

Generalized effective-medium approach to the conductivity of an inhomogeneous material*

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An old effective-medium approximation for the conductivity tensor of a randomly inhomogeneous medium is generalized to treat, in principle, materials consisting of crystallites of arbitrary shape and conductivity tensors of arbitrary symmetry. The effective-medium approximation is roughly analogous to the coherent-potential approximation (CPA) of alloy theory. The analog of the average- t -matrix approximation (ATA) is also formulated in a general way. The method is fully tractable analytically for ellipsoidal crystallites. Several applications are discussed. The effective conductivity of a polycrystal consisting of randomly oriented uniaxial crystallites is calculated as a function of the anisotropy of the grains. For a model polycrystal in an intense magnetic field, the CPA and ATA are compared, the former giving more accurate results.

I. INTRODUCTION

The transport properties of randomly inhomogeneous materials have been of interest since nearly the time of Maxwell. The reason for this interest is, of course, the enormous variety of physical systems in which random inhomogeneities occur: All polycrystalline and composite materials, for example, are randomly inhomogeneous systems. Such materials are described by a spatially varying conductivity tensor $\vec{\sigma}(\vec{x})$ which is random in some fashion. The basic problem is then the following: Given the conductivity tensor of each constituent of the inhomogeneous medium, and given the statistical laws governing the spatial variation of the conductivity, how does one calculate the effective conductivity of the medium as a whole? The problem is one of continuum physics, and is to be distinguished from the problems associated with microscopic inhomogeneities, such as impurities or vacancies, which are usually studied by scattering-theoretic techniques.

One of the most successful methods of treating the transport properties of randomly inhomogeneous materials has been a self-consistent or effective-medium approach due originally to Bruggeman,¹ and studied quantitatively by Landauer.² The virtue of the method is that it is not limited to low concentrations of inhomogeneities or to weakly varying conductivities. In recent years,³ this approach has been extended to treat the low-field Hall coefficient⁴ and the magnetoresistance⁵ of heterogeneous materials. An identical approximation can, of course, be used to treat heat transport, dielectric properties, magnetic permeability, and diffusion in inhomogeneous materials, since all these processes are governed by formally identical equations. In the past two years, the approximation has been further extended to the somewhat more complex problem of the elastic constants of heterogeneous materials by Korringa,⁶ and by

Zeller and Dederichs.⁷ The latter formulated the problem in the concise language of scattering theory and were thus able to derive the effective-medium approach in a rather elegant fashion.

The purpose of the present paper is to generalize the effective-medium approach to treat inhomogeneous media with crystallites of arbitrary shape, size, and orientation, and conductivity tensors of arbitrary symmetry. Such a fully generalized effective-medium approximation has not previously been explicitly derived. To obtain the generalization, we first develop an integral equation for the electric field within the medium, and then approximately decouple this equation. The decoupling procedure serves to make clear the mean-field character of the effective-medium approach. It also suggests a connection, previously noted by Gubernatis and Krumhansl,⁸ between this scheme and similar mean-field approximations in the theory⁹ of electronic propagation in disordered binary alloys. It is, in fact, possible to define an "average- t -matrix approximation" (ATA)¹⁰ and a "coherent-potential approximation" (CPA)⁹ in loose analogy with the alloy problem. The latter is equivalent to the effective-medium approach.

In addition to describing a generalized effective-medium approach to inhomogeneous transport problems, the present paper also gives several examples designed to illustrate the tractability of the method in a variety of special cases, and to show connection with previous work. Both the ATA and the CPA can be worked out analytically if the crystallites can be taken to be ellipsoidal in shape, even for conductivity tensors of arbitrary symmetry. For the simplest case of a two-phase medium composed of isotropic crystallites approximately spherical in shape, the CPA becomes simply a quadratic equation for σ_e , the effective conductivity, as obtained originally by Bruggeman.¹ For a true polycrystal consisting of anisotropic spherical crystallites, the method is again tractable, as is

shown by a numerical application to a polycrystal of randomly oriented uniaxial crystallites. The method can also be applied to the magnetoconductivity tensor of a polycrystalline metal in a magnetic field, for which the medium as a whole as well as its components are anisotropic. In this case, the CPA is shown to be much more accurate than the non-self-consistent ATA in the high-field limit. Finally it is pointed out that the approach is applicable to ac as well as dc problems provided the wavelength of the ac field is long compared to the linear dimensions of the inhomogeneities. Such an approach could be very useful in treating the optical properties of composites, which until now seem to have been studied only by variants of the ATA such as the well-known Maxwell-Garnett theory.¹¹

Before proceeding to the derivation and examples, we point out that the present statistical approach is designed to treat only one of several difficulties associated with inhomogeneities. We ignore, for example, boundary scattering, i. e., actual dissipation of energy at boundaries due to interaction between current carriers and defects such as dislocations. The statistical theory, in fact, takes account only of local current fluctuations due to "impedance mismatch" at boundaries. Dissipation due to scattering at boundaries, if thought important, must be treated by a different approach.

