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Self-consistent approach to electromagnetic wave propagation in composite media: Application to model granular metals

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A self-consistent method is developed to treat the propagation of electromagnetic waves in composite media. The theory reduces to the effective-medium approximation in the static limit, but unlike the latter is not necessarily limited to composites in which only electron-dipole scattering contributes. The self-consistency condition on the effective complex propagation constant $k_{\rm eff}(\omega)\equiv[\epsilon_{\rm eff}(\omega)]^{1/2}\omega/c$ reduces to the requirement that $\epsilon_{\rm eff}$ be chosen so that the "forward-scattering amplitude" of particles embedded in this medium should vanish on the average. The approximation is applied to far-infrared absorption in a model granular metal. Absorption due to induced eddy currents, properly included in the new theory, but neglected in the existing quasistatic theories, is shown overwhelmingly to dominate the classical absorption coefficient of such composites below the insulator-metal transition even for very small particles.

I. INTRODUCTION

The propagation of electromagnetic waves through composite media is often treated by ascribing to the composite an effective complex dielectric function $\epsilon_{\rm eff}(\omega)$.[1-5] Numerous approximations for calculating $\epsilon_{\rm eff}$ are available in the literature. Most, however, are based on the "quasistatic approximation"—that is, they are derived at *zero* frequency from consideration of the *static* electric field and electric displacement in the composite, and are extended to finite frequencies in a naive manner. Two well-known approaches of this kind are the Maxwell-Garnett approximation (MGA)[6] and the effective-medium approximation (EMA).[7-10] Both become exact for a composite consisting principally of one component and containing only a small volume fraction of a second, but the latter shows certain new features, for example, a metal-insulator transition in a composite consisting partly of metal and partly of dielectric. The condition for extending these approximations to finite frequencies is believed[11] to be that the characteristic particle dimension a in the composite is small compared to the characteristic wavelength λ. For shorter wavelengths, electromagnetic scattering becomes important and these theories as presently formulated certainly break down.

In this paper, we extend the EMA to finite frequencies, using a full multipole expansion to treat scattering from small particles. The main output of the theory is an effective complex wave vector $k_{\rm eff}(\omega)$ which describes the phase velocity and attenuation of a plane electromagnetic wave of frequency ω, or equivalently an " effective dielectric function" $\epsilon_{\rm eff}(\omega)$ defined by $k_{\rm eff}(\omega)=[\epsilon_{\rm eff}(\omega)]^{1/2}\omega/c$. The new theory, unlike the old, is not necessarily restricted to particles small compared to the wavelength of radiation in the composite, but could in principle continue to be useful even for quite short wavelengths, so long as the *attenuation length* [essentially $(\mathrm{Im}k_{\rm eff})^{-1}$] is large compared to characteristic particle dimensions. While in practice it might appear that this condition will be satisfied only for small-particle composites, it may also hold for larger but weak-scattering particles, or even possibly systems in which strong scattering by individual particles may sometimes tend to cancel out, still leaving quite a large attenuation length (or "photon mean free path").

To illustrate the new predictions of the "dynamic EMA" (DEMA), we have applied it to an important special case, namely, far-infrared absorption by a composite consisting of small metal particles and dielectric. We find that the static EMA is drastically in error at concentrations of metal below the so-called percolation threshold (i.e., that concentration at which the metal forms a closed conducting path). The DEMA, in contrast, predicts an absorption coefficient hundreds to thousands of times greater than the static EMA even for quite small metal particles. The extra absorption, which results from eddy currents in the metal particles (or, equivalently, induced magnetic dipole effects) is in agreement with the predictions of the classical Mie theory in the small concentration limit, for which calculations have been carried out by other workers.[4]

The new DEMA is most conveniently formulated by considering the fields generated inside the particles that make up the composite when an electromagnetic wave propagates through it. In the spirit of the EMA, these are calculated as if all the material in the composite (metal *and* dielectric) were formed into spheres embedded in a

uniform effective medium of dielectric function $\epsilon_{eff}(\omega)$ (the special assumption of spherical shape is inessential and can be removed). ϵ_{eff} is then determined self-consistently by requiring that the appropriate Fourier components $\vec{D}(\vec{q}\omega)$ and $\vec{E}(\vec{q}\omega)$ in the composite be related by a constant of proportionality $\epsilon_{eff}(\omega)$. This condition is imposed at a magnitude of $\vec{q}$ corresponding to that of the propagating electromagnetic wave, i.e., $q=[\epsilon_{eff}(\omega)]^{1/2}\omega/c \equiv k_{eff}$.

The DEMA as formulated in this way can be recast in terms of the *scattered* fields rather than the interior fields. The self-consistency condition just mentioned will be shown rigorously equivalent to the requirement that the forward-scattering amplitudes of the particles in the composite, measured relative to ϵ_{eff}, should vanish on the average. Now if ϵ_{eff} were nondissipative [$\mathrm{Im}\epsilon_{eff}=0$] the forward-scattering amplitude would be related, by the optical theorem, to the *total* cross-section (absorption plus scattering). Since $\mathrm{Im}\epsilon_{eff} \neq 0$ in the case at hand, the analogous "cross-section" can be positive or negative, and in this sense the DEMA is equivalent to choosing ϵ_{eff} so that a wave propagating through this medium shall experience, on average, no further scattering. This interpretation permits a connection of the DEMA in spirit to other self-consistent theories of disordered systems.

