Electron mobility in semiconductors

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(Received 16 March 1981; revised manuscript received 29 March 1982)

We treat the problem of a single electron interacting only with the lattice vibrations of its host crystal with and without the application of a weak electric field. A Markovian solution which applies in the limit of a large number of collisions is given to the exact integro-differential equation for the electron's density matrix. This equation was derived earlier from the path-integral representation of Feynman *et al.* for a polaron. The solution, which corresponds to the observed phenomenological description, averages out memory effects. The Einstein diffusion relation is found to hold closely, and realistic results are obtained for the temperature dependence of the mobility and for the deformation-potential coupling constants of silicon and germanium.

I. INTRODUCTION

We treat the problem of a single electron interacting only with the lattice vibrations of the crystal under the influence of a weak electric field E (linear mobility, effective-mass approximation, nondegenerate semiconductor). The desire to place electron transport in crystals on a first-principles basis has existed for a long time.[1,2] For weak electric fields there is the Kubo formula,[3] with the work, for example, by Baumann and Ranninger summing ladder diagrams to obtain the standard Boltzmann result.[4] The Boltzmann or rate-equation approach is tied to a model of electron collisions with phonons, with total energy conserved. However, the collisions may be too frequent for conservation. The question of which diagrams to retain is a difficult one.

Perhaps, one ought to recall that in a typical semiconductor at room temperature the electron's thermal velocity is $\simeq 2 \times 10^7$ cm/sec whereas with $E \simeq 100$ V/m its drift velocity may be 2000 cm/sec. Accordingly, we are suggesting trying to represent the strongly interacting electron in a different way, more closely related to the conduction phenomena as they are observed, rather than using perturbation schemes always actually based on a noninteracting situation.

In a previous publication with Heinekamp[5] we were influenced by the early experiments of Haynes and Westphal,[6] where a temporal square-wave distribution in the density of carriers injected at one end of the sample diffuses as a well-defined Gaussian, the Einstein diffusion relation $(D = kT\mu)$ being rather closely satisfied.[7] We remarked that the electron-phonon collisions are averaged over in a way which we find reminiscent of the averaging of individual collisions between the colloid particle and impinging molecules in studies of Brownian motion.[8] We showed that the bivariate solutions in velocity $\vec{u}$, coordinate $\vec{r}$ as given for Brownian motion by Chandrasekhar can be taken over into a quantum-mechanical formulation by drawing on Wigner distribution functions.[9]

We note that in the experiments evidence of individual collisions with phonons is neither sought nor observed. It thus is in harmony with the principles of quantum mechanics to try to base the problem on continuous distribution functions without probing individual collisions with phonons. After all, interaction takes place at all times with all modes. From our numerical results, however, we shall be able to infer that the "collisions" happen so often that the total energy is not well defined between them. The present treatment, unlike the earlier one,[5] no longer limits the phonon wave vectors to being small in any way except for their actual confinement to a single Brillouin zone, and is truly physical.

We start with the double path-integral expression for the density matrix $\rho(\vec{R}, \vec{R}', t)$ for a single electron developed by Feynman, Hellwarth, Iddings, and Platzman, in which the phonons appear only implicitly as harmonic modes, homogeneous and driven by the electron.[10] It follows that dielectric screening by the lattice is automatic and no explicit equivalent of renormalization procedures is called for. However, to unravel the results we will obtain in terms of those obtained with diagrammatic procedures is apt to be difficult, and beyond our aims here. Different approaches to calculating polaron mobility using the Feynman formula and a

Boltzmann and/or variational techniques[10-13] have been carried out in the past. Our approach is suggested by classical Brownian motion studies. Although the previous calculations were generally for polar coupling (the polaron), we are for the present interested in comparing with the experiments of Haynes and Westphal,[6] and the Bell Telephone Labs Transistor Summer School,[7] that is for deformation-potential coupling to the acoustic modes of silicon and germanium.

Just as the Feynman path-integral formulation of quantum mechanics can be reduced back to the Schrödinger equation, so too, as we showed earlier, can the double path-integral formula of Feynman, Hellwarth, Iddings, and Platzman be reduced to an integro-differential (id) equation, which we give below as Eq. (4).[14] We then convert this equation to Wigner's variables $\vec{r}$ and $\vec{u}$, with the density matrix becoming a Wigner function. It will be recalled that the Wigner function resembles a classical distribution function as nearly as is possible for a quantum-mechanical entity. We attempt a solution of this id equation with an ansatz which is formally only a slight generalization of Chandrasekhar's solution in classical variables $\vec{r}$ and $\vec{u}$ to Brownian motion. The program is to find from this microscopic analysis values for the parameters that characterize the ansatz, that is, mobility and diffusion constants. These will be functions of temperature and semiconductor properties, notably the deformation-potential coupling constants.

The main approximation is that the ansatz is, as is well known from Brownian motion studies, Markovian.[8] As we shall see, it splits naturally and uniquely into short-time propagators for any assigned division of time into discrete intervals. This feature allows us to substitute the ansatz into our id equation. The id equation, being exact, is non-Markovian. Nevertheless, we shall see that the ansatz is a solution to Eq. (4), exact to order $1/n$, with n the number of "elapsed collisions." [Our interest here is in "steady-state," or, perhaps, one may say macroscopic experiments, where as for Haynes and Westphal, n is typically of the order of 10^8. n is given by $\beta t'$, where β, while defined as an unknown parameter in the ansatz, will turn out to be related to the electrical mobility μ as $\mu = e/(m\beta)$. One thus knows from experiment that $\beta^{-1} \simeq 5 \times 10^{-13}$ sec. In the experiments, t', the time between injection and observation, was of the order of 10^{-4} sec.]

