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Theory of ac and dc electric conductivity by noninteracting electrons in correlated arrays of fixed scatterers

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It is shown that the procedure of averaging over positions of scatterers interacts synergetically with the application of the diagonal-projection-operator (Δ,Δ') decomposition to yield an exact expression for the ac and dc conductivity for an arbitrarily ordered array of fixed potentials. The formula is evaluated to lowest order in the scattering strength for arrays of scatterers with various degrees of order from uncorrelated to periodic; it is a function of density, frequency, and temperature. dc conductivity, for example, is a minimum for a perfectly random array, increasing to infinity for a periodic lattice at $T = 0$. Application to thermal-disorder resistivity in metals is mentioned. In appendices we discuss pervious attempts to solve this problem, simplify the quantum-mechanical Green-Kubo formula, and calculate the conductivity of classical electrons moving among dilute uncorrelated scatterers.

I. INTRODUCTION

In this paper we will calculate the electric conductivity for a simple model of a real substance. Our starting point will be the Green-Kubo formula for the ac $(\omega > 0)$ and dc $(\omega = 0)$ conductivity $\sigma(\omega)$ in terms of the integrated current-current time-correlation function. The model will consist of noninteracting electrons moving in an arbitrarily ordered array of fixed potential wells.

The obstacle with which any attempt to calculate $\sigma(0)$ is soon confronted is that in the absence of random scatterers it is infinite.[1] If perturbation theory is to be used it must be with care, because every term in the expansion in powers of the scattering strength is either zero or infinity.

Several ways of coping with this vexatious situation have been invented.[2-17] One is to forget about the Green-Kubo formula and derive a Boltzmann equation for the relevant part of the electrons' density matrix in the presence of an electric field, solve it approximately, and obtain the conductivity from the solution. Another is to manipulate the equivalent of the Green-Kubo formula into an expression for the resistivity $(\rho = \sigma^{-1})$, which vanishes for no scattering, hence promises that a perturbation expansion may be possible. Or one can parametrize divergences in the expansion by giving the frequency a positive infinitesimal imaginary part, and keeping only the most divergent terms in each order of the perturbation series. The sum of these terms yields a finite answer.

Each of these methods gives the same result for conductivity in the simple examples to which they have been correctly applied. None of them is particularly easier than the others as far as formal manipulations or numerical work are concerned, because they all involve solving an integral equation equivalent to the Boltzmann equation.

In the present work we aim to accomplish several things. First, we use the diagonal projection superoperators Δ, Δ' to transform the Green-Kubo expression for $\sigma(\omega)$ into a form suggestive of the Drude formula.[18] Second, we formally (but only implicitly) expand $\sigma(\omega)$ in a power series in λ, the scatterer strength, in order to perform the correlated average over scatterer positions. Because of the presence of the superoperators Δ, the averages of certain products, in the thermodynamic limit, become products of averages. This fact enables us to resum $\sigma(\omega)$, obtaining a formally exact result.

We will then evaluate $\sigma(\omega)$ in some interesting limits to lowest order in λ. The case of uncorrelated scatterers has been treated before, but not for all $0 \le \omega < \infty$. We also consider correlated scatterers, presenting $\sigma(\omega)$ for a liquid as a function of the structure factor, and for a periodic lattice with thermal-disorder corrections.

II. DERIVATION OF CONDUCTIVITY FORMULA

A. Superoperator formalism

The model we consider is illustrated in Fig. 1. It consists of independent electrons moving under the influence of an electric field $\vec{E}(t) = \mathrm{Re}(\vec{E}e^{i\omega t})$ in an array of fixed scatterers. The Hamiltonian is the sum of $e\vec{E}(t) \cdot \vec{r}$ and $H = H^0 + \lambda V$, with

$$V(\vec{r}) = \sum_{i=1}^{N} \phi(\vec{r} - \vec{r}_i) , \qquad (1)$$

where λ is the dimensionless strength of the scatterers, of which there are N, located at positions $\{\vec{r}_i\}$, $i = 1, \ldots, N$.

The Green-Kubo formula for the linear response to $E(t)$ gives an electric conductivity whose real

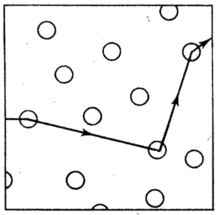

FIG. 1. Model which we consider in this paper. Independent electrons propagate under the influence of an applied electric field in an array of scatterers, whose positions may be correlated with each other.

part is[19]

$$\sigma_R(\omega) = \tfrac{1}{3}\bar{\beta} e^2 n_e \,\mathrm{Re}\int_0^\infty dt\, e^{i\omega t}\mathrm{Tr}[\rho\vec{v}\cdot\vec{v}(t)]\,, \tag{2}$$

where $\bar{\beta} = (e^{\omega\beta} - 1)/\omega$, $\beta = 1/kT$, and n_e is the electron density. The equilibrium density matrix is[20]

$$\rho = e^{-\beta H}/\mathrm{Tr}(e^{-\beta H})\,, \tag{3}$$

$\vec{v}$ is the velocity operator, and

$$\begin{aligned}\vec{v}(t) &= e^{-iHt}\vec{v}e^{iHt}\\ &= e^{\mathcal{H}t}\vec{v}\,,\end{aligned} \tag{4}$$

defining the Liouville superoperator[21] $\mathcal{H}$, which can be shown to satisfy

$$\mathcal{H}O = -i[H, O]\,, \tag{5}$$

where O is an arbitrary operator. With Eq. (4), the integral in (2) may be performed, giving

$$\sigma_R(\omega) = \bar{\beta}q\,\mathrm{Re}\,\mathrm{Tr}(\rho\vec{v}\cdot\mathcal{G}\vec{v})\,, \tag{6}$$

where $q = \frac{1}{3}e^2 n_e$ and

$$\mathcal{G} = (\epsilon - i\omega - \mathcal{H})^{-1}\,. \tag{7}$$

We have added a positive imaginary infinitesimal part to $\omega \to \omega + i\epsilon$, to insure convergence of the time integral. $\mathcal{G}$ is, like $\mathcal{H}$, a superoperator.

