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REPRINT

A NEW METHOD FOR THE EVALUATION OF ELECTRIC CONDUCTIVITY IN METALS

by

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Philosophical Magazine, **3**, 1020–1031 (1958).

[1020]

A New Method for the Evaluation of Electric Conductivity in Metals†

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[Received May 23, 1958]

Abstract

A method is developed which allows the evaluation of the closed formal expressions for electrical conductivity which have recently been developed by several authors. The case of a random set of scatterers is treated in detail and the formal solution made to yield directly the solution to the Boltzmann equation. A brief mention of the application of this method to liquids and alloys is made.

§ 1. Introduction

Recently it has been realized by several workers (Nakano 1956, Kubo 1956, Kohn and Luttinger 1957, Greenwood 1958), that the electric conductivity in, say, a metal can be written down in a closed formal expression, without going through the intermediate form of deriving a transport equation, and moreover these closed forms are exact. The usual derivation of a transport equation (cf. Peierls 1955) is rather limited in its applicability and cannot in any simple way be extended to the cases of alloys and liquids etc., and moreover, even where it is usually used, it is not at all clear (see e.g. Peierls 1955, p. 123) that there are not temperature dependent corrections which would entirely invalidate the usual solution. Now the formal exact solutions avoid all this, but carry the difficulty that they are still in a rather abstract form, and it is not clear how they are to be evaluated. This paper is concerned with the evaluation of these formulae, and will show that they can readily give the same result as the usual transport equation where the latter has been assumed to be correct, and thus dispose of the possibility of temperature dependent corrections. The use of the exact formulation in new problems will only be very briefly mentioned in this paper, and since the present object is only to illustrate the method, the simplest problem, that of the conductivity of electrons scattered by a random set of scattering centres, will be discussed.

§ 2. Formulation of the Problem

The starting point will be the formula of Greenwood and Peierls, which states that the conductivity tensor is given by

$$\sigma_{\mu\nu} = -2\pi e^2\hbar \sum_{n,m} v_{nm}{}^{\mu} v_{mn}{}^{\nu} \delta(E_n - E_m) \frac{\partial f}{\partial E_n}, \quad . \quad . \quad . \quad . \quad (1)$$

† Communicated by Professor R. E. Peierls, C.B.E., F.R.S.

where $v_{mn}{}^{\mu}$ is the matrix element of velocity, f the electron distribution function, and the δ function is to be understood in the sense that the limit $E_n \to E_m$ is taken after the system is considered so large that always there are many levels between E_n and E_m. This form as it stands is not suitable for computation, so it is rearranged by first writing it out in full:

$$v_{nm}{}^{\mu} v_{mn}{}^{\nu} = -\frac{\hbar^2}{m^2} \int \psi_n(x) \frac{\partial \psi^*(x)}{\partial x_\mu} d^3x \int \psi_m(y) \frac{\partial \psi_n{}^*(y)}{\partial y^\nu} d^3y. \quad . \quad (2)$$

Introduce units so that $(2m/\hbar^2)^{-1/2} = 1$, then

$$\sum_{m,n} v_{nm}{}^{\mu} v_{mn}{}^{\nu} = -\left(\frac{8\pi e^2}{\hbar}\right) \sum_{n,m} \iiiint \frac{\partial}{\partial x_\mu'} \{\psi_n(x)\psi_n{}^*(x')\} \frac{\partial}{\partial y_\nu'} \{\psi_m(y)\psi_m(y')\}$$
$$\times \delta(x'-y)\delta(y'-x)\, d^3x\, d^3y\, d^3x'\, d^3y'. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now $\sum_n \psi_n(x)\psi_n(x')\delta(E-E_n)$ is a Green function, the solution of the homogeneous Schrödinger equation. If the Schrödinger equation for ψ is

$$(H-E)\psi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the Green functions G_+, G_- are given by

$$\left.\begin{aligned} (H-E+i\epsilon)G_+(x,x') &= \delta(x-x') \\ (H-E-i\epsilon)G_-(x,x') &= \delta(x-x') \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where ϵ is an infinitesimal quantity used to define the contour defining the G_+, G_-, then

$$G_+(x,x') = \sum_n \psi_n(x)\psi_n{}^*(x')(E-E_n+i\epsilon)^{-1} \quad . \quad . \quad . \quad . \quad (6)$$

$$G_-(x,x') = \sum_n \psi_n(x)\psi_n{}^*(x')(E-E_n-i\epsilon)^{-1}. \quad . \quad . \quad . \quad . \quad (7)$$

From these the sum and the difference can be made

$$G_+ - G_- = 2\pi i \sum \psi_n(x)\psi_n{}^*(x')\delta(E-E_n)$$
$$= 2\pi i G \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$
$$G_+ + G_- = 2\pi i P \sum \psi_n(x)\psi_n{}^*(x')(E-E_n)^{-1}$$
$$= 2\pi i G_P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

P standing for principal part.