The formulation of the dynamical MGA is somewhat subtler and will be deferred to a subsequent publication.

We turn now to the body of the paper. The DEMA is formulated in Sec. II. The application to far-infrared absorption by granular metals is presented in Sec. III. Several mathematical details are contained in the Appendix.

II. FORMALISM

We consider a plane electromagnetic wave of frequency ω propagating through a composite such as is showin in Fig. 1(a). The wave will be attenuated and retarded as it moves through the medium, because of multiple scattering amongst the particles composing it and also because of actual absorption. We wish to take these two effects into account in an average way by means of an effective propagation constant $k_{eff}=k_1+ik_2$, or equivalently a complex dielectric function $\epsilon_{eff}(\omega)$ which we define by $\epsilon_{eff}(\omega)=c^2k_{eff}^2/\omega^2$.

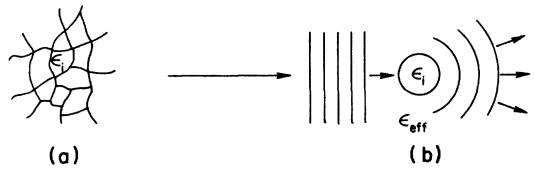


FIG. 1. Illustration of the self-consistent embedding principle as applied to electromagnetic wave propagation in composite media. The electric field and electric displacement in the ith grain are calculated as if the actual environment of the grain (a) were replaced by an effective environment of dielectric function $\epsilon_{\mathrm{eff}}(\omega)$. The requisite fields are then found by solving the boundary-value problem illustrated in (b).

We shall determine $\epsilon_{eff}(\omega)$ by means of a simple approximate argument based on self-consistency. First, we note that if wave propagation through the composite can indeed be described by an effective dielectric function, then, for a macroisotropic medium, the electric field and electric displacement associated with such a wave propagating in the z direction must be related by

$$\int \vec{D}(\vec{x}\omega)e^{-ik_{eff}z}\,d\vec{x} = \epsilon_{eff}(\omega)\int \vec{E}(\vec{x}\omega)e^{-ik_{eff}z}\,d\vec{x} \qquad (2.1)$$

where k_{eff} and ω are related by $k_{eff}=[\epsilon_{eff}(\omega)]^{1/2}\omega/c$. No averaging is necessary in (2.1), despite the randomly inhomogeneous nature of the composite, because the Fourier components already involve an effective space average. Now although (2.1) is in principle exact, it can only be evaluated approximately because the fields in the composite are spatially varying in a random way. We therefore calculate the fields in each grain as if the grain were spherical and embedded in an "effective medium" of dielectric constant $\epsilon_{eff}(\omega)$ (the requirement of spherical shape is inessential and can be removed as noted above). This embedding assumption shown schematically in Fig. 1(b), makes the problem tractable irrespective of the frequency of incident radiation or the diameter of the grain.

Consider, for example, the ith grain, which for convenience we assume to be homogeneous, of volume v_i, and centered at the origin. Under the embedding assumption described above, the electric field incident on the grain is

$$\vec{E}_{inc}=\vec{E}_0e^{ik_{eff}z-i\omega t} \qquad (2.2a)$$

and the magnetic field is

$$\vec{B}_{inc}=(\epsilon_{eff})^{1/2}\vec{E}_{inc}\times\hat{z}\,. \qquad (2.2b)$$

It is convenient to choose the incident wave to have polarization such that $\vec{E}_0=\hat{x}+i\hat{y}$. (If the components of the medium exhibit no birefringence, all the results that follow can immediately be applied to *linearly* polarized waves.) The fields inside the grain and the scattered fields can be found by expanding interior and exterior fields in a multipole series and matching boundary conditions in a standard way first developed by Mie.[12] The interior field can then be used to calculate the integral over the grain volume,

$$\vec{I}_i = \int_{v_i} \vec{E}_i e^{-i\vec{k}_{eff}\cdot\vec{x}}\, d\vec{x} \tag{2.3}$$

required to find the integrals in (2.1). As is well known from the Mie theory, an incident field of the form (2.2) will result in an integral I_i which can be written in the form

$$\vec{I}_i = (\hat{x} + i\hat{y}) I_i \,. \tag{2.4}$$

From definition (2.1) it then follows that $\epsilon_{eff} = \sum_i \epsilon_i I_i / \sum_i I_i$ or equivalently,

$$\sum_i \delta\epsilon_i I_i = 0 \,. \tag{2.5}$$

Here $\delta\epsilon_i = \epsilon_i - \epsilon_{eff}$ and the sum runs over all the grains in the sample. Note that the integral I_i can be calculated as if the ith grain were centered at the origin.

