Percussion effects and sum rules in the optical properties of composites

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(Received 31 July 1978)

The optical properties of binary composites may be affected by the presence or absence of infinite connected paths of either component. In a model composite of Drude metal and insulator, we find not only that the Drude peak in the real conductivity, \( \sigma_0(\omega) \), disappears below the metal percolation threshold, but also that the metal plasmon peak in the energy-loss function \( -\epsilon^{\prime\prime}_m(\omega) \) vanishes at the insulator threshold. The integrated strength of the percolation modes is found to vary near the percolation threshold in the limit of small damping, according to the conductivity exponents \( t \) and \( s \) as defined by Straley. These effects are illustrated by elementary calculations based on the effective medium approximation. Similar phenomena are found in other kinds of composites, and the possibility that these effects may have been observed in polarized transmission experiments is discussed. New sum rules, analogous to those of Bergman, are derived within the quasistatic approximation for \( \text{Re} \sigma_0(\omega) \) and \( -\text{Im} \epsilon^{\prime\prime}_m(\omega) \). These are used to make statements about the center of gravity of the impurity band in these quantities, and the way in which this is affected by percolation phenomena.

I. INTRODUCTION

Composites usually have optical properties (absorption coefficients, reflectivity, etc.) very different from those of their constituents, and for this reason have been extensively studied in the last several years.\(^1\) The purpose of this paper is to point out some qualitative features that are likely to occur generally in the optical spectra of small-particle composites. These are "percolation phenomena," that is, they result from the presence or absence of connected clusters of one or another constituent that extend throughout the composite. While some of these phenomena have been discussed previously,\(^2\) the present paper describes a new one associated with the percolation of insulator and provides a unified picture of these effects. It also gives explicit numerical examples of optical constants that may show percolation effects.

In addition to a discussion of percolation effects, the paper also derives new sum rules on \( \text{Im} \epsilon^{\prime\prime}_m(\omega) \) and \( \text{Im} \epsilon^{\prime\prime}_m(\omega) \), \( \epsilon^{\prime\prime}_m(\omega) \) being the effective dielectric function of the composite. These sum rules are simple analogs of those obtained by Bergman for the pole spectrum of \( \epsilon^{\prime\prime}_m(\omega) \).\(^3\) Being expressed directly in terms of frequency, they may be useful in interpreting both percolation effects and optical data in general, especially once experimental measurements have been carried far enough to permit Kramers-Kronig inversion of the data.

The paper is organized as follows. Section II describes the percolation effects and provides numerical illustrations within the effective-medium approximation. Following this, the sum rules are presented in Sec. III.

II. PERCOLATION EFFECTS

We shall first consider percolation effects in a model composite containing a fraction \( f \) by volume, of Drude metal with dielectric function

\[
\epsilon_m(\omega) = 1 - \omega_p^2 / [\omega (\omega + i/\tau)],
\]

where \( \omega_p \) is the plasma frequency, and \( \tau \) is a characteristic relaxation time. The rest of the composite will be assumed to be insulator of dielectric function \( \epsilon_i(\omega) = 1 \). The composite is assumed to lie in the "small-particle limit" \( a/\lambda \ll 1 \), where \( a \) is a typical linear dimension of interest and \( \lambda \) is the smallest of the wavelengths of interest (i.e., the incident wavelength, the wavelength of a wave in the composite, and the skin depth). For such a system it is generally assumed that the problem of wave propagation can be treated quasistatically, that is, as if \( \nabla \times \mathbf{E} = 0 \). Such an assumption means that eddy currents are ignored, an omission which may be inadmissible in certain circumstances, even in the "small-particle limit."\(^4\)\(^-7\) However, we shall in this paper neglect all such effects and take the quasistatic assumption to be justified.

With the caveats, the optical properties of the composite are described in terms of an effective dielectric function \( \epsilon^{\prime\prime}_m(\omega) \). This cannot be computed exactly for a random inhomogeneous medium, and so, for purposes of illustration, we shall assume it to be given by the effective medium approximation (EMA), which is the simplest approximation giving rise to a percolation transition in a metal-insulator composite.\(^8\)\(^-9\) The EMA is perhaps most appropriate to a composite made up of cells, such that the cells are each uniform,
together fill all space, are composed at random of metal and insulator, and are compact and roughly spherical in shape. For the metal-insulator composite described above, the EMA gives for \( \varepsilon_{\text{eff}}(\omega) \) the equation

\[
f \frac{\varepsilon_m(\omega) - \varepsilon_{\text{eff}}}{\varepsilon_m(\omega) - \varepsilon_{\text{eff}}} + (1 - f) \frac{\varepsilon_i(\omega) - \varepsilon_{\text{eff}}}{\varepsilon_i(\omega) - \varepsilon_{\text{eff}}} = 0. \tag{2.2}
\]

This quadratic has two solutions for \( \varepsilon_{\text{eff}} \), the physical branch being determined by the requirements that \( \varepsilon_{\text{eff}}(\omega) \) be continuous and that \( \text{Im}\varepsilon_{\text{eff}}(\omega) > 0 \). In applying (2.2) to the model composite, we use the uncharacteristically large value \( \omega_p\tau = 10^4 \), rather than the value \( 10^6 \) more typical of most bulk metal near room temperature. This choice makes the percolation effects more apparent.