If now a basis set $\psi_{\vec{k}}$ is introduced, with

$$H^0\psi_{\vec{k}} = E_{\vec{k}}\psi_{\vec{k}}\,, \tag{8}$$

we can deduce the tetradic[21] elements of the superoperators $\mathcal{H}^0$ and $\mathcal{V}$. From the definition (5) we find

$$\begin{aligned}(\mathcal{V}O)_{\vec{k}\vec{q}} &= \sum_{\vec{k}'\vec{q}'} \mathcal{V}_{\vec{k}\vec{q}\vec{k}'\vec{q}'}\, O_{\vec{k}'\vec{q}'}\\ &= -i\sum_{\vec{k}'}(V_{\vec{k}\vec{k}'}O_{\vec{k}'\vec{q}} - O_{\vec{k}\vec{k}'}V_{\vec{k}'\vec{q}})\,,\end{aligned}$$

from which it follows that

$$\mathcal{V}_{\vec{k}\vec{q},\vec{k}'\vec{q}'} = -i(V_{\vec{k}\vec{k}'}\delta_{\vec{q}\vec{q}'} - V_{\vec{q}'\vec{q}}\delta_{\vec{k}\vec{k}'})\,. \tag{9}$$

Similarly it is easy to show that if $\mathcal{H}^0$ is defined by

$$\mathcal{H}^0 O = -i[H^0, O]\,,$$

then

$$\mathcal{H}^0_{\vec{k}\vec{q}\vec{k}'\vec{q}'} = -i(E_{\vec{k}} - E_{\vec{q}})\delta_{\vec{k}\vec{k}'}\delta_{\vec{q}\vec{q}'}\,, \tag{10}$$

and if

$$\mathcal{G}^0 = (\epsilon - i\omega - \mathcal{H}^0)^{-1}\,, \tag{11}$$

then

$$G^0_{\vec{k}\vec{q}\vec{k}'\vec{q}'} = \delta_{\vec{k}\vec{k}'}\delta_{\vec{q}\vec{q}'}[\epsilon - i\omega - i(E_{\vec{k}} - E_{\vec{q}})]^{-1}\,. \tag{12}$$

B. Diagonal projection superoperators

In order to motivate the introduction of the Δ, Δ' superoperators,[22] one might look at the expansion of $\mathcal{G}$ in powers of λ:

$$\mathcal{G} = \mathcal{G}^0 + \lambda\mathcal{G}^0\mathcal{V}\mathcal{G}^0 + \lambda^2\mathcal{G}^0\mathcal{V}\mathcal{G}^0\mathcal{V}\mathcal{G}^0 + \cdots\,. \tag{13}$$

Comparing this with (12) it would appear that in the dc limit the "diagonal" ($E_{\vec{k}} \cong E_{\vec{q}}$) intermediate states in this expansion give an important contribution simply because $\mathcal{G}^0_{\vec{k}\vec{k}\vec{k}\vec{k}} = \epsilon^{-1}$ and we will eventually take $\epsilon \to 0$. (We will see later that it is true that there is something special about the $\vec{k} = \vec{q}$ intermediate states, but that it has nothing to do with the magnitude of $\mathcal{G}^0$.) Therefore we define a superoperator which singles out these intermediate states as follows. With O and arbitrary operator,

$$(\Delta O)_{\vec{k}\vec{q}} = \delta_{\vec{k}\vec{q}}O_{\vec{k}\vec{k}}\,, \tag{14}$$

or, for the tetradic elements of Δ,

$$\Delta_{\vec{k}\vec{q}\vec{k}'\vec{q}'} = \delta_{\vec{k}\vec{q}}\delta_{\vec{k}'\vec{q}'}\delta_{\vec{k}\vec{k}'}\,. \tag{15}$$

Δ can be described as a diagonal projection superoperator; its complement is $\Delta' = 1 - \Delta$.

We can now insert $1 = \Delta + \Delta'$ wherever we please in (13):

$$\mathcal{G} = \mathcal{G}^0 + \lambda\mathcal{G}^0(\Delta + \Delta')\mathcal{V}(\Delta + \Delta')\mathcal{G}^0 + \lambda^2\cdots\,, \tag{16}$$

and if we define a propagator $\mathcal{G}'$ with no diagonal intermediate states

$$\begin{aligned}\mathcal{G}' &= \mathcal{G}^0 + \lambda\mathcal{G}^0\Delta'\mathcal{V}\mathcal{G}^0 + \lambda^2\mathcal{G}^0\Delta'\mathcal{V}\mathcal{G}^0\Delta'\mathcal{V}\mathcal{G}^0 + \cdots\\ &= (\epsilon - i\omega - \mathcal{H}^0 - \lambda\Delta'\mathcal{V})^{-1}\\ &= (1 - \lambda\mathcal{G}^0\Delta'\mathcal{V})^{-1}\mathcal{G}^0\,,\end{aligned} \tag{17}$$

then (16) becomes

$$\mathcal{G} = \mathcal{G}' + \lambda\mathcal{G}'\Delta\mathcal{V}\mathcal{G}' + \lambda^2\cdots \tag{18a}$$

$$= (1 - \lambda\mathcal{G}'\Delta\mathcal{V})^{-1}\mathcal{G}'\,. \tag{18b}$$

The diagonal singularities have been segregated in (18a) and resummed in (18b). The only singular ($\sim\epsilon^{-1}$) factors in (18) come from $\mathcal{G}'\Delta = (1 - \lambda\mathcal{G}^0\Delta'\mathcal{V})\epsilon^{-1}\Delta$.