Although we have a solution, this does not mean that we have the steady-state solution to the equation of motion, but only the solution in a Markovian subspace—the best Markovian solution. Since it is a solution, attempts to find Markovian corrections within the stated accuracy lead to no corrections.

We base the significance of this paper on its close relationship to observation. The ansatz corresponds precisely to the situation of a diffusing electron as first observed and measured by Haynes and Westphal.

Further, the Einstein diffusion relation, which is observed to hold closely in the experiments is a hallmark of Markovian propagation. Inspection of the actual calculation will show that the influence on the "potential" (i.e., on the Feynman influence function) of fluctuations in the velocity $\vec{u}$ owing to interactions with phonons results from a very-short-time interval before the time of observation t. In typical semiconductors this interval is of order $10^{-2}\beta^{-1}$ sec or less ($\sim 10^{-15}$ sec). (It is during this short-time interval that conservation of virtual energy does not hold.) This interval is too short for the lattice to respond. Since it is the condition of the lattice which constitutes the memory, we do not foresee much recording (or screening) of the fluctuations. Thus, we do not expect that the behavior of the distribution function which is not subject to direct observation will upset the observed Markovian character of the propagation. A self-consistent Markovian distribution becomes a reasonable solution. We note that the stronger the coupling, that is, the shorter β^{-1}, the less important memory effects become, and the more suitable becomes the Markovian distribution function approach. Further discussion of these matters is best left to when we can show the nature of any non-Markovian modifications. One of the points of this calculation is that in any case it provides a representation or zero-order scheme to build on. We see it as occupying roughly the same role as an effective-field theory in the many-body problem. Correlations (memory effects) are being averaged out.

In as much as comparison with experiment is possible without very elaborate calculation, that is, without explicit attention to anisotropy, umklapp and possible departure from deformation-potential coupling, we have done so. We find in Sec. III that the results are encouraging. They agree surprisingly well with the general results of the early experiments on silicon and germanium. We feel that more detailed calculations on specific materials are best postponed until the limitations of the method suggested here can be clarified by look-

ing at non-Markovian modifications. In the next section we show how the macroscopic nature of the steady state simplified the mathematics to where we can easily get to the solution.

II. CALCULATIONS

We start with the well-known classical problem of Brownian motion on which we wish to model our quantum-mechanical approach to electrical conductivity. The Fokker-Planck equation describing Brownian motion has with a distribution function W' the well-known form[8]

$$\frac{\partial W'(\vec{r}\,',\vec{u}\,',t';\vec{r}_0',\vec{u}_0')}{\partial t'}+\vec{u}\,'\cdot\vec{\nabla}_{r'}W'$$

$$=\beta\vec{\nabla}_{u'}\cdot(W'\vec{u}\,')+q\nabla^2_{u'}W'\;,\quad(1a)$$

where q and β are here mechanical constants measuring, respectively, velocity flucutations and viscous friction. The normalized bivariate solution $W'(\vec{r}\,',\vec{u}\,';\vec{r}_0',\vec{u}_0')$ in velocity coordinates $\vec{u}\,',\vec{u}_0'$ and position coordinates $\vec{r}\,',\vec{r}_0'$ given by Chandrasekhar can be written as

$$W'(\vec{r}\,',\vec{u}\,',t';\vec{r}_0',\vec{u}_0')=(8\pi^3\Delta^{3/2})^{-1}\exp[\,-(a'Q'^2+2h'\vec{Q}\,'\cdot\vec{P}\,'+b'P'^2)/2\Delta\,]$$

$$(1b)$$

with

$$\vec{Q}\,'=\vec{u}\,'-\vec{u}_0'e^{-\beta t'}\;,\quad(1c)$$

$$\vec{P}\,'=\vec{r}\,'+\vec{u}\,'/\beta-\vec{r}_0'-\vec{u}_0'/\beta\;,\quad(1d)$$

$$a'=(2q/\beta^2)t'\;,\quad(1e)$$

$$b'=(q/\beta)(1-e^{-2\beta t'})\;,\quad(1f)$$

$$h'=-(2q/\beta^2)(1-e^{-\beta t'})\;,\quad(1g)$$

$$\Delta=a'b'-h'^2\;.\quad(1h)$$

This solution corresponds to a δ function initial condition defining the variables $\vec{r}_0',\vec{u}_0'$. For Fourier representation we shall associate with $\vec{Q}\,'$ a wave vector $\vec{k}\,'$, with $\vec{P}\,'$ a wave vector $\vec{w}\,'$. It is very convenient to go to dimensionless quantities, $t,\vec{r},\vec{u},\vec{w},\vec{k}$:

$$t=\beta t'\;,\quad(2a)$$

$$\vec{r}=\vec{r}\,'(q/\beta^3)^{-1/2}\;,\quad(2b)$$

$$\vec{u}=\vec{u}\,'(q/\beta)^{-1/2}\;,\quad(2c)$$

$$\vec{w}=\vec{w}\,'(q/\beta^3)^{1/2}\;,\quad(2d)$$

$$\vec{k}=\vec{k}\,'(q/\beta)^{1/2}\;.\quad(2e)$$

Here time is measured in units of the "relaxation time" β^{-1} and lengths in terms of the Einstein diffusion length $(q/\beta^3)^{1/2}\equiv(D/\beta)^{1/2}$, where D is the diffusion constant.

