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Theory of Electrical Resistivity

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A new general expression for the electrical resistivity of a substance is obtained with the help of projection techniques with the Liouville equation as the point of departure. No many-body detail is sacrificed and the "$\lambda^2 t$ limit" is not invoked. The first-order result in a perturbation expansion in orders of the scattering is presented in explicit form and shown to have a simple and physical appearance. It is also shown to reduce to the well-known Boltzmann expressions for simple cases.

I. INTRODUCTION

The calculation of the electrical resistivity of a substance can be performed at three different levels. The most elementary is the Drude approach,[1] wherein the electrons are assumed to be subjected to a viscous force proportional to their speed. Writing the classical Newtonian equation for each electron as

$$m \frac{d\vec{v}}{dt} = e\vec{E} - \alpha\vec{v} , \tag{1}$$

where the electron has mass m, charge e, and velocity $\vec{v}$, $\vec{E}$ is the applied electric field, and α is a constant of proportionality, we can immediately calculate the steady-state $(d\vec{v}/dt = 0)$ electrical resistivity γ as

$$\gamma = m/Ne^2\tau , \tag{2a}$$

$$\tau = m/\alpha , \tag{2b}$$

where N is the total number of electrons in the substance and τ is the "relaxation time."

Apart from the fact that the equation of motion used is a classical one, the major drawback of the Drude approach is that its implicit assumption of a constant α (and therefore of a constant τ) cannot be justified and an investigation of the origin of the viscous force cannot be carried out within its framework. One merely makes general statements asserting that the viscous force arises from collisions of the electron with the scattering centers (other electrons or different bodies) and that the "relaxation time τ" is approximately one-

half the average time between two collisions.

A more sophisticated approach starts with the Boltzmann equation,[2-7] which describes the time evolution of f, the ensemble density in μ space. The equation in its exact form is a complicated nonlinear integrodifferential one, and so approximations like "linearization" and the "relaxation-time assumption" (see for instance Ref. 3) are often used to solve for f.[8] From f one then obtains the electrical conductivity σ (which is of course $1/\gamma$) as[7]

$$\sigma = - \frac{e^2}{4\pi^3} \int \tau_k v_k^2 \frac{\partial f_k^0}{\partial \epsilon_k} d^3k , \tag{3}$$

where v_k is the component of the velocity of the electron in state k along the direction of measurement, ϵ_k is its energy, f_k^0 is the equilibrium Fermi-Dirac distribution function, d^3k is a volume element in k space, and τ_k is the relaxation time which arises out of the relaxation-time assumption.

The above approach is widely used for practical calculations and almost all discussions of electrical resistivity or related problems are carried out in its context. Under these circumstances it is easy to forget its inherent limitations and the criticisms that can be levied against it. The most serious objection to this Boltzmann approach consists of an objection to the very use of the Boltzmann equation. This equation was derived[9] on the basis of intuitive arguments which are not rigorous and attempts to obtain it deductively from more general starting points (like for

example the Liouville equation) have not been suc-
cessful to the present date. The Bogolubov
formalism, [10] which perhaps came closest to ob-
taining the Boltzmann equation from the Liouville
equation, has recently met with many objec-
tions[11-13] of a very fundamental character, and
until these are removed we cannot be said to have
any acceptable derivation of the Boltzmann equa-
tion. Also, this equation is known to be a first-
order approximation valid for low densities and
weak interactions, and the domain of validity of
its generalizations is also not completely known.
For a more detailed discussion see Refs. 14-16.