We turn now to the body of the paper. The formal generalization of the effective-medium theory is described in Sec. II. A number of examples are then worked out in Sec. III.

II. FORMALISM

We consider an inhomogeneous medium of volume V , bounded by surface S , and characterized by a spatially varying conductivity tensor $\vec{\sigma}(\vec{x})$. The conductor is assumed to be a random medium in the sense that the ensemble average of $\vec{\sigma}(\vec{x})$, denoted $\langle \vec{\sigma}(\vec{x}) \rangle$, is independent of \vec{x} . It is convenient also to make the "ergodic" hypothesis that a configuration average is equivalent to a volume average. Thus, for example, $\langle \vec{\sigma} \rangle = V^{-1} \int_V \vec{\sigma}(\vec{x}) d^3x$. Henceforth we shall evaluate all averages explicitly as volume averages.

The measurable transport properties of the conductor are determined by an effective position-independent conductivity tensor $\vec{\sigma}_e$. $\vec{\sigma}_e$ can be defined most easily by imaging that a constant electric field \vec{E}_0 is applied at the boundary of the conductor, so that the scalar potential on S is $\Phi(\vec{x}) = -\vec{E}_0 \cdot \vec{x}$. Then $\vec{\sigma}_e$ is defined by

$$\langle \vec{J} \rangle \equiv \vec{\sigma}_e \langle \vec{E} \rangle, \quad (2.1)$$

where \vec{J} is the current density. Note that $\langle \vec{E} \rangle = \vec{E}_0$, the applied field.

In order to develop approximations for $\vec{\sigma}_e$, we

now expand $\vec{\sigma}(\vec{x})$ about a constant reference conductivity $\vec{\sigma}_0$, by writing

$$\vec{\sigma}(\vec{x}) = \vec{\sigma}_0 + \delta\vec{\sigma}(\vec{x}). \quad (2.2)$$

$\vec{\sigma}_0$ is for the moment to be viewed as an arbitrary constant, and may be chosen in any convenient way. Possible choices will be discussed later. Substituting (2.2) into (2.1) yields

$$\langle \vec{J} \rangle = \vec{\sigma}_0 \langle \vec{E} \rangle + \langle \delta\vec{\sigma} \vec{E} \rangle. \quad (2.3)$$

Thus the calculation of $\vec{\sigma}_e$ requires a good approximation to the quantity $\langle \delta\vec{\sigma} \vec{E} \rangle$.

We now derive a simple integral equation for $\vec{E}(\vec{x})$ which may be decoupled in various ways to yield several approximations for $\vec{\sigma}_e$. The electrostatic equations are $\vec{\nabla} \cdot \vec{J} = 0$, $\vec{\nabla} \times \vec{E} = 0$; these combined with the constitutive relation $\vec{J}(\vec{x}) = \vec{\sigma}(\vec{x}) \vec{E}(\vec{x})$ imply that the electrostatic potential $\Phi(\vec{x})$ satisfies

$$\vec{\nabla} \cdot \vec{\sigma}(\vec{x}) \vec{\nabla} \Phi(\vec{x}) = 0. \quad (2.4)$$

The substitution (2.2) then leads to the boundary-value problem

$$\vec{\nabla} \cdot \vec{\sigma}_0 \vec{\nabla} \Phi(\vec{x}) = -\vec{\nabla} \cdot \delta\vec{\sigma}(\vec{x}) \vec{\nabla} \Phi(\vec{x}) \quad \text{in } V, \quad (2.5)$$

$$\Phi(\vec{x}) = \Phi_0(\vec{x}) \equiv -\vec{E}_0 \cdot \vec{x} \quad \text{on } S.$$

