An Elaborate dc Electric Conductivity Formula as Result of Conjunction of Two Linear Response Formulae

N. MILINSKI

Institute of Fundamental Disciplines-FTN
University of Novi Sad, 21000 Novi Sad

(Received May 21, 1990)

The principal aim of this work is to find out and explain the physics which forms the basis for the procedure by which we have obtained an elaborate expression for the dc electric conductivity $\sigma$, from the Kubo formula for the electric conductivity $\sigma(\omega)$. We show that to get an expression suitable for taking into account scattering effects in the calculation of the dc electric conductivity $\sigma$, it is not enough to put $\omega=0$ into the ac electric conductivity formula $\sigma(\omega)$, but some additional, characteristic physical content must be introduced into formula for $\sigma$. We have found such physical content in conjunction of two linear response formulae: one for the real ac conductivity $\sigma_0(\omega)$, the other one for the real susceptibility $\chi_0(\omega)$, describing polarization by the mechanism of carriers displacement, taken for $\omega\to 0$. The involvement of $\chi_0(\omega)$ into formula for $\sigma$ may be understood as an explicit appreciation of cyclic boundary conditions, which are inherent to the closed loop shape of the many particle system only in which the dc current can run, apart from the ac current which can run also in an open shaped system. Also in this work, we have applied our dc formula to determine $\sigma$ for the cases where the velocity autocorrelation functions are described by the Markoffian and by the Gaussian models.

§ 1. Introduction

One of the best known formulae in the linear response theory is the Kubo formula for transport coefficients.\textsuperscript{1,2} The Kubo formula has got a common recognition as an exact expression for studying the general properties of transport coefficients, but as a tool to calculate for these coefficients it appears to be less suitable.\textsuperscript{3} This is especially true for the case of dc transport coefficients. This strange behaviour of Kubo formula, so different when one is applying it for general and for specific purposes, results from the fact that it is not suitable for a series expansion in powers of the scattering Hamiltonian $U$. In physics there we have at our disposal well developed methods for perturbation series expansion,\textsuperscript{4} which give us a Taylor series (series with positive exponents). Perturbation series expansion in $U$ as applied to Kubo formula did not come into consideration, since it would give a Taylor series in the scattering strength $g$ ($U\sim g$), while we are seeking for the Laurent series in $g$ for the dc conductivity $\sigma$. Much effort has been spent in looking for a suitable parameter, to make the desired series expansion,\textsuperscript{5} and as a result there is a very extensive literature devoted to this problem. As parameters for this kind of series expansion we can meet in the literature: $(\hbar/\tau k_B T)$, $(\hbar/\tau k_B T_D)$, $(1/\tau \omega)$, $(\hbar/\tau E_F)$, and so on, where $\tau$, $T$, $T_D$ and $E_F$ are relaxation time, temperature, Debye temperature and Fermi energy respectively. Any of these parameters contains $\tau$, the relaxation time, a quantity which is usually introduced into transport theory to simplify the problem. However, the concept of simplification by the relaxation time approximation cannot be accepted in many cases. Therefore, approaches which go beyond this kind of simplification...
are needed. Involvement of Green functions into transport theory\(^6\) has opened promises for more adequate approximations, since it makes possible a series expansion in the inverse scattering strength\(^7\) \((1/g)\). Although the approach with Green's functions has given significant advances, it has not satisfied all expectations.

A few years ago, the author of this article, has succeeded in derivation of an expression for the \(dc\) conductivity \(\sigma\)\(^8\) which enables us to determine the coefficients of the Laurent series in \(g\) \((g\) the scattering parameter) for \(\sigma\)\(^9\) by applying the technique of the perturbation theory\(^4\). In this way, we have obtained a natural tool to take into account the effects of the scattering Hamiltonian \(U\) on \(\sigma\).

To derive our \(dc\) conductivity formula in our previous work\(^8\), we started with the Kubo formula\(^1\) for the electric conductivity \(\sigma(\omega)\) as function of frequency \(\omega\):

\[
\sigma(\omega) = \left( \frac{1}{V} \right) \left( \frac{e}{m} \right)^2 \lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \vec{P}_x(t); \vec{P}_x \rangle ,
\]

where

\[
(\vec{P}_x(t); \vec{P}_x) = \int d\lambda \text{Tr} \{ \vec{P}_x(t) - i\hbar \lambda \} \vec{P}_x ,
\]

\[
\vec{P}_x(t - i\hbar \lambda) = e^{\hat{H}_x e^{i\hbar t}} \vec{P}_x e^{-\hat{H}_x e^{-i\hbar t}} .
\]

In the above formulae, \(V\) is the volume, \(e\) and \(m\) are charge and mass of a single carrier, \(\vec{P}_x\) is operator of the carriers \(x\)-component of momentum, \((\vec{P}_x(t); \vec{P}_x)\) is the generalized scalar product of \(\vec{P}_x(t)\) and \(\vec{P}_x\), defined by the right-hand side of (1-2), and \(\hat{H}\) is Hamiltonian of the system, which is assumed to be in thermodynamic equilibrium. By twice applying partial integration in \(t\) to the right-hand side of (1-1) we converted \(\sigma(\omega)\) into:

\[
\sigma(\omega) = \left( \frac{1}{V} \right) \left( \frac{e}{m} \right)^2 \lim_{\varepsilon \to 0} \left\{ \frac{\sigma(\omega) - iz(mN)}{z^2} \right\} ,
\]

where

\[
\sigma(\omega) = \lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} dt e^{iat} \langle \vec{F}_x(t); \vec{F}_x \rangle ,
\]

\[
z = \omega - is ,
\]

\[
\vec{F}_x(t) = \left( \frac{1}{i\hbar} \right) [\vec{P}_x(t), \hat{H}] .
\]

