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Electron Transport at High Temperatures in the Presence of Impurities

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We investigate the linear transport properties of electrons in a solid when both phonon and impurity scattering are important. The problem is treated for the case where Maxwellian statistics apply and the electrons are described by a classical distribution function in position and velocity, $f(\mathbf{r},\mathbf{v})$. This function satisfies a space-dependent equation in which the interaction with the impurities is treated as part of the Hamiltonian and the phonon scattering is described by a linear Boltzmann-type collision term. This equation is solved formally in the presence of a weak external electric field in a form convenient for perturbation expansions in the relative strength of the different scattering mechanisms, some of which are carried out explicitly. We also show rigorously that the change in conductivity due to the presence of impurities is negative.

1. INTRODUCTION

THE electrical resistivity of a solid at high temperatures is often due primarily to the scattering of electrons by phonons and by impurities. It is usually assumed (Matthiessen's rule)[1] that the effect of these two contributions to the resistance are simply additive, i.e., $1/\sigma = 1/\sigma_{\text{phon}} + 1/\sigma_i$, where σ is the conductivity and σ_{phon}, σ_i are respectively the conductivities when there is *only* phonon or impurity scattering.

This additivity is true only if the effect of both impurity and phonon scattering can be represented by means of single relaxation times whose ratio is independent of velocity. Kohler has also shown[1] when both effects were represented by space independent transition probabilities, that the resistance is larger than that given by Matthiessen's rule. It is the purpose of this note to treat the action of the impurities rigorously as part of the Hamiltonian of the system while continuing to treat the effect of phonon collisions by means of stochastic transition probabilities. We now have to use a space- and velocity-dependent distribution function. This introduces important changes in the problem and there does not appear to be any simple method now for proving Kohler's result. We only show here that the addition of impurities will always decrease the conductivity.

The deviation from the results obtained by using a space independent distribution function could be especially important in the case where the effective phonon mean free path is small compared to the range of the impurity electron forces. In this case, which certainly occurs for ionized impurities in a semiconductor at high temperatures, the electrons will suffer many collisions with the phonons while traversing the field of a single impurity. We investigate this situation explicitly in Sec. 3.

We consider a sample of total volume Ω, which contains a number of (possibly charged) fixed impurities. There are to be N impurity centers in each macroscopic unit volume V, located at fixed positions $\{\mathbf{r}_i\}$, $i=1, 2, \cdots, N$. The electrons are assumed to act (effectively) independent of each other. The average number of electrons in the unit volume V is n. The number of electrons with velocity $\mathbf{v}$ lying in $d\mathbf{v}$ and position $\mathbf{r}$ lying in $d\mathbf{r}$ is $f(\mathbf{r},\mathbf{v};\{\mathbf{r}_i\})d\mathbf{v}d\mathbf{r}$. This f satisfies a classical transport equation.

A representative electron located at $\mathbf{r}$, will be acted on by forces due to (1) the externally applied electric field $\mathbf{E}$ causing transport, where $|\mathbf{E}|$ is so small that quadratic terms in $|\mathbf{E}|$ can always be neglected, and (2) the potential of interaction with the fixed impurity centers $U = U(\{\mathbf{r}-\mathbf{r}_i\})$,

$$U = \sum_i \varphi(\mathbf{r}-\mathbf{r}_i), \tag{1.1}$$

where φ is the potential energy of interaction of an electron with the impurity center at $\mathbf{r}_i$.

The effect on the electrons of collisions with the lattice will be described generally in terms of a probability density per unit time $K(\mathbf{x},\mathbf{x}')$ for an electron in a state $\mathbf{x}'=(\mathbf{r}',\mathbf{v}')$ making a transition (i.e., a discontinuous jump) to a new state $\mathbf{x}=(\mathbf{r},\mathbf{v})$. The properties of K will be discussed in the next section.

By virtue of the above assumptions the equation satisfied by the electron distribution f is

$$\frac{\partial f}{\partial t}+\mathbf{v}\cdot\frac{\partial f}{\partial \mathbf{r}}+\frac{1}{m}\left(e\mathbf{E}-\frac{\partial U}{\partial \mathbf{r}}\right)\cdot\frac{\partial f}{\partial \mathbf{v}}=\left(\frac{\delta f}{\delta t}\right)_{\text{coll}}, \tag{1.2}$$

where $(\delta f/\delta t)_{\text{coll}}$ represents the effect of phonon scattering, m is the isotropic effective mass and e the charge of the electron. We will be strictly interested only in the steady-state electron distribution $f(\mathbf{r},\mathbf{v})$ which satisfies Eq. (1.2) with $\partial f/\partial t$ set equal to zero.

The equilibrium distribution function, f_0, in the

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[1] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), Chap. 10; see also R. A. Logan and A. J. Peters, J. Appl. Phys. 31, 122 (1960).

absence of an external field $\mathbf{E}$, is $f_0(\mathbf{r},\mathbf{v};\{\mathbf{r}_i\})$

$$f_0(\mathbf{r},\mathbf{v})=n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\exp\left[\frac{-m\mathrm{v}^2}{2kT}\right]\frac{e^{-U/kT}}{Z},\qquad(1.3)$$

with T the temperature and Z the configurational partition function of the electron-impurity system,

$$Z=\int_V e^{-U/kT}d\mathbf{r}.\qquad(1.4)$$

The phonon collision term, $(\delta f/\delta t)_{\mathrm{coll}}$, must have the property that $(\delta f_0/\delta t)_{\mathrm{coll}}$ vanishes, so that f_0 is the stationary solution of Eq. (1.2) when $\mathbf{E}=0$.

The spatial integration in Eq. (1.4) is over a unit volume V which is chosen to be large enough for the system to be uniform on this scale, i.e., surface effects of V can always be neglected. The value of Z is thus independent of the location of V inside the total volume Ω of our sample.