Figure 1 shows the real part of the effective conductivity, defined by

\[
\text{Re} \varepsilon_{\text{eff}}(\omega) = \omega \text{Im} \varepsilon_{\text{eff}}(\omega)/4\pi \tag{2.3}
\]

for the model composite just described; the behavior of this quantity has previously been considered by several authors. At small \( f \), \( \text{Re} \varepsilon_{\text{eff}}(\omega) \) has a peak at \( \omega = \omega_p \) arising from absorption by standing modes excited by incident electromagnetic radiation in the small metal particles. If the composite has overall spherical symmetry this "impurity band" is centered at \( \omega = \omega_p/\sqrt{3} \). The peak is superimposed on a broad background arising from the fact that \( \tau^{*} \neq 0 \), but for our choice of \( \omega_p\tau \) this background cannot be seen. As \( f \) increases, the impurity band broadens (symmetrically within the EMA for small \( f \)) and its lower edge, at \( \omega(\omega_p) \), moves to lower frequencies, reaching \( \omega = 0 \) at \( f = \frac{1}{2} f_m \), the concentration at which, in the EMA, the metal forms an infinite cluster. For \( f > f_m \), \( \omega(\omega_p) \) again increases, but a Drude peak of half-width \( 1/\tau \) (seen as a \( \delta \)-function spike in Fig. 1) appears. This corresponds to the zero-frequency conductivity, finite for \( f > f_m \) of the infinite cluster. As \( f \) further increases, the integrated strength of the percolation mode steadily increases while that of the finite-impurity band eventually decreases. Near \( f = 1 \) the latter shrinks to a symmetric band centered at \( \omega = \sqrt{3}\omega_p \) associated with the excitation of a "void resonance" within the metal and localized in the vicinity of the dielectric "voids."

Analogous phenomena, not previously noted, occur in \( \text{Im} \varepsilon_{\text{eff}}(\omega) \), a quantity whose peaks, in ho-

FIG. 1. Real part of the effective conductivity \( \sigma_{\text{eff}}(\omega) \) for the model metal-insulator composite described in the text, as calculated within the effective-medium approximation. \( f \) is the volume fraction of metal. The heavy vertical line segments at \( \omega = 0 \) represent the Drude peaks, whose width is too narrow to be resolved on the scale of the figure for the given choice of model parameters. The height of the line segments is proportional to the integrated intensity of the Drude peaks. The dashed line denotes the plasma frequency \( \omega_p \). In this and all subsequent figures the individual curves are displaced vertically by constant amounts relative to one another.

FIG. 2. \( \text{Im} \varepsilon_{\text{eff}}^d(\omega) \) for the model metal-insulator composite, as computed within the EMA. The \( \delta \)-functionlike spikes at \( \omega = \omega_p \) represent the plasmon peaks; the height of the spikes is proportional to their integrated strength.
mogeneous metals, are usually ascribed to “plasma resonances.” At small concentration 1 - \( f \) of insulator, \(-\text{Im} \varepsilon_{\text{eff}}^1(\omega)\) is seen in Fig. 2 to have a strong sharp peak at \( \omega = \omega_p \), corresponding to the plasma resonance of the bulk metal, and also a weak impurity band (“void resonance”) which is symmetric and centered about \( \omega = \sqrt{2/3} \omega_p \). This latter peak broadens with decreasing \( f \), its upper edge, at \( \omega_{\text{L}}(f) \), moving towards \( \omega_p \) and reaching \( \omega_p \) at \( f = \frac{1}{3} \), the concentration below which, in the EMA, the insulator forms an infinite cluster. For \( f < f_\text{c} \), the plasmon peak in \(-\text{Im} \varepsilon_{\text{eff}}^1\) disappears, and \( \omega_{\text{L}}(f) \) decreases, moving away from \( \omega_p \). For small \( f \), the impurity band becomes symmetric and is identifiable with standing modes of small metal particles dispersed in an insulating host.