The crucial element in this calculation is the integral I_i. As is shown in the Appendix, this quantity is intimately connected to the *scattered* field in the forward direction. The exact relation is there shown to be

$$I_i = (4\pi i \epsilon_{eff}/k^3 \delta\epsilon_i) S_i(0) \,, \tag{2.6}$$

where $\vec{S}_i(\theta, \phi)$ is the amplitude of the scattered wave in the far (radiation) zone, defined by

$$\vec{E}_{scatt}(\theta, \phi) = (e^{ikr}/kr)\vec{S}_i(\theta, \phi) \tag{2.7}$$

and

$$\lim_{\theta \to 0} \vec{S}_i(\theta, \phi) = S_i(0)(\hat{x} + i\hat{y}) \times \hat{r} \,,$$

$\hat{r}$ being a unit vector pointing radially outward from the origin. Substitution of (2.6) into (2.5) gives

$$\sum S_i(0) = 0 \tag{2.8a}$$

or equivalently,

$$\langle S(0) \rangle = 0 \,, \tag{2.8b}$$

where the brackets denote a volume average, i.e., $\langle\ \rangle \equiv N^{-1} \sum_i$, N being the number of grains in the composite. Equation (2.8) is therefore a self-consistency condition which determines ϵ_{eff} within the (dynamic) EMA.

The result (2.8) can be used to make a connection in spirit with other approximations in the theory of disordered systems. If $\epsilon_{eff}(\omega)$ were real, then, from the optical theorem, the real part of the forward scattering amplitude $S_i(0)$ would be equal, within a constant of proportionality, to the total cross-section C_i (absorption plus scattering) for the ith particle. The exact connection is (for the phase convention used here)[13]

$$C_i = (4\pi/k^2)\, \mathrm{Re} S_i(0) \,. \tag{2.9}$$

Equation (2.9) can be viewed as defining an effective *total* cross section, but, if the embedding medium has a complex dielectric constant, the new "cross section" does not have to be positive. In this language condition (2.8) simply means that ϵ_{eff} is to be chosen so that a wave propagating through the effective medium shall experience, on the average, no further scattering. This intuitively appealing statement of the self-consistency condition is analogous in spirit to that which defines the coherent potential approximation of alloy theory.[14]

Condition (2.8) can also be interpreted from a slightly different point of view. If we consider the electric field at point $\vec{x}$ in the composite, it will be made up of the propagating wave (2.2) plus the sum of the scattered wavelets from the various grains in the composite,

$$\vec{E}(\vec{x}, t) = \vec{E}_{inc}(\vec{x}, t) + \sum_i \vec{E}^{(i)}_{scatt}(\vec{x}, t) \,,$$

where $\vec{E}^{(i)}_{scatt}$ is the wave scattered from the ith grain (cf. Fig. 2). If that grain is sufficiently far from $\vec{x}$, then the principle of self-consistent embedding shows that this scattered field at $\vec{x}$ will be of the form (2.7). In order for this picture to be self-consistent, we must require that the sum of the scattered wavelets vanish, i.e.,

$$\sum_i \vec{E}^{(i)}_{scatt}(\vec{x}, t) = 0 \tag{2.10}$$

in some average sense. If we assume that *all* the fields $\vec{E}^{(i)}_{scatt}$ can be approximated as radiation fields, then it is possible to show, using an argument based on the principle of stationary phase,[15] that the "ensemble average" of (2.10) (i.e., an average over possible environments of the point

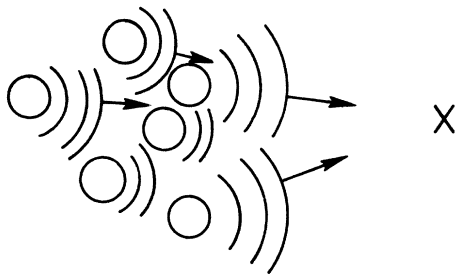


FIG. 2. Alternate way of viewing the dynamic effective-medium approximation. The field at × is the sum of the propagating wave, which has field $\vec{E}_0 e^{i(kz - \omega t)}$, plus that of all the wavelets scattered from the various inclusions. The scattered field at × is dominated on average by forward scattering from the inclusions lying in a narrow cone to the left of ×. Self-consistency then requires k to be chosen so that this forward-scattering amplitude vanishes on the average.

$\vec{x}$) is dominated by scatterers lying in a narrow cone along the negative z direction relative to the point $\vec{x}$ (cf. Fig. 2). The sum (2.10) is then found to involve an average over the forward-scattering amplitudes of the particles contained in this cone, and condition (2.10) becomes identical to (2.8). Thus condition (2.8) can be obtained by an intuitive argument based purely on *scattering* considerations, without any explicit reference to *internal* fields within the grains themselves.

It is useful to express (2.8) in a form suitable for calculation. The forward-scattering amplitude for the ith particle, which is assumed to have radius R_i and dielectric function $\epsilon_i(\omega)$, is[16]

$$S_i(0)=\frac{1}{2}\sum_{l=1}^{\infty}(2l+1)(a_l^{(i)}+b_l^{(i)}), \tag{2.11}$$

where $a_l^{(i)}$ and $b_l^{(i)}$ are the electric and magnetic multipole coefficients characterizing the scattered field. These coefficients are given by the standard expressions

$$a_l^{(i)}=\frac{\psi_l'(y_i)\psi_l(x_i)-\mu_i\psi_l(y_i)\psi_l'(x_i)}{\psi_l'(y_i)\zeta_l(x_i)-\mu_i\psi_l(y_i)\zeta_l'(x_i)}, \tag{2.12a}$$

$$b_l^{(i)}=\frac{\mu_i\psi_l'(y_i)\psi_l(x_i)-\psi_l(y_i)\psi_l'(x_i)}{\mu_i\psi_l'(y_i)\zeta_l(x_i)-\psi_l(y_i)\zeta_l'(x_i)}, \tag{2.12b}$$