C. Transformation of $\sigma_R(\omega)$

To apply Δ and Δ' to Eq. (6), we need to know how they act on the velocity operator. The simplest case occurs when $\vec{v}$ is diagonal in the $\psi_{\vec{k}}$ representation: then

$$\Delta\vec{v} = \vec{v}\,. \tag{19}$$

This is the case if $\psi_{\vec{k}}$ are plane waves; it is true up to interband mixing if $\psi_{\vec{k}}$ are Bloch states. We will take $\psi_{\vec{k}}$ to be plane waves in an $L \times L \times L$ box with periodic boundary conditions. Then

$$\psi_{k} = L^{-3/2} e^{i\vec{k}\cdot\vec{r}} ,$$
$$k_1, k_2, k_3 = \cdots - \frac{2\pi}{L},\ O,\ \frac{2\pi}{L},\ 2\times\frac{2\pi}{L},\ 3\times\frac{2\pi}{L};\ \cdots . \tag{20}$$

Whether or not $\psi_{\vec{k}}$ are plane waves, it follows from (9) and (15) that

$$\Delta \mathcal{V} \Delta = 0 . \tag{21}$$

Equation (6), with (19) and (18b) is

$$\sigma_R(\omega) = \bar{\beta} q \,\mathrm{Re}\,\mathrm{Tr}[\rho\vec{v}\cdot \mathcal{G}'(1-\lambda\Delta\mathcal{V}\mathcal{G}')^{-1}\Delta\vec{v}] . \tag{22}$$

With (17), (21), and the fact that

$$\mathcal{G}^0\Delta = (\epsilon - i\omega)^{-1}\Delta , \tag{23}$$

one can show algebraically that

$$(1-\lambda\Delta\mathcal{V}\mathcal{G}')^{-1}\Delta = (1-\lambda^2\Delta\mathcal{V}\mathcal{G}'\Delta'\mathcal{V}\mathcal{G}^0)^{-1}\Delta . \tag{24}$$

Using also the fact that

$$\mathcal{G}'\Delta = (1-\lambda\mathcal{G}^0\Delta'\mathcal{V})^{-1}\mathcal{G}^0\Delta , \tag{25}$$

one can write

$$\sigma_R(\omega) = \bar{\beta} q \,\mathrm{Re}\,\mathrm{Tr}[\rho\vec{v}\cdot(1-\lambda\mathcal{G}^0\Delta'\mathcal{V})^{-1} \times (\epsilon - i\omega - \lambda^2\Delta\mathcal{V}\mathcal{G}'\Delta'\mathcal{V})^{-1}\Delta\vec{v}] . \tag{26}$$

We emphasize that Eq. (26) is exact in the plane-wave basis; we have made no approximations whatever.

D. Average over scatterer positions

Use of the diagonal projection superoperators has forces $\sigma_R(\omega)$ into the form (26). Whether it is useful depends on whether it can be evaluated, and the first step in evaluation is to change the stochastic operators in it to operators averaged over realizations of the scatterer positions $\{\vec{r}_i\}$ of Eq. (1).[23]

Imagine that (26) is expanded in powers of λ, which not only occurs explicitly, but ρ and $\mathcal{G}'$ also depend on it. The coefficient of λ^m will contain m factors of $V(\vec{r})$, separated by operators which are diagonal in the $\psi_{\vec{k}}$ representation, so we need to average expressions like

$$\Phi_m = \sum_{i_1,\ldots,i_m=1} \phi_{\vec{k}_1\vec{k}_2}(\vec{r}_{i_1}) \times \phi_{\vec{k}_2\vec{k}_3}(\vec{r}_{i_2})\cdots\phi_{\vec{k}_m\vec{k}_1}(\vec{r}_{i_m}) . \tag{27}$$

For $\psi_{\vec{k}}$ given by (20), we can write

$$\phi_{\vec{k}_1\vec{k}_2}(\vec{r}_i) = L^{-3} e^{i(\vec{k}_1-\vec{k}_2)\cdot\vec{r}_i}\,\hat{\phi}_{\vec{k}_1-\vec{k}_2} , \tag{28}$$

where

$$\hat{\phi}_{\vec{k}} = \int d^3r\, e^{i\vec{k}\cdot\vec{r}}[\phi(\vec{r}) - \bar{\phi}]$$

with $\bar{\phi} = \int d^3\,\phi(\vec{r})$ subtracted so that a constant $\hat{\phi}_0$ may be absorbed into H^0. With (28), (27) becomes

$$\Phi_m = L^{-3m}\,\hat{\phi}_{\vec{k}_1-\vec{k}_2}\cdots\hat{\phi}_{\vec{k}_m-\vec{k}_1} \times \sum_{i_1\cdots i_m=1}^{N} e^{i(\vec{k}_1-\vec{k}_2)\cdot\vec{r}_{i_1}}\cdots e^{i(\vec{k}_m-\vec{k}_1)\cdot\vec{r}_{i_m}} . \tag{29}$$

Now define $f_m(\vec{r}_{i},\ldots,\vec{r}_{i_m})$ to be the joint distribution function for $\{\vec{r}_i\}$. f is symmetric in its arguments and

$$L^3 f_{m-1}(\vec{r}_{i_1},\ldots,\vec{r}_{i_{m-1}}) = \int d^3r_m f_m(\vec{r}_{i_1},\ldots,\vec{r}_{i_m}) \tag{30}$$

so that each f is normalized and $f_0 = 1$. Also f is assumed to be homogeneous: i.e., invariant under translation of all its arguments simultaneously. The averaging operation will be denoted by P, i.e.,

$$P\{O\} = L^{-3N}\int d^3r_1\cdots d^3r_N\, f_N(\vec{r}_1,\ldots,\vec{r}_N) \times O(\vec{r}_1,\ldots,\vec{r}_N) . \tag{31}$$

The sum in Φ_m contains mN terms. As an example of how the averaging works let us take a general term from Φ_5, which is depicted in the diagram in Fig. 2. The diagram is constructed by labeling the intermediate momenta $\vec{k}_1,\ldots,\vec{k}_5$ which connect vertices denoting interactions with scatterers at $\vec{r}_{i_1},\ldots,\vec{r}_{i_5}$.

The perturbation expansion of Eq. (26) can be written with a $\Delta + \Delta'$ projection superoperator separating each pair of $\mathcal{V}$'s. Translated to the language of Fig. 2 this means that, for example, if Δ occurs between vertices 3 and 4, $\vec{k}_4$ will be constrained; i.e., $\vec{k}_4 = \vec{k}_1$ as in Fig. 2(b).