It is thus clear that the Boltzmann approach is
not entirely satisfactory and a more rigorous and
a more general approach is necessary. This is
the Liouville approach,[17-21] whose starting point
is the Liouville equation for the density matrix.
The first analysis along these lines was carried
out by Kohn and Luttinger[17,18] but they considered
the simplified case of noninteracting electrons.
To attack the problem from a completely general
standpoint, we may begin with a many-body sys-
tem and obtain, through the Kubo formalism,[19,20]
a closed expression for the electrical conductivity.

$$\sigma = (e^2/m^2 kT) \int_0^\infty dt \, J(t) , \tag{4a}$$

$$J(t) = \tfrac{1}{2} \operatorname{Tr}\rho\{FF(t) + F(t)F\} , \tag{4b}$$

$$F(t) = e^{itL} F , \tag{4c}$$

$$L\iota = [H, \iota] \quad \text{for any } \Theta , \tag{4d}$$

where k is the Boltzmann constant, T is the tem-
perature, ρ is the equilibrium density matrix and
H is the system Hamiltonian, both before the ap-
plication of the electric field, and F is the com-
ponent of the total momentum of the electrons
along the direction of the applied electric field
and of the measured current.[22] (In this paper,
we treat only the diagonal component of the con-
ductivity tensor for the sake of simplicity.)

The advantages of this procedure over the
Boltzmann approach are many. Here one begins with
the very general Liouville equation and sacrifices
no many-body detail to obtain the expression
[Eq. (4a)] for the electrical conductivity. In the
Boltzmann approach on the other hand, we "de-
scend" from the Γ space to the μ space (borrow-
ing from classical terminology) and thus we lose
information. However, as may be expected the
compact but highly formal expression (4) is ex-
tremely hard to calculate. One is forced there-
fore to make some sort of approximation. This
however is beset with difficulties because if a
straightforward perturbation expansion of σ in
powers of the scattering interaction is sought, one
quickly meets with failure. The reason is that the

σ without the scattering is infinite (for obvious
physical reasons), and each successive term in the
expansion is also found to be infinite.

The expansion thus turns out to be purely formal
and completely useless. There are two remedies
to this situation: one is the "$\lambda^2 t$ limit"[20,21,23-25] of
Van Hove, and the other is the content of this pa-
per.

The "$\lambda^2 t$ limit" of Van Hove has been explained
in great detail in Refs. 20, 21, 23-35 and it has been
used by Chester and Thellung[21] and by Verboven[20]
for the present purpose. It essentially consists of
a rearrangement of the formal expansion described
above. If certain mathematical properties of the
scattering interaction are assumed, the limit
$\lambda \to 0$, $t \to \infty$, $\lambda^2 t = \text{const}$ (λ denotes the strength
parameter of the scattering interaction) leads to
an expansion of σ in which each term is finite.

While some indications of the physical motivation
of the "$\lambda^2 t$ limit" exist,[25] the procedure has not
really been justified and the physical meaning of the
limit remains somewhat mysterious. In this pa-
per we bypass this limit completely and present a
different method of calculating the electrical re-
sistivity from the Kubo formula [Eq. (4a)].

II. DIFFERENT METHOD

The basic reasoning is as follows. In the expan-
sion of the electrical conductivity

$$\sigma(\lambda) = \sigma(0) + \lambda\sigma_1 + \lambda^2\sigma_2 + \cdots , \tag{5}$$

$\sigma(0)$, σ_1, σ_2... all turn out to be divergent. One
may however ask the question: What would happen
if an expansion of the quantity $\gamma \equiv 1/\sigma$ is sought in
successive powers of λ:

$$\gamma(\lambda) = \gamma(0) + \lambda\gamma_1 + \lambda^2\gamma_2 + \cdots . \tag{6}$$

It is clear that while the conductivity with zero scat-
tering $\sigma(0)$ is infinite, the resistivity $\gamma(0)$ with zero
scattering is zero. The expansion in Eq. (6) thus
at least starts off with a noninfinite unperturbed
quantity [unlike the expansion in Eq. (5)]. If there-
fore γ_1, γ_2,... also turn out to be noninfinite, we
have a perfectly valid way of calculating γ or σ
from Eq. (6)—hoping of course that the terms in the
expansion are successively smaller. We shall now
show that such a development can in fact be carried
out with the help of a special use of the Zwanzig
projection techniques.[26] We shall obtain specifically
the first-order result and show that it can be put
in complete correspondence with the Drude re-
sult [Eq. (2a)]. Our procedure starts with the
Liouville equation, proceeds through the Kubo
formalism to Eq. (4a), and then makes no other
assumption except the interchangeability of the
orders of a certain limit and an integration. The
result we arrive at [Eq. (12a)] is thus subject
only to the validity of the above operation and of

the Kubo formula. We then make the usual as-sumption of the possibility of an expansion in λ and obtain the lowest-order expression.