In the absence of potentials these functions are just

$$(4\pi r)^{-1} e^{i\sqrt{(E)}r}, \qquad (4\pi r)^{-1} e^{-i\sqrt{(E)}r}, \qquad i(4\pi^2 r)^{-1} \sin\sqrt{(E)}r,$$
$$i(4\pi^2 r)^{-1} \cos\sqrt{(E)}r, \qquad (r = |\mathbf{X}-\mathbf{X}'|), \quad . \quad . \quad . \quad . \quad (10)$$

assuming that one already is dealing with an infinite system, i.e., a continuum of energy so that the sums over n become integrals. So if G is used for the difference of G_+ and G_-, (8) the sine like function, and also

we now specialize to the case of a diagonal σ, we have

$$\sigma = \frac{1}{3}\left(\frac{8\pi e^2}{\hbar}\right)\sum_{n,m}\iiiint (\partial G_n(x,x')/\partial x_\mu)(\partial G_m(y,y')/\partial y_\mu) \times \delta(E_n - E_m)(\partial f/\partial E_n)\delta(x'-y)\partial(y'-x)\, d^3x\, d^3y\, d^3x'\, d^3y' \quad . \quad (11)$$

where $G_n(x,x')$ is $G(E_n; x, x')$. The problem now is to find G and f in the presence of the scattering potential, and finally to average σ over all configurations of this potential†. It is convenient to express this in the following way: the Schrödinger equation is now

$$(\nabla^2 - E \pm i\epsilon + V(\mathbf{x}))G_\pm(x,x') = \delta(x-x'), \quad . \quad . \quad . \quad (12)$$

where

$$V(\mathbf{x}) = \sum_\alpha u(\mathbf{x} - \mathbf{X}_\alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

X_α being the positions of the scattering centres, and u the potential they exert on the electron. It is convenient to use the Fourier transform of this potential, defining

$$\rho_{\mathbf{k}} = \sum_\alpha e^{i\mathbf{k}\mathbf{X}_\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$V(x) = \int u(k)\, e^{i\mathbf{k}\mathbf{x}} \rho_{\mathbf{k}}^*\, d^3k. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Now if the $\mathbf{X}_\alpha$ are random, it can be shown by standard probability theory that the distribution function for the ρ's is

$$\left.\begin{aligned} P(\rho_{\mathbf{k}}) &= \xi \exp\Big[- \iint R(\mathbf{k},\mathbf{j})\rho_{\mathbf{k}}\rho_{\mathbf{j}}\, d^3k\, d^3j \\ &\quad - \iiiint Q(\mathbf{k},\mathbf{j},\mathbf{l},\mathbf{m})\rho_{\mathbf{k}}\rho_{\mathbf{j}}\rho_{\mathbf{l}}\rho_{\mathbf{m}}\, d^3k\, d^3j\, d^3l\, d^3m - \ldots \Big] \\ R(\mathbf{k},\mathbf{j}) &= N^{-1}\delta(\mathbf{k}+\mathbf{j}) + O(N^{-3}) \\ Q(\mathbf{k},\mathbf{j},\mathbf{l},\mathbf{m}) &= N^{-3}\left(\frac{1}{24}\right)\Big[\delta(\mathbf{k}+\mathbf{j}+\mathbf{l}+\mathbf{m}) - 3\sum_{\text{perm}}\delta(\mathbf{k}+\mathbf{j})\delta(\mathbf{l}+\mathbf{m})\Big] + O(N^{-5}) \end{aligned}\right\}, \quad . \quad . \quad . \quad (16)$$

where N is the total number of scatterers, and ξ the normalization to give total probability unity. When N is large, this can be used with k running over the whole continuum of k space. So we reach the final formula

$$\sigma = \frac{1}{3}\left(\frac{8\pi e^2}{\hbar}\right)\int \ldots \int \xi P(\rho_{\mathbf{k}})(\partial G_n(x,x')/\partial x_\mu)(\partial G_m(y,y')/\partial y_\mu) \times \delta(E_n - E_m)(\partial f/\partial E_n)\delta(x-y')\delta(y-x')\, d^3x\, d^3y\, d^3x'\, d^3y' \prod d\rho_{\mathbf{k}}\, d\rho_{\mathbf{k}}^*. \quad (17)$$

This form has the great advantage that it is essentially the same form as that of electrons interacting with the quantized electromagnetic field, and so techniques for evaluating it are already in existence. Moreover, there are none of the divergence problems of electrodynamics here and the various approximate techniques of electrodynamics can be applied with confidence.

