BREAKDOWN OF THE CONCENTRATION EXPANSION FOR THE IMPURITY RESISTIVITY OF METALS*

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It has been discovered recently that the transport coefficients for classical gases do not possess simple expansions in powers of the density n.[1-5] In contrast to the virial expansion for equilibrium properties, it turns out that the transport coefficients contain singular terms of the form $n^s \ln n$, where the lowest power s depends on the dimensionality of the system. The purpose of the present note is to report that a similar phenomenon occurs in the quantum-mechanical problem of expressing the zero-temperature resistivity of a metal as a function of n_i, the concentration of impurities. In particular, we have shown that the power-series expansion for the resistivity ρ breaks down at order n_i^3 in three dimensions, and that the leading term at that order is of the form $n_i^3 \ln n_i$.

The mechanism leading to the breakdown of the series expansion is fairly easy to understand. With only minor oversimplification, one can say that the term in ρ formally of order n_i^s is determined by the scattering of an electron from an isolated cluster of s impurities. This term must be averaged over all configurations of the cluster; and for $s \geq 3$, the resulting integration diverges at large impurity separations. The cure for this divergence lies in the observation that it is not meaningful to speak of a "cluster" of impurities when the cluster is of a size larger than the electron mean free path; i.e., an electron will not propagate as an unattenuated plane wave between two widely separated impurity sites. The mathematical problem, then, is to deduce an effective cutoff for the cluster integral in a systematic and consistent fashion.

Our analysis is based on a quantum formalism originally introduced by Edwards[6] and developed by one of us (J.S.L.)[7] for application to problems in which electron-electron interactions are taken into account. The many-body aspects of the problem are not significant here, and will be neglected; but the systematics of the transport calculation as outlined in the previous paper[7] are of crucial importance.

The central result of this formalism is the expression of the transport coefficient as a sum of diagrams of the form shown in Fig. 1. Each open circle here represents an impurity site and carries a factor n_i. Each wavy line is the amplitude (t matrix) for an electron scattering at an impurity site. The rule is that the total momentum transfer at an open circle must be zero. Each solid line represents a single-electron propagator which we finally shall have to take to be the exact Green's function in the impurity field averaged over configurations of impurities. We have found no anomalies in the concentration expansion of the single-particle self-energy function; and this is consistent with the fact that the classical expansions break down only for transport and not equilibrium properties.

The sum of all diagrams of the form shown in Fig. 1 may be obtained by solving the obvious integral equation (a sort of Bethe-Salpeter equation) which, in this theory, transforms into a generalization of the Boltzmann equation.[8] It turns out that the serious divergences occur in the kernel of this integral equation, i.e., in third and higher order contributions to the irreducible interaction part, W. At given order in n_i, the most divergent contributions to W may be shown to come from the completely crossed diagrams drawn in Fig. 2(a). To see the nature of this difficulty, it is convenient to reverse the upper electron lines, obtaining the simple ladder diagrams shown in Fig. 2(b). Such a ladder diagram with s rungs makes a contribution to W formally of order at least n_i^s; and the coefficient of n_i^s should be obtained by letting n_i go to zero in each of the electron lines, i.e., using unperturbed prop-

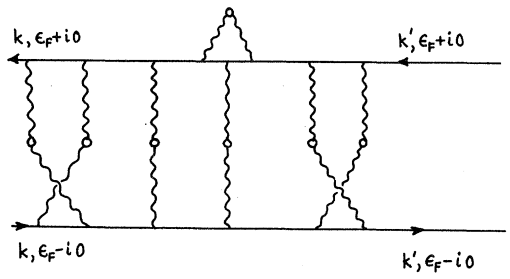

FIG. 1. Typical diagram in the expansion of the electrical conductivity.

agators. If, for demonstration purposes, we approximate each scattering amplitude by a constant, say v, then it requires only a short calculation to obtain for the sth-order contribution an expression of the form

$$(n_i v^2)^s \left[\sum_{\vec{q}} \frac{1}{(\vec{k}-\vec{q})^2 - k_F^2 + i0} \frac{1}{(\vec{k}'+\vec{q})^2 - k_F^2 - i0} \right]^{s-1} \propto \frac{(n_i v^2)^s}{|\vec{k}+\vec{k}'|^{s-1}} \quad (1)$$

which, for $s \geq 3$, has a nonintegrable singularity at $\vec{k} = -\vec{k}'$. Here k_F is the Fermi momentum, and we have set $\hbar = 2m = 1$. It should be emphasized that the right-hand side of this equation is correct only when the energy variables for the two electron lines have small imaginary parts of opposite sign. This mathematical situation is characteristic of nonequilibrium calculations and has no analog in equilibrium problems.

The resolution of the divergence difficulty is perhaps more obvious here than in the classical problem. As dictated by the formalism,[7] one must correct the single-electron propagators to account for random scattering in the impurity field. The important effect of this correction is the replacement of the small imaginary parts $\pm i0$ in the electron propagators by $\pm i\Gamma$, where Γ is the single-particle relaxation rate, proportional to n_i in lowest order. Then the right-hand side of Eq. (1) becomes

$$(n_i v^2)^s \left[\frac{1}{|\vec{k}+\vec{k}'|} \tan^{-1} \left(\frac{k_F |\vec{k}+\vec{k}'|}{\Gamma} \right) \right]^{s-1}, \quad (2)$$

which clearly contains the desired cutoff. To continue the calculation, W must be evaluated for $\vec{k}$ and $\vec{k}'$ near the Fermi surface and integrated over the angle between $\vec{k}$ and $\vec{k}'$. On performing this integration, we find that the $s = 2$ term makes a finite contribution of order n_i^2 as expected; but there are corrections to this term of the form $n_i^3 \ln n_i$, n_i^3, etc. From $s = 3$ we obtain contributions of the form $n_i^3 \ln n_i$, n_i^3, etc. Each of the terms for $s \geq 4$ contains a contribution of order n_i^3; thus, to obtain the complete n_i^3 contribution it is necessary to sum all of the completely crossed diagrams. These results, including the logarithmic terms, carry over directly into the final expression for the resistivity ρ.