where

$$x_i=\frac{\omega R_i}{c}[\epsilon_{\rm eff}(\omega)]^{1/2},$$

$$y_i=\frac{\omega R_i}{c}[\epsilon_i(\omega)]^{1/2},$$

$$\mu_i=[\epsilon_i(\omega)/\epsilon_{\rm eff}(\omega)]^{1/2}=y_i/x_i,$$

$$\psi_l(x)=xj_l(x),$$

$$\zeta_l(x)=xh_l^{(1)}(x),$$

and the primes denote differentiation with respect to the argument. j_l and $h_l^{(1)}$ are spherical Bessel and Hankel functions. With (2.12), approximation (2.8) is explicitly described in the form of a transcendental equation (or, in the case of a collection of particles described by some continuously varying parameter such as radius, an integral equation).

III. NUMERICAL EXAMPLE

To illustrate some of the new effects predicted by the formalism of the preceding section, we consider the special case of electromagnetic waves propagating through a composite made up of particles small in comparison to the wavelength of light in the medium. In that case, the various spherical Bessel functions can be expanded in powers of their arguments, and it is found that the sum in (2.8) is very rapidly convergent. For illustrative purposes, we shall neglect all terms but the electric and magnetic dipole coefficients $a_1^{(i)}, b_1^{(i)}$ and keep only the leading terms in these in an expansion in powers of x_i. The result of such an expansion is

$$a_1^{(i)}=-\tfrac{2}{3}ix_i^3\frac{\epsilon-\epsilon_{\rm eff}}{\epsilon+2\epsilon_{\rm eff}}; \tag{3.1a}$$

$$b_1^{(i)}=-\frac{i}{45}x_i^5\left(\frac{\epsilon}{\epsilon_{\rm eff}}-1\right), \tag{3.1b}$$

where $x_i=(\omega R_i/c)(\epsilon_{\rm eff})^{1/2}$ as before. Substituting (3.1) into (2.11) and (2.8) gives

$$\sum_i n_i\left[\tfrac{2}{3}x_i^3\frac{\epsilon_i-\epsilon_{\rm eff}}{\epsilon_i+2\epsilon_{\rm eff}}+\tfrac{1}{45}x_i^5\left(\frac{\epsilon_i}{\epsilon_{\rm eff}}-1\right)\right]=0, \tag{3.2}$$

where n_i is the number of particles per unit volume of type i. This can be simplified to the form

$$\sum_i f_i\left[\frac{\epsilon_i-\epsilon_{\rm eff}}{\epsilon_i+2\epsilon_{\rm eff}}+\frac{1}{30}\left(\frac{\omega R_i}{c}\right)^2(\epsilon_i-\epsilon_{\rm eff})\right]=0, \tag{3.2}$$

where f_i is the *volume fraction* occupied by particles of type i. If the magnetic dipole term were neglected, only the first term in brackets would remain (that is, the result would correspond to setting $\omega R_i/c=0$). The corresponding "static limit" would then read

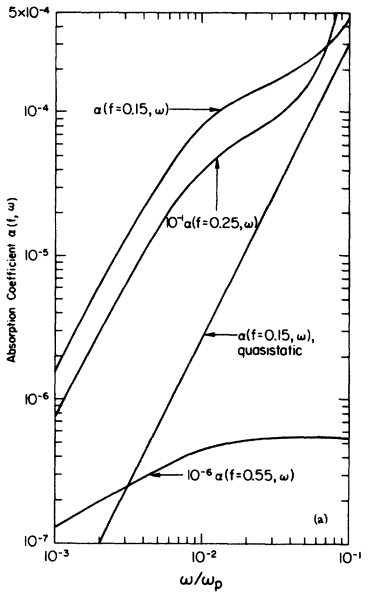
$$\sum_i f_i\frac{\epsilon_i-\epsilon_{\rm eff}}{\epsilon_i+2\epsilon_{\rm eff}}=0, \tag{3.3}$$

in agreement with the static "effective-medium approximation" of Bruggeman,[7] Landauer,[8] and various subsequent workers. However, the new term arising from the induced magnetic dipole moments has a profound influence under certain conditions as will be illustrated shortly.

We shall assume, for purposes of illustration, that the composite consists of only two types of particles, of dielectric function ϵ_A and ϵ_B, and present in volume fractions $f_A=f$ and $f_B=1-f$. We also assume for mathematical simplicity that each type of particle is formed into approximately spherical shapes of the same radius R. [If a range of radii is present then (3.2) is evidently an integral equation.] Then (3.2) takes the simple form

$$f\left(\frac{\epsilon_A-\epsilon_{\rm eff}}{\epsilon_A+2\epsilon_{\rm eff}}+\gamma(\epsilon_A-\epsilon_{\rm eff})\right)$$
$$+(1-f)\left(\frac{\epsilon_B-\epsilon_{\rm eff}}{\epsilon_B+2\epsilon_{\rm eff}}+\gamma(\epsilon_B-\epsilon_{\rm eff})\right)=0, \tag{3.4}$$

where $\gamma=\frac{1}{30}\omega^2R^2/c^2$. Equation (3.4) is seen to be a cubic equation for $\epsilon_{\rm eff}$, which reduces to a well-known quadratic in the static limit ($\gamma=0$). The material we shall study is a composite in which material A is a free-electron metal and material