† The meaning of the averaging is discussed in detail by Kohn and Luttinger (1957).

§ 3. Evaluation

The essential difference between (1) and (17) is that the averaging over the scatterers can be carried out before the integrations over coordinates and allows manipulations which are meaningless when applied to (1). Although one can, on the basis of (17), derive integral equations for the average of $G(x,x')$, $G(y,y')$, it is simplest to consider the perturbation expansion of the G's, from which the structure of the integral will become clear. However, one should emphasize that there is no need to approach the evaluation by a perturbation approach and the results to be obtained below can be got directly.

Consider firstly a simpler problem, that of obtaining the average of just one G alone. This is the difference of the averages of G_+ and G_-, which are more convenient to consider. Now in perturbation theory one can write, using $G^{(0)}$ for the ρ-independent functions (10),

$$G_+(x,x') = G_+^{(0)}(x,x') - \iint G_+^{(0)}(x,y)u(\mathbf{k})\,e^{i\mathbf{k}y}\rho_{\mathbf{k}}{}^*G_+^{(0)}(y,x')\,d^3y\,d^3k$$

$$+ \iiiint G_+^{(0)}(x,y)u(\mathbf{k})\,e^{i\mathbf{k}y}\rho_{\mathbf{k}}{}^*G_+^{(0)}(y,z)u(\mathbf{j})\,e^{i\mathbf{j}z}\rho_{\mathbf{j}}{}^*G_+^{(0)}(z,x')$$

$$\times d^3y\,d^3z\,d^3k\,d^3j + \ldots . \quad . \quad . \quad (18)$$

Upon averaging, using brackets for average value

$$\langle\rho_{\mathbf{k}}\rangle = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$\langle\rho_{\mathbf{k}}\rho_{\mathbf{j}}\rangle = N\delta(\mathbf{k}+\mathbf{j}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

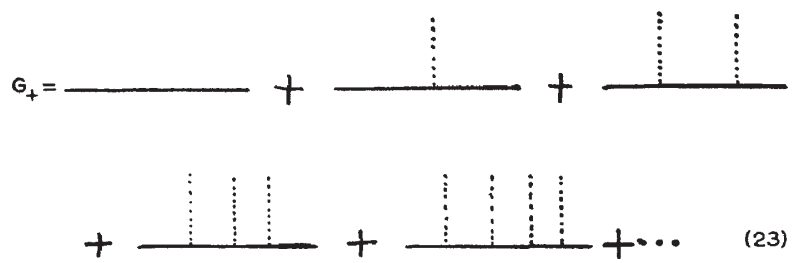
$$\langle\rho_{\mathbf{k}}\rho_{\mathbf{j}}\rho_{\mathbf{l}}\rho_{\mathbf{m}}\rangle = N^2\sum_{\text{perm}}\delta(\mathbf{k}+\mathbf{j})\delta(\mathbf{l}+\mathbf{m}) + N\delta(\mathbf{k}+\mathbf{j}+\mathbf{l}+\mathbf{m}) \quad . \quad . \quad (21)$$

and so on, neglecting terms relatively of order N^{-1}. This can be obtained directly of course, without using the expansion (16). This gives

$$\langle G_+(x,x')\rangle = G_+^{(0)}(x,x') + \iiint NG_+^{(0)}(x,y)\,e^{ik(y-z)}u^2(\mathbf{k})$$