These percolation effects are easily understood as follows. We imagine the composite placed between plates of a capacitor. For \( f < f_\text{m} \) metal is present only in the form of isolated clusters and no current can flow at zero frequency. For \( f > f_\text{m} \) metal and insulator are connected in parallel, zero-frequency current can flow, and \( \Re \varepsilon(0) > 0 \). Hence the Drude peak must reappear. The same arguments hold at \( \omega = \omega_p \), \( \varepsilon_m = 0 \) and \( \varepsilon_\text{p} = 1 \).

Thus at this frequency the metal has zero conductivity for displacement current. For \( f > f_\text{m} \), insulator is present only in isolated clusters and displacement current cannot flow, so that \( \varepsilon_{\text{eff}}(\omega_p) = 0 \). A peak must therefore be present in \(-\text{Im} \varepsilon_{\text{eff}}^1\). For \( f < f_\text{c} \), the infinite insulating cluster can carry displacement current, so that \( \varepsilon_{\text{eff}}(\omega_p) \neq 0 \) and the peak in \(-\text{Im} \varepsilon_{\text{eff}}^1(\omega)\) must disappear.

The approach of \( \omega_{\text{L}}(f) \) to \( \omega_p \) at \( f = f_\text{m} \) and of \( \omega_{\text{L}}(f) \) to \( \omega_p \) at \( f = f_\text{c} \) has been predicted on general grounds by Bergman and Imry.\(^{14}\) For \( f < f_\text{m} \), one might speculate that the low-frequency modes at the bottom of the band with resonances in long metal fibers (of very small depolarization factors) which become infinitely long at \( f = f_\text{m} \), and for \( f > f_\text{m} \) with long “dead ends” or isolated metal fibers which become shorter as \( f \) further increases.\(^{15}\) Similar considerations would apply to the high-frequency modes near \( f = f_\text{c} \), with dielectric fibers playing the same role as metal fibers near \( f = f_\text{m} \).

Figure 3 shows the normal incidence reflectivity \( R \) of the metal composite as computed in the EMA from

\[ R = \left| \frac{\langle \varepsilon_{\text{eff}}(\omega) \rangle - 1}{\langle \varepsilon_{\text{eff}}(\omega) \rangle + 1} \right|^2. \] (2.4)

The percolation effects just described are readily apparent. At \( \omega = 0 \), \( R < 1 \) for \( f < f_\text{m} \) and \( R = 1 \) for \( f > f_\text{m} \). When \( f > f_\text{m} \), \( R \) remains nearly unity for \( \omega < \omega_{\text{L}}(f) \); above this frequency, \( R \) falls off as \( \omega - \omega_{\text{L}}(f) \)^{1/2}.\(^{16}\) When \( f < f_\text{m} \), on the other hand, \( R < 1 \) for \( \omega < \omega_{\text{L}}(f) \). A similar transition can be seen near \( \omega = \omega_p \) at \( f > f_\text{c} \). When \( f > f_\text{c} \), \( R \) is 1 in the frequency range \( \omega_{\text{L}}(f) < \omega < \omega_p \). This range decreases to zero at \( f = f_\text{c} \) and for \( f < f_\text{c} \), there is no frequency range above \( \omega_{\text{L}}(f) \) where \( R = 1 \). In a realistic model of a composite, this sharp relectivity edge is, of course, likely to be much smoother (perhaps to the point of near-invisibility) because of the much smaller \( \omega_p \).

Percolation effects are also conspicuous in certain transmission experiments. Figure 4 shows the transmission, through a film of thickness \( d \), of light incident at an angle \( \theta \) to the normal and polarized parallel to the plane of incidence. This has been calculated from a formula that correctly includes multiple internal reflections. The parameters chosen in Fig. 4 are \( \theta = 45^\circ \) and \( \omega_p/c = 0.25 \), and the \( y \) axis actually shows \( -\log_2 T_x \), the “absorption.” As is well known, \( T_x \) is sensitive not only to the poles but also to the zeros of \( \varepsilon_{\text{eff}}(\omega) \),\(^{17}\) these appearing as peaks in \(-\log_2 T_x \), because the obliquely incident light has a component of electric field parallel to the film surface which can excite longitudinal surface excitations (“surface plas-
mons") occurring at frequencies near the zeroes of $\epsilon_{\text{eff}}$.

The percolation effects described above are clearly visible in Fig. 4. For $f > f_i = \frac{3}{5}$, the figure shows (i) a Drude peak centered at $\omega = 0$; (ii) a "plasmon" peak centered at $\omega = \omega_T$; and (iii) a broad impurity band between the two. Peak (ii) disappears at $f = f_i$, peak (i) at $f = f_m$, indicating that these are, in fact, related to the "percolation modes" described above.