Next we will introduce an Ursell-Mayer cluster expansion for

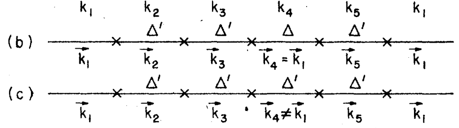

FIG. 2. Diagrams of terms in Φ_5.

f_m, namely,

$$
\begin{aligned}
f_1(\vec r_1) &= u_1(\vec r_1)\,,\\
f_2(\vec r_1,\vec r_2) &= u_1(\vec r_1)u_1(\vec r_2)+u_2(\vec r_1,\vec r_2)\,,\\
f_3(\vec r_1,\vec r_2,\vec r_3) &= u_1(\vec r_1)u_1(\vec r_2)u_1(\vec r_3)+u_1(\vec r_1)u_2(\vec r_1,\vec r_2)\\
&\quad +u_1(\vec r_2)u_2(\vec r_1,\vec r_3)\\
&\quad +u_1(\vec r_3)u_2(\vec r_1,\vec r_2)+u_3(\vec r_1,\vec r_2,\vec r_3)\,, \qquad (32)\\
&\;\;\vdots\;,
\end{aligned}
$$

where $u_1(\vec r_1)=1$, and $u_m(\vec r_1,\vec r_2,\ldots,\vec r_m)\to 0$ whenever the difference between any pair of its arguments exceeds some correlation length r_c. This defines clusters according to scatterer label; what we actually want is an expansion according to position in Φ_m (or along the line in Fig. 2) because (i_1,i_2,i_3,i_4,i_5) may not all be distinct. We want a cluster expansion in which two scatterers at $\vec r_i$ and $\vec r_j$ are in the same cluster if either $i=j$ or $\vec r_i$ and $\vec r_j$ are both arguments of a u_m. If, for example, a term in Φ_5 has $i_1=i_2$ and $i_4=i_5$ one can define

$$f_5(\vec r_1,\vec r_2,\vec r_3,\vec r_4,\vec r_5)=\delta(\vec r_1-\vec r_2)\delta(\vec r_4-\vec r_5)f_3(\vec r_1,\vec r_3,\vec r_4)\,, \qquad (33)$$

which can then be expanded in u's according to (32).

With clusters defined in this way, one can see that any term in the average of Φ_5 corresponding to Fig. 2(b) in which no cluster straddles the Δ (intermediate momentum $\vec k_1$) is the same as would have been obtained if (1, 2, 3) and (4, 5) were averaged independently. That is, (1, 2, 3) and (4, 5) are uncoupled if no cluster includes scatterers from both groups. Also, because $f_3(\vec r_1,\vec r_2,\vec r_3)$ and $f_2(\vec r_4,\vec r_5)$ are independent of the center-of-mass of (1, 2, 3) and (4.5), respectively, the averages over them enforce momentum conservation, i.e., both yield factors $\delta_{\vec k_1-\vec k_4}$.

On the other hand, if Δ occurs within a cluster, then the averages do not enforce momentum conservation, and the result of this contribution of Fig. 2(b) to the average of Φ_5 is the same as the contribution of Fig. 2(c) for $\vec k_4$ close to $\vec k_1$.[24] The number of such $\vec k_4$'s is of order $\epsilon L|\partial k/\partial E_k|$, so if the thermodynamic limit $L\to\infty$ is taken before $\epsilon\to 0$, the contribution of Fig. 2(b) for straddled Δ's can be dropped.

The argument can be extended straighforwardly to the general term in Φ_m; the result can be concisely expressed as follows. If A and B are any operators which may be expanded in Φ's, then with P as defined in Eq. (31)

$$P\{A_{\vec k\vec k}B_{\vec q\vec q}\}=P\{A_{\vec k\vec k}\}P\{B_{\vec q\vec q}\}\,. \qquad (34)$$

It follows that Eq. (26), after averaging, can be written

$$
\begin{aligned}
\sigma_R(\omega)=\bar\beta q\,\mathrm{Re}\,\mathrm{Tr}[P\{\rho\vec v\cdot(1-\lambda\mathcal{G}^0\Delta'\mathcal{V})^{-1}\}\\
\times(\epsilon-i\omega-\lambda^2P\{\Delta\mathcal{V}\mathcal{G}'\Delta'\mathcal{V}\Delta\})^{-1}\vec v]\,; \qquad (35)
\end{aligned}
$$

that is, the superoperator in the denominator is no longer stochastic, and can in principle be evaluated.

We emphasize that Eq. (35) is still exact, valid for any density or degree of correlation of scatterers, in the thermodynamic limit.

III. EVALUATION OF $\sigma_R(\omega)$

We will now evaluate Eq. (35) to lowest order in λ for several systems of fixed scatterers from randomly disordered to periodic arrays. Consider the factor

$$\vec A=(\epsilon-i\omega-\lambda^2P\{\Delta\mathcal{V}\mathcal{G}'\Delta'\mathcal{V}\Delta\})^{-1}\vec v \qquad (36)$$

which occurs in (35). Replacing $\mathcal{G}'$ with $\mathcal{G}^0$ and using (9) and (12), one gets

$$P\{\Delta\mathcal{V}\mathcal{G}^0\Delta'\mathcal{V}\Delta\}_{\vec k\vec q\vec k'\vec q'}=-2\delta_{\vec k\vec q}\delta_{\vec k'\vec q'}\delta_{\vec k\vec k'}\sum_{k''}\frac{(\epsilon-i\omega)P\{|V_{\vec k\vec k''}|^2\}}{(\epsilon-i\omega)^2+(E_{\vec k}-E_{\vec k''})^2}+2\delta_{\vec k\vec q}\delta_{\vec k'\vec q'}\frac{(\epsilon-i\omega)P\{|V_{\vec k\vec k'}|^2\}}{(\epsilon-i\omega)^2+(E_{\vec k}-E_{\vec k'})^2}\,, \qquad (37)$$

which, with (36), gives

$$\vec A_{\vec k\vec k}+2\lambda^2\sum_{k'}\frac{P\{|V_{\vec k\vec k'}|^2\}(A_{\vec k\vec k}-A_{\vec k'\vec k'})}{(\epsilon-i\omega)^2+(E_{\vec k}-E_{\vec k'})^2}=\vec v_{\vec k\vec k}/(\epsilon-i\omega)\,, \qquad (38)$$