In terms of these dimensionless quantities

$$W(\vec{r},\vec{u},t;\vec{r}_0,\vec{u}_0)\equiv W'(\vec{r}\,',\vec{u}\,',t';\vec{r}_0',\vec{u}_0')$$

has a simple Fourier representation. We have

$$W(\vec{r},\vec{u},t;\vec{r}_0,\vec{u}_0)\equiv\int\int d^3k\,d^3w\,e^{i\vec{k}\cdot\vec{Q}}$$

$$\times e^{i\vec{w}\cdot\vec{P}}\,\hat{W}(\vec{k},\vec{w},t)\;,$$

$$(3a)$$

$$\hat{W}(\vec{k},\vec{w},t)=(\beta^2/q)^3(2\pi)^{-6}e^F\;,\quad(3b)$$

$$F=-\tfrac{1}{2}(bk^2-2h\vec{k}\cdot\vec{w}+aw^2)\;,\quad(3c)$$

$$a=2t\;,\quad(3d)$$

$$b=1-e^{-2t}\;,\quad(3e)$$

$$h=-2(1-e^{-t})\;.\quad(3f)$$

We may note that as $t\to\infty$ and starting conditions are damped out one finds that W becomes the simple product of a spatial Einstein diffusion with diffusion constant $D=q/\beta^2$, and a Maxwell velocity distribution providing $(q/kT)=(\beta/m)$, m mass of diffusion particle,[8] i.e.,

$$W\to\exp[\,-\beta^2(\vec{r}\,'-\vec{r}_0')^2/4qt'\,]$$

$$\times\exp(\,-\beta u'^2/2q\,)\;.\quad(3g)$$

As mentioned in the Introduction, Feynman et al. carry out a calculation in which they eliminate from the problem the phonon system. The latter is assumed to be in thermal equilibrium at time $t=0$ when the electron is introduced. No further information about the phonons becomes evident beyond this initial time. (With only one electron in the crystal, we, presumably, need not be concerned with the fact that the system is closed, and no heat dissipation to surroundings is provided for.) Feynman et al. replace the ordered operators which appear in their expression, thereby obtaining the density matrix ρ in the form of a double path-

integral. This new form is certainly easier to work with. We shall find convenient the following abbreviations:

$$\rho(t,0) \equiv \rho(\vec{R}, \vec{R}\,'; t; \vec{R}_0, \vec{R}_0') \, ,$$

$$\rho(t,s,0) \equiv \rho(\vec{R}, \vec{R}\,'; t; \vec{R}_s, \vec{R}_s', s; \vec{R}_0, \vec{R}_0') \, .$$ (4a)

Here $\vec{R}, \vec{R}\,'; \vec{R}_s, \vec{R}_s', \vec{R}_0, \vec{R}_0'$ are the coordinate parameters at times $t, s, 0$, respectively. $\rho(t;s;0)$ is $\rho(t;0)$

"opened" at time s,[14] i.e., the integrals over the coordinates $\vec{R}_s, \vec{R}_s'$ in the path integral which yields $\rho(t,0)$ have not been taken. Thus

$$\rho(t;0) = \int \int \rho(t;s;0) d^3R_s d^3R_s' \, .$$ (4b)

The work of Feynman et al. gives explicit expression for ρ opened everywhere, that is for the kernel of the path-integral, which, therefore, is defined. The integro-differential equation for ρ derived earlier reads[5,14]:

$$\frac{\partial \rho(\vec{R}, \vec{R}\,'; t; \vec{R}_0, \vec{R}_0')}{\partial t} + \hbar/(2mi)(\nabla_R^2 - \nabla_{R'}^2)\rho(\vec{R}, \vec{R}\,'; t; \vec{R}_0, \vec{R}_0')$$

$$= \frac{-1}{i} \int \int_{-\infty}^{\infty} S_1 v_1 \rho(t;s;0) d^3R_s d^3R_s' - \int \int_{-\infty}^{\infty} S_2 v_2 \rho(t;s;0) d^3R_s d^3R_s' \, .$$ (4c)

S_1, S_2 are, respectively,

$$S_1, S_2 = \frac{2}{\hbar\beta} \int_0^t ds \sum_K |C_K|^2 \left[\sin\frac{\omega_K}{\beta}(t-s), \xi_K \cos\frac{\omega_K}{\beta}(t-s) \right]$$ (4d)

and

$$v_{1,2} = e^{-\vec{K}\cdot(\vec{R} - \vec{R}_s)} - e^{i\vec{K}\cdot(\vec{R}\,' - \vec{R}_s)} \pm e^{i\vec{K}\cdot(\vec{R} - \vec{R}_s')} \mp e^{i\vec{K}\cdot(\vec{R}\,' - R_s')} \, .$$ (4e)

$\xi_K = 2\bar{n}_K + 1$, $\bar{n}_K$ is the thermal number of phonons in longitudinal mode $\vec{K}$, and ω_K is the mode frequency. The sums over $\vec{K}$ and the integral over s in S_1, S_2 extend to all relevant quantities on their right.