It should be pointed out that percolation effects are not limited to metal-insulator composites. They can occur, for example, in composites made up partly of a Drude-Lorentz insulator and partly of some inert material of unit dielectric constant. The former may have a dielectric function of the form

$$\epsilon_{DL} = \epsilon_\\infty + A/(\omega_0^2 - \omega^2 - i\omega\gamma),$$

where $A$ is a constant describing the strength of the oscillator, $\omega_0$ is its natural frequency, and $\gamma$ is a damping parameter. Salts such as NaCl, for example, are reasonably well described by (2.5) in certain frequency regimes. In such cases, $\omega_0$ may be interpreted as a TO phonon frequency, while the principal peak in $-\text{Im} \epsilon_{DL}(\omega)$ corresponds to an LO phonon.

Figure 5 shows $T_\theta(\theta, d, \omega)$ for a composite made up of a volume fraction $f$ of an insulator described by (2.5) and $1 - f$ of material of dielectric of unit dielectric constant. We have chosen $A = 2.77\omega_0^2$, $\gamma = 0.1i\omega_0$, and $\epsilon_\\infty = 2.25$, values characteristic of bulk NaCl, and have solved for $\epsilon_{eff}(\omega)$ by means of (2.2). As is evident, $-\log_{10} T_\theta$ again shows peaks at $\omega = \omega_{TO}$ and at $\omega = \omega_{LO}$, the latter being given by $\epsilon_{DL}(\omega_{LO}) = 0$ or $\omega_{LO}^2 = \omega_{TO}^2 + A$. Between these two peaks is a broad maximum in the absorption arising from the impurity band. Again, as in the model granular metal, the peak associated with $\omega = \omega_{LO}$ disappears for $f > \frac{3}{5}$, that of $\omega = \omega_{TO}$ at $f < \frac{3}{5}$. These features are expected to be general in granular Drude-Lorentz insulators, although the critical concentrations are likely to differ from $\frac{3}{5}$ and $\frac{3}{5}$.

It is of interest to ask if the percolation effects described above have been observed in optical experiments. We shall discuss here only the possibility that the more novel effect arising

\[\]
from insulator percolation may have been seen in the oblique-incidence transmission experiments carried out by Priestley et al. on granular Ag(SiO₂)$_x$ films. Figure 6 shows the measured transmission through films of thickness 400 Å at $f = 0.92$ and $f = 0.39$. Also shown are two attempts at calculating the transmission via the EMA and via the so-called "Maxwell-Garnett" approximation (MGA) (which is equivalent to the Clausius-Mossotti approximation). This is believed to be most suitable when the composite consists of a volume fraction $f$ of spheres of dielectric constant $\varepsilon_S$ embedded in a background, volume fraction $1-f$, of $\varepsilon_B$, and gives for such a material

$$\varepsilon_{\text{eff}} = \varepsilon_B + 3f\varepsilon_B \frac{\varepsilon_A - \varepsilon_S}{\varepsilon_A(1+f) + \varepsilon_B(2-f)}. \quad (2.6)$$

In applying the EMA and MGA to Ag$_x$(SiO$_2$)$_{1-x}$ we have used for SiO$_2$ the constant value $\varepsilon = 2.2$ and for Ag the experimental dielectric function of bulk Ag. For $f = 0.92$ we assume for $\varepsilon_{\text{eff}}$ SiO$_2$ spheres embedded in Ag host and for $f = 0.39$ the reverse.

We consider first $f = 0.92$. At this concentration the insulator does not yet form a connected path, and, therefore, we expect a sharp metallic plasmon peak in the absorption, as in pure Ag, plus a blurred or broad impurity band. The sharp peak can be seen in the experiment but the impurity band cannot be distinguished (except conceivably by subtracting the absorption of perpendicularly polarized radiation as done by Priestley et al.).

The MGA gives a fairly sharp peak at about the right frequency. The MGA gives two sharp peaks, one corresponding to the "bulk plasmon" and one to an "impurity plasmon" which in the MGA is not broadened. If, however, we correct $\varepsilon_{\text{eff}}$ for "surface scattering" by reducing the lifetime that characterizes the Drude contribution, then these two lines become one, as indicated by dashes, and the transmission looks very much like that calculated in the EMA. In contrast, the EMA transmission is negligibly affected by this reduction in $\tau$.