to be solved for the diagonal matrix $\vec A$. This equation is equivalent to the Boltzmann equation of conductivity theory. If the system is isotropic, so that $P\{|V_{\vec k\vec k'}|^2\}$ is invariant under a simultaneous rotation of $\vec k$ and $\vec k'$, then (38) can be solved[25] as follows. We consider $\vec A_{\vec k\vec k}$ to be a vector in coordinate space; by symmetry it must be in the $\vec k$ direction. Make the replacements

$$\vec A_{\vec k\vec k}\to\alpha_k\hat k,\quad \vec v_{\vec k\vec k}\to v_k\hat k\,, \qquad (39)$$

where $|\hat k|=1$. Then (38) becomes, with $\cos\theta_{\vec k\vec k'}=\hat k\cdot\hat k'$,

$$\alpha_k+2\lambda^2\sum_{\vec k'}\frac{P\{|V_{\vec k\vec k'}|^2\}(\alpha_k-\alpha_{k'}\cos\theta_{\vec k\vec k'})}{(\epsilon-i\omega)^2+(E_k-E_{k'})^2}=\frac{v_k}{\epsilon-i\omega} \qquad (40)$$

and, if we further assume that the energy dependence of α is weak, as will be the case at moderate temperatures where only E_k's close to E_F are important, an approximate solution of (40) is

$$\alpha_k = v_k \left(\epsilon - i\omega + \sum_{\vec{k}'} W_{\vec{k}\vec{k}'}(1 - \cos\theta_{\vec{k}\vec{k}'})\right)^{-1}, \tag{41}$$

where

$$W_{\vec{k}\vec{k}'} = \frac{2(\epsilon - i\omega)\lambda^2 P\{\,|V_{\vec{k}\vec{k}'}|^2\}}{(\epsilon - i\omega)^2 + (E_k - E_{k'})^2}\ . \tag{42}$$

If now we let $\epsilon \to 0+$ in (42), it becomes (with $\mathcal{P}$ denoting principal value)

$$\begin{aligned} W_{\vec{k}\vec{k}'} = \lambda^2 P\{\,|V_{\vec{k}\vec{k}'}|^2\}\Big\{ &-2i\omega\mathcal{P}\frac{1}{(E_k - E_{k'})^2 - \omega^2} \\ &+ \pi[\delta(E_k - E_{k'} - \omega) \\ &+ \delta(E_k - E_{k'} + \omega)]\Big\}, \end{aligned} \tag{43}$$

whose real part is the familiar Fermi-golden-rule transition probability, split into components for emission and absorption of ω. Its imaginary part vanishes for $\omega = 0$.

We define δ_k, τ_k^+, and τ_k^- as follows:

$$\delta_k = 2\lambda^2 \sum_{\vec{k}'} P\{\,|V_{\vec{k}\vec{k}'}|^2\}\mathcal{P}\frac{1 - \cos\theta_{\vec{k}\vec{k}'}}{(E_k - E_{k'})^2 - \omega^2}, \tag{44}$$

$$\begin{aligned} \frac{1}{\tau_k^{\pm}} = \pi\lambda^2 \sum_{\vec{k}'} P\{\,|V_{\vec{k}\vec{k}'}|^2\}&(1 - \cos\theta_{\vec{k}\vec{k}'}) \\ &\times \delta(E_k - E_{k'} \pm \omega)\,. \end{aligned} \tag{45}$$

The Eq. (35), to lowest order in λ, can be written

$$\sigma_R(\omega) = \bar{\beta} q \sum_k \rho_{kk}\, v_k^2\, \frac{\tau_k^{-1}}{\omega^2(1 + \delta_k)^2 + \tau_k^{-2}} \tag{46}$$

which is a generalization of the Drude formula for conductivity. Here we have put

$$1/\tau_k = 1/\tau_k^+ + 1/\tau_k^-\ . \tag{47}$$

IV. COMPUTATION OF $\tau_k^{\pm}$ FOR CORRELATED SYSTEMS

From (1) and (28)

$$V_{\vec{k}\vec{k}'} = L^{-3} \sum_{i=1}^{N} e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_i}\,\hat{\phi}_{\vec{k}-\vec{k}'}\ , \tag{48}$$

so, if $n_s = N/L^3$, the density of scatterers,

$$\begin{aligned} P\{\,|V_{\vec{k}\vec{k}'}|^2\} &= n_s L^{-3}\,|\hat{\phi}_{\vec{k}-\vec{k}'}|^2 \left(1 + n_s L^{-3}\int d^3r_1 d^3r_2 u_2(\vec{r}_1, \vec{r}_2) e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}_1 - \vec{r}_2)}\right) \\ &= n_s L^{-3}\,|\hat{\phi}_{\vec{k}-\vec{k}'}|^2 S(\vec{k} - \vec{k}') \end{aligned} \tag{49}$$

where $S(\vec{q})$ is the liquid structure factor,

$$S(\vec{q}) = \frac{1}{N} P\left(\sum_{i,j=1} e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)}\right). \tag{50}$$

For an uncorrelated array, $S(\vec{q}) = 1$. For a liquid $S(\vec{q})$, for small $\vec{q}$, is typically much less.[15] The effects of the correlations are therefore to increase σ_R for small ω and decrease it for large ω, relative to the randomly disordered system.