As stated in the Introduction we are proposing to use Wigner functions and Wigner variables $\vec{r}$ and $\vec{u}$ in our treatment. We define $\rho_w(\vec{r}, \vec{u}, t; \vec{r}_0, \vec{u}_0)$ and these variables in Eq. (5) below. We recall that the Wigner scheme is close to classical statistics in that integrating $\rho_w(\vec{r}, \vec{u})$ over u will give the true quantum-mechanical spatial distribution,[9,15] the procedure we follow. Likewise, integrating $\rho_w(\vec{r}, \vec{u})$ over $\vec{r}$ would give the true momentum distribution.

The Wigner variables are defined by first letting

$$\vec{r} = (\vec{R} + \vec{R}\,')/2 \, ,$$ (5a)

$$\vec{y} = (\vec{R} - \vec{R}\,') \, .$$ (5b)

We then have

$$\rho_w(\vec{r}, \vec{u}, t; \vec{r}_0, \vec{u}_0) = (m/h)^3 \int \int \exp[-im/\hbar(\vec{y}\cdot\vec{u} - \vec{y}_0\cdot\vec{u}_0)]$$

$$\times \rho(\vec{r} + \vec{y}/2, \vec{r} - \vec{y}/2, t; \vec{r}_0 + \vec{y}_0/2, \vec{r}_0 - \vec{y}_0/2) d^3y \, d^3y_0 \, .$$ (5c)

If we need to close at an intermediate time $s < t$, it can be done in the Wigner representation (using u_s rather than y). We insert the operator

$$O_p \equiv \delta^3(\vec{y}\,' - \vec{y}_s) = (m/h)^3 \int_{-\infty}^{\infty} e^{-im(\vec{u}_s/\hbar)\cdot(\vec{y}\,' - \vec{y}_s)} d^3u_s \, .$$ (5d)

This gives, omitting the $\vec{r}$ arguments, for ρ expressed in variables $\vec{y}$,

$$\int_{-\infty}^{\infty} \rho(\vec{y}, \vec{y}_s)\rho(\vec{y}_s, \vec{y}_0) d^3y_s = \int_{-\infty}^{\infty} \rho(\vec{y}, \vec{y}\,') O_p \rho(\vec{y}_s, \vec{y}_0) d^3y_s d^3y'$$ (5e)

$$= \int_{-\infty}^{\infty} \rho(\vec{y}, \vec{u}_s)\rho(\vec{u}_s, \vec{y}_0) d^3u_s \, .$$ (5f)

With these definitions we change Eqs. (4) to Wigner variables by transforming both sides of Eq. (4c). The change from $\vec{y}$ to $\vec{u}$ of the factor $e^{i\vec{K}\cdot(\vec{R}-\vec{R}_s)}$ on the right of Eq. (4c), for example, involves the integral

$$(m/h)^3 \int e^{i\vec{K}\cdot(\vec{r}-\vec{r}_s)} e^{i[\vec{K}\cdot\vec{y}/2 - m\vec{u}\cdot\vec{y}/\hbar - \vec{K}\cdot\vec{y}_s/2]} \rho(\vec{r}+\vec{y}/2,\vec{r}-\vec{y}/2)d^3y \ . \tag{6a}$$

The factor $\exp i\vec{K}\cdot\vec{y}/2$ thereby has the effect of attaching a recoil of $-h\vec{K}/2m$ to $\vec{u}$ in $\rho_w(\vec{r},\vec{u})$. Similar recoils attach to $\vec{u}_s$ at intermediate times s. For example, using Eq. (5d),

$$\int_{-\infty}^{\infty} \rho(\vec{y},\vec{y}_s)e^{-i\vec{K}\cdot\vec{y}_s/2}\rho(\vec{y}_s,\vec{y}_0)d^3y_s = \int_{-\infty}^{\infty} \rho(\vec{y},\vec{y}_s)e^{im\vec{u}_s/\hbar\cdot(\vec{y}_s-\vec{y}')}e^{-i\vec{K}\cdot\vec{y}_s/2}\rho(\vec{y}',\vec{y}_0)d^3y_s d^3u_s d^3y'$$

$$= \int_{-\infty}^{\infty} \rho(\vec{y},\vec{u}_s - \hbar\vec{K}/2m)\rho(\vec{u}_s,\vec{y}_0)d^3u_s \ . \tag{6b}$$

In this sense instantaneous electron-phonon collisions are being represented on the right-hand side of Eq. (4c).

As explained in the Introduction we are proposing to use a slightly generalized form of Eq. (1b) as a trial solution for our quantum-mechanical problem of an electron interacting with lattice vibrations, by altering Eqs. (3d) and (3f) to read

$$a = a_0 2t \ , \tag{7a}$$

$$h = -2h_0(1-e^{-t}) \ , \tag{7b}$$

all other features of Eqs. (3) remaining the same. As we shall see a_0, h_0 which are dimensionless, will, for our materials, not depart much from unity. We shall see that their actual values are of physical significance. It might be thought that Eqs. (3) are encumbered with complications needless for our purposes. We show in Appendix A, then, in fact, they are necessary either for expediency or for physical consistency.

Also, as noted, the actual problem is not Markovian, the deformable lattice acts as a memory storing the effects of the motion (path) of the electron. That this is the case is evident from the form of Eq. (4c), where $\rho(t,0)$ is obtained in terms of $\rho(t,s,0)$, i.e., ρ opened at time s, and, similarly, one can derive an equation for ρ opened at one place in terms of ρ opened at two places, and so on. This situation is very similar to the electron-gas problem as discussed, for example, in the well-known paper of Martin and Schwinger.[16] This memory effect is averaged out in the Brownian motion problem where the random medium is assumed unaffected by the particle. As already stated, our Markovian ansatz contains the corresponding limitation.