III. PROJECTION TECHNIQUES

The projection techniques of Zwanzig[26] are a means of formally extracting partial information from the evolution equation of a quantity $x(t)$, when one is interested not in the entire $x(t)$ but only in a part of it. The techniques have been used in various contexts by a number of au-thors,[26-31] and the details of the particular man-ner in which they are used here may be found in an earlier paper.[30]

Our use of the projection techniques for the present purpose proceeds through the following steps. We first observe that by the cyclic per-mutation of the operators within the trace, it is possible to rewrite the $J(t)$ appearing in Eq. (4) as

$$J(t) = \text{Tr} FK(t) , \tag{7a}$$

where $K(t)$ obeys the Liouville-like equation

$$K(t) = e^{itL} K(0) \tag{7b}$$

and

$$K(0) = \tfrac{1}{2}(\rho F + F\rho) . \tag{7c}$$

It is thus possible to express $J(t)$ as a quantity projected out of another, the latter being governed by a Liouville-like equation. We now define the linear time-independent idempotent projection op-erator P through

$$P\Theta \equiv K(0)\,\text{Tr}\,F^1\Theta \quad \text{for any } \Theta , \tag{8a}$$

$$F^1 \equiv [1/J(0)]\,F . \tag{8b}$$

This particular choice immediately simplifies the Zwanzig equation[26]

$$i\,\frac{\partial PK(t)}{\partial t} = PL\,PK(t) + PLG(t)(1-P)K(0)$$

$$-i\int_0^t ds\,PLG(s)(1-P)LPK(t-s) , \tag{9a}$$

$$G(t) = e^{it(1-P)L} , \tag{9b}$$

and reduces it to (see Ref. 30 for further details)

$$\frac{\partial J(t)}{\partial t} = -\int_0^t ds\,\mathcal{Q}\,(t-s)J(s) , \tag{10a}$$

$$\mathcal{Q}(t) = [1/J(0)]\,\text{Tr}[FLG(t)(1-P)LK(0)] . \tag{10b}$$

We can solve[30] Eq. (10a) by Laplace transforms to yield

$$\int_0^\infty dt\,e^{-\epsilon t} J(t) = J(0)/\left[\epsilon + \int_0^\infty dt\,e^{-\epsilon t}\mathcal{Q}(t)\right] . \tag{11}$$

This result is exact and is a direct consequence of the Kubo formula [Eq. (4a)]. We now take the

limit as $\epsilon \to 0$ and assume that the orders of the limit and the integration may be interchanged. If this is permissible we immediately have a formula for the electrical resistivity:

$$\gamma = [m^2 kT/e^2 J(0)^2] \int_0^\infty dt\,Q(t) , \tag{12a}$$

$$Q(t) = \text{Tr}[FLG(t)(1-P)LK(0)] . \tag{12b}$$

This is in the form required for the Eq. (6) and we shall find that while an expansion of $J(t)$ and therefore of σ in powers of the scattering interac-tion gives rise to divergences, a similar expan-sion of $Q(t)$ and thus of γ does not. In fact we shall derive an explicit formula for the resistivity to the lowest order in the scattering.