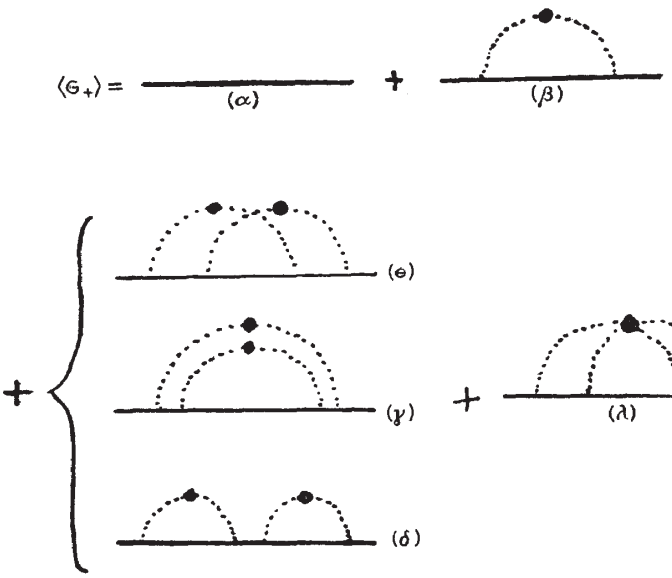
$$\times G_+^{(0)}(y,z)G_+^{(0)}(z,x')\,d^3y\,d^3z\,d^3k + \ldots . \quad . \quad . \quad (22)$$

This is conveniently expressed in diagrams, which are slightly different from those of electrodynamics. Consider $G(x,x')$ before averaging, draw a full line for every $G_+^{(0)}$ and a dotted line for every $u\rho$. Then the expansion of $G(x,x')$ is written



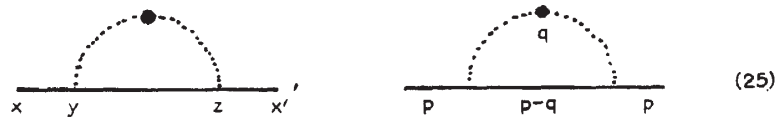
(23)

The averaging process joins the loose dotted line ends up, and places the value N at a join of two, N at a join of four, and so on. Mark these joins by a large dot. Then the average appears as



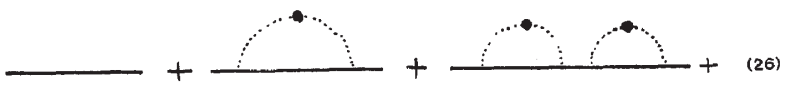
(24)

These diagrams can readily be labelled in configuration or momentum space



(25)

the dot having significance only when diagrams like the last in eqn. (24) appear which incidentally has no analogue in electrodynamics†, which is effectively the case of N infinite. Now concentrate attention upon the series



(26)

This is a simple expansion of the series

$$\left(G_+^{(0)-1}(p) - N\int G_+^{(0)}(q)u^2(\mathbf{p}-\mathbf{q})\,d^3q\right)^{-1}. \quad . \; . \; . \quad (27)$$

† In electrodynamic language the G_+ is S_F, the dotted line the vertex Γ, the dot the photon Green function D_F.

Since $G_+^{(0)}(q) = (2\pi)^{-3}(q^2 - E + i\epsilon)^{-1}$ the integral can be written

$$\tfrac{1}{2}P\int G_+(q)u^2(p-q)\,d^3q + \frac{i\pi}{(2\pi)^3}\int \delta(q^2-E)u^2(p-q)\,d^3q. \qquad (28)$$

If now u is taken as isotropic so that u^2 is $u^2(p^2+q^2-2pq\cos\theta)$ this can be written as $A+iB$, where A, B are real

$$A = \tfrac{1}{2}NP\int (q^2-E)^{-1}u^2(p^2+q^2-2pq\cos\theta)\,d^3q \quad . \quad . \quad . \quad (29)$$

$$B = (2\pi)^{-3}\pi N\int \delta(q^2-E)u^2(p^2+q^2-2pq\cos\theta)\,d^3q. \quad . \quad . \quad (30)$$

These can be expanded as series in p^2-E so that this approximation to $\langle G\rangle^{-1}$ is in the form

$$(p^2 - E + i\epsilon + a_1 + ib_1 + (p^2-E)(a_2+ib_2) + \ldots) \quad . \quad . \quad . \quad (31)$$

where

$$a_1 = \tfrac{1}{2}(2\pi)^{-3}NP\int (q^2-E)^{-1}u^2(E+q^2-2q\sqrt{(E)}\cos\theta)\delta(p^2-E)\,d^3q\,d^3p \quad (32)$$

$$b_1 = N\sqrt{E}(8\pi)^{-1}\int \sin\theta\,d\theta\,u^2(2E(1-\cos\theta)). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

u^2 is in fact the differential scattering probability in Born approximation, $w_0(\theta) = (4\pi^2)^2 2\pi\hbar^{-1}u^2(2E(1-\cos\theta))$

$$b_1 = (2\pi)^{-6}\sqrt{(E)}\hbar N\int \sin\theta\,w_0(\theta)\,d\theta. \quad . \quad . \quad . \quad . \quad (34)$$