The \(dc\) conductivity \(\sigma\) has been determined as the limiting value of (1-4) taken for \(z \to 0\):

\[
\sigma = \lim_{z \to 0} \sigma(z) = \lim_{\omega \to 0} \sigma(\omega) .
\]

The order of limits on the right-hand side of (1-8) shows that we conceived \(\sigma\) as the limit of a continuous function \(\sigma(\omega)\) at the point \(\omega = 0\). The finiteness of the right-hand side of (1-4) has required the fulfilment of the next two necessary and sufficient conditions:
An Elaborate dc Electric Conductivity Formula

\[ a = a(0) = 0, \quad (1.9) \]
\[ a' = a'(0) = i(mN), \quad (1.10) \]

where \( a \) is the value of the expression (1.5) taken for \( \omega \to 0 \):

\[ a = a(0) = \lim_{\xi \to 0} \int_{-\infty}^{0} dt e^{st}(\tilde{F}_{x}(t); \tilde{F}_{x}), \quad (1.11) \]

and \( a' \) is the derivative in \( \omega \) of (1.5) taken for \( \omega \to 0 \):

\[ a' = a'(0) = \lim_{\xi \to 0} \int_{-\infty}^{0} dt e^{st}(it)(\tilde{F}_{x}(t); \tilde{F}_{x}). \quad (1.12) \]

Applying the L'Hospital rule\(^{10} \) to (1.4) in one rather sophisticated way, we finally have derived for the \( dc \) conductivity \( \sigma \) the next expression:

\[ \sigma = \left( \frac{1}{V} \right)(eN)^{2} \left[ \frac{-\alpha''}{2(a')^{2}} \right], \quad (1.13) \]

where \( \alpha'' \) is the second derivative in \( z \) of (1.5) taken for \( \omega \to 0 \):

\[ \alpha'' = \alpha''(0) = \lim_{\xi \to 0} \int_{-\infty}^{0} dt e^{st}(-i^{2})(\tilde{F}_{x}(t); \tilde{F}_{x}). \quad (1.14) \]

Before our work,\(^{9} \) formula (1.4) has appeared in some other works,\(^{3,11} \) at least in an implicit form (see formula (8.6) in Ref. 11), but it never had been elaborated for the \( dc \) case, as it was done in our work.\(^{8} \) The derivation of formula (1.13) in our previous work\(^{3} \) was quite formal, and the physics underlying it remained unclear. The principal aim of this work is to find out and explain this physics.

In § 2 of this article, we reinterpret our calculations in terms of real physical quantities, and there it becomes clear that formula (1.13) comes out of a specific kind of conjunction of two linear response formulae, one for the real electric conductivity \( \sigma_{R}(\omega) \), the other one for the real electric susceptibility \( \kappa_{R}(\omega) \). In § 3 formula (1.13) is applied to simple models (Markoffian and Gaussian models of relaxation), which can be solved exactly by both the Kubo formula and our formula. This section is very useful for a better understanding of features of the formula (1.13). In § 4 we give an exhaustive discussion of our results.

§ 2. Real quantities picture

By decomposing the complex conductivity \( \sigma(\omega) \) into real part \( \sigma_{R}(\omega) \) and imaginary part \( \sigma_{I}(\omega) \):

\[ \sigma(\omega) = \sigma_{R}(\omega) + \sigma_{I}(\omega) \cdot i, \quad (2.1) \]

we can find out some important points about the physics involved in the derivation of our \( dc \) conductivity formula (1.13).

The complex conductivity \( \sigma(\omega) \) is the factor of proportion between the complex external electric field \( E(t) \) and the complex current density \( j(t) \):\(^{12} \)

\[ j(t) = \sigma(\omega) \cdot E(t), \quad (2.2) \]
where
\[ E(t) = E_x e^{i\omega t} = E_x \cos(\omega t) + E_x \sin(\omega t) \cdot i, \]
\[ j(t) = j_R(t) + j_i(t) \cdot i. \]

For the sake of clarity, let us take \( t = 0 \). Then the complex field \( E(t) \) reduces to its maximum real value \( E_x \), \( E(0) = E_x \), while the complex density of current \( j(0) \), given by (2.1) and (2.2) expressed as:
\[ j(0) = \sigma_r(\omega) \cdot E_x + \sigma_i(\omega) \cdot E_x \cdot i. \]