We insist that the steady-state distribution f that we are looking for must have the property that if $A(\mathbf{v},\mathbf{r})$ is any vector or tensor that is itself uniform in $\mathbf{r}$ over V, then

$$\int_V d\mathbf{r}\,\mathrm{div}\int A(\mathbf{v},\mathbf{r})fd\mathbf{v}=0.\qquad(1.5)$$

This insistence [which is analogous to the assumption that in the case of vanishing U, $f=f(\mathbf{v})$ only], reflects the physical fact that in our sample of volume Ω we are dealing with an open system with electrons entering one side and leaving the other. In the limit, as Ω approaches infinity in such a way that the density of electrons and impurities remains constant, we are dealing with an infinite system which *is uniform* on the scale of V. An alternate approach corresponds to assuming periodic boundary conditions, this necessitates using an electric field produced by a changing magnetic field, which does not essentially affect the results.[2]

This requirement of uniformity can be made more precise, and some other complications avoided as well, by considering an ensemble of systems in which the distribution of impurity centers is governed by an *a priori* joint probability (density) distribution, $P_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)$.[3] The expectation value of any physical quantity Q in our system will then be found by averaging Q both over f and over P_N. The averaging over P_N will eliminate the dependence of the macroscopic quantities on the $\{\mathbf{r}_i\}$ and *also* on r, assuring complete uniformity. Thus, for example, the current density is given by

$$\mathbf{j}=e\int_V^{(N)}\cdots\int\int\mathbf{v}f(\mathbf{r},\mathbf{v};\{\mathbf{r}_i\})P_N(\{\mathbf{r}_i\})d\mathbf{v}\prod_{i=1}^{N}d\mathbf{r}_i$$

$$=e\int\mathbf{v}\langle f(\mathbf{v})\rangle_N d\mathbf{v},\qquad(1.6)$$

where

$$\langle f(\mathbf{v})\rangle_N=\int_V^{(N)}\cdots\int P_N f d\mathbf{r}_1,\cdots,d\mathbf{r}_N;$$

the $\langle\cdots\rangle_N$ always denoting averaging over P_N.

In Sec. 2 we find a general expression for the conductivity. In Sec. 3 we carry out some explicit calculations for the change in conductivity due to impurity scattering when the phonon collisions dominate. There we make use of a simple relaxation time approximation for the phonon collisions, writing

$$(\delta f/\delta t)_{\mathrm{coll}}=(f_0-f)/\tau.\qquad(1.7)$$

In Sec. 4 we discuss the relation of our results to Matthiessen's rule using the electron velocity autocorrelation functions.

2. GENERAL TRANSPORT EQUATION AND CONDUCTIVITY

The transport Eq. (1.2) can be written

$$\frac{\partial f}{\partial t}+(f,H)=\int K(\mathbf{x},\mathbf{x}')f(\mathbf{x}')d\mathbf{x}'-\frac{f(\mathbf{x})}{\tau(\mathbf{x})}-\frac{e\mathbf{E}}{m}\cdot\frac{\partial f}{\partial\mathbf{v}},\qquad(2.1)$$

with H the single electron, impurity centers Hamiltonian

$$H=\tfrac{1}{2}m\mathrm{v}^2+U,\qquad(2.2)$$

(f,H) is the complete Poisson bracket with respect to the electron coordinates $\mathbf{r}$, $\mathbf{v}$ and the kernel $K(\mathbf{x},\mathbf{x}')$ is the transition probability per unit time from $\mathbf{x}'$ to $\mathbf{x}$ describing the electron scattering due to the lattice. As usual

$$\frac{1}{\tau(\mathbf{x})}=\int K(\mathbf{x}',\mathbf{x})d\mathbf{x}',\qquad(2.3)$$

with the integrations in Eqs. (2.1) and (2.3) being taken over the electron phase space. Since $(\delta f_0/\delta t)_{\mathrm{coll}}$ vanishes, we must have

$$\int K(\mathbf{x},\mathbf{x}')f_0(\mathbf{x}')d\mathbf{x}'=\int K(\mathbf{x}',\mathbf{x})f_0(\mathbf{x})d\mathbf{x}'=\frac{f_0(\mathbf{x})}{\tau(\mathbf{x})}.\qquad(2.4)$$

We shall also assume that K yields detailed balancing in equilibrium which implies

$$K(\mathbf{x},\mathbf{x}')f_0(\mathbf{x}')=K(\mathbf{x}',\mathbf{x})f_0(\mathbf{x})=W(\mathbf{x},\mathbf{x}')=W(\mathbf{x}',\mathbf{x}).\qquad(2.5)$$

In general we expect that "collisions" with phonons will change the momentum of an electron but not its position

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[2] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

[3] This reduces to the previous situation of specific location for the impurity centers when P_N is chosen to be a product of delta functions, $P_N(\mathbf{r}_1',\cdots,\mathbf{r}_N')=\Pi_{i=1}^{N}\,\delta(\mathbf{r}_1'-\mathbf{r}_i)$. However in order to make the system manifestly uniform P_N should be a function of the $(\mathbf{r}_i-\mathbf{r}_j)$.

so that K will have the form[4]

$$K(\mathbf{x},\mathbf{x}')=\tilde{K}(\mathbf{v},\mathbf{v}';\,\mathbf{r},\{\mathbf{r}_i\})\delta(\mathbf{r}-\mathbf{r}_i), \tag{2.6}$$

where $\tilde{K}$ is the transition rate from one momentum state to another which may depend on the position of the electron in the vicinity of an impurity. We note here however that the relaxation-time approximation [of Eq. (1.7) discussed in Sec. 3] does not correspond to a K having this form.[4] In this case the probability that an electron will have the phase space coordinates $\mathbf{r}$ and $\mathbf{v}$ after a collision is equal to $f_0(\mathbf{r},\mathbf{v})$, which means that the position of the electron may also change abruptly in a collision.

We seek solutions of Eq. (2.1) which retain terms of order $|\mathbf{E}|$ but neglect all higher powers of $|\mathbf{E}|$. To this end, we set

$$f=f_0(1+\varphi), \tag{2.7}$$

where f_0 is the electron equilibrium distribution Eq. (1.3) and $\varphi(\mathbf{x},t;\{\mathbf{r}_i\})$ is a correction term satisfying

$$f_0(\partial\varphi/\partial t)+f_0(\varphi,H)=\mathfrak{A}\varphi+e\beta\mathbf{E}\cdot\mathbf{v}f_0, \tag{2.8}$$

with $\beta=1/kT$ and $\mathfrak{A}$ is an operator such that

$$\mathfrak{A}\varphi=\int d\mathbf{x}'\,W(\mathbf{x},\mathbf{x}')[\varphi(\mathbf{x}')-\varphi(\mathbf{x})]. \tag{2.9}$$

It is convenient to break up the correction term φ into two additive contributions $q(\mathbf{x},t)$ and $h(\mathbf{x},t)$. $q(\mathbf{x},t)$ characterizes the lattice scattering of the electrons, i.e., $q(\mathbf{x},t)$ satisfies the inhomogeneous equation

$$f_0\partial q/\partial t=\mathfrak{A}q+e\beta\mathbf{E}\cdot\mathbf{v}f_0. \tag{2.10}$$

Actually q will still depend on the impurities through f_0 and possibly also through $K(\mathbf{v},\mathbf{r};\mathbf{v}',\mathbf{r}')$. Only when the two processes are completely independent, i.e., $\tilde{K}$ in Eq. (2.6) is independent of $\mathbf{r}$, and also in the constant relaxation time approximation, does q become the same as in the complete absence of impurities. The other term $h(\mathbf{x},t)$ gives the further correction due to the presence of the impurity centers and must satisfy by virtue of Eqs. (2.8) and (2.10) the inhomogeneous equation

$$f_0\partial h/\partial t=f_0(H,h)+\mathfrak{A}h+f_0(H,q). \tag{2.11}$$

We are interested in the stationary solutions of Eqs. (2.8), (2.10), and (2.11), which will be denoted by $\varphi(\mathbf{x})$, $q(\mathbf{x})$, and $h(\mathbf{x})$, and which are obtained by setting the time derivatives equal to zero in these equations.