The situation is reversed at $f = 0.39$, where the insulator certainly forms a connected path (this is obvious from the fact that these samples are insulating in dc experiments). Since the metallic plasmon peak should now have disappeared, we expect only a single plasmon peak in the absorption, resulting from the "impurity band" plasmon. As may be seen from the experimental plot, this peak is considerably broader than that of the host metallic peak, and indeed can only be unambiguously distinguished by subtracting the perpendicular-polarized absorption from the parallel-polarized. The EMA seems to describe this broadening adequately. This is very surprising because the EMA does not describe the strong absorption maximum which occurs at a wavelength of about 0.46 μm at this concentration, and which arises from the peak in $\varepsilon_{\text{eff}}$, not $-\varepsilon_{\text{eff}}^{-1}$. The MGA, which better describes the latter, gives too sharp a peak in the parallel-polarized absorption. This peak is much reduced but not eliminated by surface-scattering corrections, as indicated by the dashed curve. Note that neither the MG nor EM approximations give two plasmon peaks; this is because both correctly model at $f = 0.39$ the percolation of the insulator. We conclude, however, that neither approximation is adequate to describe the oblique-incidence absorption of Ag$_x$(SiO$_2$)$_{1-x}$ over the entire optical range at this concentration of metal.

The published experimental results do not indicate whether this percolation effect is likely to appear abruptly at $f_t$. It seems likely that such a concentration may be difficult to distinguish experimentally. If we believe the EMA, then the impurity peak in $-\varepsilon_{\text{eff}}^{-1}$ is quite sharp near $f_t$. 

\[\text{FIG. 6. As in Fig. 4, but for the composite Ag}_x\text{(SiO}_2\text{)}_{1-x}. \text{ Angle of incidence is 60° and the film thicknesses are 400 Å. The "experimental" curves were obtained by a crude tracing of the published data of Ref. 17, on the assumption that the vertical scale indicated in that reference represents } -\log_{10} T. \text{ Dashed curves labeled "MGA" result when the Drude lifetime obtained from fitting the dielectric function of bulk Ag (Ref. 26) is reduced by a factor of ten (an upper limit) to account for surface scattering.}\]
III. SUM RULES

Additional information about the percolation effects just described can be found with the help of various sum rules that we now derive. These sum rules are based on the quasistatic approximation, but are otherwise quite general, independent of particular structural models of the composite.

Consider a heterogeneous dielectric made up of two components, A and B, with dielectric functions \( \epsilon_A(\omega) \) and \( \epsilon_B(\omega) \), present in volume fractions \( f \) and \( 1-f \). At high frequencies we assume that

\[
\epsilon_A(\omega) - 1 - M_A/\omega^2 + O(1/\omega^3),
\]

\[
\epsilon_B(\omega) - 1 - M_B/\omega^2 + O(1/\omega^3).
\]  

(3.1)

Thus \( |\epsilon_A - \epsilon_B| \lesssim 1/\omega^2 \) in this regime and an expansion of \( \epsilon_{\text{eff}} - \epsilon_{\text{in}} \) in powers of this parameter is rapidly convergent at sufficiently high frequencies \( \epsilon_{\text{in}} = f \epsilon_A + (1-f) \epsilon_B \). Such an expansion, for an isotropic composite, yields

\[
\epsilon_{\text{eff}} - \epsilon_{\text{in}} = \frac{1}{3}(1-f)(\epsilon_A - \epsilon_B)^2 + O(1/\omega^2).
\]  

(3.2)

or, expressing the right-hand side as an expansion in powers of \( 1/\omega^2 \),

\[
\epsilon_{\text{eff}} - \epsilon_{\text{in}} = f(1-f)(M_A - M_B)^2/3\omega^4 + O(1/\omega^7).
\]  

(3.3)

The sum rules for \( \epsilon_{\text{eff}} \) now follow from the Kramers-Kronig relations

\[
\text{Re} \epsilon_{\text{eff}}(\omega) = P \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\text{Im} \epsilon_{\text{eff}}(\omega')}{\omega^2 - \omega'^2} d\omega',
\]  

(3.4)

which in turn follows from the requirement that \( \delta \epsilon_{\text{eff}}(\omega) \equiv \epsilon_{\text{eff}}(\omega) - \epsilon_{\text{in}}(\omega) \) be analytic in the upper half of the complex plane. Expanding left- and right-hand sides in powers of \( 1/\omega^2 \) at large \( \omega \), using (3.3) and equating coefficients of \( \omega^2 \) and \( \omega^4 \), gives

\[
\int_{-\infty}^{\infty} \omega' \text{Im} \epsilon_{\text{eff}}(\omega') d\omega' = 0
\]  

(3.5a)

\[
\int_{-\infty}^{\infty} \omega'^2 \text{Im} \epsilon_{\text{eff}}(\omega') d\omega' = \frac{1}{2} \pi f(1-f)(M_A - M_B)^2.
\]  