The real part \( j_R(0) \):
\[ j_R(0) = \sigma_r(\omega) \cdot E_x, \]
where
\[ \sigma_r(\omega) = \left( \frac{1}{V} \right) \left( \frac{e}{m} \right)^2 \lim_{\delta \to 0^+} \int_0^\delta dt e^{i\omega t} \cos(\omega t)(\bar{P}_x(t); \bar{P}_x), \]
is the density of current in the literal physical meaning,\(^\text{12}\) therefore \( \sigma_r(\omega) \), given by (2.7), is the conductivity in the literal physical meaning. The imaginary part \( j_i(0) \):
\[ j_i(0) = \sigma_i(\omega) \cdot E_x, \]
where
\[ \sigma_i(\omega) = \left( \frac{1}{V} \right) \left( \frac{e}{m} \right)^2 \lim_{\delta \to 0^+} \int_0^\delta dt e^{i\omega t} \sin(\omega t)(\bar{P}_x(t); \bar{P}_x), \]
does not represent density of current in the literal meaning, but rather represents the polarization of the system due to the spatial displacement of the carrier system. This interpretation comes out from the relationship:
\[ \varepsilon_0 \kappa_r(\omega) = \left( \frac{1}{\omega} \right) \sigma_i(\omega), \]
which connects the imaginary part \( \sigma_i(\omega) \) of the complex conductivity \( \sigma(\omega) \) to the real susceptibility of the carrier system \( \kappa_r(\omega) \). The relationship (2.10) most elegantly can be derived by linear response theory.\(^\text{13}\) (For clarity let us add, that the relationship (2.10) is most often applied to dielectrics, where both polarization and current come up from oscillations of ions around their balance positions. In the case of conducting materials, we have in addition to ionic polarization the polarization of the carriers. This mechanism of polarization is usually omitted, when the electric current is considered. In the relationship (2.10) \( \kappa_r(\omega) \) and \( \sigma_i(\omega) \) belong to the same mechanism, specifically here we are interested in applying it to the carrier system mechanism.) Therefore, it is the polarization \( \mathcal{P} \), \( \mathcal{P} = \varepsilon_0 \kappa_r(\omega) \cdot E_x \), due to the spatial displacement of the carrier system, which is determined by \( \sigma_i(\omega) \):
\[ \mathcal{P} = \left( \frac{1}{\omega} \right) \sigma_i(\omega) \cdot E_x, \]
Now let us turn to the expression (1·4). By decomposing it into its real and imaginary parts we get the next expressions for $\sigma_R(\omega)$ and for $\sigma_i(\omega)$:

$$\sigma_R(\omega) = \left(\frac{1}{V}\right)^2 \frac{e^2}{m^2} \left(\frac{\alpha_R}{\omega^2}\right),$$  \hspace{1cm} (2·12)

$$\sigma_i(\omega) = \left(\frac{1}{V}\right)^2 \frac{e^2}{m^2} \left(\frac{\alpha_i(\omega) - \omega (mN)}{\omega^2}\right),$$  \hspace{1cm} (2·13)

where

$$\alpha_R(\omega) = \lim_{\omega \to 0} \int_0^\infty dt e^{\omega t} \cos(\omega t) (\bar{F}_x(t) - \bar{F}_x),$$  \hspace{1cm} (2·14)

$$\alpha_i(\omega) = \lim_{\omega \to 0} \int_0^\infty dt e^{\omega t} \sin(\omega t) (\bar{F}_x(t) - \bar{F}_x).$$  \hspace{1cm} (2·15)

The terms $\alpha_R(\omega)$ and $\alpha_i(\omega)$ are the real and imaginary parts respectively of the complex quantity $a(\omega)$, $a(\omega) = \alpha_R(\omega) + i \cdot \alpha_i(\omega)$.

The dc conductivity $\sigma$ is the limit of $\sigma_R(\omega)$ for $\omega \to 0$.10 In accordance with the physical meaning of $\sigma_i(\omega)$, one could expect that the dc conductivity $\sigma$ has nothing to do with $\sigma_i(\omega)$, and therefore one should not expect $\sigma_i(\omega)$ to be directly involved in the derivation of the formula for $\sigma$. However, in our derivation8 of formula for $\sigma$ we have made use not only of $\sigma_R(\omega)$ but also of $\sigma_i(\omega)$. To see quite clearly how $\sigma_i(\omega)$ is involved into our formula for $\sigma$, we have given in the Appendix an alternative derivation to that given in our previous work.

As for the involvement of $\sigma_i(\omega)$ into our derivation of formula for $\sigma$, the question may be raised up now: Whether the condition (A·2) and the relation (A·3), express something physically true. To answer this question let us consider a conducting many particle system in a closed electric circuit, as presented in Fig. 1. The many particle system is contained in the conducting wire from surface 1 to surface 2. The source of electromotive force labeled by EMF does not belong to the system, but is an external technical device which plays two roles as follows: First, it creates the external electric field $E_x$; second, it enables the carriers to leave the many particle system at the surface 2 and to enter the system at the surface 1. The technical way of preparing the boundary conditions to which the system concerned is submitted. Due to this second role of EMF and the loop shape of the system, the electric polarization of this system due to the carriers displacement does not change in time, when the dc current is flowing. In the considered system, the polarization $\mathcal{P}$ and the susceptibility $\kappa_R(\omega)$ must be limited, and therefore the imaginary part $\sigma_i(\omega)$ of the complex conductivity $\sigma(\omega)$ must vanish for $\omega \to 0$, in accordance with (2·10).
Therefore we are expressing something physically true, when imposing the condition (A-2) and the relation (A-3), as far as we are describing the system presented by Fig. 1.

Now the next question may be raised up: Does the condition (A-2) and the relation (A-4) on which our formula for $\sigma$ hangs up, express something sporadic and not necessarily true for all cases of the dc current? Apart from the ac current which can run even in an open, non-loop shaped conducting system, the dc current can run only in a closed-loop shaped systems. (A circuit with a capacitor connected in series, is an example of an open, non-loop shaped conducting system through which the ac current can run and the dc current cannot. An antenna in another such example.) Therefore, in all cases of dc current, the displacement polarization is finite quantity, and the imaginary part of the complex conductivity vanishes, i.e., $\sigma_i(\omega) \rightarrow 0$ for $\omega \rightarrow 0$. For the ac case we always have $\sigma_i(\omega) \neq 0$. The difference between the ac and the dc cases is exactly here, in different values of the imaginary parts of their complex conductivities, as we just have explained. Since the Kubo formula is the same expression for the ac and for the dc conductivity, obviously it has not taken into consideration yet the difference between the ac and the dc cases. To specify Kubo formula to the dc case we have to take into consideration the specific feature of the dc case, as we have done it, by the condition (A-2) and by explicitly building it into $\sigma$ by the relation (A-4).