Following Kohler,[1] we now define

$$\begin{aligned}\{a,b\}&\equiv-\int\int a(\mathbf{x})W(\mathbf{x},\mathbf{x}')[b(\mathbf{x}')-b(\mathbf{x})]d\mathbf{x}d\mathbf{x}'\\&=-\int a\mathfrak{A}b\,d\mathbf{x}=\frac{1}{2}\int\int W(\mathbf{x},\mathbf{x}')\\&\quad\times[a(\mathbf{x}')-a(\mathbf{x})][b(\mathbf{x}')-b(\mathbf{x})]d\mathbf{x}d\mathbf{x}'\\&=\{b,a\}.\end{aligned} \tag{2.12}$$

Since $\{c,c\}$ is always positive, we can easily show by letting $c=\lambda a+b$ that

$$\{a,a\}\{b,b\}\geq\{a,b\}^2. \tag{2.13}$$

It follows further that the correct φ which is the stationary solution of Eq. (2.8) satisfies

$$\begin{aligned}\{a,\varphi\}&=\beta e\mathbf{E}\cdot\int f_0a\mathbf{v}d\mathbf{x}-\int af_0(\varphi,H)d\mathbf{x}\\&=\{\varphi,a\},\end{aligned} \tag{2.14}$$

and in particular, see Eq. (1.6) (where we omit here and wherever it is not important the indication of averaging over P_N),

$$\begin{aligned}\{\varphi,\varphi\}&=\beta e\mathbf{E}\cdot\int\int f_0\varphi\mathbf{v}d\mathbf{v}d\mathbf{r}=\beta\mathbf{E}\cdot\int\mathbf{j}d\mathbf{r}\\&=\beta\mathbf{E}\cdot\mathbf{J}=\beta\mathbf{E}\cdot\boldsymbol{\sigma}\cdot\mathbf{E}.\end{aligned} \tag{2.15}$$

Here $\mathbf{J}$ is the total current, since we are always integrating over a unit volume, and $\boldsymbol{\sigma}$ is the conductivity tensor. The last equation was derived by noting that

$$f_0(\varphi,H)=-\frac{1}{\beta}(\varphi,f_0), \tag{2.16}$$

and

$$\begin{aligned}\int&\varphi(\varphi,f_0)d\mathbf{x}\\&=\frac{1}{2}\int(\varphi^2,f_0)d\mathbf{x}\\&=\frac{1}{2}\int d\mathbf{x}\left[\frac{\partial}{\partial\mathbf{v}}\cdot\left(f_0\frac{\partial\varphi^2}{\partial\mathbf{r}}\right)-\frac{\partial}{\partial\mathbf{r}}\cdot\left(f_0\frac{\partial\varphi^2}{\partial\mathbf{v}}\right)\right].\end{aligned} \tag{2.17}$$

The first term in the last integral of Eq. (2.17) vanishes by virtue of the fact that f_0 goes to zero for large velocities and the second term vanishes in accordance with Eq. (1.5).

We have similarly for the stationary q of Eq. (2.10),

$$\{a,q\}=\beta\mathbf{E}\cdot\int f_0a\mathbf{v}d\mathbf{x}. \tag{2.18}$$

Thus,

$$\{q,q\}=\beta\mathbf{E}\cdot\mathbf{J}_{\text{phon}}=\beta\mathbf{E}\cdot\boldsymbol{\sigma}_{\text{phon}}\cdot\mathbf{E}, \tag{2.19}$$

and

$$\{\varphi,q\}=\beta\mathbf{E}\cdot\mathbf{J}=\{\varphi,\varphi\}, \tag{2.20}$$

where $\boldsymbol{\sigma}_{\text{phon}}$ is the conductivity in the absence of impurities. [See the discussion after Eq. (2.10).]

Replacing now a and b in Eq. (2.13) by φ and q, we find

$$\{\varphi,\varphi\}\{q,q\}\geq\{q,\varphi\}^2, \tag{2.21}$$

or

$$\beta\mathbf{E}\cdot\boldsymbol{\sigma}_{\text{phon}}\cdot\mathbf{E}=\{q,q\}\geq\{q,\varphi\}=\beta\mathbf{E}\cdot\boldsymbol{\sigma}\cdot\mathbf{E}. \tag{2.22}$$

Since $\boldsymbol{\sigma}_{\text{phon}}$ and $\boldsymbol{\sigma}$ are both symmetric the above implies

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[4] E. P. Gross, Phys. Rev. **97**, 395 (1955).

that the eigenvalues of $\boldsymbol{\sigma}_{\text{phon}}$ are greater than those of $\boldsymbol{\sigma}$, which is what we wanted to prove. Combining Eqs. (2.14), (2.15), and (2.19), we also find

$$\begin{aligned}(\mathbf{J}-\mathbf{J}_{\text{phon}})\cdot\mathbf{E}&\\ &=-1/\beta\int qf_0(\varphi,H)d\mathbf{x}=-1/\beta\int f_0\varphi(H,q)d\mathbf{x}\\ &=-1/\beta\int f_0h(H,q)d\mathbf{x}=\mathbf{E}\cdot\Delta\boldsymbol{\sigma}\cdot\mathbf{E},\end{aligned}\tag{2.23}$$

where the last two equalities follow by arguments similar to those developed after Eq. (2.15).