With the introduction of the Green's function $G(\vec{x}, \vec{x}')$ defined by

$$\vec{\nabla} \cdot \vec{\sigma}_0 \vec{\nabla} G(\vec{x}, \vec{x}') = -\delta(\vec{x} - \vec{x}') \quad \text{in } V, \quad (2.6)$$

$$G(\vec{x}, \vec{x}') = 0, \quad \vec{x}' \text{ on } S,$$

$\Phi(\vec{x})$ can be written as

$$\Phi(\vec{x}) = \Phi_0(\vec{x}) + \int_V G(\vec{x}, \vec{x}') \vec{\nabla}' \cdot \delta\vec{\sigma}(\vec{x}') \vec{\nabla}' \Phi(\vec{x}') d^3x'. \quad (2.7)$$

Integrating by parts and taking the gradient of each side, one obtains

$$\vec{E}(\vec{x}) = \vec{E}_0 - \int_V [\delta\vec{J}(\vec{x}') \cdot \vec{\nabla}'] \vec{\nabla} G(\vec{x}, \vec{x}') d^3x', \quad (2.8)$$

where $\delta\vec{J}(\vec{x}') = \delta\vec{\sigma}(\vec{x}') \vec{E}(\vec{x}')$, and we have used the fact that $G(\vec{x}, \vec{x}') = G(\vec{x}', \vec{x})$. Equation (2.8) can be written in the compact form

$$\vec{E}(\vec{x}) = \vec{E}_0 + \int d^3x' \vec{\mathcal{G}}(\vec{x}, \vec{x}') \delta\vec{\sigma}(\vec{x}') \vec{E}(\vec{x}'), \quad (2.9)$$

where the tensor $\vec{\mathcal{G}}(\vec{x}, \vec{x}')$ is defined by

$$\mathcal{G}_{\alpha\beta}(\vec{x}, \vec{x}') = \frac{\partial}{\partial x'_\alpha} \frac{\partial}{\partial x_\beta} G(\vec{x}, \vec{x}'). \quad (2.10)$$

An exact formal solution for $\vec{\sigma}_e$ can now be written down. From Eq. (2.9),

$$\delta\vec{\sigma}(\vec{x}) \vec{E}(\vec{x}) = \delta\vec{\sigma}(\vec{x}) \vec{E}_0 + \delta\vec{\sigma}(\vec{x}) \int d^3x' \vec{\mathcal{G}}(\vec{x}, \vec{x}') \delta\vec{\sigma}(\vec{x}') \vec{E}(\vec{x}') \quad (2.11)$$

or, defining a tensor $\vec{\chi}(\vec{x})$ by

$$\delta\vec{\sigma}(\vec{x}) \vec{E}(\vec{x}) = \vec{\chi}(\vec{x}) \vec{E}_0, \quad (2.12)$$

we have

$$\vec{\chi}(\vec{x}) = \delta \vec{\sigma}(\vec{x}) + \delta \vec{\sigma}(\vec{x}) \int d^3x' \vec{G}(\vec{x}, \vec{x}') \vec{\chi}(\vec{x}'). \quad (2.13)$$

Comparison of (2.1) and (2.3) with (2.12) indicates that

$$\vec{\sigma}_e = \vec{\sigma}_0 + \langle \vec{\chi} \rangle. \quad (2.14)$$

The problem thus reduces to the (formidable) task of computing $\langle \vec{\chi} \rangle$.

The nature of the approximations that may be derived from this formalism depends on some extent on the precise character of the inhomogeneous medium under consideration. We consider here polycrystalline or composite media, i. e., materials consisting of a random assembly of cells or crystallites, each of which is individually pure, with well-characterized transport coefficients. The crystallites may differ in shape, size, composition, and orientation of crystallographic axes.

For such a system, a class of approximations can be written down as follows. Let \vec{x} lie in the i th crystallite, and let that crystallite have volume v_i . Then Eq. (2.13) may be written

$$\begin{aligned} \vec{\chi}(\vec{x}) &= \delta \vec{\sigma}_i + \delta \vec{\sigma}_i \int_{v_i} d^3x' \vec{G}(\vec{x}, \vec{x}') \vec{\chi}(\vec{x}') \\ &+ \delta \vec{\sigma}_i \int_{V-v_i} d^3x' \vec{G}(\vec{x}, \vec{x}') \vec{\chi}(\vec{x}'), \end{aligned} \quad (2.15)$$

