Comments and Addenda

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Comparison of the effective medium and the Maxwell-Garnett predictions for the dielectric constants of granular metals*

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It is shown that, in the case of granular metals, the Maxwell-Garnett theory provides a good approximation to the dielectric constant of granular metals, while the effective-medium theory does not apply.

In a recent paper Stroud[1] has shown that the effective-medium theory[2] (EMT) and the Maxwell-Garnett theory[3] (MGT) can be obtained as different approximations to a generalized transport theory of composite systems.

In this note we compare the predictions of the two theories with experiment for the case of granular metals.[4-7] These materials[8] consist of metal dispersions such as colloids,[4] cermets,[5,6] and discontinuous metal films.[7] Granular metals exhibit a strong absorption peak in the optical region which is absent in the bulk metal. An example of this is given by Au colloidal particles suspended in glass in which the absorption peak gives rise to a characteristic ruby-red color.

In the derivation of the MGT and EMT it is assumed that the composite material consists of grains that are much smaller than the wavelength of light, but are large enough so that they can be characterized by macroscopic dielectric constants. Approximate solutions to the integral equation from which the dielectric constant is determined are obtained by neglecting multiple scattering of the electric field by the grains.[1] This approximation is equivalent to a mean-field theory in which the effect of all the grains on a given grain is represented by a uniform field. In the EMT approximation the two components, A and B, of the granular metal are treated in an equivalent manner. Grains of A and B are assumed to be embedded in an effective medium whose dielectric constant is ϵ_S, the same as that of the composite material. The choice of the dielectric constant of the effective medium is such that the average field acting on a grain due to all the other grains averages to zero. The dielectric constant of the composite system ϵ_S in the case where grains of A and B are spherical is given by the relation[1]

$$x \frac{\epsilon_A - \epsilon_S}{\epsilon_A + 2\epsilon_S} + (1-x)\frac{\epsilon_B - \epsilon_S}{\epsilon_B + 2\epsilon_S} = 0 , \tag{1}$$

where x is the volume fraction of component A, and ϵ_A and ϵ_B are the dielectric constant of the individual grains.

In the MGT approximation it is assumed that the grains of one component are embedded in the matrix of the other component. This theory, unlike the effective-medium theory, treats the two components in an asymmetric manner. The field acting on a grain due to all the other grains, is assumed to be given by the Lorentz local field. The expression for ϵ_S, generalized to the case where the grains of A (embedded in matrix B) are rotational ellipsoids identical in shape and orientation (but not necessarily in size), is given by[5]

$$\frac{\epsilon_S - \epsilon_B}{L\epsilon_S + (1-L)\epsilon_B} = x \frac{\epsilon_A - \epsilon_B}{L\epsilon_A + (1-L)\epsilon_B} , \tag{2}$$

where L is the characteristic depolarization factor. For spherical grains ($L = \frac{1}{3}$) Eq. (2) reduces to the usual Maxwell-Garnett result.[3]

Inspection of Eqs. (1) and (2) shows that their forms are entirely different: Eq. (1) is quadratic in ϵ_S and symmetric in ϵ_A and ϵ_B while Eq. (2) is linear in ϵ_S and asymmetric in ϵ_A and ϵ_B. The different ways in which the two theories treat the components A and B lead to gross differences in the predicted optical properties. We illustrate this for two cases: a hypothetical granular metal consisting of isolated spherical grains of a Drude metal, dispersed in a dielectric medium with a dielectric constant of unity,[9] and for the case of a granular Ag film. In Fig. 1 is given the MGT dielectric constant [Eq. (2)] for the Drude metal dispersion. It should be noted that its behavior is analogous to that of the dielectric constant of ionic crystals near the restrahlen band. As the volume fraction of the metal increases, the amplitude of the anomaly in ϵ_S grows, and the wavelength λ_A at which the anomaly occurs moves to larger values. Figure 2 shows the dielectric constant of the same Drude metal dispersion obtained from the EMT [Eq. (1)]. The behavior of ϵ_S is in this case very different. For $x=0.4$, the real part of ϵ_S is metal-like (negative at long wavelength and changing sign at the plasma frequency) and for $x=0.20$ it is insulatorlike (positive at all wavelengths). The transition from metallic to dielectric behavior takes place at $x=\frac{1}{3}$.