The stationary value $h(\mathbf{x})$ may be written formally as the value of $h(\mathbf{x},t)$ as $t\rightarrow\infty$. This leads to the expression

$$f_0h(\mathbf{x})=\int_0^\infty ds\int P(\mathbf{x},\mathbf{x}'|s)\times[H(\mathbf{x}'),q(\mathbf{x}')]f_0(\mathbf{x}')d\mathbf{x}',\tag{2.24}$$

where the Green's function $P(\mathbf{x},\mathbf{x}'|s)$ is the solution of the homogeneous equation,

$$\frac{\partial P}{\partial s}+(P,H)=\int d\mathbf{x}''[K(\mathbf{x},\mathbf{x}'')P(\mathbf{x}'',\mathbf{x}'|s)-K(\mathbf{x}'',\mathbf{x})P(\mathbf{x},\mathbf{x}'|s)],\tag{2.25}$$

under the initial condition,

$$P(\mathbf{x},\mathbf{x}'|0)=\delta(\mathbf{x}-\mathbf{x}').\tag{2.26}$$

$P(\mathbf{x},\mathbf{x}'|s)d\mathbf{x}$ is thus the probability that an electron initially at the phase point $\mathbf{x}'$ will be found in the region $d\mathbf{x}$ about $\mathbf{x}$ at time s later. Substitution of Eq. (2.24) into Eq. (2.23) yields the autocorrelation function expression,

$$\begin{aligned}\mathbf{E}\cdot\Delta\boldsymbol{\sigma}\cdot\mathbf{E}&=-1/\beta\int_0^\infty ds\int\langle Q(\mathbf{x})P(\mathbf{x},\mathbf{x}'|s)Q(\mathbf{x}')f_0(\mathbf{x}')\rangle_N d\mathbf{x}'\\ &=-1/\beta\int_0^\infty ds\langle\langle Q(\mathbf{x}'|s)Q(\mathbf{x}'|0)\rangle_N\rangle_0,\end{aligned}\tag{2.27}$$

with

$$Q(\mathbf{x})=Q(\mathbf{x}|0)=(H,q),$$

and $\langle\cdots\rangle_0$ representing, as usual, an average over the equilibrium electron distribution, and the $\langle\cdots\rangle_N$ representing an ensemble average over the impurity distribution.

Now since we are dealing here with a stationary stochastic process, we have

$$\begin{aligned}\langle\langle G_Q(s)\rangle_N\rangle_0&=\langle\langle Q(s)Q(0)\rangle_N\rangle_0\\ &=\lim_{T\rightarrow\infty}1/T\int_0^T\langle\langle Q(t+s)Q(t)\rangle_N\rangle_0 dt,\end{aligned}\tag{2.28}$$

where $Q(t+s)$ and $Q(s)$ are the values assumed by the function Q (thought of here as a random variable) at the times s and $t+s$. Use of the Wiener-Khintchin theorem now yields

$$\langle\langle G_Q(s)\rangle_N\rangle_0=\int_0^\infty\langle\langle G_Q(\nu)\rangle_N\rangle_0\cos 2\pi\nu s d\nu,\tag{2.29}$$

where $G_Q(\nu)$ is the power spectrum

$$G_Q(\nu)=\lim_{T\rightarrow\infty}2/T\left\{\int_0^T Q(t)e^{-2\pi i\nu t}dt\times\int_0^T Q(t)e^{2\pi i\nu t}dt\right\},\tag{2.30}$$

which is assumed to exist. This yields finally

$$\mathbf{E}\cdot\Delta\boldsymbol{\sigma}\cdot\mathbf{E}=-(1/\beta)\pi\langle\langle G_Q(0)\rangle_N\rangle_0,\tag{2.31}$$

where G_Q is positive.

For the case where the kernel randomizes velocities,[5] i.e.,

$$K(\mathbf{x},\mathbf{x}')=K(\mathbf{x}^*,\mathbf{x}'),\tag{2.32}$$

with $\mathbf{x}^*=(\mathbf{r},-\mathbf{v})$, $q(x)$ is given by

$$q(\mathbf{x})=\tau(\mathbf{x})e\beta\mathbf{E}\cdot\mathbf{v}.\tag{2.33}$$

This yields

$$\boldsymbol{\sigma}_{\text{phon}}=e^2\beta\int\langle\tau\mathbf{v}^2f_0\rangle_N d\mathbf{x}\,\mathbf{1},\tag{2.34}$$

and

$$Q=e\beta(H,\tau\mathbf{v})\cdot\mathbf{E}.\tag{2.35}$$

3. RELAXATION-TIME APPROXIMATION

In the relaxation-time approximation the equation satisfied by f is

$$\frac{\partial f}{\partial t}+(f,H)=\frac{f_0-f}{\tau}-\frac{e\mathbf{E}}{m}\cdot\frac{\partial f}{\partial\mathbf{v}}.\tag{3.1}$$

For τ constant this corresponds to the choice

$$K(\mathbf{x},\mathbf{x}')=f_0(\mathbf{x})/\tau,$$

while there is no choice of K which would yield Eq. (3.1) for τ not constant. This may be seen most easily by noting that the correct collision term conserves the total number of particles while the relaxation time approximation does so only for τ a constant. While it is true that when K randomizes velocities, the form of q would be unchanged if one used Eq. (3.1) with the correct $\tau(\mathbf{x})$, i.e.,

$$q=-\tau e\beta\mathbf{E}\cdot\mathbf{v},$$

this would no longer be true of h. We shall therefore consider here only the case τ constant, for which

$$P(\mathbf{x},\mathbf{x}'|s)=e^{-s/\tau}\delta(\mathbf{x}_{-s}-\mathbf{x}')+(1-e^{-s/\tau})f_0(\mathbf{x}),\tag{3.2}$$

where

$$\mathbf{x}_{-t}=\mathbf{x}(\mathbf{x},-t)\tag{3.3}$$

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[5] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

are the phase space coordinates, $\mathbf{x}_{-t}=(\mathbf{r}_{-t},\mathbf{v}_{-t})$ of an electron, moving solely under the action of the forces due to the impurities, at time $-t$ when its coordinates are $\mathbf{x}$ at $t=0$. From the time reversibility of the equations of motion derived from the Hamiltonian H it follows that

$$\begin{aligned}\mathbf{r}_{-t}&=\mathbf{r}(\mathbf{r},\mathbf{v};-t)=\mathbf{r}(\mathbf{r},-\mathbf{v};+t),\\ \mathbf{v}_{-t}&=\mathbf{v}(\mathbf{r},\mathbf{v};-t)=-\mathbf{v}(\mathbf{r},-\mathbf{v};t).\end{aligned}\tag{3.4}$$