IV. SIMPLIFICATION OF $Q(t)$

From Eq. (12b),

$$Q(t) = \text{Tr}[FLG(t)LK(0) - \text{Tr}FLG(t)PLK(0)] . \tag{13}$$

But from Eq. (8),

$$PLK(0) = K(0)\,\text{Tr}[F^1 LK(0)] , \tag{14}$$

and from Eq. (7c), we can easily show that

$$\text{Tr}[F^1 LK(0)] = 0 . \tag{15}$$

Then we have

$$Q(t) = \text{Tr}[FLG(t)LK(0)] . \tag{16}$$

We now write

$$H = H_0 + V , \tag{17a}$$

$$L = L_0 + L_V , \tag{17b}$$

where H_0 is the Hamiltonian of the system in the absence of the scattering mechanism and V con-tains the scattering. It should be noted, in par-ticular, that H_0 need not be simple and may cer-tainly have a complicated many-body character.

For most systems of interest, we shall have

$$[F, H_0] = 0 . \tag{18}$$

It is clear that for any two operators Θ_1 and Θ_2

$$\text{Tr}[\Theta_1 L\Theta_2] = -\text{Tr}\,\Theta_2 L\Theta_1 . \tag{19}$$

Using Eqs. (17b)-(19) in (16), we have

$$Q(t) = \text{Tr}[FL_V G(t)LK(0)] . \tag{20}$$

This result for $Q(t)$ is exact. To get an ex-plicit expression out of Eq. (20) we now make the weak-coupling approximation. Before that we should note that taking the equilibrium density matrix to be canonical, we may write the follow-ing approximate equations,[32] which are valid to the first order in the interaction V:

$$\rho \equiv e^{-\beta(H_0 + V)} \approx \rho_0 + \rho_V , \tag{21a}$$

$$\rho_0 = e^{-\beta H}{}_0 \ , \tag{21b}$$

$$\rho_V = \rho_0 W \ , \tag{21c}$$

$$K(0) \approx K_0 + K_V \ , \tag{22a}$$

$$K_0 = \tfrac{1}{2}(F\rho_0 + \rho_0 F) \ , \tag{22b}$$

$$K_V = \tfrac{1}{2}(F\rho_0 W + \rho_0 WF) \ , \tag{22c}$$

$$W = \int_0^{-\beta} dx \, e^{-xH_0} V e^{xH_0} \ . \tag{23}$$

The weak-coupling approximation[26] consists in replacing $G(t)$ by $G_0(t)$, where

$$G_0(t) = e^{it(1-P)L}{}_0 \ . \tag{24}$$

Using Eqs. (21)–(24) in (20) and retaining the lowest-order terms,

$$Q(t) = \text{Tr}[FL_V G_0(t)(L_0 K_V + L_V K_0)] \ . \tag{25}$$

The above expression which still contains projection operators may now be rid of them by noting that for any operator Θ,

$$G_0(t)\Theta = \Theta + itL_0\Theta - itPL_0\Theta + \cdots \ . \tag{26}$$

However, from the definition (8a) of P and from the results of Eqs. (18) and (19), we have

$$PL_0\Theta = 0 \quad \text{for any } \Theta \ . \tag{27}$$

Substituting Eq. (27) in the expansion in Eq. (26), the projection operators all disappear, yielding

$$G_0(t)\Theta = e^{itL}{}_0\,\Theta \quad \text{for any } \Theta \tag{28}$$

and

$$Q(t) = \text{Tr}[FL_V e^{itL}{}_0 (L_0 K_V + L_V K_0)] \ . \tag{29}$$

V. EXPLICIT CALCULATION

We now proceed to calculate the trace explicitly. Writing

$$Q(t) = \psi_{01}(t) + \psi_{10}(t) \ , \tag{30a}$$

$$\psi_{01}(t) = \text{Tr}(FL_V e^{itL}{}_0 L_0 K_V) \ , \tag{30b}$$

$$\psi_{10}(t) = \text{Tr}(FL_V e^{itL}{}_0 L_V K_0) \ , \tag{30c}$$

and choosing the representation of the simultaneous eigenstates ξ, μ, etc., of F and H_0, we have

$$\psi_{01}(t) = - \sum_{\xi,\mu} \langle \xi | L_V F | \mu \rangle \langle \mu | L_0 K_V | \xi \rangle e^{it(E_\mu - E_\xi)} \ , \tag{31a}$$

$$\psi_{10}(t) = - \sum_{\xi,\mu} \langle \xi | L_V F | \mu \rangle \langle \mu | L_V K_0 | \xi \rangle e^{it(E_\mu - E_\xi)} \ . \tag{31b}$$