We now draw attention to the factor $\exp(-aw^2/2)$ or $\exp(-w^2t)$ in F of Eq. (3). This is the Fourier representation of $\exp-(\vec{r}-\vec{r}_0)^2/4t$, simple diffusion in dimensionless variables. Recalling from the Introduction that we want $t \sim 10^8$ we

see that w, confined to be of the order of $t^{-1/2}$, will be small. At the same time we are only interested in the electron's mobility, i.e., its spatial distribution, which means we finally integrate our distribution function over $\vec{u}$.

This gives $\vec{k} = -\vec{w}$, so that we may restrict ourselves to small values of $\vec{k}$ throughout the calculation. [We note from Eq. (3b) that the wave vector associated with $\vec{u}$ is $(\vec{k}+\vec{w})$. In the usual bare electron-phonon representation, barring umklapp, quasimomentum is conserved in collisions, and the electron wave vector changes by $\pm\vec{K}$, the phonon wave vector. In the Wigner variable scheme $(\vec{k}+\vec{w})$ is conserved, the recoil attaching itself to $\vec{u}$, as we have seen in connection with Eqs. (6).] These are the underlying reasons that $\vec{w}$ and $\vec{k}$ will be vanishingly small, and one can find a Markovian solution accurate to within factors of order $1/t$.

The small modification in Eqs. (7a) and (7b) is the only change we need make to Eqs. (3) to define the trial ansatz $\rho_{wa}(\vec{r},\vec{u},t;\vec{r}_0,\vec{u}_0)$ and its Fourier transform $\hat{\rho}_{wa}(\vec{k},\vec{w},t)$.

In Wigner variables the left-hand side of Eq. (4c) is just[5] $\partial\rho_{wa}/\partial t + \vec{u}\cdot\vec{\nabla}_r\rho_{wa}$. Substitution of Eqs. (3a)–(3d) and Eqs. (7a) and (7b) for ρ_{wa} yields for the left-hand side of Eq. (4c) (see Appendix B):

$$\frac{\partial\rho_{wa}}{\partial t} + \vec{u}\cdot\vec{\nabla}_r\rho_{wa} = \int d^3k\,d^3w\,e^{i\vec{K}\cdot\vec{Q}}e^{i\vec{w}\cdot\vec{P}}$$

$$\times \hat{\rho}_{wa}(\vec{k},\vec{w},t)q(\vec{k},\vec{w}) \ , \tag{8a}$$

$$q(\vec{k},\vec{w}) = [\vec{k}\cdot\vec{w} + w^2(-a_0 + 2h_0)] \ . \tag{8b}$$

The right-hand side of Eq. (4c) is first transformed to Wigner variables, as shown for the first term by Eqs. (6a) and (6b). The ansatz of Eqs. (1) has the properties of a Markovian propagator as can be best seen from its Fourier transform.

$\rho_{wa}(t,s,0)$ is the product of $\rho_{wa}(t,s)$ and $\rho_{wa}(s,0)$. Since Fourier representations for $\rho_{wa}(t,s), \rho_{wa}(s,0)$ are available from Eqs. (3) it is a straightforward matter to integrate over $\vec{r}_s$ and $\vec{u}_s$, now replacing $\vec{R}_s$ and $\vec{R}'_s$ at intermediate time s, giving the usual conservation of wave vectors there. In Appendix B we exhibit this calculation. We now expand the right side in a Taylor series in $\vec{k}, \vec{w}$ to second order. No constants appear in the expansion, and reflection symmetry in phonon wave-vector space eliminates odd-order terms. From what we have said about the confinement of $\vec{w}$ and $\vec{k}$ to values $\simeq 1/\sqrt{t}$, higher-order even terms in the Taylor expansion can be expected to lead to corrections in ρ_w of at most order t^{-1}. Straightforward but somewhat tedious calculation now yields a result having exactly the same form as the right-hand side of Eq. (8a). However, in the resulting quadratic form q in k^2, $\vec{k} \cdot \vec{w}, w^2$, the coefficient of k^2 does not formally vanish. Since this result and the right-hand side of Eq. (8a) are supposed to represent the same function, i.e., have equal Fourier components, we equate coefficients in the two forms q. This yields Eqs. (9a)−(9c):

$$h_0 = (1+a_0)/2 ,\tag{9a}$$

$$a_0 = \frac{-LG_1 \exp(-T)}{\{G_2[1-\exp(-T)]\}} ,\tag{9b}$$

$$1 = (2L/\beta)[2a_0 G_2(T) + LG_1] ,\tag{9c}$$

$$G_1 = (S_1 \sin\Lambda - S_2 \cos\Lambda)(K^2/3)\exp(-R) ,\tag{9d}$$

$$G_2 = (S_1 \cos\Lambda + S_2 \sin\Lambda)(K^2/3)\exp(-R) ,\tag{9e}$$

$$R = a_0 K^2 [\exp(-T) - 1 + T]$$
$$\simeq a_0 Y^2/2 ,\tag{9f}$$

$$\Lambda = LK^2 [1 - \exp(-T)] \simeq LKY ,\tag{9g}$$

$$L = \hbar\beta/(2k_B T_p), \quad Y = KT, \quad T = t - s ,\tag{9h}$$

where T_p is temperature, and Y rather than T is the natural variable of integration.