By using Eq. (3.2), Eq. (2.27), giving the change in conductivity due to the presence of the impurity centers $\Delta\boldsymbol{\sigma}$, becomes

$$\Delta\boldsymbol{\sigma}=-e^2\beta\int_0^\infty ds\,\langle\langle\mathbf{Q}_\tau(\mathbf{x})e^{-s/\tau}\mathbf{Q}_\tau(\mathbf{x}_{-s})\rangle_N\rangle_0,\tag{3.5}$$

where $\mathbf{Q}_\tau(\mathbf{x})$ is given by

$$\mathbf{Q}_\tau(\mathbf{x})=\tau(H,\mathbf{v})=-(\tau/m)\mathbf{F}(\mathbf{r}).\tag{3.6}$$

Thus

$$\Delta\boldsymbol{\sigma}=-\frac{e^2\beta\tau^2}{m^2}\int_0^\infty ds\,e^{-s/\tau}\langle\langle\mathbf{F}(\mathbf{r}_s)\mathbf{F}(\mathbf{r})\rangle_N\rangle_0\tag{3.7}$$

$$=-\frac{e^2\beta\tau^2}{m^2}\int_0^\infty ds\,e^{-s/\tau}\langle\langle\mathbf{F}(\mathbf{r})\mathbf{F}(\mathbf{r}_s)\rangle_N\rangle_0.\tag{3.8}$$

To derive the last equality we have made use of time reversibility, $\mathbf{F}(\mathbf{r}_{-s})=\mathbf{F}(\mathbf{r},-\mathbf{v};-s)$ and of the time invariance of f_0. Thus $\Delta\boldsymbol{\sigma}$ is equal to its transpose, i.e., $\Delta\boldsymbol{\sigma}$ is symmetric as expected in general. We note also that in Eq. (3.7) the effect on $\Delta\boldsymbol{\sigma}$ of the electron-phonon interaction is "separated" from that due to the forces exerted on the electron by the impurity centers. For central forces and an isotropic distribution of impurity centers, it follows from symmetry, that

$$\langle\langle\mathbf{F}(\mathbf{r}_s)\mathbf{F}(\mathbf{r})\rangle_N\rangle_0=\langle\langle\mathbf{F}(\mathbf{r}_s)\cdot\mathbf{F}(\mathbf{r})\rangle_N\rangle_0\mathbf{1},$$

or

$$\langle\mathbf{G}_F(s)\rangle_0=\langle G_F(s)\rangle_0\mathbf{1},\tag{3.9}$$

with $G_F(s)$ the autocorrelation function of any component of $\mathbf{F}$ and $\mathbf{1}$ the unit tensor. By virtue of the Wiener-Khintchin theorem used in the last section we can now write in analogy to Eq. (2.29)

$$\begin{aligned}\Delta\boldsymbol{\sigma}&=-\frac{e^2\beta\tau^2}{m^2}\mathbf{1}\int_0^\infty d\nu\int_0^\infty ds\,\langle\langle G_F(\nu)\rangle_N\rangle_0e^{-s/\tau}\cos(2\pi\nu s)\\ &=-\frac{\tau e^2\beta}{2\pi m}\mathbf{1}\int_0^\infty d\omega\frac{\langle\langle G_F(\omega)\rangle_N\rangle_0}{(\omega^2+1/\tau^2)}>0,\end{aligned}\tag{3.10}$$

with $\omega=2\pi\nu$, and

$$G_F(\nu)=\lim_{T\to\infty}2/T\left|\int_0^T F(t)e^{-i\omega t}dt\right|^2>0.\tag{3.11}$$

These results can also be obtained quite directly from the solution of Eq. (3.1), $f=f_0(1+\varphi)$

$$\varphi(\mathbf{r},\mathbf{v},t)=e\beta\int_0^t ds\,\exp\{-s[1/\tau+i\mathcal{L}]\}\mathbf{v}\cdot\mathbf{E}+\exp\{-t[1/\tau+i\mathcal{L}]\}\varphi(\mathbf{r},\mathbf{v},0),\tag{3.12}$$

where $i\mathcal{L}=(\ ,H)$. The stationary solution is obtained from the above by letting $t\to+\infty$,

$$\begin{aligned}\varphi(\mathbf{r},\mathbf{v})&=\lim_{t\to\infty}\varphi(\mathbf{r},\mathbf{v},t)=e\beta\mathbf{E}\cdot\int_0^\infty ds\,\exp\{-s[1/\tau+i\mathcal{L}]\}\mathbf{v}\\ &=e\beta\mathbf{E}\cdot\int_0^\infty ds\,e^{-s/\tau}\mathbf{v}_{-s},\end{aligned}\tag{3.13}$$

as could also have been found by solving directly the steady-state equation satisfied by this φ,

$$(i\mathcal{L}+1/\tau)\varphi=e\beta\mathbf{v}\cdot\mathbf{E}.\tag{3.14}$$

Two limiting cases of Eq. (3.13) are of interest: (1) when there are no impurities, $U=0$, i.e., $\mathbf{v}_{-s}=\mathbf{v}$ (though we shall formally leave U inside f_0), then

$$\varphi(\mathbf{r},\mathbf{v})\,|_{U=0}=q=e\beta\tau\mathbf{E}\cdot\mathbf{v},\tag{3.15}$$

and (2) when lattice scattering is negligible, in which case

$$\varphi(\mathbf{r},\mathbf{v})\,|_{1/\tau\to0}=e\beta\mathbf{E}\cdot\int_0^\infty\mathbf{v}_{-s}ds.\tag{3.16}$$

For what follows, it is convenient to integrate Eq. (3.13) by parts, using the relation

$$\mathbf{F}(\mathbf{r}_{-s})=-m(d/ds)\mathbf{v}_{-s},\tag{3.17}$$

to obtain

$$\varphi(\mathbf{r},\mathbf{v})=q-\frac{\tau e\beta}{m}\mathbf{E}\cdot\int_0^\infty ds\,e^{-s/\tau}\mathbf{F}(\mathbf{r}_{-s}).\tag{3.18}$$

Substituting Eq. (3.18) into the current given by Eq. (2.19), one finds that

$$\sigma_{\text{phon}}=(\sigma)_{U=0}=ne^2\tau/m,\tag{3.19}$$

while from Eq. (2.23)

$$\Delta\boldsymbol{\sigma}=-\frac{\tau e^2\beta}{m}\int_0^\infty ds\,e^{-s/\tau}\langle\langle\mathbf{v}\mathbf{F}(\mathbf{r}_{-s})\rangle_N\rangle_0.\tag{3.20}$$

Carrying out an integration by parts of Eq. (3.20) and using the facts that (a) the equilibrium distribution is invariant with respect to time translation by the operator $\exp(i\mathcal{L})$ so that

$$\langle\mathbf{v}\mathbf{F}(\mathbf{r}_{-s})\rangle_0=\langle\mathbf{v}_s\mathbf{F}\rangle_0,\tag{3.21}$$

and (b) noting that there is no correlation between the instantaneous value of $\mathbf{F}$ and $\mathbf{v}$ at equilibrium,

$$\langle\mathbf{v}\mathbf{F}\rangle_0=0,\tag{3.22}$$

we recover Eq. (3.7).