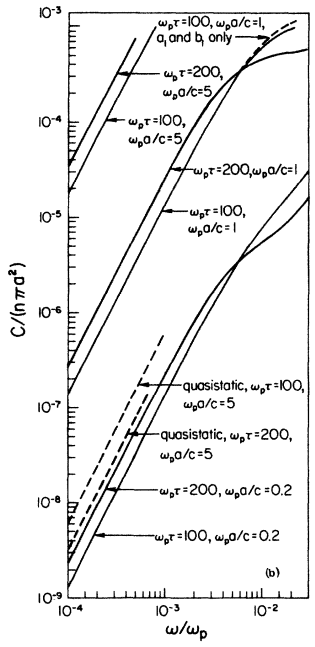


FIG. 3. (a) Absorption coefficient $\alpha(f,\omega)$ calculated for the model granular metal described in the text. The effect of magnetic dipoles (eddy currents) can be seen by comparison of $\alpha(f=0.15,\omega)$ with the corresponding quantity calculated in the quasistatic approximation. Units of α are such that $\omega_p=1$ and $c=1$; to convert to cm^{-1}, multiply by $\omega_p(\mathrm{sec}^{-1})/3\times10^{10}$. (b) Extinction coefficient per unit number density of metal spheres, in units of πa^2, plotted for a dilute collection of metal spheres in vacuum. Except where shown, all calculations were carried out by summing the full Mie series to convergence. The corresponding coefficient, calculated with only the dominant parts of a_1 and b_1, is shown as a dashed curve for $\omega_p\tau=100$ and $\omega_p a/c=1$.

B is a dielectric of dielectric constant unity. We take $\epsilon_A(\omega)$ to be a Drude dielectric function,

$$\epsilon_A(\omega)=1-\omega_p^2/[\omega(\omega+i/\tau)]\equiv\epsilon_m(\omega), \tag{3.5}$$

where ω_p is the plasma frequency and τ is a relaxation time. Such a composite is representative of a variety of granular metals[2,4,5] which have been of considerable experimental and theoretical interest in recent years.

The far-infrared attenuation constant $\alpha=\mathrm{Im}(\omega/c)[\epsilon_{\mathrm{eff}}(\omega)]^{1/2}$ resulting from the solution of (3.4) and (3.5) is shown in Fig. 3(a) for several values of f and for a scaled particle radius $\omega_p a/c=1$ and relaxation time $\omega_p\tau=100$. (This radius would correspond to a particle of radius ~100 Å in Al.) The constant α is essentially the inverse of the effective "skin depth" of the composite. As calculated here, it takes into account, in an average way, both absorption and scattering of energy out of the incident beam, but at the long wavelengths considered here the scattered component is very small and α is certainly almost entirely a measure of absorption.

At low concentrations ($f<\frac{1}{3}$) and sufficiently low frequencies ($\omega\ll1/\tau$), it is evident from Fig. 3(a) that α is proportional to ω^2. This is in accord with previous results in this regime,[11] but the magnetic dipole term (b_1) enormously enhances the predicted absorption, as is illustrated by a plot of the "quasistatic" absorption coefficient ($\gamma=0$) for $f=0.15$, shown in the same figure.

The enhancement factor due to magnetic dipole effects can be obtained analytically in the limit of small f by expanding Eq. (3.4) in powers of f, and retaining terms up to first order only. This procedure gives

$$\epsilon_{\mathrm{eff}}\sim1+3f[(\epsilon_m-1)/(\epsilon_m+2)+\gamma(\epsilon_m-1)]. \tag{3.6}$$

The corresponding attenuation constant is (to lowest order in f)

$$\alpha=\frac{3}{2}\frac{\omega}{c}f\,\mathrm{Im}\left[\frac{1}{1-3\omega(\omega+i/\tau)/\omega_p^2}-\frac{1}{30}\left(\frac{\omega_p a}{c}\right)^2\frac{1}{1+i/\omega\tau}\right]$$

on using (3.5). In the far-infrared region ($\omega\ll\omega_p$ but not necessarily $\omega\ll1/\tau$) this may be expanded in powers of ω/ω_p to give

$$\alpha\sim\frac{9}{2}\frac{f}{c}\frac{\omega^2}{\omega_p^2\tau}+\frac{1}{20}\frac{f}{c}\left(\frac{\omega_p a}{c}\right)^2\frac{\omega^2\tau}{1+(\omega\tau)^2}. \tag{3.7}$$

The first term is due to the induced electric dipole, while the second results from the magnetic dipole. In the regime $\omega\tau\ll1$ both vary as ω^2 with the magnetic and the electric coefficients contributing in the ratio

$$\frac{\alpha_m}{\alpha_e}=\frac{1}{90}(\omega_p\tau)^2\left(\frac{\omega_p a}{c}\right)^2. \tag{3.8}$$

For the parameters chosen in Fig. 3 this ratio is about 110. For larger particles the ratio is even larger, increasing as a^2 if τ is assumed independent of particle size. At higher frequencies ($1/\tau \lesssim \omega \ll \omega_p$) the magnetic contribution saturates but the electric coefficient continues to increase as ω^2. This leads to the "shoulder" in α near $\omega = 1/\tau$, seen in Fig. 3. Eventually, the electric coefficient becomes dominant again, at a frequency which depends on τ and a. In Fig. 3, this return occurs near $\omega\tau = 0.1$. But at this frequency a pure ω^2 behavior is no longer seen; instead, the absorption curves begin to be influenced by the well-known electric dipole resonance whose peak occurs in the vicinity of $0.5\omega_p$. In the EMA the resonant absorption sets in at lower frequencies for $f = 0.25$ than for $f = 0.15$, as can be seen from Fig. 3.