Although our assumptions made in Sec. III included isotropy and a maximum correlation distance r_c, we can still apply our formulas to microcrystalline[26] substances as long as the maximum size is $\ll L$. Isotropy in the large is then satisfied. Imagine that the scatterers are arranged on a regular lattice; in fact we shall use the Einstein model and specify that their displacements from equilibrium are distributed according to a Boltzmann factor

$$e^{-(\kappa\delta_i^2/kT)/2}\ , \tag{51}$$

with $\vec{\delta}_i = \vec{r}_i - \vec{r}_i^{\,0}$. Then from (48)

$$\begin{aligned} \frac{L^6|V_{\vec{k}\vec{k}'}|^2}{|\phi_{\vec{k}-\vec{k}'}|^2} &= \sum_{j,j'=1}^{N} e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}_j^{\,0} - \vec{r}_{j'}^{\,0} + \vec{\delta}_j - \vec{\delta}_{j'})} \\ &= N + \sum_{j\neq j'} e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}_j^{\,0} - \vec{r}_j^{\,0} + \vec{\delta}_j - \vec{\delta}_{j'})}\,. \end{aligned} \tag{52}$$

The second term can be averaged using (51); for $j \neq j'$, $\vec{\delta}_j$ and $\vec{\delta}_{j'}$ are independent,

$$\begin{aligned} P\left(e^{i(\vec{k}-\vec{k}')\cdot(\vec{\delta}_j - \vec{\delta}_{j'})}\right) &= e^{-(\vec{k}-\vec{k}')^2\langle\delta^2\rangle} \\ &= e^{-(\vec{k}-\vec{k}')^2 kT/\kappa} \end{aligned} \tag{53}$$

and the right-hand side of (52) becomes[27]

$$\begin{aligned} &N(1 - e^{-(\vec{k}-\vec{k}')^2\langle\delta^2\rangle}) \\ &\qquad + e^{-(\vec{k}-\vec{k}')^2\langle\delta^2\rangle} \sum_{j,j'=1} e^{i(\vec{k}-\vec{k}')\cdot(\vec{r}_j^{\,0} - \vec{r}_{j'}^{\,0})}\,. \end{aligned} \tag{54}$$

The unrestricted sum in (54) vanishes unless $\vec{k} - \vec{k}' = 0$ or a reciprocal-lattice vector. $\vec{k} - \vec{k}' = 0$ does not contribute because $\hat{\phi}_0 = 0$, and if the temperature is moderate interband transitions may be neglected, so for this case (45) becomes[28]

$$\begin{aligned} \frac{1}{\tau_k^{\pm}} = \pi\lambda^2 n_s L^{-3} \sum_{k'} &|\phi_{\vec{k}-\vec{k}'}|^2 (1 - \cos\theta_{\vec{k}\vec{k}'}) \\ &\times (1 - e^{-(\vec{k}-\vec{k}')^2 kT/\kappa}) \\ &\times \delta(E_k - E_{k'} \pm \omega)\,. \end{aligned} \tag{55}$$

For moderate temperatures Eq. (55) predicts that the scattering rate τ^{-1} will be proportional to T, and will saturate at high temperatures at a value equal to that attained by a random array of scatterers. This intuitively reasonable state of affairs was anticipated by Allen[29] from the deviation from linearity of the temperature-dependent metallic resistivity.

V. RECAPITULATION AND DISCUSSION

Starting with the Green-Kubo formula for the electric conductivity, with the help of the superoperator fomalism and using the Δ, Δ' projection superoperators, we have derived an exact expression for the ac and dc conductivity of noninteracting electrons in an array of fixed scatterers. We have shown that the form of this result is preserved when the positions of the scatterers are averaged over, independent of the degree of correlations, from random disorder to periodic lattices. To accomplish this it was necessary to expand in a perturbation series, but the resummation was exact in the thermodynamic limit. No use was made of $\lambda^2 t$ (or λ^2/ϵ) diagonal singularity arguments to justify resummation, and our results are valid for all ω.

We have shown that the conductivity can be cast into the Drude form, with inverse lifetime τ^{-1} simply expressible in terms of a Fermi-golden-rule transition probability. We have performed the average over scatterer positions for two cases: liquids with isotropic correlations, and the periodic lattice with thermal disorder.

We believe that the results above and the ease with which they have been obtained illustrate the power and utility of the Δ, Δ' method. The algebraic manipulations, while nearly trivial, yield exact expressions to which the random averaging may be applied, and whose structure is exactly preserved under the random averaging operation.

This is the key to the success of the method. Often random averaging is awkward and approximate, here it is easy and exact. The pattern of occurrence of diagonal terms in the perturbation series, enforced by the Δ, Δ' algebraic manipulations, is in fact reasserted by the random averaging.

Actual evaluation of the exact expression (35) for the conductivity is, of course, still difficult, except in the lowest order in λ, which is the only case for which we have done it. Higher-order calculations must not only take account of the explicit λ dependence of (35), but also must expand $\mathcal{G}'$ and the density matrix ρ in powers of λ.

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APPENDIX A: REMARKS ABOUT DIAGONAL SINGULARITIES

Consider the factor (24) which occurs in the expression (26) for the conductivity:

$$\mathcal{G}^0(1-\lambda^2\Delta\mathcal{V}\mathcal{G}'\Delta'\mathcal{V}\mathcal{G}^0\Delta)^{-1} = \sum_{m=0}^{\infty} \frac{\lambda^{2m}}{(\epsilon - i\omega)^{m+1}} (\Delta\mathcal{V}\mathcal{G}'\Delta'\mathcal{V}\Delta)^m , \quad (\mathrm{A1})$$

which is a geometric series in the diagonal superoperator $\Delta\mathcal{V}\mathcal{G}'\Delta'\mathcal{V}\Delta$. Suppose we want to evaluate this sum for $\omega = 0$, to lowest order in λ, and suppose further that we do not know the complete structure of (A1), but that we wish to evaluate

$$\sum_{m=0}^{\infty} \frac{\lambda^{2m}}{\epsilon^{m+1}} \mathcal{B}_m(\lambda, \epsilon) , \quad (\mathrm{A2})$$

where we know only that

$$\mathcal{B}_m(\lambda, \epsilon) = [\Delta\mathcal{V}\mathcal{G}^0(\epsilon=0)\Delta'\mathcal{V}\Delta]^m + O(\lambda) + O(\epsilon) . \quad (\mathrm{A3})$$