where $\delta \vec{\sigma}_i = \vec{\sigma}_i - \vec{\sigma}_0$, $\vec{\sigma}_i$ being the conductivity tensor of the i th cell. The approximation consists of replacing the last integral in (2.15) by its average. Thus in (2.15) we write

$$\begin{aligned} \delta \vec{\sigma}_i \int_{V-v_i} d^3x' \vec{G}(\vec{x}, \vec{x}') \vec{\chi}(\vec{x}') \\ \approx \delta \vec{\sigma}_i \int_{V-v_i} d^3x' \vec{G}(\vec{x}, \vec{x}') \langle \vec{\chi} \rangle \end{aligned} \quad (2.16)$$

for \vec{x} in the i th cell. Equation (2.16) closes the integral equation for $\vec{\chi}$ and enables $\chi(\vec{x})$ to be calculated in terms of $\langle \vec{\chi} \rangle$, which can be determined in turn from $\vec{\chi}(\vec{x})$.

Approximation (2.16) is not unique but depends on the choice of reference conductivity $\vec{\sigma}_0$. Of these choices, the "best" is presumably the self-consistent choice which ensures that

$$\langle \vec{\chi} \rangle = 0. \quad (2.17)$$

With this choice, and with Eq. (2.14), $\vec{\sigma}_e = \vec{\sigma}_0$. Equation (2.17) defines a loose analog of the coherent-potential approximation (CPA) which has been used successfully to treat electron states in disordered binary alloys. In effect, the actual medium surrounding each crystallite is replaced by a self-consistently determined effective medium. The various non-self-consistent approximation defined by Eq. (2.16) may be viewed collectively as the analogs of the average- t -matrix approximation (ATA) of alloy theory.

The class of approximations just defined may be applied, in principle, to composites consisting of crystallites of arbitrary shape and to conductivity tensors of arbitrary symmetry. If, however, the grains are taken to be ellipsoids, approximation (2.16) leads to a $\vec{\chi}(\vec{x})$ which is uniform within each grain,¹² and $\vec{\sigma}_e$ can be determined in a very compact form. To see this, we substitute (2.16) into (2.15), integrate by parts the two integrals in (2.15), and use the boundary condition in (2.6) to obtain

$$\begin{aligned} \chi_i^{\alpha\beta} &= \delta \sigma_i^{\alpha\beta} - \delta \sigma_i^{\alpha\gamma} \left(\oint_{S'} d^2x' \frac{\partial}{\partial x_\gamma} G(x, x') n'_\beta \right) \\ &\times (\chi_i^{\delta\beta} - \langle \chi \rangle_{\delta\beta}), \end{aligned} \quad (2.18)$$

where χ_i is the value of $\vec{\chi}(\vec{x})$ for x within the i th grain, and n'_β is a component of \hat{n}' , a unit normal outward from S' . In Eq. (2.18) Greek subscripts and superscripts denote Cartesian components, and repeated indices are summed over. In the limit of large volume, $G(\vec{x}, \vec{x}')$ goes over to the free-space Green's function, satisfying the differential equation (2.6) and the boundary condition $G(\vec{x}, \vec{x}') \rightarrow 0$ as $|\vec{x} - \vec{x}'| \rightarrow \infty$. It thus becomes a function only of $\vec{x} - \vec{x}'$. The surface integral is then a constant, independent of \vec{x} , and (2.18) takes the form

$$\vec{\chi}_i = \delta \vec{\sigma}_i + \delta \vec{\sigma}_i \vec{\Gamma}_i (\vec{\chi}_i - \langle \vec{\chi} \rangle), \quad (2.19)$$

where

$$\vec{\Gamma}_i^{\alpha\beta} = - \oint_{S'} \frac{\partial}{\partial x_\alpha} G(\vec{x} - \vec{x}') n'_\beta d^2x'. \quad (2.20)$$

Solving (2.19) for $\vec{\chi}_i$ in terms of $\langle \vec{\chi} \rangle$ yields

$$\vec{\chi}_i = (\vec{\Gamma} - \delta \vec{\sigma}_i \vec{\Gamma}_i)^{-1} \delta \vec{\sigma}_i (\vec{\Gamma} - \vec{\Gamma}_i \langle \vec{\chi} \rangle), \quad (2.21)$$

where $\vec{\Gamma}$ is the 3×3 unit matrix.