(3.5b)

Now the Kramers-Kronig relations for \( \epsilon_A \) and \( \epsilon_B \) give

\[
\int_{-\infty}^{\infty} \omega' \text{Im} \epsilon_i(\omega') d\omega' = \pi M_i, \quad i = A, B.
\]  

(3.6)

From (3.6) and from the fact that all the integrands of (3.5) and (3.6) are even functions of \( \omega' \), we get

\[
\int_{0}^{\infty} \omega' \text{Im} \epsilon_{\text{eff}}(\omega') = \frac{1}{3} \pi f(M_A + (1-f)M_B),
\]  

(3.7a)

\[
\int_{0}^{\infty} \omega'^3 \text{Im} [\epsilon_{\text{eff}}(\omega') - \epsilon_{\text{in}}(\omega')] d\omega' = \frac{1}{8} \pi f(M_A - M_B)^2.
\]  

(3.7b)

Equations (3.7) are the desired sum rules for \( \epsilon_{\text{eff}}(\omega) \). The first of these is nothing more than a statement that the integrated oscillator strength of the composite is the average of the integrated oscillator strengths of the components. However, the second equality is a nontrivial statement about the effects of composite inhomogeneity on the center of gravity of the oscillator strength. It is the analog of that derived by Bergman for the pole spectrum of \( \epsilon_{\text{eff}}(\omega) \). While eddy current absorption, and to some extent multipole scattering at higher frequencies (where \( \alpha/\lambda \) may no longer be a small parameter), will produce corrections to these quasistatic sum rules, nonetheless they seem likely to remain approximately valid and to provide useful information about many realistic small-particle composites.

Results analogous to (3.7) can be obtained for \( \text{Im} \epsilon_{\text{eff}}(\omega) \). From Eq. (3.3) we deduce

\[
\text{Im} \epsilon_{\text{eff}}(\omega) - \text{Im} \epsilon_{\text{in}}(\omega) = \frac{f(1-f)(M_A - M_B)^2}{3\omega^4} + O(1/\omega^7),
\]  

(3.8)

[upon using \( \epsilon_{\text{in}}(\omega) \rightarrow 1 \) as \( \omega \rightarrow \infty \)] and hence the sum rules

\[
\int_{0}^{\infty} \omega' \text{Im} \frac{1}{\epsilon_{\text{eff}}(\omega')} d\omega' = -\frac{1}{2} \pi f(M_A + (1-f)M_B),
\]  

(3.9a)

\[
\int_{0}^{\infty} \omega'^3 \text{Im} \left( \frac{1}{\epsilon_{\text{eff}}(\omega')} - \frac{1}{\epsilon_{\text{in}}(\omega')} \right) d\omega' = -\frac{1}{8} \pi f(M_A - M_B)^2.
\]  

(3.9b)

Again the effect of inhomogeneity is to push up some of the oscillator strength in \( -\text{Im} \epsilon_{\text{eff}}(\omega) \) relative to that of \( -\text{Im} \epsilon_{\text{in}}(\omega) \).

To show the usefulness of the sum rules (3.7) and (3.9), we shall use them to interpret some of the percolation behavior described in Sec. II. We consider the model granular metal of Sec. III, but initially consider the limit \( 1/\tau \rightarrow 0 \). In this way we insure that the "impurity" band can be unambiguously distinguished from the percolation modes. Thus \( \epsilon_{\text{in}} = \epsilon_{\text{eff}} = 1 - \omega^2/\omega_{\text{in}}^2 \) and \( \epsilon_{\text{in}} = 1 \), and the sum rules (3.7) and (3.9) take the forms
\[
\int_0^\infty \omega' \text{Im} \varepsilon_{\text{eff}}(\omega') d\omega' = \frac{1}{\lambda} \pi f \omega_p^2 = I_1, \quad (3.10a)
\]
\[
I_1^\text{imp} = \frac{3}{2} \pi \omega_p^2 \left( \frac{1}{2} - f \right) \quad (f > f_m), \quad (3.16a)
\]
\[
\omega_\text{imp} = \omega_p \sqrt{\frac{3}{2} f}. \quad (3.16b)
\]

In the limit \(1 - f < 1\), both (3.15) and (3.16) are exact to order \(1 - f\) for spherical voids in an otherwise homogeneous metal. However, if the inclusions have shapes other than spherical, we are not aware of a proof that these results still hold, even to order \(1 - f\). For \(f \approx f_m\), the ratio \(\sigma(f)/\sigma(1)\) is believed to exhibit power-law behavior
\[
\sigma(f)/\sigma(1) \sim (1 - f)^t, \quad (3.17)
\]
where \(t = 1.7, 2.6\) (The EMA gives \(t = 1\)).