A rather more refined treatment is to expand not in terms of p^2-E but $p^2-E+a_1+ib_1$ an important step in electrodynamics where only a_1-E is defined, but here it makes little odds as we are anyway taking all the a's to be small, and the effect of the terms a_2, b_2 etc. will come out very small. So it has been found that this series summed gives effectively a complex displacement of the energy E

$$\langle G_+(E)\rangle \cong G_+(E+\delta E) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where
$$\begin{aligned}(E+\delta E)^{1/2} &= (E+a_1+ib_1)^{1/2}\\ &\cong \sqrt{E} + (a_1+ib_1)/2\sqrt{E}\\ &= \sqrt{E'} + i\Gamma. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)\end{aligned}$$

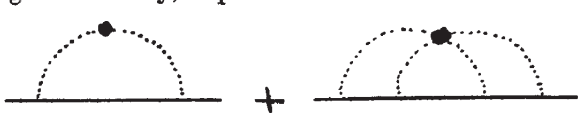
So in configuration space

$$\langle G_+\rangle = (4\pi r)^{-1}\,\mathrm{e}^{-i\sqrt{(E')}r - \Gamma r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

(cf. Bardeen 1956). If this calculation had been performed for G_- the result would have been

$$\langle G_-\rangle = (4\pi r)^{-1}\,\mathrm{e}^{i\sqrt{(E')}r - \Gamma r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

Now consider to what extent one can take the forms (26), (37) as adequate approximations to the whole series. Consider first those terms containing one dot only, in particular the series



(39)

This series is in fact building up the exact scattering of one electron by one scattering centre, instead of its first Born approximation, and if instead of taking the unit

in the series (26) one took all one dot diagrams one would just replace the Born approximation scattering by the true differential scattering cross section in (34), $w(\theta)$. This can be important in strong interaction, and this way of looking at it will be valuable if one can think of the electron in strong interaction with the scattering centres one at a time, as is usually considered to be the case. In a dense system, however, the electron interacts with many centres at once, and one cannot disentangle the scattering with one centre from that of all the others, i.e. the other terms to be discussed below. Henceforward these diagrams will be ignored except inasmuch as the differential scattering cross section can be understood as the true one rather than Born approximation. Now turn to the other terms in (24), in particular, say, (δ) and (ϵ). The electrical conductivity based on the approximate sum (31) and further calculations to be given below comes out to be of order Γ^{-1}, i.e. inversely with the square of the interaction. Terms like (δ), (ϵ) and the higher terms, if included, give a series in the interaction, but do not alter the first term which will still dominate the calculation. To see this it is perhaps simplest to look at G_+ in configuration space. The series which has been considered so far (26) amounts to

$$(4\pi r)^{-1}\,\mathrm{e}^{i\sqrt{(E')}r-\Gamma r}=(4\pi r)^{-1}\,\mathrm{e}^{i\sqrt{(E)}r}(1+Lr+\tfrac{1}{2}L^2r^2+\ldots) \tag{40}$$

where

$$L=i(\sqrt{E'}-\sqrt{E})-\Gamma. \tag{41}$$

The inclusion of terms like (δ), (ϵ) etc. adds in terms so that in first order Lr is corrected by a constant, in second order $\frac{1}{2}L^2r^2$ is corrected by a term in r, and so on, always a power of r less in any order, so that summing on the basis of (31) one has

$$\langle G_+\rangle=(4\pi r)^{-1}\,\mathrm{e}^{(i\sqrt{E'}-\Gamma)r}(1+k_0r+k_1r^2+\ldots) \tag{42}$$

and, as will appear below, this affects the conductivity by second and higher terms in u^2

$$\sigma\sim O(\Gamma^{-1})+O(1)+O(\Gamma)+O(\Gamma^2)+\ldots. \tag{43}$$

Thus (37) is a good basis for the evaluation of $\langle G_+\rangle$ and hence, of course, $\langle G\rangle$.