Of course, the closed loop shape of the many particle system through which the dc current is flowing, and the cyclic boundary conditions requires one to describe the carriers in terms of periodic functions.

§ 3. Markoffian and Gaussian models of the velocity autocorrelation functions

Kubo has divided the set of all autocorrelation functions $\Phi(t) = \langle v_x(t) v_x(0) \rangle$, into two classes as follows:

a) The class of functions in which the dynamical coherence dominates. The simplest example of this kind is the Gaussian model, for which $\Phi(t)$ reads:

$$\Phi(t) = \langle v_x^2 \rangle e^{-\Delta^2 t^2/2},$$  \hspace{1cm} (3-1)

where $\Delta = \text{const}$, is the characteristic parameter of the function $\Phi(t)$, and $\langle v_x^2 \rangle$ is the statistical mean value of the square of the x-component of a single carrier's velocity:

$$\langle v_x^2 \rangle = \left( \frac{1}{\beta m} \right).$$  \hspace{1cm} (3-2)

b) The class of functions in which the dynamical coherence is lost at an early stage, and the stochastic decay predominates over the most part of the time. The simplest example of this kind is the Markoffian model, for which $\Phi(t)$ reads:

$$\Phi(t) = \langle v_x^2 \rangle e^{-|t|/\tau} = \langle v_x^2 \rangle \left\{ e^{(t/\tau)} \Theta(-t) + e^{-(t/\tau)} \Theta(t) \right\},$$  \hspace{1cm} (3-3)

where $\tau$ is the relaxation time, and $\Theta(t)$ means the step function.

At first let us investigate the Markoffian model. Classical dynamics and elastic scatterings are assumed here. The generalized scalar product ($\vec{F}_x(t); \vec{F}$) is given by
Due to the relations:
\[ \langle \dot{v}_x(t) \dot{v}_x(0) \rangle = -\langle \dot{v}_x(t) v_x(0) \rangle = -\dot{\Phi}(t) \]
(3.5)
\[
(\vec{F}_x(t); \vec{F}_x) = \beta (N m^2) (\dot{\Phi}(t))
\]
(3.6)
By double differentiation in \( t \), from (3.3) we get for \( \dot{\Phi}(t) \):
\[
\dot{\Phi}(t) = \langle v_x^2 \rangle \left\{ \frac{1}{r^2} e^{(r^2)} \Theta(-t) - \frac{1}{r^2} \delta(t) \right\}
\]
(3.7)
The sketches of graphs for functions \( \Phi(t) \), \( \dot{\Phi}(t) \) and \( (\vec{F}_x(t); \vec{F}_x) \) are given in Figs. 2A) \sim C), respectively. The function \( \dot{\Phi}(t) \) is an odd function of \( t \) with discontinuity at \( t = 0 \), while \( \Phi(t) \) and \( (\vec{F}_x(t); \vec{F}_x) \) are even functions of \( t \).

The scalar product \( (\vec{F}_x(t); \vec{F}_x) \) can be divided into two components:
\[
(\vec{F}_x(t); \vec{F}_x) = (\vec{F}_x(t); \vec{F}_x)_\parallel + (\vec{F}_x(t); \vec{F}_x)_\perp,
\]
(3.8)
where
\[
(\vec{F}_x(t); \vec{F}_x)_\parallel = \beta (N m^2) \langle v_x^2 \rangle (1/r^2) \Theta(-t)
\]
(3.9)
\[
(\vec{F}_x(t); \vec{F}_x)_\perp = -\beta (N m^2) \langle v_x^2 \rangle (1/r^2) \left\{ e^{(r^2)} \Theta(-t) + e^{(-r^2)} \Theta(t) \right\}
\]
(3.10)
The first component given by (3.9) is called the autocorrelation function of orthogonal forces.\(^{15,16}\) In this Markoffian case, the width of \( (\vec{F}_x(t); \vec{F}_x)_\parallel \) is zero, it is a positive delta impulse at \( t=0 \). The second component given by (3.10) is called the autocorrelation function of secular forces.\(^{16}\) It is a negative quantity, smoothly going to zero with increase of \( t \); it is the long time tail of the correlation function \( (\vec{F}_x(t); \vec{F}_x) \). From the literature we know that these two components cancel each other in the expression (1.11) for \( a \). However, the same thing does not happen with \( a' \) and \( a'' \) as given by (1.12) and (1.14) respectively. The integration in (1.12) for \( a' \) can be written down as
\[
\lim_{\delta \rightarrow 0} \int_{-\infty}^{0} dt e^{\delta t} (\vec{F}_x(t); \vec{F}_x) = \lim_{\delta \rightarrow 0} \int_{-\infty}^{0} dt e^{\delta t} (\vec{F}_x(t); \vec{F}_x)_\parallel
\]
Since the relation: \( t(\bar{F}_x(t); \bar{F}_x) \sim t \cdot \delta(t) \) holds here, we immediately conclude that the first integral on the right-hand side of (3.11) is zero. Therefore, \( \alpha' \) receives nonzero contributions only from the long time tail of the correlation function \( \bar{\phi}(t) \). By performing the calculations prescribed by the formula (1.12), we get for \( \alpha' \) the value \( \alpha' = imN \), in accordance with the condition (1.10). In a similar way, due to the relation: \( t^2(\bar{F}_x(t); \bar{F}_x) \sim t^2 \cdot \delta(t) \), we conclude that \( \alpha'' \) also does not receive nonzero contribution from \( (\bar{F}_x(t); \bar{F}_x)_\perp \), but only from the long time tail of \( \bar{\phi}(t) \). Formula (1.14) here gives the value: \( \alpha'' = 2(Nm)r \). With these values of \( \alpha' \) and \( \alpha'' \), formula (1.13) gives for the dc conductivity:

\[
\sigma = (N/V)e^2(\tau/m).
\]

(3.12)

Kubo formula (1.1) gives the same result as (3.12).