The following identities have been proved in the Appendix:

$$\langle \xi | L_V F | \mu \rangle = \langle \xi | V | \mu \rangle (F_\mu - F_\xi) \ , \tag{32a}$$

$$2\langle \mu | L_0 K_V | \xi \rangle = \langle \mu | V | \xi \rangle (F_\mu + F_\xi)(e^{-\beta E_\mu} - e^{-\beta E_\xi}) \ , \tag{32b}$$

$$\langle \mu | L_V K_0 | \xi \rangle = \langle \mu | V | \xi \rangle (F_\xi e^{-\beta E_\xi} - F_\mu e^{-\beta E_\mu}) \ , \tag{32c}$$

$$(F_\mu + F_\xi)(e^{-\beta E_\mu} - e^{-\beta E_\xi}) + 2(F_\xi e^{-\beta E_\xi} - F_\mu e^{-\beta E_\mu})$$

$$= (F_\xi - F_\mu)(e^{-\beta E_\xi} + e^{-\beta E_\mu}) \ , \tag{32d}$$

where F_μ is the diagonal element $\langle \mu | F | \mu \rangle$.

Substituting Eqs. (32a)–(32c) in Eqs. (30a) and (31) and using Eq. (32d), we obtain

$$Q(t) = \tfrac{1}{2} \sum_{\xi,\mu} e^{it(E_\mu - E_\xi)} |\langle \xi | V | \mu \rangle|^2 (F_\mu - F_\xi)^2$$

$$\times (e^{-\beta E_\xi} + e^{-\beta E_\mu}) \ . \tag{33}$$

Substituting Eq. (33) in Eq. (12a), taking the thermodynamic limit first, and writing (the principal part of $1/x$ does not contribute to the following expressions)

$$\int_0^\infty dt \, e^{itx} = \pi\delta(x) \ , \tag{34}$$

we obtain the expression for the resistivity

$$\gamma = \int dE \, e^{-\beta E} \, \alpha(E) / \int dE \, e^{-\beta E} \, g(E) \ , \tag{35a}$$

$$\alpha(E) = \frac{m^2 \pi k T}{e^2 J(0)^2} \sum_{\xi,\mu} |\langle \xi | V | \mu \rangle|^2 (F_\mu - F_\xi)^2$$

$$\times \delta(E - E_\xi)\delta(E - E_\mu) \ , \tag{35b}$$

where $g(E)$ is the many-body density of states given by $\sum_\xi \delta(E - E_\xi)$.

The quantity $J(0)$ appearing in Eq. (35b) also depends on the scattering V, and we must therefore carry out an expansion of it in orders of V and, for the sake of consistency in the expression for γ, retain only the lowest order term. We shall now carry out this calculation.

From Eqs. (7),

$$J(0) = \text{Tr}\rho FF \ , \tag{36}$$

and in the lowest order of V (the zeroth order) this is

$$J(0) \approx \text{Tr}\rho_0 FF \ . \tag{37}$$

The well-known Kubo identity,[19] which may be written in our notation here as

$$-im[\rho_0, X] = \rho_0 \int_0^\beta ds \, F(-is) \ , \tag{38}$$

with X as the relevant component of the "total position operator," takes the following form in the zeroth order of V:

$$-im[\rho_0, X] = \beta \rho_0 F, \tag{39}$$

and Eq. (37) can therefore be written

$$J(0) \approx -imkT \, \text{Tr}[\rho_0, X] F \ . \tag{40}$$

Cyclic permutation of operators within the trace and the use of the basic commutation relations between the position and the momentum operators