To summarize in a rather formal way the above discussion, consider the identity

$$\begin{aligned}G_+(x,x')=G_+^{(0)}(x,x')-\iint G_+^{(0)}(x,y)\,\mathrm{e}^{i\mathbf{k}y}u(\mathbf{k})\rho_{\mathbf{k}}G_+^{(0)}(y,x')\,d^3y\,d^3k\\+\iiiint G_+^{(0)}(x,y)\,\mathrm{e}^{i\mathbf{k}y}u(\mathbf{k})\rho_{\mathbf{k}}G_+^{(0)}(y,z)u(\mathbf{j})\,\mathrm{e}^{i\mathbf{j}z}G_+(z,x')\\\times d^3y\,d^3z\,d^3k\,d^3j.\end{aligned} \tag{44}$$

Then

$$\langle G_+(x,x')\rangle = G_+^{(0)}(x,x') - \iint G_+^{(0)}(x,y)\, e^{iky} u(\mathbf{k}) \langle \rho_{\mathbf{k}} \rangle G_+^{(0)}(y,x')\, d^3y\, d^3k$$
$$+ \iiiint G_+^{(0)}(x,y)\, e^{i\mathbf{k}y} u(\mathbf{k}) \langle \rho_{\mathbf{k}} G_+^{(0)}(y,z) u(\mathbf{j})\, e^{i\mathbf{j}z} \rho_{\mathbf{j}} G_+(z,x')\rangle$$
$$\times d^3y\, d^3z\, d^3k\, d^3j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

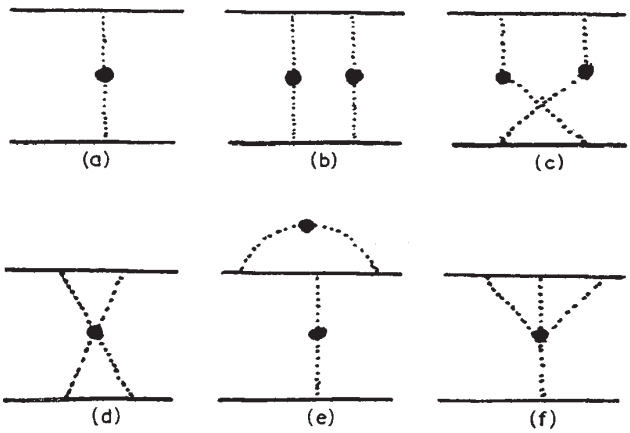
$$= G_+^{(0)}(x,x') + \iiiint G_+^{(0)}(x,y) v(\mathbf{k}) v(\mathbf{j})\, e^{i\mathbf{k}y + i\mathbf{j}z} G_+^{(0)}(y,z)$$
$$\times \langle \rho_{\mathbf{k}} \rho_{\mathbf{j}} G_+(z,x')\rangle\, d^3y\, d^3z\, d^3k\, d^3j \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

$$= G_+^{(0)}(x,x') - \iint G_+^{(0)}(x,y) \Sigma(y,z) \langle G_+(z,x')\rangle\, d^3y\, d^3z, \quad . \quad (47)$$

which defines $\Sigma(y,z)$. Then symbolically

$$[(G_+^{(0)})^{-1} + \Sigma]\langle G_+\rangle = \delta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

The discussion above has shown that when the interaction is weak, an evaluation of Σ by perturbation theory is adequate. So far all the discussion has concerned $\langle G_+\rangle$, but (17) involves the evaluation of $\langle G_n' G_m' \partial f/\partial E\rangle$, and the two G's and the f will interfere. The dependence of f upon the p's in the averaging does not affect the answer in its leading term, so it is ignored for the present. Since the problem is already being considered for an infinitely large conductor the distinction between n and m can be dropped at this stage. Consider at first the quantity $\langle G(x,x')G(y,y')\rangle$. In terms of the diagrams, this consists of two full lines, with dotted lines leaving and entering both, in particular, in addition to the types of series (24) one also has types



(49)

Types (*d*), (*f*) clearly belong to the same category as those of (24, λ) and will be considered no further. Also disregard type (*e*) which is an interference between type (α) and (β), and corresponds to the Lamb shift in electrodynamics: it can readily be found to be small when the interaction is weak. Of the remainder, types (*a*), (*b*) are again the first two of a simple

series analogous to (β), (γ) of (24). Assuming then that terms like (a), (b) do not interfere with terms like (β), (γ) one has the equation for $\langle GG\rangle$:

$$\langle G(x,x')G(y,y')\rangle = \langle G(x,x')\rangle\langle G(y,y')\rangle + N\iiint \langle G(x,z)\rangle\langle G(y,w)\rangle u^2(\mathbf{k}) \times e^{i\mathbf{k}(\mathbf{z}-\mathbf{w})}\langle G(z,x')G(w,y')\rangle\, d^3k\, d^3z\, d^3w, \quad . \quad (50)$$

or in the spirit of (48) the exact equation can be written symbolically in terms of a generalized ' interaction ' I

$$\langle GG\rangle = \langle G\rangle\langle G\rangle + \langle G\rangle\langle G\rangle I\langle GG\rangle \quad . \ . \ . \ . \quad (51)$$

and as in (48), by explicit calculation of the errors, one finds that I can be evaluated by perturbation theory if the interaction is weak. The first approximation, the sum of (a), (b) . . ., is then (51) with

$$I(\alpha,\beta) = N\int d^3k u^2(\mathbf{k})\, e^{i\mathbf{k}(\alpha-\beta)}. \quad . \ . \ . \ . \ . \ . \quad (52)$$