In the literature we encounter another conductivity formula which can be written as

\[
\sigma_\perp = (N/V)e^2\left( \frac{1}{m} \right) \left( \frac{mN}{\alpha_\perp} \right).\]

(3.13)

Mori\(^{16}\) has shown that formula (3.13) becomes an exact expression for \( \sigma \), \((\sigma_\perp = \sigma)\), if \( \alpha_\perp \) is calculated from the formula (1.11) but with generalized scalar product \((\bar{F}_x(t); \bar{F}_x)\) replaced by its orthogonal component \((\bar{F}_x(t); \bar{F}_x)_\perp\). Under certain conditions\(^{11,13}\) formula (3.13) can be used with \( \alpha_\perp \) found from the whole scalar product \((\bar{F}_x(t); \bar{F}_x)\), but then the integration in \( t \) must be restricted to a narrow interval \((-\infty, 0)\), instead of \((-\infty, 0)\). This latter use of formula (3.13) is known as Kirkwood's formula.\(^{17}\) Kirkwood's formula is just an approximation \((\sigma_\perp \approx \sigma)\). In this Markovian case, formula (3.13) with \((\bar{F}_x(t); \bar{F}_x)_\perp\), as given by (3.9), leads to the result given in (3.12), therefore here is \( \sigma_\perp = \sigma \).

Our formula (1.13) and formula (3.13) in this specific case have shown some kind of complementarity. Namely, our formula (1.13) describes \( \sigma \) from the long time tail of the correlation function \((\bar{F}_x(t); \bar{F}_x)_\perp\), while formula (3.13) describes \( \sigma \) from the short time component of the correlation function \((\bar{F}_x(t); \bar{F}_x)_\perp\).

Now let us turn to the Gaussian model. In this model \((\bar{F}_x(t); \bar{F}_x)\) is given by

\[
(\bar{F}_x(t); \bar{F}_x) = \beta(Nm^2)v_x^2(\Delta^2)(e^{-\Delta^2t/2} - (\Delta^2t^2)e^{-\Delta^2t/2}).
\]

(3.14)

The sketches of graphs of \( \phi(t), \Phi(t) \) and \((\bar{F}_x(t); \bar{F}_x)\) for this case are given in Figs. 3 A)~C). All the three functions here are continuous and well defined in the usual mathematical sense. The scalar product \((\bar{F}_x(t); \bar{F}_x)\) here also may be divided into two components as before:

\[
(\bar{F}_x(t); \bar{F}_x) = (\bar{F}_x(t); \bar{F}_x)_\perp + (\bar{F}_x(t); \bar{F}_x)_\parallel,
\]

(3.15)

where

\[
(\bar{F}_x(t); \bar{F}_x)_\perp = \beta(Nm^2)v_x^2(\Delta^2)e^{-\Delta^2t/2},
\]

(3.16)
An Elaborate dc Electric Conductivity Formula

Fig. 3. Qualitative behaviour of autocorrelation functions for Gaussian model: A) $\Phi(t)$; B) $\Phi(t)$; C) $(\bar{F}_x(t); \bar{F}_x)\sim(-\Phi(t))$. See text for details.

The component $(\bar{F}_x(t); \bar{F}_x)_||$ is positive and has rather sharp maximum at $t=0$, but its width is finite, while the component $(\bar{F}_x(t); \bar{F}_x)_\perp$ is negative long time tail of the correlation function. In the expression (1-11), these two components cancel each other giving $a=0$, in accordance with condition (1-9). The quantity $a'$ from (1-12), with $(\bar{F}_x(t); \bar{F}_x)$ given by (3-14) has the value $a'=i(mN)$, in accordance with the condition (1-10). The quantity $a''$ from (1-14), with $(\bar{F}_x(t); \bar{F}_x)$ given by (3-14) receives value of $a''=(mN)(\sqrt{2\pi}) (1/A)$, leading by (1-13) to the following expression for the dc conductivity $\sigma$:

$$\sigma=(N/V)e^2\left(\frac{1}{m}\right)\sqrt{\frac{\pi}{2}} \left(\frac{1}{A}\right).$$  \hspace{1cm} (3.18)

Kubo formula (1-1) gives the same result (3.18).

Formula (3.13), used in the sense of Mori's formula, with $(\bar{F}_x(t); \bar{F}_x)_\perp$ given by (3-16), gives the value:

$$\sigma_\perp=(N/V)e^2\left(\frac{1}{m}\right)\sqrt{\frac{2}{\pi}} \left(\frac{1}{A}\right),$$  \hspace{1cm} (3.19)

a result which is in discrepancy with the exact result given by (3.18). Here we are obliged to say, that the short time living component $(\bar{F}_x(t); \bar{F}_x)_\perp$, as given by (3-16) has not been determined by the procedure prescribed for finding the orthogonal forces time correlation function,\textsuperscript{15} but rather intuitively. Application of Mori's procedure for getting $(\bar{F}_x(t); \bar{F}_x)_\perp$ in this Gaussian case is not at all a simple task, as it was in the case of the Markoffian model. Kirkwood's approach is not applicable here since the correlation function $(\bar{F}_x(t); \bar{F}_x)$ is no longer as sharp at the point $t=0$, as it was in the case of the Markoffian model.