yield,[33] from Eq. (40),

$$J(0) \approx NmkT . \qquad (41)$$

Substitution of Eq. (41) in Eq. (35a) gives our

final expression for the electrical resistivity γ correct to the lowest order in the scattering V. It can then be cast into the exact form of Drude [Eq. (2a)] with the relaxation time τ given by

$$\frac{1}{\tau} = \frac{\pi}{NmkT} \int dE \, e^{-\beta E} \sum_{\xi, \mu} |\langle \xi | V | \mu \rangle|^2 (F_\mu - F_\xi)^2 \delta(E - E_\xi) \, \delta(E - E_\mu) \Big/ \int dE \, e^{-\beta E} \sum_\xi \delta(E - E_\xi) . \qquad (42)$$

VI. REDUCTION TO BOLTZMANN FORMULAS

The final expression for the electrical resistivity, the conjunction of Eqs. (2a) and (42), has in spite of its many-body character an extremely familiar form and the recovery of the usual Boltzmann-like formulas for simple cases is quite trivial. While the details are absolutely straightforward and will not therefore be given here, an outline of such a reduction is perhaps in order and will be briefly sketched for the model of elastic scattering of noninteracting electrons from fixed impurities.

Expressing the operators V, F, and H_0 in the second quantized form,

$$V = \sum_{m,n} V_{mn} a_m^\dagger a_n , \qquad (43a)$$

$$F = \sum_k k_x a_k^\dagger a_k , \qquad (43b)$$

$$H_0 = \sum_k \epsilon_k a_k^\dagger a_k , \qquad (43c)$$

the expression for γ [Eq. (42)] can be shown to reduce to a sum over single-electron states, of a product of two factors, one of which is the statistical manifestation of the exclusion principle and the other consists of, among other quantities, the transition probability $|V_{mn}|^2$. The statistical factor is $f_k^0(1 - f_k^0)$, and when multiplied by $1/kT$ [see Eq. (42)] it yields $\partial f_k^0 / \partial \epsilon_k$. The Boltzmann expression (3) is then exactly obtained with its τ_k corresponding to a part of the other factor (not containing the statistics) in our formula.

Scattering from phonons may also be treated in an identical manner, and the corresponding Boltzmann formula obtained from Eq. (42).

VII. DISCUSSION

In summary, our procedure consists of starting with the Liouville equation, arriving (with Kubo) at Eq. (4a), applying projection techniques to yield Eq. (11), and making the assumption of the interchangeability of the orders of the limit and the integration to give Eq. (12a). Equation (12a) is really our central result. We then derive

an explicit expression for the resistivity [Eq. (42) with (2a)] to the lowest order in the scattering interaction: Results correct to higher orders may be obtained by treating $Q(t)$ and $J(0)$ to higher orders.

Our method differs from the existing[20, 21, 23-25] derivations from the Liouville equation in that it entirely bypasses the "$\lambda^2 t$ limit" and consequently avoids the problems of its justification and physical interpretation. When the final result is placed vis-a-vis the Drude expression, the relaxation time τ featuring in our formula is seen to have a simple and physical appearance: One encounters, in Eq. (42), a product of the transition probability between two many-body states and the square of the difference between the expectation values of the total momentum component in the two states. As we have shown in Sec. VI, it is also a straightforward matter to simplify our Eq. (42) for the noninteracting case and obtain a Boltzmann-like formula for the conductivity. As it stands however, Eq. (42) has the complete many-body character. It does not require H_0, the Hamiltonian without the scattering, to be a sum of single-particle Hamiltonians, and it is correct as long as H_0 satisfies Eq. (18). Furthermore, it is possible[34] to modify the procedure and to obtain by a straightforward extension of our method a slightly different formula when Eq. (18) is not satisfied. Another general feature of Eq. (42) is that it is independent of the statistics of the constituents of the system. The latter have to be fed into the formula through the states ξ, μ, etc.