Before going on to discuss numerical results, we take up the seemingly arbitrary choice of the functions $a(t), b(t), h(t)$. If we had left $a(t), b(t), h(t)$ as undetermined functions, the three algebraic equations leading to (9a)−(9c) would be replaced by three coupled integro-differential equations with independent variable t, closely related to Volterra's equation of the second type. Like that equation they would have unique solutions[17]—the same as we took from the Brownian motion problem.

III. RESULTS

One can show that the inclusion of an electric field $\vec{E}$ in Eq. (4c) will shift $\vec{r}$ by exactly $-(e\vec{E}t'/m\beta)$ (see Appendix C). The spatial distribution of ρ_{wa} upon integrating Eq. (1) over u, will thus assume the form

$$\exp\left[\frac{-\beta^2(\vec{r}' - \vec{r}'_0 - e\vec{E}t'/m\beta)^2}{(4qt'a_0)}\right] .$$

As we discuss in the next paragraph, ultimately we must set q/β equal to $k_B T_p/m$, k_B being Boltzmann's constant. It follows that the Einstein diffusion relation,

$$D \equiv qa_0/\beta^2 = \mu k_B T_p/e \equiv k_B T_p/(m\beta) ,$$

where μ is the mobility, is satisfied providing $a_0 = 1$. Somewhat closer examination of Eq. (9b) shows that a_0 will generally be close to unity, and computer calculations yield a self-consistent solution [a_0 also appears on the right in Eq. (9f)] of 1.02 for $m = m_e$ Ge electrons, and 1.03 for heavy-mass silicon electrons, the latter in exact agreement with measurement.[11]

Equation (9c) is insufficient to determine both q and β. We believe that our assumption that a steady-state evolution for the density matrix is occuring brings about the necessity of an *ad hoc* introduction of the constant lattice temperature, already contained in the parameters ξ_K [see Eq. (4)]. To avoid this procedure one would have to study the actual relaxation process of an electron to thermal equilibrium. Integration of Eq. (1) over $\vec{r}$ yields the Maxwell velocity distribution for electrons, or alternatively, the fluctuation-dissipation theorem, providing we set q/β equal to $k_B T_p/m$. The latter theorem is an exact result for small electric fields[18] which limits our treatment to the small-E (or linear) problem. (Possible extension to hot electrons suggests itself here, but this leads to many questions which we cannot answer at this point.) We can now use Eq. (9c) to determine the temperature dependence for β, and, using experimental room-temperature mobilities,[19] find the deformation potentials E as a measure of electron-phonon coupling.[20] Performing our Y and K integrations on a computer, we find that the values of β follow a $T_p^{3/2}$ dependence to within 5% between 150 and 450 K for both semiconductors, and virtually no dependence of this result on m. We find values of 1.91 $(m/m_e)^{-3/4}$ eV for E_{Ge} and 2.32 $(m/m_e)^{-3/4}$ eV for E_{Si}, m_e being the free-

electron mass, assuming isotropic masses.

A ubiquitous factor $K^3\exp(-K^2L^2/2)$ appears upon integrating over $\vec{Y}$ if one uses the closely approximate forms for R and Λ in Eqs. (9). [See Appendix D. As we show there this factor as integrand in Eq. (9c) yields a $T_p^{3/2}$ dependence for β when the B zone is extended to infinity.] As a result the greatest contributions to integrals defining G_1 and G_2 come at $K\simeq\sqrt{3}/L$ and drop off rapidly thereafter, or at about 100 for Si and 300 for Ge at room temperature, and in the Y integrals at $Y=KT\simeq1$. Remembering that T is measured in units of $(1/\beta)$, we have an interaction time T which is only a small fraction of the relaxation time. We are not at all dealing with semiclassical collisions, and are far from energy conservation [recoil energy $(hK)^2/2m\simeq0.2$ eV]. In viewing the experimental $T_p^{-1.66}, T_p^{-2.6}$ temperature variations for germanium and silicon electrons, respectively, we note that at room temperature $\sqrt{3}/L$ for Ge extends over $\frac{1}{6}$ of the Brillouin zone for $m=1$ whereas $\sqrt{3}/L$ for Si extends over $\frac{1}{3}$, both ratios increasing as $m^{-1/2}$ for smaller masses. Thus, the complicated energy-band topology, umklapp, and any departure from deformation-potential coupling with increasing K may become very serious only for silicon. We believe it will be worthwhile and possible to extend this calculation to include these complications, as well as to use the method in other transport calculations.

ACKNOWLEDGMENTS

APPENDIX A: PHYSICAL CONSISTENCY OF TRIAL SOLUTION

We have pointed out that a solution to the equation of motion which satisfies initial and boundary conditions must be unique, and commented on the unique character of the functions $a(t), b(t), h(t)$. The physical grouping of variables as (i) $\vec{u}e^{\beta t}$ and (ii) $\vec{r}+\vec{u}/\beta$ helps to give the solution a simple form. By virtue of the choice (i), i.e., the occurrence of the difference $e^{\beta t}(\vec{u}-\vec{u}_0e^{-\beta t})$, we get ready thermalizing of initial velocity transients, and by virtue of (ii) we are assured of correct bivariate boundary conditions as $u\to\infty$. Finally, for internal physical consistency, we check the continuity equation.

$$\partial\rho(\vec{R},\vec{R}',t)/\partial t+\vec{\nabla}\cdot\vec{S}=0, \tag{A1}$$

$$S=\hbar/(2im)[\ \vec{\nabla}_R\rho(\vec{R},\vec{R}',t)$$
$$-\vec{\nabla}_{R'}\rho(\vec{R},\vec{R}',t)]\ |_{\vec{R}=\vec{R}'}. \tag{A2}$$