The idea of the diagonal singularity method of van Hove[30] ($\lambda^2 t$ or λ^2/ϵ method) is to keep, for each order λ^n in the expansion of (A2), only the coefficient of the highest negative power of ϵ, because it will give the biggest contribution when $\epsilon \to 0$. This means that the contributions of $O(\lambda)$ and $O(\epsilon)$ in (A3) are neglected, and (A2) becomes

$$\sum_{m=0}^{\infty} \frac{\lambda^{2m}}{\epsilon^{m+1}} \mathcal{B}_m(0,0) = [\epsilon - \lambda^2\Delta\mathcal{V}\mathcal{G}^0(\epsilon=0)\Delta'\mathcal{V}\Delta]^{-1} , \quad (\mathrm{A4})$$

which, when $\epsilon = 0$, is exactly what (A1) becomes to lowest order in λ with $\epsilon = 0$. Our point here is that (A4) is a divergent series when $\epsilon \to 0$, which is the case of interest. It is a summable divergent series, so Eq. (A4) is true, but theorems of termwise comparison do not hold for divergent series: in particular one cannot legitimately drop high-order terms in (A3). The reader can easily convince himself that this is true by considering

$$\sum_{m=0}^{\infty} \frac{\lambda^{2m}}{\epsilon^{m+1}} \left(1 + \frac{a\lambda^2}{(m+1)!} + \frac{b\epsilon}{m!}\right) = (\epsilon - \lambda^2)^{-1} + a(e^{\lambda^2/\epsilon} - 1) + be^{\lambda^2/\epsilon} \quad (\mathrm{A5})$$

for $\epsilon \to 0$. The reason that the λ^2/ϵ method works to lowest order in this case [i.e., (A4) and (A1) agree] is the lucky accident that (A1) can be expressed as a geometric series for any ϵ and λ^2.

The rationale of the diagonal singularity method, namely, that the diagonal energy denominators are smallest and hence give the biggest contributions to the sum, is valid only in the absence of degeneracies and for finite level spacings. But minimum level spacings vanish as $L \to \infty$, and it is well known that the order of limits in evaluating the Green-Kubo expressions must be $L \to \infty$

before $\epsilon \to 0$.

Divergent series cannot be avoided in calculation of dc conductivity.[31] In Sec. II D we implicitly expanded into and subsequently resummed a divergent series, in order to perform the random averaging. But the terms we dropped between expansion and resummation vanished in the thermodynamic limit, so our resummation was exact.

APPENDIX B: CLASSICAL LORENTZ GAS

Because of its pedagogical felicity, a discussion of the evaluation of the Green-Kubo formula for a classical electron moving in a dilute gas of small scatterers is appended here. Equation (2) is directly applicable, with the trace replaced by an integral over a distribution function.

$$\sigma = \tfrac{1}{3}\beta e^2 n_e \int^{\infty} dt\, e^{-i\omega t} \int d^3v\, f(\vec{v}) \langle\langle \vec{v}\cdot\vec{v}(t)\rangle\rangle\ , \qquad \text{(B1)}$$

where $f(\vec{v})$ is the equilibrium velocity distribution function such that

$$\int f(\vec{v}) d^3v = 1\,.$$

Implied by the double brackets in (B1) is an average over initial positions of the electron, and over all possible realizations of the random scatterers. The orbits are assumed to be straight lines between scatterings, which occur at times $t_1, t_2, t_3 \ldots$. The velocity is $\vec{v}_0 = \vec{v}$ for $0 < t < t_1$, $\vec{v}_1$ for $t_1 < t < t_2 \ldots$, where $\vec{v}_i^2 = \vec{v}^2$, $i = 0, 1, \ldots$ because the scatterings are all elastic. If each scattering is described by a rotation matrix R_i, then

$$\vec{v}_i = R_i \vec{v}_{i-1}, \quad i = 1, 2 \ldots\,.$$

If now successive scatterings are assumed to be independent, all we need to know about the matrix R_i is its average value

$$\langle R_i\rangle = \langle \cos\theta_i\rangle = \langle\cos\theta\rangle\ .$$

Then

$$\int dt\, e^{-i\omega t}\vec{v}(t) \to \sum_{i=1}^{\infty} \vec{v}_0 \frac{e^{-i\omega t_{i-1}} - e^{-i\omega t_i}}{i\omega} \langle\cos\theta\rangle^{i-1}\ . \qquad \text{(B2)}$$

Now if the intervals $\Delta t_i = t_i - t_{i-1}$ are distributed according to the Poisson distribution

$$P(\Delta t) = \tau^{-1} e^{-\Delta t/t}\,,$$

then

$$\langle\langle e^{-i\omega t_i}\rangle\rangle = \left\langle\left\langle \exp\left(-i\omega \sum_{j=1}^{i} \Delta t_j\right)\right\rangle\right\rangle = \left(\tau^{-1}\int_0^{\infty} e^{-\Delta t/t}\, d\Delta t\, e^{-i\omega\Delta t}\right)^i = (1 + i\omega\tau)^{-i}\,.$$

Thus

$$\int_0^{\infty} dt\, e^{-i\omega t}\vec{v}(t) \to \frac{\tau\vec{v}}{1+i\omega\tau} \sum_{i=0}^{\infty} \frac{\langle\cos\theta\rangle^i}{1+i\omega\tau} = \frac{\vec{v}}{i\omega + \tau^{-1}\langle 1 - \cos\theta\rangle}\ ,$$

and finally

$$\sigma = \tfrac{1}{3}\beta e^2 n_e \int f(\vec{v}) d^3v \frac{v^2}{i\omega + \tau^{-1}\langle 1 - \cos\theta\rangle} \qquad \text{(B3)}$$

which has the same form as Eq. (46) as must be the case at least in the high-temperature limit.