We see that the differences in sharpness of the correlation functions $(\bar{F}_x(t); \bar{F}_x)$ in the two considered models, do not affect the correctness of our formula (1-13) in any way. The only difference between the Markoffian and the Gaussian cases in our formula is that in the Markoffian case $a'$ and $a''$ receive nonzero contributions from the long time tail $(\bar{F}_x(t); \bar{F}_x)_\parallel$ exclusively, while in the Gaussian case $a'$ and $a''$ do from both $(\bar{F}_x(t); \bar{F}_x)_\parallel$ and $(\bar{F}_x(t); \bar{F}_x)_\perp$. Therefore, the exactness of our formula

\begin{equation}
(\bar{F}_x(t); \bar{F}_x)_\parallel = -\beta(Nm^2)\langle u_x^2 \rangle \langle A^2 \rangle \langle A^2 t^2 \rangle e^{-A^2 t^2/2}.
\end{equation}

\textsuperscript{(3.17)}
(1·13) is not restricted by the conditions prescribed for the Kirkwood’s type formula (3·13). On the other hand, in using our formula (1·13) we are not faced with the difficult problem of application of Mori’s procedure to separate from \( \langle F_x(t); F_x \rangle \) the orthogonal component \( \langle F_x(t); F_x \rangle_\perp \).

§ 4. Discussion and conclusion

It is more or less customary in transport theory, to keep the dc and the ac cases under the same roof. Kubo formula (1·1) has settled the things in the same way. This custom can be quite right as long as the effects of the scattering Hamiltonian \( U \) are taken exactly into account, but as soon as the effects of \( U \) are calculated by some approximate method, this custom becomes very inconvenient. The reasons are as follows: The single carrier’s velocity \( v \) is a quantity which is accumulated in time, when the carrier is coupled with an external driving force. (To be quite precise, this is true for the drift part of the full velocity \( v \).) There are two factors resisting the accumulation of \( v \): The inertia of the carrier (its mass \( m=0 \)), and the scattering, when \( g=0 \) \( (U=g) \). When the scattering disappears, \( g \to 0 \) \( (U \to 0) \), remains the inertia of carriers since always \( m \neq 0 \). In the ac case, \( \omega \neq 0 \), the direction of the external driving force regularly changes sign from time to time, and in this case the carrier’s velocity \( v \), being a cumulative quantity of contributions with opposite signs, always remains bounded, even if \( g \to 0 \) \( (U \to 0) \). The same is valid for the density of an ac current. Therefore, if \( \omega \neq 0 \) the conductivity \( \sigma(\omega) \) is bounded for any \( g \), including \( g=0 \). The situation is quite different in the dc case, \( \omega=0 \). The intensity and the direction of the external driving force are kept constant all the time, and in an infinitely long period of time \( T \to +\infty \), the carrier’s velocity \( v \), and the dc current density \( j \), increase without limit if the scattering disappears, \( g \to 0 \) \( (U \to 0) \). Therefore, if \( \omega=0 \) the conductivity \( \sigma \) has singularity at \( g=0 \). (We are in the framework of a non-relativistic theory; relativistic effects are not described by the usual transport theory. Of course, the boundless character of \( \sigma \) for \( g \to 0 \), has to be understood as an asymptotic behaviour, which must be seen in the mathematical expressions for \( \sigma \). In practical cases however small, always \( g \neq 0 \).)

By applying the perturbation series expansion in \( U \) to the generalized scalar product \( \langle \vec{P}_x(t); \vec{P}_x \rangle \) or \( \langle \vec{F}_x(t); \vec{F}_x \rangle \), contained in the expressions for conductivity \( \sigma(\omega) \), and by performing time integration and Traces process, we really get a power series in \( g \) for \( \sigma(\omega) \). The point around which the series expansion is made in this way is \( g=0 \). These series have different nature for the ac and for the dc conductivity. In the ac case, the point \( g=0 \) is a regular point \( (\sigma(\omega) \) is bounded for \( g=0) \), and the corresponding series is a Taylor series. In the dc case, the point \( g=0 \) is a singular point \( (\sigma \) is boundless for \( g=0) \), and the corresponding series is a Laurent series. If the dc case is kept as particular case (for \( \omega=0 \)) in the general expression \( \sigma(\omega) \), then we have a single object at our disposal, and by perturbation series expansion we get a single series, adequate for the general case, therefore it is a Taylor series in \( g \). Unfortunately, this Taylor series will not convert into a Laurent series automatically, if we apply it for \( \omega=0 \). The well-known Van Hove’s procedure, followed by many authors, in essence may be described as an attempt to convert this Taylor series into
the lowest order term of a Laurent series for \( \sigma \). We do not think these attempts have ever been quite correctly and transparently done. Therefore, the approach in which the same expression for the ac and for the dc case is used for series expansion in \( U \), cannot be a good one. If we start with the same expression for the ac and for the dc case, like Kubo formula, before making series expansion in \( U \) we must separate from \( \sigma(\omega) \) some specified expression for \( \sigma \), on the level while \( \sigma(\omega) \) is still exact in \( U \). The series expansion in \( g \) then has to be applied to this specified expression for \( \sigma \). Then this series automatically appears to be a Laurent series. This is exactly what we have done in our work.