The quantity required has $x'=y$, $y'=x$, so let Δ be $\langle GG\rangle$ in this case. Then if Δ is written in momentum space, the quantity required in (17) is, where Ω is the total volume,

$$\Omega\int \mathbf{p}\cdot\mathbf{q}\Delta(\mathbf{p},\mathbf{q})\, d^3p\, d^3q \quad . \ . \ . \ . \ . \ . \quad (53)$$

where (52) becomes, putting

$$\langle G(p)\rangle\langle G(-p)\rangle = g(p) \quad . \ . \ . \ . \ . \ . \quad (54)$$

$$\Delta(\mathbf{p},\mathbf{q}) = g(p)\delta(\mathbf{p}-\mathbf{q}) + N\int g(p)u^2(\mathbf{p}-\mathbf{s})\Delta(\mathbf{s},\mathbf{q})\, d^3s. \quad . \ . \quad (55)$$

Let

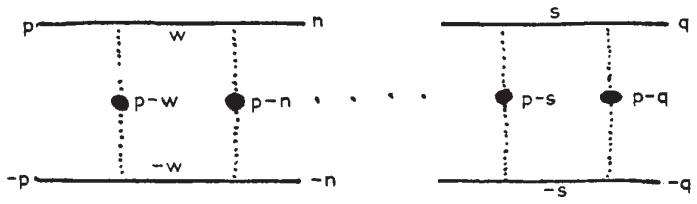
$$\int \mathbf{p}\cdot\mathbf{q}\Delta(\mathbf{p},\mathbf{q})\, d^3q = K(p) \quad . \ . \ . \ . \ . \ . \quad (56)$$

then

$$K(p) = p^2g(p) + N\int g(p)u^2(\mathbf{p}-\mathbf{s})\mathbf{p}\cdot\mathbf{q}\Delta(\mathbf{s},\mathbf{q})\, d^3s\, d^3q \quad . \ . \ . \quad (57)$$

$$= p^2g(p) + 2\pi N\int g(p)u^2(p^2+\delta^2-2ps\cos\theta)\cos\theta\sin\theta \times K(s)s^2\, ds\, d\theta. \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (58)$$

The fact that $\mathbf{p}\cdot\mathbf{q} = pq\cos\theta_{pq}$ effectively contributes $pq\cos\theta_{ps}$ is seen by writing all the quantities concerned in spherical harmonics, or perhaps simpler by considering the series of which (52) is the sum, consisting of terms like



The integration over $\mathbf{q}$ with $\cos\theta_{pq}$ leaves a $\cos\theta_{ps}$ for the s integration, and so right through the diagram, which is in effect (58).

Now $g(p)$, apart from the displacement Γ is just a function with $p=\sqrt{E}$ or more accurately $p=\sqrt{E'}$. $K(p)$ has essentially this same feature, so to the accuracy that has been used so far, the solution of (58) can be written down at once

$$K(p)=p^2g(p)\left[1-2\pi N\int u^2(2E(1-\cos\theta))\cos\theta\sin\theta\int q(s)\delta^2\,ds\right]^{-1}. \qquad (59)$$

The integral of K can be obtained by contour integration or by the discussion below in equations (64)–(66).

$$\int K(p)\,d^3p=\frac{E'/2\Gamma'}{1-\Gamma'/\Gamma} \qquad (60)$$

$$=\frac{E'}{2}(\Gamma-\Gamma')^{-1} \qquad (61)$$

where

$$\Gamma'=(8\pi)^{-1}N\hbar\int u^2(2E'(1-\cos\theta))\sin\theta\cos\theta\,d\theta \qquad (62)$$

or in the notation of (34)

$$\Gamma'=\tfrac{1}{2}(2\pi)^{-6}N\hbar\int\cos\theta\sin\theta\,w_0(\theta)\,d\theta. \qquad (63)$$