We shall now investigate the explicit form of Eq. (3.13) and Eq. (3.7) for the case when lattice scattering is dominant, i.e., τ is small compared to τ_i. This will be accomplished by expanding φ and $\Delta\boldsymbol{\sigma}$ in powers of τ. To this end we note that

$$\mathbf{r}_{-s}=\mathbf{r}-s\mathbf{v}+1/m\int_0^{-s}ds'\int_0^{s'}\mathbf{F}_{s''}ds''$$

$$=r-s\mathbf{v}+(1/2)\frac{s^2}{m}\mathbf{F}(r)+O(s^3), \qquad (3.23)$$

which when substituted in Eq. (3.18) yields

$$\varphi(\mathbf{r},\mathbf{v})=\frac{\tau e\beta}{m}E\cdot\left\{m\mathbf{v}-\tau\mathbf{F}(\mathbf{r})+\tau^2\mathbf{v}\cdot\frac{\partial}{\partial\mathbf{r}}\mathbf{F}(\mathbf{r})+\cdots\right\}. \qquad (3.24)$$

The physical parameter of expansion which is used here is essentially the change in the electron impurity centers potential over one phonon mean free path, δU, divided by kT. In this approximation the velocity distribution of an electron can be written as

$$\psi(\mathbf{v})=\frac{1}{V}\int_V^{(N)}\cdots\int d\mathbf{r}_1,\cdots,d\mathbf{r}_N P_N\int_V f(\mathbf{r},\mathbf{v})d\mathbf{r}$$

$$=\psi_M(\mathbf{v})[1+X(\mathbf{v})], \qquad (3.25)$$

where ψ_M is the Maxwellian distribution,

$$\psi_M(\mathbf{v})=n(2\pi mkT)^{-\frac{3}{2}}\exp[-\beta m\mathbf{v}^2/2], \qquad (3.26)$$

and

$$X(\mathbf{v})=\frac{\tau e\beta}{m}\mathbf{E}\cdot\{m\mathbf{v}-\tau^2\beta\mathbf{v}\cdot\langle\langle\mathbf{F}(\mathbf{r})\mathbf{F}(\mathbf{r})\rangle_N\rangle_0+\cdots\}. \qquad (3.27)$$

Corresponding formulas for $\Delta\boldsymbol{\sigma}$ can be obtained by substituting Eq. (3.24) in Eq. (2.23) by expanding directly Eq. (3.7) or by expanding Eq. (3.11), $(\tau\ll\omega^{-1})$, noting that

$$\frac{1}{2\pi}\int_0^\infty d\omega\langle\langle\mathbf{G}_F(\omega)\rangle_N\rangle_0$$

$$=\lim_{T\to\infty}\frac{1}{2T}\int_{-\infty}^{\infty}\langle\langle\mathbf{F}(t)F(t)\rangle_N\rangle_0 dt$$

$$=\langle\langle\mathbf{F}(\mathbf{r})\mathbf{F}(\mathbf{r})\rangle_N\rangle_0$$

$$=\int\left[\int_V^{(N)}\cdots\int d\mathbf{r}_1,\cdots,d\mathbf{r}_N P_N f_0(\mathbf{r},\mathbf{v})\frac{\partial U}{\partial\mathbf{r}}\frac{\partial U}{\partial\mathbf{r}}\right]d\mathbf{v}. \qquad (3.28)$$

All three of these methods give directly the desired relation

$$\Delta\boldsymbol{\sigma}=-\frac{\tau^3e^2}{m^2}\beta\langle\langle\mathbf{F}(\mathbf{r})\mathbf{F}(\mathbf{r})\rangle_N\rangle_0+O(\tau^5). \qquad (3.29)$$

After some integration by parts, the last identity of Eq. (3.28) simplifies to read, for central forces,

$$\langle\langle\mathbf{F}(\mathbf{r})F(\mathbf{r})\rangle_N\rangle_0=\beta^{-1}\rho r\int g(r')\nabla\nabla\varphi(r')d\mathbf{r}' \qquad (3.30)$$

with $\rho=N/V$ (V is a unit volume) and $g(r')$, the radial distribution function for an impurity center-electron pair,

$$g(\mathbf{r}-\mathbf{r}_1)=\frac{\displaystyle\int_V^{(N-1)}\cdots\int P_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)\exp[-\beta\sum_{k=1}^N\varphi(|\mathbf{r}-\mathbf{r}_k|)]d\mathbf{r}_2\cdots d\mathbf{r}_N}{\displaystyle\int_V^{(N+1)}\cdots\int P_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)\exp[-\beta\sum_{k=1}^N\varphi(|\mathbf{r}-\mathbf{r}_k|)]d\mathbf{r}d\mathbf{r}_1\cdots d\mathbf{r}_N}. \qquad (3.31)$$

Thus, if g is known, Eq. (3.30) in Eq. (3.29) gives us the limiting change of conductivity $\Delta\boldsymbol{\sigma}$ for sufficiently small τ valid to all powers of ρ.

Unfortunately the problem of carrying out the integrations shown in Eq. (3.31) is not easier than the corresponding problem in the theory of fluids. Just as in that theory, progress can be made if the system is sufficiently attenuated, i.e., ρ is very small and we are dealing with a dilute "impurity gas." Expanding g straightforwardly in a power series in the density of impurities ρ, one obtains

$$g(r')=e^{-\beta\varphi(r')}[1+O(\rho)], \qquad (3.32)$$

which when substituted in Eq. (3.30) gives, retaining only first-order terms in ρ,

$$\langle\langle\mathbf{F}\mathbf{F}\rangle_N\rangle_0=\beta^{-1}\rho n\int e^{-\beta\varphi(r')}\nabla\nabla\varphi(r')d\mathbf{r}'$$

$$=\mathbf{1}\frac{4\pi\rho}{3}n\int e^{-\beta\varphi(r')}\left[\frac{d\varphi(r')}{dr'}\right]^2 r'^2dr'. \qquad (3.33)$$