Considering the dominant influence of the magnetic dipole term as illustrated in Fig. 3(a), it may appear insufficient to truncate the Mie series as done in Eq. (3.1). However, this truncation is adequate at least in the long wavelength limit. In that regime x_i and y_i are small and the coefficients $a_l^{(i)}$ and $b_l^{(i)}$ vary as x_i^{2l+1} and x_i^{2l+3}, respectively. Since $\epsilon_m(\omega)$ varies as $1/\omega$ at lower frequencies, one must keep all terms through order x_i^5 to avoid missing any part of the ω^2 absorption coefficient. Only a_1, a_2 and b_1 contribute in this order; the appropriate expansion (see, for example, p. 144 of Ref. 13) can be used to show that in fact only the terms included in (3.1) actually contribute to the ω^2 coefficient, so that the present expansion is indeed adequate in the far infrared. The adequacy of (3.1) can also be numerically confirmed for $f \ll 1$. In this regime, the self-consistency condition (2.5) can be shown to reduce to

$$\epsilon_{\text{eff}}(\omega) = 1 + \frac{4\pi i n}{(\omega/c)^3} S_m(0)\,, \tag{3.9}$$

where n is the number of metal spheres per unit volume, and we have used the fact that for a dielectric sphere of radius R, $I_i = v_i$, the volume of the sphere. This corresponds to an *extinction coefficient* [Eq. (2.9)]

$$C = \frac{4\pi}{(\omega/c)^2} n\, \mathrm{Re} S_m(0)\,, \tag{3.9a}$$

which is precisely the extinction coefficient of a collection of n metal spheres of radius a in unit volume.[13] Thus, the effective dielectric function calculated from the DEMA gives the correct extinction coefficient in the low-f limit. The values of the dimensionless constant $C/n\pi a^2$, as calculated from (3.9a), using the full Mie expansion,[12] are shown in Fig. 3(b) for $\omega_p\tau = 100$ and $\omega_p a/c = 1$. As may be seen, when $\omega \lesssim 1/\tau$, the exact results for $\omega_p a/c = 1$ and $\omega_p\tau = 100$ are nearly indistinguishable from those based on retention of only the leading portions of the a_1 and b_1 coefficients. (This is no longer the case, of course, at larger ω, but even for $\omega_p a/c$ as large as 5 and $\omega \sim \omega_p$ the Mie series converges in only a few terms.) For reference, we also show in Fig. 3(b) the far-infrared values of C as calculated in the noninteracting limit for several other choices of $\omega_p\tau$ and $\omega_p a/c$, using the full Mie series.

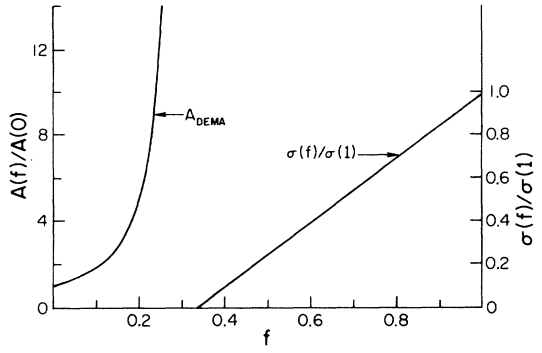


FIG. 4. Left-hand scale: the function $A(f) = \alpha(f, \omega = 0.001)/f\omega^2)$ plotted for the DEMA. Right-hand scale: $\sigma(\omega = 0.001, f)/\sigma(\omega = 0.001, f = 1)$, as calculated within the DEMA.

Although α at low frequencies reduces to the "noninteracting limit" as $f \to 0$, it shows progressive departures from that limit as f increases. This is shown in Fig. 4 where we plot $A(f, \omega) = \alpha/(f\omega^2)$ versus f at $\omega = 0.001\ \omega_p$. In the noninteracting limit this quantity would remain a constant, independent of f. As may be seen, the ratio instead increases rapidly with f, becoming singular at $f = \frac{1}{3}$. This is the concentration at which a metal-insulator transition occurs in the *static* EMA. This concentration is unchanged when "dynamic" effects are included in the theory. The behavior of $A(f, \omega)$ can be obtained analytically for $f < f_c$ and $\omega \ll 1/\tau$ by multiplying out (3.4), making a low-frequency expansion of all terms, and setting the coefficients of ω^{-1} and ω^0 equal to zero. This gives

$$\epsilon_s(f) \equiv \lim_{\omega \to 0} \mathrm{Re}\epsilon_{\text{eff}}(f, \omega) = (1 - 3f)^{-1}\,, \tag{3.10a}$$

$$\epsilon_2 \equiv \lim_{\omega \to 0} \omega^{-1}\, \mathrm{Im}\epsilon_{\text{eff}}(f, \omega) = \frac{9f(1-f)}{\omega_p^2\tau(1-3f)^3} + \frac{1}{10}\left(\frac{a}{c}\right)^2 \frac{f(1-f)}{(1-3f)^2}\,, \tag{3.10b}$$

and hence that

$$A(f,\omega)=\epsilon_2/(2fc\sqrt{\epsilon_s})$$
$$=\frac{9}{2c}\frac{1-f}{\omega_p^2\tau(1-3f)^{5/2}}+\frac{1}{20}\left(\frac{a}{c}\right)^2\omega_p^2\tau\frac{1-f}{(1-3f)^{3/2}}, \quad (3.10c)$$

which diverges near f_c as expected.[17,18]