Equation (3.12) indicates that \(I_1^\text{perc}\) will vanish according to the same power law.

The sum rules (3.10c) and (3.10d) give information about percolation effects in \(-\text{Im} \varepsilon_{\text{eff}}\). For \(f < f_i\), the oscillator strength in this function is entirely concentrated in an impurity band centered at frequency
\[
\bar{\omega}_\text{imp} = \sqrt{I_2/I_1} = \omega_p \sqrt{3(1 + 2f)} \quad (f < f_i). \quad (3.18)
\]

For \(f > f_i\), some of the oscillator strength is soaked up by the plasmon peak which appears at \(\omega = \omega_p\).

As is argued in the Appendix, the latter has integrated strength \(\omega_\text{p}\) given by
\[
I_1^\text{perc} = \frac{3}{2} \pi \omega_p^2 \bar{\sigma}(1)/\bar{\sigma}(f) \quad (f > f_i), \quad (3.19)
\]
where \(\bar{\sigma}(f)\) is what the dc conductivity of the composite would be if the insulating portion had infinite conductivity and the metal portion had conductivity \(\bar{\sigma}(1)\). Since \(f(f)\) diverges as \(f - f_i\) from above, \(I_1^\text{perc}\) goes to zero near this threshold, according to the power law
\[
I_1^\text{perc} \sim (f - f_i)^s \quad (f > f_i), \quad (3.20)
\]
where \(s\) is the exponent introduced by Straley and governing conductivity of a resistor lattice consisting of randomly placed elements of unit and zero resistance. Network calculations give \(s \approx 0.7, 2.6\).

From (3.14), (3.10c), and (3.10d) one deduces
\[
\bar{\omega}_\text{imp} = \sqrt{I_2/I_1^\text{imp}} \bar{\omega}_\text{imp} = \omega_p \sqrt{3f/(1 - f)} \quad (f > f_i), \quad (3.21a)
\]
\[
\bar{\omega}_\text{imp} = \omega_p \sqrt{3f} \quad (f > f_i). \quad (3.21b)
\]

Thus in the limit \(f \rightarrow 1\), \(\bar{\omega}_\text{imp} = \omega_p \sqrt{3f}\), i.e., there is a peak in \(-\text{Im} \varepsilon_{\text{eff}}\) at this frequency in the EMA. As noted above, this result is rigorously valid at
least for isolated spherical voids in an otherwise homogeneous metal. Figure 7 shows the various information that can be deduced about the model metal-insulator composite on the basis of the sum rules and the EMA. The solid lines represent the band limits \( \omega(f) \) and \( \omega_s(f) \) as calculated within the EMA. The touch \( \omega = 0 \) and \( \omega = \omega_s \) at \( f = \frac{1}{2} \) and \( f = \frac{3}{2} \). The heavy solid lines at these frequencies denote the poles in \( \text{Im} \epsilon_{\text{eff}}(\omega) \) and \( -\text{Im} \epsilon_{\text{eff}}(\omega) \). The dashed lines correspond to \( \omega_{\text{imp}} \) and \( \omega_{\text{imp}}^\text{c} \), they are deduced from the sum rules for \( f < f_m \) and \( f < f_i \), and from the sum rules combined with the EMA above these frequencies. Finally, the dot-dashed line corresponds to the maximum in \( -\text{Im} \epsilon_{\text{eff}}(\omega) \) for \( f < f_i \), as calculated in the EMA. As can be seen in Fig. 2, and as discussed in Sec. II, this peak is rather sharp, especially for \( f > f_i \), for reasons not understood.

The sum rules (3.5) and (3.7) can also be used, for example, to treat composites of Drude-Lorentz insulators embedded in a dielectric of unit dielectric constant. Let the dielectric function of the former be described by Eq. (2.5) with \( \gamma = 0 \). Then a straightforward application of arguments such as those just used to treat a metal-insulator composite gives the following results for the impurity phonon band appearing in the range \( \omega_0^s < \omega < \omega_0^s + A \):

\[
J_1^{\text{imp}} = \frac{1}{2} \pi fA \quad (f < f_m)
\]

\[
= \frac{\pi}{2} A \left( f - \frac{\bar{\sigma}(f)}{\sigma(1)} \right) - \frac{\pi}{4} (1 - f) (f > f_m),
\]

(3.22a)

\[
\omega_1^\text{imp} = \frac{1}{2} f(1 - f) A \quad (f < f_m)
\]

\[
= \frac{\pi}{2} A \left( f - \frac{\bar{\sigma}(f)}{\sigma(1)} \right) - \frac{\pi}{4} (1 - f) (f > f_m),
\]