In this double limit of small ρ and τ, Eq. (3.29) reduces by virtue of Eq. (3.33) to $\Delta\boldsymbol{\sigma}=\mathbf{1}\Delta\sigma$,

$$\Delta\sigma=-\frac{\tau^3e^2}{m^2}\beta n\frac{4\pi\rho}{3}\int e^{-\beta\varphi}\left(\frac{d\varphi}{dr}\right)^2 r^2dr. \qquad (3.34)$$

Equation (3.34) can be explicitly evaluated if the force $-\varphi'$, between the electron and the impurity center is known. Possible choices for the potential φ for charged impurities are suggested by current theory of electrolytes. For example, in the case of a negatively charged impurity center φ can be given by the Debye shielded Coulomb potential $\varphi_{\mathrm{D.S.}}$ and in the case of a positively charged impurity center (of effective positive charge $+Ze$), imbedded in the solid of effective dielectric constant D, φ can be the Bogoljubow potential φ_B,[6] viz.

$$\varphi_{\mathrm{D.S.}}=+\frac{Ze^2}{Dr}\exp[-r/\lambda_D],$$

$$\varphi_B=-\frac{Ze^2}{Dr}(1-e^{-\alpha r})\exp[-r/\lambda_D],$$

the latter remains finite as r vanishes, with α a distance of the order of the effective Bohr radius and λ_0 the Debye shielding distance. A mathematically simpler choice is that the force is given by Coulomb's law with appropriate cutoffs, which are necessary to satisfy the conditions of the expansion. For an impurity center of effective charge Ze imbedded in an impure solid whose effective dielectric constant is D, we set

$$\begin{aligned}-\varphi'(r)&=0 &&\text{for}\quad r<a \text{ and } r>\lambda_D,\\ &=-Ze^2/Dr^2 &&\text{for}\quad a<r<\lambda_D,\end{aligned}\tag{3.35}$$

where a and λ_D are the lower and upper cutoff distances. Substituting Eq. (3.35) into Eq. (3.34), we find

$$\begin{aligned}\Delta\sigma&=-\frac{4\pi\rho n\tau^3}{3m^2}\frac{Ze^4}{D}[\exp(\beta Ze^2/Da)-\exp(\beta Ze^2/D\lambda_D)]\\ &=\frac{4\pi}{3}\sigma_{\mathrm{phon}}\left(\frac{\rho\tau^2}{m}\frac{Ze^2}{D}\right)\\ &\qquad\times[\exp(\beta Ze^2/Da)-\exp(\beta Ze^2/D\lambda_D)]\end{aligned}\tag{3.36}$$

where we have assumed for simplicity that all the impurities have the same charge; otherwise their effect is additive in this approximation.

The upper cutoff λ_D may be chosen, as in the Conwell-Weisskopf theory,[7,8] to be one-half the average distance between impurity centers, $\lambda_D=\frac{1}{2}\rho^{-\frac{1}{3}}$, and $\Delta\sigma$ will generally not be too sensitive to its exact value. The lower cutoff distance, a, presents a serious problem in the case of negatively charged impurities where $\Delta\sigma$ given by Eq. (3.36) goes to infinity as a vanishes. The origin of this difficulty is related to the complete trapping of the electrons by the $-1/r$ potential. This is true, classically, for any potential with an infinite depth, but this complete trapping does not occur in a true quantum mechanical theory. Even with the cutoff we do not treat correctly the electrons with negative energies, which ought not contribute to the current at all, but which do in our theory, a little. It would seem reasonable to choose a to be of the order of the Bohr radius $D\hbar^2/me^2$. The further elucidation of this question requires a quantum mechanical treatment which we are carrying out.

At sufficiently high temperatures, $\beta|Z|e^2/Da\ll 1$, Eq. (3.36) reduces to

$$\frac{\Delta\sigma}{\sigma_{\mathrm{phon}}}=-\frac{4\pi}{3}\frac{\tau^2}{mkT}\left(\frac{Ze^2}{D}\right)^2\frac{1}{a}\left(1-\frac{a}{\lambda_D}\right)\rho.\tag{3.37}$$

We note here that if a is taken to be independent of the temperature then $\Delta\sigma/\sigma_{\mathrm{phon}}$ has a temperature dependence which goes as $(\sigma_{\mathrm{phon}})^2/T$, while Matthiessen's rule predicts a temperature dependence of $\Delta\sigma/\sigma_{\mathrm{phon}}\approx\sigma_{\mathrm{phon}}/\sigma_i$.

Note added in proof. The calculation carried through in Sec. 3 for the constant relaxation time approximation can also be done quantum-mechanically in the density matrix formalism. When the impurity-electron interaction is represented by a screened Coulomb potential $\varphi_{\mathrm{D.S.}}$ and only the lowest order terms in φ are kept, then the quantum formula corresponding to Eq. (3.37) here is

$$\frac{\Delta\sigma}{\sigma_{\mathrm{phon}}}=-\frac{\tau^2}{\hbar(mkT)^{\frac{1}{2}}}\left(\frac{Ze^2}{D}\right)^2\left(\frac{128}{(18\pi)^{\frac{1}{2}}}I(\gamma)\right).\tag{3.37$'$}$$

Here, γ is $(3/16\pi^2)(\lambda/\lambda_D)^2$ where λ is the de Broglie wavelength of the electron, $\lambda=h/(3mkT)^{\frac{1}{2}}$, and

$$I=\int_{-\omega}^{\omega}dx\frac{x^3\exp(-\frac{1}{2}x^2)}{(x^2+\gamma^2)^2}\int_{-\omega}^{\omega}\exp(-\tfrac{1}{2}y^2)\frac{\sinh(xy)}{y}dy\xrightarrow[\gamma\to 0]{}(8\pi)^{\frac{1}{2}}\ln(\lambda/\lambda_D)$$

and the other symbols have the same meaning as in Eq. (3.37).

4. CONDUCTIVITY AND VELOCITY AUTOCORRELATION FUNCTION

In this section we continue the analysis of the conductivity in the relaxation time approximation, particularly in reference to the extent to which this conductivity departs from Matthiessen's rule. Using the stationary value of φ (see Sec. 2), one finds after some manipulation assuming isotropicity, that

$$\begin{aligned}\sigma&=\frac{\beta e^2}{3}\int_0^\infty\int\int\mathbf{v}\cdot\langle P(\mathbf{x},\mathbf{x}'|s)\mathbf{v}'f_0(\mathbf{x}')\rangle_N d\mathbf{x}d\mathbf{x}'ds\\ &=\frac{ne^2}{m}\int_0^\infty C(s)ds,\end{aligned}\tag{4.1}$$

where $C(s)$ is the normalized velocity autocorrelation function,

$$C(s)=\langle\langle\mathbf{v}(s)\cdot\mathbf{v}\rangle_N\rangle_0/\langle\mathbf{v}\cdot\mathbf{v}\rangle_0,\tag{4.2}$$

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[6] See for example, G. Kelbg, Wiss. Univ. Rostock, Math.-Naturw. Reihe **9**, 4 (1959).