In Wigner variables Eqs. (A1) and (A2) assume the physically satisfying form[9]:

$$\frac{\partial}{\partial t}\int\rho_w(\vec{r},\vec{u},t)d^3u+\int\vec{u}\cdot\vec{\nabla}_r\rho_w(\vec{r},\vec{u},t)d^3u=0. \tag{A3}$$

The left-hand side of Eq. (4c) in Wigner variables, i.e., the left-hand side of Eq. (8a), averaged over $\vec{u}$ must vanish. We have already noted that integrating over $\vec{u}$ requires that $\vec{k}\,\mathrm{expt}=-\vec{w}$. We then see from Eq. (8b) that Eq. (A3) is satisfied providing

$$a_0+1-2h_0=0. \tag{A4}$$

This gives a physical meaning to Eq. (9a), which is the same as Eq. (A4).

APPENDIX B: DERIVATION

Some details of the calculations in Sec. II are given below. The right-hand side of Eq. (8b) is obtained by observing in the notation of Eq. (3c) that

$$\vec{u}\cdot\vec{\nabla}_r\rho_{wa}(\vec{r},\vec{u};\vec{r}_0,\vec{u}_0)=\vec{u}\cdot\int\int d^3k\,d^3w\,e^{i\vec{k}\cdot\vec{Q}}e^{i\vec{w}\cdot\vec{P}}\hat{\rho}_{wa}(\vec{k},\vec{w},t).$$

Further, focusing on the right-hand side above,

$$\int\int d^3k\,d^3w\,e^{i\vec{k}\cdot\vec{Q}}e^{i\vec{w}\cdot\vec{P}}i\vec{u}\hat{\rho}_{wa}=\int\int d^3k\,d^3w\,e^{i\vec{k}\cdot\vec{Q}}e^{i\vec{w}\cdot\vec{P}}(\vec{\nabla}_k e^{i\vec{k}\cdot\vec{u}})\ \{\hat{\rho}_{wa}(\vec{k},\vec{w},t)e^{-i\vec{k}\cdot\vec{u}}\}$$

$$=-\int\int d^3k\,d^3w\,e^{i\vec{k}\cdot\vec{Q}}e^{i\vec{w}\cdot\vec{P}}e^{i\vec{k}\cdot\vec{u}}\vec{\nabla}_k[\hat{\rho}_{wa}(\vec{k},\vec{w},t)e^{-i\vec{k}\cdot\vec{u}}]$$

$$=\int\int d^3k\,d^3w\,e^{i\vec{k}\cdot\vec{Q}}e^{i\vec{w}\cdot\vec{P}}[b\vec{k}-h\vec{w}]\hat{\rho}_{wa}(\vec{k},\vec{w},t).$$

Straightforward differentiation under the integral sign $\int d^3k\, d^3w$ yields $\partial \rho_{wa}/\partial(\beta t)$. Dropping transients, i.e., terms multiplied by extra factors $e^{-\beta t'}$, we arrive at Eqs. (8).

The term on the right-hand side of Eq. (4c), T', is given by

$$T' = -2/(\hbar\beta) \int_0^t ds \sum_K |C_K|^2 \sin(w_K/\beta)(t-s) T'_{1K} ,$$

$$T'_{1K} = \int \int e^{i\vec{K}\cdot(\vec{R}-\vec{R}_s)} \rho_{wa} d^3R_s d^3R'_s .$$

Transforming to variables $\vec{r}$ and $\vec{y}$, Eqs. (5a) and (5b), we get

$$T'_{1K} = \int \int e^{i\vec{K}\cdot(\vec{r}-\vec{r}_s)} e^{i\vec{K}/2\cdot(\vec{y}-\vec{y}_s)} \rho_{wa} d^3r_s d^3y_s ,$$

since the relevant Jacobian is 1. Using Eqs. (5c)–(5f) to transform to Wigner variables, we have

$$T_{1K} = (m/h)^3 \int \int e^{-i(m/\hbar)(\vec{y}\cdot\vec{u}-\vec{y}_0\cdot\vec{u}_0)} T'_{1K} d^3y\, d^3y_0$$

$$= \int \int e^{i\vec{K}\cdot(\vec{r}-\vec{r}_s)} \rho(\vec{r},\vec{u}-\hbar\vec{K}/2m\,;\vec{r}_s,\vec{u}_s-\hbar\vec{K}/2m)\rho(\vec{r}_s,\vec{u}_s;\vec{r}_0,\vec{u}_0) d^3r_s d^3u_s .$$