Equation (2.21) may now be averaged and solved for $\langle \vec{\chi} \rangle$. The result may be substituted into (2.14) to yield

$$\vec{\sigma}_e = \vec{\sigma}_0 + \langle (\vec{\Gamma} - \delta \vec{\sigma} \vec{\Gamma})^{-1} \delta \vec{\sigma} \rangle, \quad (2.22)$$

where

$$\langle (\vec{\Gamma} - \delta \vec{\sigma} \vec{\Gamma})^{-1} \delta \vec{\sigma} \rangle = \lim_{V \rightarrow \infty} V^{-1} \sum_i v_i (\vec{\Gamma} - \delta \vec{\sigma}_i \vec{\Gamma}_i)^{-1}, \quad (2.23)$$

$$\langle (\vec{\Gamma} - \delta \vec{\sigma} \vec{\Gamma})^{-1} \delta \vec{\sigma} \rangle = \lim_{V \rightarrow \infty} V^{-1} \sum_i v_i (\vec{\Gamma} - \delta \vec{\sigma}_i \vec{\Gamma}_i)^{-1} \delta \vec{\sigma}_i.$$

Equation (2.22) is the desired ATA solution for $\vec{\sigma}_e$ in the special case of ellipsoidal grains. The CPA is defined by

$$\langle (\vec{\Gamma} - \delta \vec{\sigma} \vec{\Gamma})^{-1} \delta \vec{\sigma} \rangle = 0. \quad (2.24)$$

From a practical point of view, the ATA is easily executed. Once a convenient $\vec{\sigma}_0$ has been chosen, the tensors $\delta \vec{\sigma}_i$ and $\vec{\Gamma}_i$ become readily calculated properties of the various individual crystallites

and the evaluation of the averages in (2.23) is only a matter of straightforward matrix algebra. The self-consistency required by the CPA normally entails only a slight degree of additional computation.

It may be objected that space cannot be filled by an assembly of ellipsoidal grains and hence the approximation just described is inapplicable to any realistic composite. The counterargument to this objection is that many crystallites may, in fact, be reasonably approximated by ellipsoids. The simplification can be viewed as spiritually akin to the Wigner-Seitz approximation in band theory, wherein the Wigner-Seitz cell is approximated for computational reasons by a sphere of equal volume. If the grains are predominantly snakelike or spiderlike in shape, a different approach might be desirable. Rodlike grains, however, should be reasonably approximated by ellipsoids. If the grains are known to be of some specific, nonellipsoidal shape—for example, cubes—then it might be appropriate to apply the ATA or CPA, but with the actual shapes of the grains, rather than ellipsoidal estimates of them.

III. EXAMPLES

In this section we discuss several simple applications of the formalism just developed. The purpose of the discussion is to illustrate the usefulness of the effective-medium approximation in a variety of circumstances, and to compare the method with previous work in several cases. Detailed numerical studies of real systems will be deferred to a subsequent publication.

A. Two-phase medium, spherical isotropic crystallites

We begin with the simplest example, namely, a two-phase medium composed of a fraction c , by volume, of material A , and a fraction $1 - c$ of material B . The two constituents are assumed to have scalar conductivities $\vec{\sigma}_A = \sigma_A \vec{1}$ and $\vec{\sigma}_B = \sigma_B \vec{1}$, where $\vec{1}$ is again the 3×3 unit tensor, and both are taken to be present in the form of approximately spherical crystallites. Then $\vec{\sigma}_e$ will also be a scalar, $\vec{\sigma}_e = \sigma_e \vec{1}$, and the elements of the tensor $\vec{\Gamma}$ (which is the same for each crystallite, since all crystallites are by hypothesis the same shape) will be given by the surface integral (2.20). The Green's function $G(\vec{x}, \vec{x}')$ that enters the surface integral is the free-space solution to the differential equation (2.6):

$$G(\vec{x} - \vec{x}') = + \frac{1}{4\pi\sigma_e} \frac{1}{|\vec{x} - \vec{x}'|}. \quad (3.1)$$

