2g/\partial\eta\partial\epsilon)$ by g evaluated at $\epsilon=\eta=0$ for normalization. Therefore, this does not contribute to G_1, the first correction of G from G_0, and we omit it. The other terms are later to be multiplied by a function of $t-s=u$ only, and integrated on t and s. Hence, we let $t=u+s$ and integrate on all s's to get [note $Y_0(-\nu)=Y_0^*(\nu)$,

$A_0(-\nu)=A_0(\nu)]$

$$r(K,t-s)=\left\{-\frac{K^2}{12\pi^2}\int 2(1-\cos\nu u)Y_0(\nu)\right.$$
$$\left.[Y_0(\nu)+2iA_0(\nu)]e^{i\nu(\tau-\sigma)}d\nu\right\}$$
$$\times\exp\left[\frac{iK^2}{2\pi}\int(1-\cos\nu u)(Y_0+iA_0)d\nu\right] \quad \text{(B3)}$$

This will make a contribution to $G_1(\tau-\sigma)$. It is already in the form of a Fourier transform so for the contribution to $G_1(\nu)$ we omit the integral on ν and the factor $e^{i\nu(\tau-\sigma)}$. According to (29) we must next multiply $r(K,t-s)$ by $y(\omega_K,u)+ia(\omega_K,u)$ and integrate on u. This is best done by dividing the range of u from 0 to ∞ and from $-\infty$ to 0, and in the latter putting $u\rightarrow -u$ so that all integrals are over positive u only.

The integral in the exponent is $-K^2/2$ times

$$-\frac{i}{\pi}\int(1-\cos\nu u)[Y_0(\nu)+iA_0(\nu)]d\nu$$
$$=+i[\mathbf{Y}_0(u)+\mathbf{Y}_0(-u)]+2[\mathbf{A}_0(0)-\mathbf{A}_0(u)] \quad \text{(B4)}$$

[where $\mathbf{Y}_0(t)$, $\mathbf{A}_0(t)$ are the inverse transforms of $Y_0(\nu)$, $A_0(\nu)$]. Expression (46) is equal to $D(u)$, defined in (35c) for $u>0$, and $D(-u)$ for $u<0$, since $\mathbf{Y}_0(u)=0$ for $u<0$. Thus, this term in $r(K,t-s)$ contributes a piece

$$-\frac{K^2}{3\pi}Y_0(\nu)[Y_0(\nu)+2iA_0(\nu)]$$
$$\times\int_0^\infty(1-\cos\nu u)[y(\omega_K,u)+y(\omega_K,-u)$$
$$+2ia(\omega_K,u)]e^{-\frac{1}{2}K^2D(u)}du. \quad \text{(B5)}$$

Adding the three other corresponding pieces from $\exp\{i\mathbf{K}\cdot[\mathbf{X}'(t)-\mathbf{X}'(s)]\}$, etc., multiplying by $|C_K|^2$, and integrating over K [see Eq. (30)] gives the first term in (35). The second term is gotten in an analagous way from Φ_0. We need to expand our expression for $r(K,t-s)$ just to first order in K^2. The terms like $e^{-\frac{1}{2}K^2D(u)}$ are replaced by one. The resulting expression is an integral on u, $\int_0^\infty(1-e^{i\nu u})S_0(u)du$, where

$$S_0(u)=\mathrm{Im}C\left(e^{iwu}+\frac{2\cos wu}{e^{\beta w}-1}\right)=C\sin wu.$$

The integral on u gives $C\nu^2/w(\nu^2-w^2)$, as in the last term of (34).

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Phonon Frequency Distribution in Vanadium at Several Temperatures

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The energy spectrum of a beam of 4 Å neutrons scattered by vanadium has been measured using a conventional time-of-flight technique. Analysis of the results using the methods described by Placzek and Van Hove has been carried out to determine the frequency distribution of phonons in vanadium. The sample was held at 206, 300, and 860°K, and the effect of temperature on the phonon spectrum was observed.

The lower part of this spectrum is not "Debye" in form, but the departures from this simple shape become less at increasing temperatures. The upper peak in the phonon spectrum previously observed is relatively insensitive to temperature. A high-energy tail to the observed neutron spectrum is discussed; it is probable that this indicates a tail to the phonon distribution, which previous measurements at room temperature had failed to reveal.

1. INTRODUCTION

SINCE Born and von Kármán[1] published their theory of vibrations in crystal lattices, considerable attention has been devoted to the calculation of the distribution of frequencies and the variation of specific heat with temperature. Blackman[2] has given a review of the techniques of calculation, the results of the calculations, and their comparison with measured specific heat curves. Recently, frequency distributions have been studied by neutron scattering techniques which allow much more detailed information to be obtained than with the older methods. Scattering data obtained using vanadium can be interpreted without difficulty, as the scattering is almost entirely incoherent. This material has been the subject of experiments by Stewart and Brockhouse[3] and by Eisenhauer *et al.*[4] Unfortunately (as discussed below), these experiments lack the pre-

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