We must hasten to add that while our method has avoided the $\lambda^2 t$ limit, it has introduced in its place a new assumption, viz., the one about the interchangeability of the orders of the limit and integration in Eq. (11). However, we believe that this appears to be a much more reasonable assumption. It is nothing more than requiring that as $\epsilon \to 0$ the limit of the Laplace transform of the correlation function be equal to the $t = 0$ to $t = \infty$ integral of the correlation function.

As a side remark it is interesting to note the following result. Multiplying and dividing Eq. (4) by $J(0)$ one may write

$$\sigma = Ne^2 \tau / m , \qquad (44a)$$

$$\tau = \zeta \int_0^\infty dt\, J(t)/J(0) \;, \tag{44b}$$

$$\zeta = J(0)/NmkT \;. \tag{44c}$$

This simple manipulation shows that if the resistivity γ, as appearing in the Kubo formalism, is put in the Drude form, τ acquires a particularly transparent and nonartificial form. Apart from the parameter ζ, it is just the zero-to-infinity time integral of the "normalized" correlation function. [Two simple details may be easily checked: The dimensions of τ are obviously those of time, since both ζ and $J(t)/J(0)$ are dimensionless; and the right-hand side of Eq. (44b) gives τ apart from ζ for the simple case of a single universal relaxation time, i.e., if $J(t)$ equals $J(0)e^{-t/\tau}$.]

The problem to which one then requires to address oneself is the calculation of the right-hand side of Eq. (44b). The Van Hove method consists of expanding $J(t)$, considering the integral in Eq. (44b) with t' ($\neq \infty$) as the upper limit, rearranging the expansion and taking the limit as $\lambda \to 0$, $t' \to \infty$, $\lambda^2 t' = \text{const}$. Our method, on the other hand, consists of handling the entire object $\int_0^\infty dt\, J(t)$. From the structure of $J(t)$ [Eq. (7a)], we write a separate equation for $J(t)$ [Eq. (10a)], which we arrive at through projection techniques. Laplace-transforming the equation we obtain an expression for the entity $\int_0^\infty dt\, J(t)$ as a reciprocal of another $t = 0$ to $t = \infty$ integral. This latter integral turns out to be amenable to a nondivergent expansion [unlike $\int_0^\infty dt\, J(t)$]. The central idea of our method is thus extremely simple. Since for the case of no scattering, $\tau = \infty$ but $1/\tau = 0$, we expand $1/\tau$ rather than τ in orders of the scattering.

Our final expression is for the resistivity γ rather than for the conductivity σ. It is therefore particularly useful whenever a direct γ expression (as opposed to a σ expression) is required. This happens, for instance, in an investigation[16] of the Matthiessen's rule.[35] This and the treatment of the nondiagonal components of the conductivity tensor, which require a slight modification of our method, will be reported elsewhere.

We conclude by stating that while our method is perfectly general and can in principle tackle the magnetoresistance problem, our final expression as exhibited in Eq. (42) is not valid for such a situation. This is because of the assumption in Eq. (18) which is not correct when the Hamiltonian without the scattering involves a magnetic field. A modification of the simplifying procedure initiated in Eq. (18) must thus be undertaken to treat the problem of magnetoresistance. Such an analysis can be carried out[34] and will be reported in another paper.