This surface integral can be evaluated using (3.1) to yield

$$\Gamma_{\alpha\beta} = -\delta_{\alpha\beta}/3\sigma_e. \quad (3.2)$$

The self-consistency condition (2.23) takes the

form

$$c[1 - (\vec{\sigma}_A - \vec{\sigma}_e)\vec{\Gamma}]^{-1}(\vec{\sigma}_A - \vec{\sigma}_e) + (1 - c)[1 - (\vec{\sigma}_B - \vec{\sigma}_e)\vec{\Gamma}]^{-1}(\vec{\sigma}_B - \vec{\sigma}_e) = 0, \quad (3.3)$$

which, upon substitution of (3.2), simplifies to a quadratic equation for σ_e :

$$c \frac{\sigma_A - \sigma_e}{\sigma_A + 2\sigma_e} + (1 - c) \frac{\sigma_B - \sigma_e}{\sigma_B + 2\sigma_e} = 0. \quad (3.4)$$

Equation (3.4) has previously been obtained by several workers.^{1,2} It has been extensively investigated by Landauer,² who finds that it adequately describes the effective conductivity of a two-phase medium even if the conductivities of the components differ by a factor of 100.

B. Polycrystalline medium, anisotropic crystallites

The effective-medium approximation is easily generalized to the discussion of truly polycrystalline materials. We consider as an example a polycrystalline material consisting of approximately spherical crystallites of identical composition but anisotropic conductivity tensor, and we assume that the principal axes of the crystallites are randomly oriented, that is, they have equal probability of pointing in any direction. The effective conductivity of the medium will be a scalar, $\vec{\sigma}_e = \sigma_e \vec{1}$, and the tensor $\vec{\Gamma}$ will again be given by Eq. (3.2). The self-consistency condition determining σ_e takes the form

$$\langle [1 + (1/3\sigma_e)(\vec{\sigma} - \sigma_e \vec{1})]^{-1}(\vec{\sigma} - \sigma_e \vec{1}) \rangle = 0, \quad (3.5)$$

where the brackets denote an average over possible crystallite orientations.

Equation (3.5) is particularly easy to evaluate when the crystallites are uniaxial. If the coordinate axes are parallel to the principal axes of the crystallite, $\vec{\sigma}$ will then be of the form

$$\vec{\sigma} = \sigma_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \alpha \end{pmatrix}. \quad (3.6)$$

In other coordinate systems, $\vec{\sigma}$ will be related to (3.6) by a similarity transformation. It may readily be shown in this case that Eq. (3.3) reduces to a quadratic equation for σ_e which can be solved to yield simply

$$x = \frac{1}{4}[-3 + (9 + 8\epsilon)^{1/2}]. \quad (3.7)$$

Here, $x = \sigma_e/\sigma_0 - 1$, and $\epsilon = \alpha - 1$. For small ϵ , the solution of Eq. (3.7) is $x = \frac{1}{3}\epsilon - \frac{2}{27}\epsilon^2$, in agreement with the result obtained from the second-order perturbation approach of Herring.³ Note that at large ϵ , $x \sim (\alpha/2)^{1/2}$, whereas in the limit $\epsilon \rightarrow -1$, $x \rightarrow -\frac{1}{2}$ or $\sigma_e/\sigma_0 \rightarrow +\frac{1}{2}$. It is amusing to observe that σ_e as determined by Eq. (3.7) is the same, within

the CPA, as that of a composite of isotropic spherical crystallites, two-thirds having conductivity σ_0 and one-third $\alpha\sigma_0$.

C. Polycrystalline metal in an applied magnetic field

We turn next to a more complex example of considerable practical interest, namely, the effective conductivity of a polycrystalline metal in an applied magnetic field $\vec{H} = H\hat{z}$. In such a material, $\vec{\sigma}_e$ is not a scalar but instead takes the form¹³

$$\vec{\sigma}_e = \begin{bmatrix} \sigma_e^{xx} & \sigma_e^{xy} & 0 \\ -\sigma_e^{xy} & \sigma_e^{xx} & 0 \\ 0 & 0 & \sigma_e^{zz} \end{bmatrix}. \quad (3.8)$$

In spite of the added complexity, the differential equation (2.6) can still be solved for $G(x-x')$ by means of a scale transformation with the result

$$G(\vec{x}, \vec{x}') = + \frac{1}{4\pi\sigma_e^{xx}(\sigma_e^{zz})^{1/2}} \times \left(\frac{(x-x')^2}{\sigma_e^{xx}} + \frac{(y-y')^2}{\sigma_e^{xx}} + \frac{(z-z')^2}{\sigma_e^{zz}} \right)^{-1/2}. \quad (3.9)$$