Equation (B3) affords an easy way to see exactly where several attempts in recent years to calculate resistivity in the dc case have erred. Since a straightforward perturbation theory for σ is then obviously impossible attention was focused on the resistivity, which vanishes for no scattering and therefore may be amenable to perturbation calculation. We define an effective scattering frequency

$$\nu = \langle 1 - \cos\theta\rangle/\tau \approx \langle\theta^2\rangle/2\tau\ .$$

First, expand ($B3$) for finite ω as a perturbation series in ν, keeping the first-order term.

$$\sigma = \frac{e^2 n_e}{i\omega m}\left(1 - \frac{\beta m}{3i\omega} \int d^3v f(\vec{v}) v^2 \nu\right)\ . \qquad \text{(B4)}$$

Then take the inverse to get the resistivity:

$$R = \sigma^{-1} = \frac{i\omega m}{e^2 n_e}\left(1 + \frac{\beta m}{3i\omega} \int d^3v\, f(\vec{v}) v^2 \nu\right)\ . \qquad \text{(B5)}$$

Here we have again made a perturbation expansion, keeping only the first-order term in ν. Equation (B5) is well behaved for $\omega \to 0$ and we have accomplished the removal of the divergent terms in (B4) for $\omega \to 0$. So (B5) says

$$\sigma(0) = \frac{e^2 n_e}{m} \langle\nu\rangle_f^{-1}\ , \qquad \text{(B6)}$$

whereas (B3) says

$$\sigma(0) = \frac{e^2 n_e}{m}\langle\nu^{-1}\rangle_f\ ,$$

where the brackets are now defined

$$\langle g\rangle_f = \int d^3v\, f(\vec{v}) v^2 g(\vec{v}) \Big/ \int d^3v\, f(v) v^2\,.$$

These two expressions for $\sigma(0)$ are equal if $f(\vec{v})$ is a δ function in energy, as is the case in the degenerate electron system at $T = 0$. But as has been pointed out by Huberman and Chester,[1] they are quite different in other situations. Equation (B6) is wrong; the reason it is wrong is obvious from the derivation. Similar mistakes, well hidden, have been made in each of the papers in which its equivalent has been derived.

APPENDIX C: SIMPLIFICATION OF THE QUANTUM-MECHANICAL GREEN-KUBO FORMULA

The usual form for an isotropic system is

$$\sigma(\omega)=\tfrac{1}{3}e^2n_e\int_0^\infty dt\,\mathrm{Tr}\left(\rho\vec{v}\cdot\int_0^\beta d\beta'\,\vec{v}(t+i\beta')\right)e^{i\omega t}\,. \tag{C1}$$

From this we will derive Eq. (2). We first change variables $t'=t+i\beta'$, and decompose the integrals, with $i\beta''=t'$,

$$\int_0^\beta d\beta'\int_0^\infty dt \rightarrow -i\int_0^\beta d\beta'\int_0^{\beta'} d\beta''+\int_0^\beta d\beta'\int_0^\infty dt'\,.$$

Then, after reversing the order of integration in the first term, and letting $q=\frac{1}{3}e^2n_e$, we get

$$\sigma(\omega)=iq\int_0^\beta d\beta''(e^{\omega(\beta-\beta'')}-1)\omega^{-1}\mathrm{Tr}[\rho\vec{v}\cdot\vec{v}(i\beta'')] + q\sigma_0(\omega)(e^{\omega\beta}-1)/\omega\,, \tag{C2}$$

where

$$\sigma_0(\omega)=q\int_0^\infty dt\,e^{i\omega t}\,\mathrm{Tr}[\rho\vec{v}\cdot\vec{v}(t)]\,.$$

It is easy to show that the first term in (C2) is pure imaginary, so if $\sigma=\sigma_R+i\sigma_I$, then $\sigma_R(\omega)=q\beta\,\mathrm{Re}\sigma_0(\omega)$, which is Eq. (2).

Because $\sigma(\omega)$ is a causal response,[32] its real and imaginary parts are related, according to the Titchmarsh theorem,[33] by the Hilbert transform

$$\sigma_I(\omega)=-\frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{\infty}d\omega'\,\frac{\sigma_R(\omega')}{\omega'-\omega}\,.$$

Although $\sigma_R(\omega)$ as given above is not a manifestly even function of ω, one can demonstrate it as follows. First, observe that the trace in Eq. (C1) is a real, even function of t. It then follows that $\sigma^*(\omega)=\sigma(-\omega)$, so $\sigma(\omega)+\sigma^*(\omega)$ is even.

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[19] A simple derivation of generalized Green-Kubo formulas may be found in W. M. Visscher, Phys. Rev. A 10, 2461 (1974). The elimination of the integral over temperature is performed in Appendix C. It is also discussed in Ref. 4.

[20] We use the density matrix in the canonical ensemble for simplicity. No difficulties in principle are involved in using the grand-canonical density matrix, which is necessary to properly treat Fermi-Dirac statistics. We would then need a second-quantized formalism with anticommuting electron creation-annihilation operators. As it stands our analysis applies only to independent electrons; the changes needed for a degenerate gas of noninteracting electrons are straightforward.

[21] The superoperator technique was exploited by R. W. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, B. W. Downs, and J. Downs (Interscience, New York, 1961), Vol. 3, p. 106. They are discussed by Zwanzig also in Physica (Utr.) 30, 1109 (1964). If the operators H, V have an $N\times N$ matrix representation, the superoperators $\mathcal{H}, \mathcal{V}$ are represented by $N^2\times N^2$ matrices (tetradics). Their matrix elements can be specified by 4 indices.

[22] The notation we use here for the Zwanzig projection superoperators is that of Ref. 11.

[23] Careful discussions of averaging procedures in similar problems are given by W.L. Schaich, Phys. Status Solidi B 64, 649 (1974). See also Ref. 2 and A. W. B. Taylor, Physica (Utr.) 32, 2030 (1966).

[24] By close we mean within the Lorentzian width of $|\mathcal{G}^0_{\vec{k}\vec{q}\vec{k}\vec{q}}|^2=[\epsilon^2+(\omega+E_{\vec{k}}-E_{\vec{q}})^2]^{-1}$.

[25] The method used to solve (38) is that of Ref. 2.

[26] For a perfect macroscopic crystal, the random averaging can be dispensed with entirely, and Eq. (26) could be evaluated directly.

[27] $\langle\delta^2\rangle$ is proportional to kT for Boltzmann statistics [Eq. (51)]; one could instead use Bose-Einstein statistics for phonons in the Einstein or Debye model.

[28] In the thermodynamic limit $L^{-3}\sum_{\vec{R}'}\rightarrow(2\pi)^{-3}\int d^3k'$. Equation (55) shows that at low temperatures, where $E_k=E_F$, measurement of ac conductivity is a direct probe of the electronic density of states, because $\delta(E_F-E_k+\omega)=(dk/dE_k)\delta(k-k(E_F+\omega))$.

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