Using the Fourier representation, Eqs. (3a) and (3b) give

$$T_{1K} = (\beta^2/q)^6 (2\pi)^{-12} \int \int \int \int \int \int d^3u_s d^3r_s d^3k'' d^3w\, d^3k' d^3w'$$

$$\times \exp i[\,\vec{K}\cdot(\vec{r}-\vec{r}_s) + \vec{w}\,'\cdot(\vec{r}-\vec{r}_s+\vec{u}-\vec{u}_s)$$

$$+ \vec{w}\cdot(\vec{r}_s+\vec{u}_s-\vec{r}_0-\vec{u}_0) + \vec{k}\,'\cdot(\vec{u}-\vec{u}_s e^{-(t-s)} - \vec{C}_{1ts})$$

$$+ \vec{k}\,''\cdot(\vec{u}_s-\vec{u}_0 e^{-s})]$$

$$\times \exp[\,-\tfrac{1}{2}(b_{ts}k'^2 - 2h_{ts}\vec{k}\,'\cdot\vec{w}\,' + a_{ts}w'^2$$

$$+ b_{s0}k''^2 - 2h_{s0}\vec{k}\,''\cdot\vec{w} + a_{s0}w^2)] ,$$

where

$$a_{t0} \equiv a = 2a_0 t, \quad a_{ts} = 2a_0(t-s), \quad b_{t0} \equiv b, \quad b_{ts} = (1-e^{-2(t-s)}), \text{ etc.} ,$$

$$\vec{C}_{1ts} = \hbar\vec{K}/(2m)(1-e^{-(t-s)}) .$$

Integration on r_s leads to

$$\vec{K} + \vec{w}\,' = \vec{w}$$

and on u_s to

$$\vec{k}\,'e^{-(t-s)} + \vec{w}\,' = \vec{w} + \vec{k}\,''$$

or

$$\vec{k} \equiv \vec{k}\,' + \vec{w}\,' - \vec{w} = \vec{k}\,' - \vec{K} .$$

We get, leaving out transient terms in u_0 and r_0

$$T_{1K} = [\beta^2/(2\pi q)]^6 \int \int d^3k\, d^3w\, e^{i\vec{w}\cdot(\vec{r}+\vec{u})} e^{i\vec{k}\cdot\vec{u}} e^{-i(\vec{k}+\vec{K})\cdot\vec{C}_{1ts}}$$

$$\times \exp{-\tfrac{1}{2}[a_{t0}w^2 - 2h_{t0}\vec{k}\cdot\vec{w} + b_{t0}k^2]} \exp[-(R+R_1)/2] ,$$

$$R = b_{s0}K^2f^2 + b_{ts}K^2 + 2h_{ts}K^2 + a_{ts}K^2 ,$$

$$R_1 = 2\vec{k}\cdot\vec{K}fb_{s0}e^{-(t-s)} + 2\vec{k}\cdot\vec{K}b_{ts} - 2h_{s0}\vec{K}\cdot\vec{w}f + 2h_{ts}\vec{k}\cdot\vec{K} - 2h_{ts}\vec{w}\cdot\vec{K} ,$$

$$f = (e^{-(t-s)} - 1) ,$$

$$\vec{C}_{1ts} = \hbar\vec{K}/(2m)(1-e^{-(t-s)}) .$$

The other seven terms on the right-hand side of Eq. (4c) are evaluated in the same way, and, then, as stated in Sec. II, a systematic Taylor expansion of the result in $\vec{k}$ and $\vec{w}$ is carried out.

APPENDIX C: INFLUENCE OF THE ELECTRIC FIELD

We discuss the influence of the electric field. A term $(i\hbar)^{-1}e\vec{E}\cdot(\vec{R}-\vec{R}')$ on the left-hand side of Eq. (4c) becomes in Wigner variables $(e\vec{E}/m)\cdot\vec{\nabla}_{u'}\rho_{wa}$.[5] With an electric field we change the exponentials $e^{i\vec{k}'\cdot\vec{Q}'}e^{i\vec{w}'\cdot\vec{P}'}$ to

$$[\exp\{i\vec{k}'\cdot[\vec{u}'e^{\beta t'}-(e\vec{E}/m\beta)(e^{\beta t'}-1)]\}$$

$$\times\exp\{i\vec{w}'\cdot[\vec{r}'+\vec{u}'/\beta-(e\vec{E}/m\beta)t']\}] ,$$

all else remaining unchanged. The differentiation $\partial\rho_{wa}/\partial t'$ now brings down an extra term $(ie\vec{E}/m)\cdot(\vec{k}\exp\beta t'+\vec{w})$ to cancel the effect of $(e\vec{E}/m)\cdot\vec{\nabla}_{u'}\rho_w$.

APPENDIX D: $T_p^{3/2}$ DEPENDENCE FOR β

In this appendix we indicate how the $T_p^{3/2}$ dependence for β comes about. The most important and a typical contribution to the right-hand side of Eq. (9c) is

$$I=\left[\frac{2L}{\beta}\right]2a_0S_2(\sin\Lambda)(K^2/3)[\exp(-R)]T$$

$$\propto\frac{L}{\beta^2}\left[\frac{\beta^3}{q}\right]^2\int_0^{K_{max}}K^5\xi_KI_K'dK ,$$

where we have $|C_K|^2$ proportional to K' (deformation-potential coupling), and have converted all vectors K' to dimensionless form, including those in K'^2dK', the density of states. We have

$$I_K'=\int_0^\infty \cos pKT\,(\sin\Lambda)T\exp(-R)dT$$

with p given by $s\sqrt{\beta/q}$, s the speed of the acoustic waves. We write

$$I_K'\approx K^{-2}\int_0^\infty \sin LKY\,e^{-Y^2/2}Y\,dY$$

$$=L/K\sqrt{\pi/2}e^{-L^2K^2/2} .$$

We note that $\xi_K\approx(LpK)^{-1}$ and that the peak in the K integrand occurs at only a fraction of the Brillouin-zone radius so that we need

$$\int_0^\infty K^3e^{-L^2K^2/2}dK=2/L^4 .$$

If we now set I equal to unity, Eq. (9c), we have indeed $\beta\propto T_p^{3/2}$.

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