The breakdown of the concentration expansion for electrical resistivity seems to indicate that transport phenomena in strongly disordered systems are more complicated and more difficult to describe mathematically than had previously been hoped. The appearance of the logarithmic terms in quantum problems seems especially significant because it opens for investigation a wide range of physical situations in which the nonanalytic properties of transport coefficients may be of importance. We mention as examples electron transport in highly doped semiconductors, liquid metals, and normal metals in which the impurities have scattering resonances at the Fermi surface. Needless to say, it is not very likely that the coefficient of the term $n_i^3 \ln n_i$ can be computed accurately and compared directly to experimental data. It may be hoped, however, that the insight gained in studying these higher order terms may lead to better and more comprehensive theories.

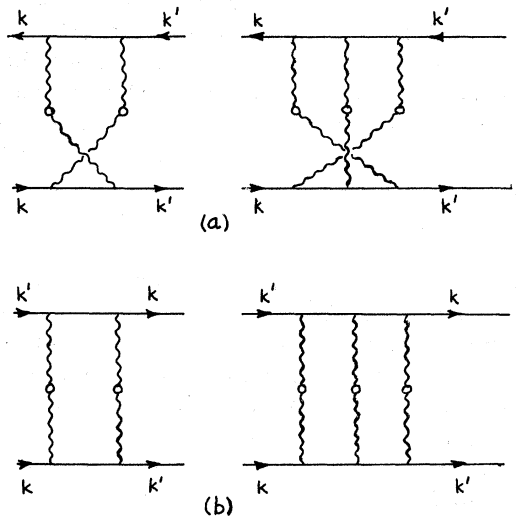

FIG. 2. (a) Completely crossed diagrams in the expansion of the irreducible interaction part W. (b) The crossed diagrams with upper electron line reversed.

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SECOND-HARMONIC GENERATION OF LIGHT IN REFLECTION FROM MEDIA WITH INVERSION SYMMETRY

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The second-harmonic generation (SHG) of light in reflection[1] has been extensively studied in crystals lacking a center of inversion.[2] In media with inversion symmetry, the second-harmonic source terms are smaller in magnitude and have magnetic-dipole and/or electric-quadrupole character.[3] Recently, reflected second-harmonic light from metallic silver[4] and from silicon and germanium[5] has been reported. Some discussion has arisen whether the effect in silver is due mostly to the free-electron plasma[6-8] or whether core electrons contribute significantly to the observed second-harmonic intensity.[5,9,10] It is the purpose of this note to present new theoretical and experimental evidence that the latter viewpoint is correct.

In general one may expect that, if both conduction electrons and core electrons make comparable contributions to the linear dielectric constant, they will also make comparable contributions to the nonlinear susceptibilities.[11] It is well known that the linear dielectric constant in silver at the second-harmonic frequency of ruby-laser light contains about equal and opposite contributions from the intraband (conduction electron) and interband (core) transitions.[12] A general formula for the nonlinear source current density incorporates both contributions.[13] An expansion into multipole moment contributions has been made.[3,14]

For an isotropic medium[15] the important source terms at the second-harmonic frequency may be written in the pheonomenological form

$$\vec{P}^{NL}(2\omega) = \alpha(\vec{E}\times\vec{H}) \equiv (\alpha_{pl} + \alpha_c)(\vec{E}\times\vec{H}), \tag{1}$$

$$-\nabla\cdot Q^{NL}(2\omega) = -\nabla\cdot(\beta_{pl}' + \beta_c')\vec{E}\vec{E}. \tag{2a}$$

The divergence of the volume quadrupolarization may be transformed into a surface term of the form used by Jha,[7]

$$\vec{P}_{eff}^{NL} = +(\beta_{pl} + \beta_c)\vec{E}(\nabla\cdot\vec{E}), \tag{2b}$$

with

$$\beta_{pl} + \beta_c = -(\beta_{pl}' + \beta_c')/(\epsilon_{(\omega)} - 1).$$

All values of the fields should be taken inside the medium. They are related to the incident laser field by the linear Fresnel equations. The magnitude of the quadrupole volume term is equivalent to that of a dipole term restricted to a single atomic layer at the surface.

It must be emphasized that these phenomenological relationships hold equally well for free as for bound electrons. Any attempt to decide on the basis of polarization properties alone that a pure plasma effect is involved has no validity. The symmetry properties of the core electrons are the same as for the conduction electrons. We have indeed found that the polarization properties, the variation with angle of incidence, as well as the magnitude of the reflected harmonic intensity from Si and Ge are very similar to those from Ag, Au, Cu, and other metals.

The suggestion that the laser beam first creates a plasma in Si and Ge in our experiments has been disproved as follows. The reflectivity of the Si and Ge samples was monitored with a continuous beam at 6328 Å from a He-Ne laser. No observable change in reflectivity occurred during the ruby-laser pulse which created the second harmonic. The induced plasma density is negligible at the power levels used in our experiment. Furthermore, the SHG was found to be strictly proportional to the square of the laser intensity. If a