In contrast to the far-infrared behavior of α in the insulating composite ($f<\frac{1}{3}$), the behavior on the metallic side is not grossly affected by inclusion of dynamic terms in the EMA. By way of example, Fig. 3 shows $\alpha(\omega)$ plotted for $f=0.55$, in the metallic regime. At very low frequencies, α exhibits typical metallic behavior $[\alpha=A'(f)\sqrt{\omega}]$. We find numerically that the proportionality constant $A'(f)$ diminishes with f and approaches zero near $f=\frac{1}{3}$ according to the law $A'(f)\propto(f-f_c)^{1/2}$. This behavior corresponds to a metal in which the static conductivity diminishes linearly with f, approaching zero as $(f-f_c)^{1.0}$ at $f=f_c$, as can be seen from Fig. 4, where we plot $\sigma(f,\omega=0.001)/\sigma(f=1, \omega=0.001)$ versus f for $f>\frac{1}{3}$. This is precisely the behavior predicted by the static EMA.

Another type of behavior can be investigated by studying of $\epsilon_{eff}(\omega)$ and $\alpha(\omega)$ at $f=f_c=\frac{1}{3}$. The behavior of $\alpha(\omega)$ at very low frequencies ($\omega\ll 1/\tau$) is shown in Fig. 5. We have found numerically that real and imaginary parts of $\epsilon_{eff}(\omega)$ obey power laws; these are found numerically to be

$$\mathrm{Re}\,\epsilon_{eff}(f_c,\omega)\sim\omega^{-1/2}; \quad (3.11)$$
$$\mathrm{Im}\,\epsilon_{eff}(f_c,\omega)\sim\omega^{-1/2},$$

or, if we introduce an effective frequency-dependent conductivity by $\sigma_{eff}=(\omega/4\pi)\mathrm{Im}\epsilon_{eff}(\omega)$, then $\sigma_{eff}\sim\omega^{+1/2}$. The corresponding behavior of α is

$$\alpha(f_c,\omega)\sim\omega^{3/4}. \quad (3.12)$$

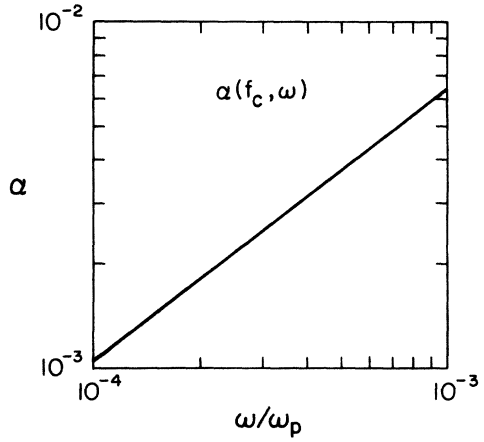


FIG. 5. $\alpha(f=f_c=\frac{1}{3},\omega)$ vs ω, calculated within the DEMA. The corresponding quasistatic result is nearly indistinguishable from that shown.

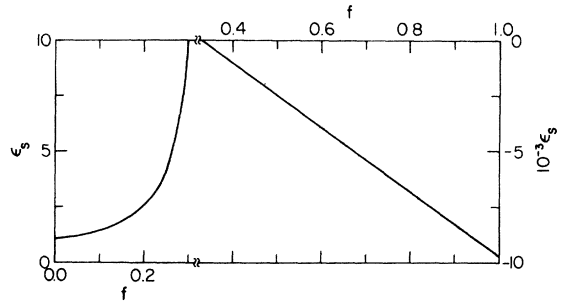


FIG. 6. Static dielectric constant $\epsilon_s=\lim_{\omega\to 0}\mathrm{Re}\epsilon_{\mathrm{eff}}(\omega)$ from the EMA or the DEMA. Note change of scale.

These results are in accord with the previous results of Webman *et al.*,[11] based on the quasistatic EMA. Moreover, the coefficient of $\omega^{3/4}$ proves to be nearly identical in the two cases. Certainly, the true values of the exponents are expected to deviate from the present mean-field numbers.

The DEMA can also be used to compute the static dielectric constant, $\mathrm{Re}\epsilon_{eff}(\omega=0)=\epsilon_s$. This quantity is obviously given by the static EMA [Eq. (2.5) with $\gamma=0$]. The result is shown in Fig. 6 as a function of f. In the dielectric regime ($f<\frac{1}{3}$), ϵ_s is a positive and an increasing function of f, diverging as $(f_c-f)^{-1}$ near $f=f_c$, as noted above. In the metallic region, ϵ_s is negative, as is illustrated. The anomaly near $f=f_c=\frac{1}{3}$, ϵ_s first increasing, then falling through zero, is characteristic of a continuous metal-insulator transition, as previously discussed by several authors.[10,19] The discontinuity at $f=\frac{1}{3}$ only occurs in systems where the dielectric component of the composite has strictly zero conductivity.