In the Appendix, we show that our formula (1·13) for \( \sigma \) comes out from a specific kind of conjunction of two linear response formulae: The first one for the real conductivity \( \sigma_r(\omega) \) and the second one for the real susceptibility \( \kappa_r(\omega) \) of the spatial displacement of the carrier system. In some way, this conjunction is equivalent to summation of some class of diagrams in the perturbation theory, when we, in advance, know the value of that partial sum. By inserting the right-hand side of (A·4) into (2·12) we really have restricted the behaviour of \( \sigma_r(\omega) \) for \( \omega \to 0 \). In this manner, our formula for \( \sigma \) is more convenient than the Kubo formula \( \sigma_r(\omega) \) taken for \( \omega = 0 \) without any additional restriction. This is the key to understanding why the two formulae behave differently as regards a Laurent series expansion: Our formula (1·13) makes possible the calculation of the coefficients of the Laurent series in \( g \) by direct application of the technique of perturbation series expansion in \( U \) to the generalized scalar product \( (\tilde{F}_x(t); \tilde{F}_x) \), while Kubo formula (1·1) does not allow such a procedure to apply to the corresponding generalized scalar product \( (\tilde{P}_x(t); \tilde{P}_x) \).

One of the most severe critics\(^{21}\) of the linear response theory has put up a number of objections onto this theory, amongst which we here recall the one in which he says: "Linear response theory does provide expressions for the phenomenological coefficients, but I assert that it arrives at these expressions by a mathematical exercise rather than by describing the actual mechanism which is responsible for the response." What are those mechanisms which are missing in the Kubo formula? Several authors\(^{21,22}\) think it is its stochastic and irreversible character. These authors\(^{22}\) make alterations to the Kubo formula to improve it in accord with their objections. Our objection against their treatment of Kubo formula is that the basic idea of the linear response theory, and that is: To be thoroughly consistent with the microscopic dynamics, has been abandoned half way by their treatment. Instead, in our approach we attempt to keep the basic ideas and character of the Kubo formula, and we try to get the improvement by another route. We do admit, that the Kubo formula as applied to the \( dc \) case is a half way between the Liouville von Neumann equation and the final expression which is useful for calculations. In § 2 we saw that the physics which is presumably missing from the Kubo formula as applied to the \( dc \) case, is the explicit appreciation of the boundary conditions. Our intervention on the Kubo formula may be interpreted as a procedure for extracting the particular solution for the corresponding boundary condition out of the general solution given by the Kubo formula. Our formula (1·13) for the \( dc \) conductivity \( \sigma \) has been derived without explicitly including any classical elements of stochasticity or irreversibility. We think the sources of stochasticity and irreversibility are in the quantum mechani-
N. Milinski

cal dynamics, to which the microparticles are submitted. The very fact that our formula for $\sigma$ enables us to get the Laurent series expansion in $g$ by itself shows that it is possible to obtain expressions for phenomenological coefficients without taking into account any classical sources of stochasticity or irreversibility.

The second topic of our discussion here relates to the nature of Eqs. (1·9) and (1·10), with $a$ and $a'$ given by (1·11) and (1·12) respectively. Equation (1·9) has been subject to wide disputes in the past. Those authors who claim that (1·9) is true have not presented Eq. (1·9) as a condition for $\sigma(W)$ to be bounded as $W \to 0$, but in opposite, taking as granted that $\sigma(W)$ is bounded as $W \to 0$ for all cases, they concluded that (1·9) must be true in all cases. So far we have no general proof of (1·9) which would be independent of the supposition that $\sigma(W)$ is bounded for $W \to 0$. The question whether (1·9) is an identity, true for all systems, has not received yet clear answer in the literature. We think that (1·9) is not an identity true for all systems, but an equation true only for some systems, depending on the Hamiltonian of the system. The same is true for Eq. (1·10). These two equations should be considered as necessary and sufficient conditions for $\sigma$ to be bounded, as observed in our work. These two equations supply us the means to control whether our Hamiltonians are correctly chosen. If these equations are not satisfied, the chosen Hamiltonian does not describe a system with bounded electric conductivity. Unfortunately, to check whether these equations are fulfilled is a difficult problem. But in principle, we have found a theoretical mean to test a given Hamiltonian for finiteness of the electric conductivity of a system.

In conclusion we would like to point out a few additional things. First, formula (1·13) is strictly quantum mechanical in concept. Second, for the $dc$ case it is an expression as exact as the Kubo formula. Third, to our knowledge, it is the only formula for $\sigma$ which allows a Laurent series expansion in the scattering parameter $g(U \sim g)$. This last property makes formula (1·13) suitable for investigation of transport problems in those cases where the investigation starts with the Hamiltonian (as usually granted). We already have demonstrated the way in which it can be done. In earlier work we applied formula (1·13) to determine the electric resistivity of liquid metals and the mobility of carriers in nondegenerate semiconductors, limited due to the coupling to phonons and charged impurities. Our experience from these calculations is that inelastic processes play a greater role in the transport phenomena than it is usually assumed. It leads us to suppose that the dynamical coherence plays a bigger role in these processes than it is usually assumed. The relaxation time approximation does not seem to be acceptable in the aforementioned cases. The exact result that we have obtained in the case of the Gaussian model in § 3, certainly raises our confidence in the applicability of formula (1·13) to the cases where the dynamical coherence plays a significant role. We believe that formula (1·13) is a starting point for practical calculations of real interest, and to go beyond the relaxation time approximation.

Acknowledgements

Thanks are due to Professor M. Skrinjar for helpful discussions. The author is
An Elaborate dc Electric Conductivity Formula

indebted to the unknown referee, who has given valuable suggestions to improve this article. This article is based on work supported by the U.S.-Yugoslav Joint Fund for Scientific and Technological Cooperation, in cooperation with the Department of Energy, under Grant (JFP-555/DOE).