It is perhaps useful to look at (60) in configuration space. Without scattering the conductivity is

$$\sigma=\frac{1}{3}\left(\frac{8\pi e^2}{\hbar}\right)\frac{\Omega}{(2\pi)^4}\sum_E\int\nabla\frac{\sin\sqrt{E}r}{r}\nabla\frac{\sin\sqrt{E}2}{r}(\partial f/\partial E)\,d^3r. \qquad (64)$$

This diverges at large distances where the integral over r looks like

$$\sim\int^{\infty}dr.$$

When the scattering is introduced, the term $\sin\sqrt{(E)}r$ is replaced by $\sin\sqrt{(E')}re^{-\Gamma r}$ and also the averaging process introduces the cross term $e^{\Gamma' r}$ giving altogether, at large distances,

$$\int e^{-2(\Gamma-\Gamma')r}\,dr \qquad (65)$$

$$\sigma=\Omega e^2/(12\pi^2\hbar(\Gamma-\Gamma')). \qquad (66)$$

This, of course, is the usual answer (cf. Peierls 1955, eqns. (6.16), (6.20)); Peierls w is our Nw/Ω, in particular for free electrons where $\partial f/\partial E$ is approximately a δ function at the Fermi surface, so integration over the Fermi surface gives the final result

$$\sigma=e^2n_e\left(4\pi mn_s\int w(\theta)(1-\cos\theta)\sin\theta\,d\theta\right)^{-1} \qquad (67)$$

where n_e is the density of electrons, and n_s the density of the scatterers.

The dependence of f upon the configuration of scatterers can be expressed by expanding it in a power series in the density of scatterers and adding in the terms so produced. These corrections are of the same order as those in (43), and since they are well defined at $T=0$, do not involve the temperature in any critical form.

It is worth remarking that in averaging over all configurations, one includes those configurations for which the conductivity is infinite, for example an ordered lattice system. The method of calculating presented here automatically gives these configurations negligible weight, but a rigorous treatment would require a more careful treatment.

§ 4. Discussion

It has been shown that the exact formal solution of the equation of motion can be evaluated to give the usual solution of the Boltzmann transport equation, and within the framework of weak interaction it is quite easy to write down higher order corrections, though of course these rapidly become very numerous. Of more interest is the possibility of evaluating formula (11) in cases where perturbation theory is not applicable. An example, which is still far from being the most general state of affairs but is of physical interest, is the case when the distribution of scatterers (which may be lattice vibrations, etc.) is known through a partition function, and the electrons still interact weakly with the scattering centres. This is a model of a liquid or an alloy. For a liquid, eqns. (20), (21) and so on, are not satisfied, and the averages can only be found from the partition function. If it could be assumed to a reasonable degree of approximation that

$$\langle \rho_{\mathbf{k}} \rho_{\mathbf{j}}^* \rho_{\mathbf{l}} \rho_{\mathbf{m}}^* \rangle = \sum_{\text{perm}} F(\mathbf{k}-\mathbf{j}) F(\mathbf{l}-\mathbf{m}) \quad . \quad . \quad . \quad . \quad (68)$$

where

$$F(\mathbf{k}-\mathbf{j}) = \langle \rho_{\mathbf{k}} \rho_{\mathbf{j}}^* \rangle \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (69)$$

then one could immediately write down the conductivity by replacing

$$\int w(\theta)(1-\cos\theta)\sin\theta \, d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

by

$$\int F(2E(1-\cos\theta)) w(\theta)(1-\cos\theta)\sin\theta \, d\theta \quad . \quad . \quad . \quad (71)$$

in (67). Since one is dealing with smooth averages this approximation may be adequate for this problem, even if it is not so for the theory of liquids as a whole. In general, however, the conductivity will involve not only the two body correlation function F, which is available experimentally, but the whole partition function, which at present is not available. There are models available for alloys, however, in particular for super lattice forming alloys and this problem is being considered further. Methods are in existence for evaluation of formulae like (17) in cases where perturbation methods are inapplicable, but a discussion of these will be left until they have been successfully applied.

ACKNOWLEDGMENTS

The author would like to thank Professor Peierls for suggesting this problem and for helpful discussions during its solution. He would also like to thank Drs. G. V. Chester and A. Thellung, who have also considered the evaluation of the exact formulation from a different viewpoint, for helpful discussions, and Professor J. M. Luttinger for pointing out some inadequacies of the first version of the work and for drawing the author's attention to the work of Bardeen.

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