It is of some interest, finally to compare the preceding far-ir predictions with experiment. The major prediction is of course the enhancement in absorption arising from the induced magnetic dipoles in the metal spheres. This enhancement is apparently insufficient to explain anomalously large far-ir absorption seen in ~50-Å Al particles[4] but may suffice to explain the order of magnitude of the absorption data on larger particles of Pd embedded in KCl.[20] These latter data also exhibit the "shoulder" in the absorption curve predicted here. (The Al data may require consideration of other effects, such as quantum size effects[21] or absorption in amorphous oxide overcoatings.[22]) The present calculations also predict that the absorption per particle is strongly dependent on concentration (cf. Fig. 2). Thus the absorption is predicted to be enhanced if the metal particles in the composite are "clustered" in regions of locally high concentration, as may be the case in some granular metals.

We conclude by pointing out some further possible extensions of the present approach. Treatment of shapes other than spheres would require only a straightforward application of Eq. (2.8), although the multipole coefficients would then become much more difficult to calculate. The method could also be used to treat composites made of *coated* particles.[23,24] Such particles are often present in real metal-dielectric composites, in which it is often found that the metal is coated with oxide or the dielectric itself. For example, in the composite $Ag_{0.4}(SiO_2)_{0.6}$,[25] electron microscopy reveals a "correlated" structure in which most metal grains are coated with dielectric, and not the "random" or "cellular" structure presupposed by the EMA and the DEMA as formulated above. The presence of correlations raises the concentration of the metal-insulator transition to $f_m \sim 0.5$ rather than the value $f_m \sim 0.15$ characteristic of a random cellular composite. If the medium is supposed *entirely* correlated, so that *all* the dielectric is present in the form of coatings on metal spheres, and if the ratio of coating thickness to the diameter of metal particles is assumed to be the same for each particle in the composite, then the self-consistent embedding procedure leads, in the quasistatic regime, to an effective dielectric function which is identical to the Maxwell-Garnett form.[26] That is, the MGA is in effect the EMA applied to highly correlated composites. And, indeed, the MGA is much more successful than the (random) EMA for calculating the optical density of $Ag_{0.4}(SiO_2)_{0.6}$.[25] Extension of the DEMA to such correlated systems would be straightforward and probably useful in the study of systems of this kind.

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APPENDIX

The integral defined in (2.4) can be written

$$I_i = \frac{1}{2\delta\epsilon_i}\int_{v_i} \vec{E}_0^*(z)\cdot\delta\epsilon_i\vec{E}(\vec{x})\,d\vec{x}, \tag{A1}$$

where

$$\vec{E}_0(z) = (\hat{x}+i\hat{y})e^{ikz} = k^{-1}\vec{\nabla}\times\vec{E}_0(z) \tag{A2}$$

and $\delta\epsilon_i = \epsilon_i - \epsilon_{eff}$. (We shall compute I_i for real k. The resulting value can then be analytically continued to complex k). Extending the volume of integration to a large sphere V of radius R, integrating by parts, and using (A2), we get

$$I_i = \frac{1}{2k^2\delta\epsilon_i}\int_V \vec{E}_0^*(z)\cdot\vec{\nabla}\times\vec{\nabla}\times(\delta\epsilon_i\vec{E})\,d\vec{x}. \tag{A3}$$

Now Maxwell's equations for a source-free region of space can be combined to take the form

$$(\nabla^2+k^2)\vec{D} = -\vec{\nabla}\times\vec{\nabla}\times(\delta\epsilon_i\vec{E}), \tag{A4}$$

where $k=(\omega/c)(\epsilon_{eff})^{1/2}$ as before. Substitution of (A4) into (A3) and use of Green's theorem gives

$$I_i = -\frac{\epsilon}{2k^2\delta\epsilon_i}\oint_S\left(\vec{E}_0^*\cdot\frac{\partial\vec{E}_{scatt}}{\partial r} - \frac{\partial\vec{E}_0^*}{\partial r}\cdot\vec{E}_{scatt}\right)dS \tag{A5}$$

S being the surface of the sphere. In deriving (A5) we have used the relation $(\nabla^2+k^2)\vec{E}_0 = 0$ and have written $\vec{D} = \epsilon_{eff}(\vec{E}_0+\vec{E}_{scatt})$ outside the sphere. Substitution of the asymptotic form (2.7) for $\vec{E}_{scatt}$ gives

$$I_i = -\frac{\epsilon_{eff}}{2k^2\delta\epsilon_i}\oint_s i\,dS\,g_i(\theta,\phi)\frac{e^{ikR(1-\cos\theta)}}{R}, \tag{A6a}$$

where

$$g_i(\theta,\phi) = (1+\cos\theta)(\hat{x}-i\hat{y})\cdot\vec{S}_i(\theta,\phi). \tag{A6b}$$

The integral can be evaluated asymptotically to order R^0, the other terms dropping out in the limit $R\to\infty$, and the result for I_i is Eq. (2.6) as desired.

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