The surface integral (2.20) can be evaluated for the elements of $\vec{\Gamma}$. For example, if the crystallites are spherical, it yields a diagonal $\vec{\Gamma}$, with nonzero matrix elements

$$\Gamma_{zz} = -\frac{1}{\sigma_e^{zz}\epsilon} \left(1 - (1-\epsilon)^{1/2} \frac{\sin^{-1}\sqrt{\epsilon}}{\sqrt{\epsilon}} \right), \quad (3.10)$$

$$\Gamma_{xx} = \Gamma_{yy} = -\frac{1}{2} \left(\Gamma_{zz} + \frac{1}{(\sigma_e^{xx}\sigma_e^{zz})^{1/2}} \frac{\sin^{-1}\sqrt{\epsilon}}{\sqrt{\epsilon}} \right).$$

Here $\epsilon = 1 - \sigma_e^{xx}/\sigma_e^{zz}$, and we have assumed $\epsilon > 0$, as is usually the case. Equations (3.10) can then be substituted into the self-consistency condition (2.23) to yield a set of three equations which can be solved for σ_e^{xx} , σ_e^{yy} , and σ_e^{zz} .

To illustrate the utility of the method, we apply Eq. (3.10) to a simplified version of a model which has been proposed¹⁴ to account for the galvanomagnetic properties of polycrystalline Cu. We imagine a metal composed of a fraction $1-c$ of spherical crystallites of free-electron metal, and a fraction c of spherical crystallites with open orbitals. The free-electron crystallites have conductivity tensor,

$$\vec{\sigma}_{fe} = \sigma_0 \begin{pmatrix} (1-\xi^2)^{-1} & \xi(1+\xi^2)^{-1} & 0 \\ -\xi(1+\xi^2)^{-1} & (1+\xi^2)^{-1} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (3.11)$$

where $\xi = \omega_c\tau$, τ is a relaxation time characteristic of the metal, and $\omega_c = eH/mc$ is the cyclotron frequency. The open-orbit crystallites have, in addition to a free-electron conductivity, an additional contribution arising from the ability of the open or-

bits to carry current in a direction perpendicular to the open-orbit direction and to the magnetic field. We shall simply approximate these open orbits by transverse short circuits, i. e., by infinite conductivities in the two directions perpendicular to the field.

The effective-medium theory may now be applied to this model. The self-consistency condition (2.18) takes the form

$$(1-c)[1 - (\vec{\sigma}_{fe} - \vec{\sigma}_e)\vec{\Gamma}]^{-1}(\vec{\sigma}_{fe} - \vec{\sigma}_e) + c[1 - (\vec{\sigma}_{oo} - \vec{\sigma}_e)\vec{\Gamma}]^{-1}(\vec{\sigma}_{oo} - \vec{\sigma}_e) = 0, \quad (3.12)$$

where $\vec{\sigma}_{oo}$ is the diagonal conductivity tensor of the open-orbit crystallites, with elements given by

$$\sigma_{oo}^{xx} = \sigma_{oo}^{yy} = \infty, \quad \sigma_{oo}^{zz} = \sigma_0. \quad (3.13)$$

Since $\vec{\Gamma}$ is a diagonal tensor, σ_e^{zz} is evidently equal to σ_0 (there being no randomness in the z component of the conductivity tensor), while σ_e^{xx} and σ_e^{yy} are determined by the condition

$$(1-c)[1 - (\vec{\sigma}_{fe} - \vec{\sigma}_e)\vec{\Gamma}]^{-1}(\vec{\sigma}_{fe} - \vec{\sigma}_e) - c(\vec{\Gamma})^{-1} = 0, \quad (3.14)$$

where now Eq. (3.14) is to be interpreted as a "2×2" matrix equation consisting of the projection of Eqs. (3.12) on the xy subspace.

Equation (3.14) may be solved analytically in the high-field limit ($\xi \gg 1$). In that regime, Γ_{xx} , determined by Eqs. (3.10), becomes

$$\Gamma_{xx} = \Gamma_{yy} = -\frac{\pi}{2} \frac{1}{(\sigma_e^{xx}\sigma_e^{zz})^{1/2}} = -\frac{\pi}{2} \frac{1}{(\sigma_e^{xx}\sigma_0)^{1/2}}. \quad (3.15)$$