Note added in proof. After this paper was written, it was pointed out to us that some of our methods

are similar to the ones employed by H. Mori, Progr. Theoret. Phys. <u>33</u>, 423 (1965); <u>34</u>, 399 (1965). In these interesting articles, Mori provides a rigorous foundation to the Langevin equation in the theory of Brownian motion. In this process he employs projection techniques and derives equations that resemble some of the equations in the first part of the present paper. Indeed Eqs. (5.3) through (5.4) in Mori's second paper are almost identical to our Eqs. (11) and (12). (The difference lies in the meaning of the projection operators.) However, Mori did not obtain an explicit usable expression for the resistivity, which does not contain projection operators. Also, the spirit of his investigation and his use of the projection techniques are quite different from ours. A detailed comparison showing the interrelationship of the two approaches will be presented elsewhere. Here we merely state the following chief differences: (i) Mori applies projections to the Heisenberg equation of motion of an operator corresponding to an observable, and containing no statistical element, while we start with the Liouville equation already containing the statistics and obeyed by $K(t)$, a quantity which is obtained in a simple manner from the density matrix. (ii) Whereas we choose such projections as will make the initial-value term in the Zwanzig equation equal zero, Mori's projections make the first term (called the "proper term" in Ref. 16) zero, and in his approach the initial-value term plays an important role, viz., that of the fluctuating random force. This is a fundamental difference and means that the projection operators are quite different in the two cases. (iii) Equations corresponding to our Eq. (11) look different in Mori's and our approaches in the general case and are alike only in the special case of *auto*correlation functions. (iv) The projected equation is directly obeyed by a correlation function in our method, while Mori's equation features a currentlike operator, whose correlation we consider. (v) The quantities described by the original equation and the projected equation are the same in Mori's approach but different [$K(t)$ and $J(t)$, respectively] in ours. (vi) Finally, the techniques of Mori are particularly well suited to the investigation of Brownian motion while ours are effective for transport parameters. We have also been informed that P. N. Argyres and J. Siegel have recently obtained some results similar to ours. We wish to thank Professors R. Kubo and P. N. Argyres for drawing our attention to these investigations.

APPENDIX

We present here the details of the calculations that lead to Eqs. (32a)–(32d).

The relation

$$L_V F = VF - FV \qquad (A1)$$

and the fact that F is diagonal in states μ, ξ, etc., yield Eq. (32a) quite trivially. We note from Eq. (23) that

$$\langle \mu | W | \xi \rangle = \int_0^{-\beta} dx \langle \mu | V | \xi \rangle e^{-x(E_\mu - E_\xi)} . \qquad (A2)$$

Carrying out the integration we get

$$\langle \mu | W | \xi \rangle = e^{\beta E_\mu} \frac{e^{-\beta E_\xi} - e^{-\beta E_\mu}}{E_\xi - E_\mu} \langle \mu | V | \xi \rangle . \qquad (A3)$$

From Eq. (22c), we have

$$\langle \mu | K_V | \xi \rangle = \tfrac{1}{2} e^{-\beta E_\mu} (F_\mu + F_\xi) \langle \mu | W | \xi \rangle . \qquad (A4)$$

Substituting Eqs. (A3) and (A4) in

$$2 \langle \mu | L_0 K_V | \xi \rangle = 2 \langle \mu | K_V | \xi \rangle (E_\mu - E_\xi) , \qquad (A5)$$

we obtain Eq. (32b). Also, since

$$\langle \mu | L_V K_0 | \xi \rangle = \langle \mu | V | \xi \rangle (\langle \xi | K_0 | \xi \rangle - \langle \mu | K_0 | \mu \rangle) , \qquad (A6)$$

Eq. (32c) is easily obtained. Finally (32d) can be established through a straightforward calculation.

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[32]In Eqs. (21a)–(22c) and in the results derived from them, we do not display the normalizing factor in the density matrix (which makes $\mathrm{Tr}\rho = 1$) merely for the sake of convenience. We hope this will not create any confusion. The factor reappears from Eq. (35a) onwards.

[33]At first sight, $J(0)$ might seem to equal the statistical average of the kinetic energy of the system, and one might, therefore, expect it not to equal $NmkT$ (in lowest order), except for a classical system wherein equipartition holds. It is however possible to show that this is not true and that the reason lies in the indistinguishability of the particles in a quantum mechanical system. A detailed clarification has been given elsewhere (Ref. 34).

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