(3.22b)

\[
F_1^{\text{imp}} = \frac{1}{2} \pi fA \quad (f < f_i)
\]

\[
= \frac{\pi}{2} A \left( f - \frac{\bar{\sigma}(f)}{\sigma(1)} \right) - \frac{\pi}{4} (1 - f) (f > f_i),
\]

(3.22c)

\[
\tilde{\omega}_1^{\text{imp}} = \frac{1}{2} (1 + 2f) A \quad (f < f_i)
\]

\[
= \frac{\pi}{2} A \left( f - \frac{\bar{\sigma}(f)}{\sigma(1)} \right) - \frac{\pi}{4} (1 - f) (f > f_i),
\]

(3.22d)

where the expressions to the right of the arrows are based on the EMA for \( \sigma(f)/\sigma(1) \) and \( \bar{\sigma}(f)/\bar{\sigma}(1) \).

We consider, finally, the potential usefulness of these sum rules in applications to real composites. As in pure metals, one expects in composites that \( \text{Im} \epsilon_{\text{eff}} \) will remain nonzero to quite high frequencies. If experimental data are not available to such frequencies, one may have to consider partial quantities, i.e., integrals of \( \omega \text{Im} \epsilon_{\text{eff}} \) and similar quantities to some finite upper limit. In pure materials, these definite integrals can be interpreted in terms of total number of electrons contributing to the oscillator strength below a certain frequency defined by the upper limit of the integral. Con-
ceivably similar techniques can be used in conjunction with the sum rules to unfold optical data in small-particle composites.

ACKNOWLEDGMENTS

I should like to thank the Division of Applied Science at Harvard University, and particularly Professor Henry Ehrenreich, for their hospitality during the period when this work was initiated. This work was supported in part by NSF under Grant No. 76-10846.

APPENDIX

We wish to argue that the strength of the Drude peak in Re$\sigma$, for the model metal-insulator composite of Sec. II, varies as $\sigma(f)/\sigma(1)$. To this end, we consider $\epsilon_m = 1 - \omega_P^2/\omega^2$ and $\epsilon_f = 1$ at a fixed filling fraction $f$ above the percolation threshold $f_m$. It is clear on physical grounds that the behavior of $\epsilon_{\text{eff}}$ is dominated, under these circumstances, for sufficiently small $\omega$ (where $\epsilon_m \ll \epsilon_f$) by $\epsilon_m$

alone. (This is equivalent to the assumption that, for small $\omega$ and $f > f_m$, all the displacement current is confined to the metal.) It follows that, for sufficiently small $\omega$, we must have

$$\epsilon_{\text{eff}}(\omega) \sim -\left[\sigma(f)/\sigma(1)\right] (\omega^2/\omega_p^2)$$

(A1)

and hence the strength of the pole in $\text{Im} \omega_{\text{eff}}(\omega)$ at $\omega = 0$ varies as $\sigma(f)/\sigma(1)$. Similar arguments can be used to deduce the strength of the metal "plasmon" pole at $\omega = \omega_p$.

For fixed $f > f_i$ and $\omega$ sufficiently near $\omega_p$, we have $\epsilon_m \approx \epsilon_f$. Since, however, the insulator does not form a connected path across the sample, it acts essentially as a short circuit across localized portions of the composite and can be treated as if it has infinite dielectric constant. Thus, for $f > f_i$, we have for $\omega = \omega_p$

$$\epsilon_{\text{eff}}(\omega) = \epsilon_m(\omega) \delta(f)/\delta(1)$$

(A2)

and hence the strength of the pole in $-\text{Im} \omega_{\text{eff}}$ at $\omega = \omega_p$ varies as $\delta(1)/\delta(f)$.

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1A number of articles and references may be found in Proceedings of the Conference on Electrical Transport and Optical Properties of Inhomogeneous Media, edited by J. C. Garland and D. B. Tanner (American Institute of Physics, New York, 1978).


10This "regime of validity" has yet to be stated in any clear mathematical way, unfortunately.

11J. C. Maxwell--Garnett, Phil. Trans. R. Soc. Lond. 203, 385 (1904).


14See, for example, L. D. Landau and E. M. Lifshitz, Electrodynamics of Continuous Media (Pergamon, New York, 1960).

15See, for example, D. Pines, Elementary Excitations in Solids (Benjamin, New York, 1962), p. 292. Equation (2.4) follows from Pines' formula upon using $\delta \epsilon (\omega_p') = \delta \epsilon (\omega_p)$.