Substitution of (3.15) and (3.11) into (3.14) yields

$$\sigma_e^{xx} = \frac{1}{\pi^2}\sigma_0 \left[c + \left(c^2 + \frac{\pi^2}{\xi^2} \right)^{1/2} \right], \quad (3.16)$$

$$\sigma_e^{yy} = \xi^{-1}\sigma_0.$$

Thus in the field limit ($\xi \rightarrow \infty$), $\sigma_e^{xx} \propto c^2$. This result corresponds to a saturating transverse magnetoresistance, $\rho_e^{xx} = (\vec{\sigma}_e^{-1})_{xx} \rightarrow \text{const}$ as $\xi \rightarrow \infty$, a behavior which differs from the linear magnetoresistance observed in actual samples of polycrystalline Cu.¹⁵ Nevertheless, there is little doubt that Eq. (3.16) does indeed represent the correct asymptotic behavior of the model. This is strongly suggested by consideration of the expected high-field current pattern of the polycrystal. In this regime, the free-electron portion of the medium carries current only in the direction parallel to the applied field. The current can make progress in the transverse direction only by "hopping" from one open-orbit crystallite to another. A simple scaling argument, based on a network analog, can be used to suggest that the transverse conductivity associated with this mechanism is indeed proportional

to c^2 .

It is interesting to compare the predictions of the self-consistent or effective-medium approximation with those of the non-self-consistent or average- t -matrix approach. In the present, highly anisotropic regime, they give qualitatively different results. We consider the ATA, as defined by Eq. (2.22), using as a reference medium the pure free-electron metal. The effective conductivity in the ATA is given by

$$\vec{\sigma}_e = \vec{\sigma}_{te} + c(\vec{1} + c \vec{t}\vec{1})^{-1} \vec{t}, \quad (3.17)$$

where

$$\vec{t} = [\vec{1} - (\vec{\sigma}_{oo} - \vec{\sigma}_{te}) \vec{1}]^{-1} (\vec{\sigma}_{oo} - \vec{\sigma}_{te}). \quad (3.18)$$

In a manner similar to that used to find $\vec{\sigma}_e$ in the self-consistent approximation, it may be shown that that in the high-field regime σ_e^{xx} is given by

$$(\sigma_e^{xx})_{ATA} = \text{const}(c/\xi). \quad (3.19)$$

This prediction differs qualitatively from that of the self-consistent approximation and moreover is evidently incorrect, since in the high-field limit σ_e^{xx} must become field independent. Thus, in this instance at least, it is evident that self-consistency makes an important difference in the calculation of effective conductivity.

D. Optical properties

We conclude this discussion of examples by noting that both the CPA and the ATA can be used to discuss ac as well as dc effects in heterogeneous materials, provided that the wavelength of the ac signal is large compared to a typical linear dimension of the crystallites. For such effects it is often more convenient to talk in terms of frequency-dependent dielectric functions than in terms of conductivities. In a two-phase medium, for example,

the relevant CPA self-consistency condition determining $\epsilon_e(\omega)$ is Eq. (3.4) with all σ 's replaced by ϵ 's. Thus $\epsilon_e(\omega)$ satisfies

$$c \frac{\epsilon_A(\omega) - \epsilon_e(\omega)}{\epsilon_A(\omega) + 2\epsilon_e(\omega)} + (1-c) \frac{\epsilon_B(\omega) - \epsilon_e(\omega)}{\epsilon_B(\omega) + 2\epsilon_e(\omega)} = 0. \quad (3.20)$$

If there are absorptive processes, ϵ_A , ϵ_B , and ϵ_e may have both real and imaginary parts.

It is instructive to compare Eq. (3.20) with the analogous ATA equation. If we take material B as the reference medium, Eq. (2.22) reduces to

$$\epsilon_e(\omega) = \{\epsilon_B(\omega) + c\delta\epsilon(\omega)/[1 + (1-c)\delta\epsilon(\omega)/3\epsilon_B(\omega)]\} \vec{1}, \quad (3.21)$$

where $\delta\epsilon(\omega) = \epsilon_A(\omega) - \epsilon_B(\omega)$. Equation (3.21) is identical to the equation originally derived by Maxwell-Garnett¹¹ to describe the optical properties of a composite medium, and since used extensively by a number of workers¹⁶ to describe the optical properties of assorted composites. Equation (3.21) is not necessarily limited to small concentrations c , although it does not treat A and B on the same footing. It would be most interesting to compare the predictions of the ATA equation (3.21) with the self-consistent equation (3.20), which apparently has not been used previously to describe optical properties of inhomogeneous media. It is hoped to present such a comparison in a subsequent publication.

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