[7] E. Conwell and F. Weisskopf, Phys. Rev. **69**, 258 (1946).

[8] H. Brooks, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, New York, 1955), Vol. 7, p. 85.

and

$$\langle \mathbf{v}\cdot\mathbf{v}\rangle_0 = 3nkT/m. \tag{4.3}$$

For the relaxation-time approximation, P is given by Eq. (3.2) which yields immediately

$$C(s)=e^{-s/\tau}C_i(s)=C_{\text{ph}}(s)C_i(s), \tag{4.4}$$

where $C_i(s)$ is the velocity autocorrelation in the absence of phonon scattering, i.e., $\tau^{-1}\to 0$ and $C_{\text{ph}}(s)$ is similarly defined as $C(s)$. For Matthiessen's rule to hold, $C_i(s)$ would also have to be of the form $\exp(-s/\tau_i)$.

Our point now is that there is an essential difference between the behavior of $C_i(s)$ and $C_{\text{ph}}(s)$ near $s=0$. For while $C_{\text{ph}}(s)$ has a cusp at the origin,

$$C_{\text{ph}}(s)=e^{-|s|/\tau}=1-\frac{|s|}{\tau}+O(s^2), \tag{4.5}$$

$C_i(s)$ must be a smooth even function of s near the origin. More explicitly,

$$C_i(s)=1-\frac{3\beta}{2nm}\langle\langle \mathbf{F}^2\rangle_N\rangle_0 s^2+O(s^4), \tag{4.6}$$

which leads back to Eq. (3.29) for $\Delta\sigma$.

The origin of this different behavior lies in the fact that the interaction of the electrons with the phonons has been treated as impulsive while that with the impurities has been retained as part of a continuous Hamiltonian (neglecting any slight complications that might arise from a finite cutoff). It is generally believed though, in the case of atoms moving in fluids or solids, and the same reasoning ought to apply here too, that for large times $C_i(s)$ ought to decay exponentially. A conjectured form of this function which exhibits the proper behavior for small and large s,[9] whose consequences we shall investigate here briefly, is

$$C_i(s)=\operatorname{sech}(s\pi/\tau_i), \tag{4.7}$$

where the factor π has been put in so that σ_i, the conductivity when $\tau_i \ll \tau$, is given by

$$\sigma_i=\frac{ne^2}{m}\int_0^\infty C_i(s)ds=\frac{ne^2}{m}\tau_i. \tag{4.8}$$

The impurity relaxation time τ_i appearing in $C_i(s)$ may be identified, in this approximation, from Eq. (4.6) as

$$\tau_i^{-2}=\langle\langle \mathbf{F}^2\rangle_N\rangle_0/(3m\pi^2kT). \tag{4.9}$$

It is clear from this equation that the identification of $(ne^2/m)\tau_i$ with the conductivity in the limit $\tau_i\ll\tau$, can possibly be true only when there is a high concentration of impurities. For at low densities of impurities $1/\tau_i^2$ given by this equation is proportional to ρ [cf. Eq. (3.34)] and the resistance would not be linear in ρ. The full conductivity σ is now given by

$$\begin{aligned}\sigma&=\frac{ne^2}{m}\int_0^\infty\frac{2\exp(-s/\tau)ds}{\exp(\pi s/\tau_i)+\exp(-\pi s/\tau_i)}\\&=\frac{ne^2\tau_i}{m}\left\{\cos\left(\frac{\tau_i}{\tau}\right)+\frac{1}{2\pi}\left[\psi\left(\frac{3}{4}+\frac{\pi}{4}\frac{\tau_i}{\tau}\right)\right]\right.\\&\qquad\left.-\psi\left(\frac{3}{4}-\frac{\pi}{4}\frac{\tau_i}{\tau}\right)\right\},\end{aligned} \tag{4.10}$$

with

$$\psi(z)=\Gamma'(z)/\Gamma(z);\quad \Gamma(z)=\int_0^\infty e^{-t}t^{z-1}dt. \tag{4.11}$$

In the two limiting cases of $\tau\ll\tau_i$ and $\tau_i\ll\tau$, we have

$$\sigma=\begin{cases}\dfrac{ne^2\tau}{m}\left[1-\dfrac{\pi^2}{2}\left(\dfrac{\tau}{\tau_i}\right)^2+\cdots\right]\\ \quad=\dfrac{ne^2\tau}{m}\left[1-4.95\left(\dfrac{\tau}{\tau_i}\right)^2+\cdots\right], & \tau\ll\tau_i,\\ \dfrac{ne^2\tau_i}{m}\left[1-\dfrac{\psi'(\frac{3}{4})}{4}\left(\dfrac{\tau_i}{\tau}\right)+\cdots\right]\\ \quad=\dfrac{ne^2\tau_i}{m}\left[1-0.63\left(\dfrac{\tau_i}{\tau}\right)+\cdots\right], & \tau_i\ll\tau,\end{cases} \tag{4.12}$$

while for comparison Matthiessen's rule gives

$$\sigma=\begin{cases}\dfrac{ne^2\tau}{m}\left[1-\dfrac{\tau}{\tau_i}+\cdots\right], & \tau\ll\tau_i,\\ \dfrac{ne^2\tau_i}{m}\left[1-\dfrac{\tau_i}{\tau}+\cdots\right], & \tau_i\ll\tau.\end{cases} \tag{4.13}$$

We see that in the case $\tau_i\ll\tau$, the two essentially agree. This corresponds to the case where the probability of scattering by a phonon during the transversal by an electron of an impurity atom is very small and the two processes therefore add up in the resistance. [Our choice of $C_i(s)$ rules out the case where τ_i is small because there are very strong long range forces between an electron and an impurity center. Rather τ_i small corresponds to having a large concentration of impurities.] On the other hand, for $\tau\ll\tau_i$, where there are many phonon collisions during a transversal time, the deviation from Matthiessen's rule will be very large in this approximation, and actually corresponds to a larger conductivity. We should mention again though, that this last discussion depends on the particular form chosen for $C_i(s)$.

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[9] D. C. Douglass, J. Chem. Phys. (to be published).