Appendix

Here we define the dc conductivity $\sigma$ by the limit of $\sigma_\epsilon(\omega)$ for $\omega \to 0$.

The aim of this appendix is to show clearly the way in which we have involved the expression for $\sigma_\epsilon(\omega)$ into this limit.

From the very definitions of $a_\epsilon(\omega)$ and of $\alpha_\epsilon(\omega)$, as given by expressions (2·14) and (2·15) respectively, we conclude that the power series in $\omega$ of $a_\epsilon(\omega)$ contains terms of even exponents only, while the power series in $\omega$ of $\alpha_\epsilon(\omega)$ contains terms of odd exponents only. Therefore, the necessary and sufficient condition for $\sigma_\epsilon(\omega)$ to converge in the limit $\omega \to 0$, is as follows:

$$a_\epsilon(0) = 0.$$  \hspace{1cm} (A·1)

The necessary and sufficient condition for $\sigma_\epsilon(\omega)$ to vanish in the limit $\omega \to 0$ is as follows:

$$a'(0) = (mN) ,$$  \hspace{1cm} (A·2)

where $a'(0)$ is the first derivative in $\omega$ of (2·15) as counted for $\omega = 0$. The condition (A·2) is equivalent to the requirement that the numerator $(a_\epsilon(\omega) - \omega m N)$ of the ratio (2·13) for $\sigma_\epsilon(\omega)$ must be some function $\vartheta(\omega)$ of $\omega$:

$$\vartheta(\omega) = (a_\epsilon(\omega) - \omega m N) ,$$  \hspace{1cm} (A·3)

whose power series in $\omega$ must not contain terms of order lower than 3, therefore, $\vartheta(\omega) = k_3 \cdot \omega^3 + k_5 \cdot \omega^5 + \cdots$. From (A·3) the next expression for $\omega$ follows:

$$\omega = \left( \frac{1}{mN} \right) (a_\epsilon(\omega) - \vartheta(\omega)) .$$  \hspace{1cm} (A·4)

Now by inserting the right-hand side of (A·4) for $\omega$ into the right-hand side of (2·12), we get

$$\sigma_\epsilon(\omega) = \left( \frac{1}{V} \right) (eN)^2 \frac{a_\epsilon(\omega)}{\left( a_\epsilon(\omega) - \vartheta(\omega) \right)^2} .$$  \hspace{1cm} (A·5)

Of course, (A·5) is still an indeterminate ratio $(0^2/0^2)$ for $\omega \to 0$, like (2·12). Now we apply the L'Hospital rule to (A·5) in the way as follows:

$$\lim_{\omega \to 0} \sigma_\epsilon(\omega) = \left( \frac{1}{V} \right) (eN)^2 \lim_{\omega \to 0} \frac{a''(\omega)}{\left( a_\epsilon(\omega) - \vartheta(\omega) \right)^3}$$

$$= \left( \frac{1}{V} \right) (eN)^2 \lim_{\omega \to 0} \frac{(a''(\omega))}{\left( 2(a_\epsilon(\omega) - \vartheta(\omega)) + 2(a_\epsilon(\omega) - \vartheta(\omega))(a''(\omega) - \vartheta''(\omega)) \right)} .$$
where we took into consideration that for \( \omega \to 0 \), we have \( \vartheta'(\omega) \to 0 \), \( (a_i(\omega) - \vartheta(\omega)) \to 0 \), while \( (a_i'(\omega) - \vartheta''(\omega)) \) is finite. Therefore, for the dc conductivity \( \sigma \), we have got

\[
\sigma = \left( \frac{1}{V} \right) (eN)^2 \left\{ \frac{\alpha_i'}{2(a_i')^2} \right\},
\]

where \( \alpha_i' \) and \( \alpha_i \) are the second and first derivative in \( \omega \), of \( a_R(\omega) \) and of \( a_i(\omega) \), as given by (2·14) and (2·15) respectively, calculated at \( \omega = 0 \). Of course, the expressions (1·13) and (A·7) are the same expressions for \( \sigma \), since the first derivative of \( a_R(\omega) \) and the second derivative of \( a_\omega(\omega) \) are equal to zero for \( \omega = 0 \).

If we had left out of consideration what happens to \( a_R(\omega) \) in the limit \( \omega \to 0 \) (i.e., with polarization \( \mathcal{P} \) of the system) then we would be missing Eq. (A·4), and we would not be able to derive formula (A·7) for \( \sigma \). Instead of (A·5), we would have to apply L'Hospital rule to (2·12), and we would obtain:

\[
\sigma = \left( \frac{1}{V} \right) \left( \frac{e}{m} \right)^2 \left( \frac{\alpha_i'}{2} \right),
\]

an expression which has been obtained before in another work,\(^3\) but which does not make it possible to get a Laurent series expansion for \( \sigma \), by the use of the technique of perturbation series expansion in \( U \).\(^4\) The expression (A·8) differs from the expression (1·1) taken for \( \omega = 0 \), due to explicit appreciation of the condition (A·1), which is directly concerned with \( \sigma_R(\omega) \). To get our formula (1·13) or equivalently formula (A·7), in addition to the condition (A·1) we must also explicitly include the condition (A·2), a condition which concerns \( \sigma_i(\omega) \), i.e., the real susceptibility \( \kappa_R(\omega) \). Therefore we may say, our formula for the dc conductivity \( \sigma \) comes out of a specific kind of conjunction of two linear response formulae, the first one for the real conductivity \( \sigma_R(\omega) \), and the second one for the real susceptibility \( \kappa_R(\omega) \).

References

2) D. N. Zubarev, Nonequilibrium Statistical Thermodynamics (Moskow, Nauka, 1971).