In Fig. 3 are compared the computed and measured optical densities of an Ag-SiO_2 film. The theoretical curves were computed using for ϵ_A the complex dielectric constant of Ag,[10] and for ϵ_B the dielectric constant of SiO_2 ($\epsilon_B=2.2$) and the experimental points from the work of Cohen *et al.*[5] The MGT [Eq. (2)] predicts reasonably well the position of the observed absorption peak (λ_A) although the predicted height of the peak is larger than observed. In addition, the MGT predicts correctly the compositional variation of the

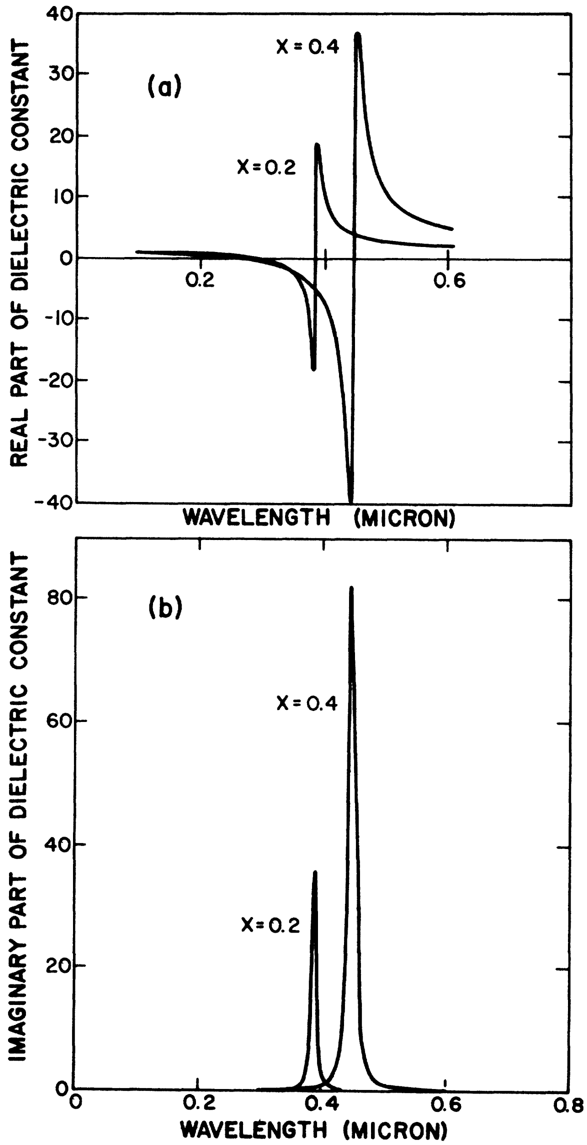

FIG. 1. MGT dielectric constant ϵ_S of spherical metal grains in vacuum for two different volume fractions of the metal, x; calculated from Eq. (2) assuming $\epsilon_B=1.0$ and for ϵ_A the complex dielectric constant of a Drude metal with a plasma frequency of 1.5×10^{15} sec^{-1} and a relaxation time of 1×10^{-14} sec; (a) real part, and (b) imaginary part of the dielectric constant.

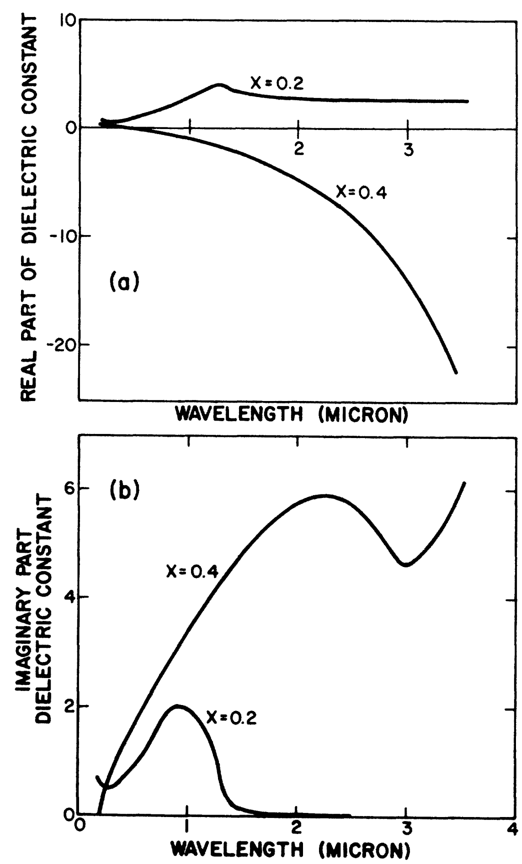

FIG. 2. EMT dielectric constant of spherical metal grains in vacuum; calculated from Eq. (1) using the same parameters as in Fig. 1; (a) real part, and (b) imaginary part of the dielectric constant.

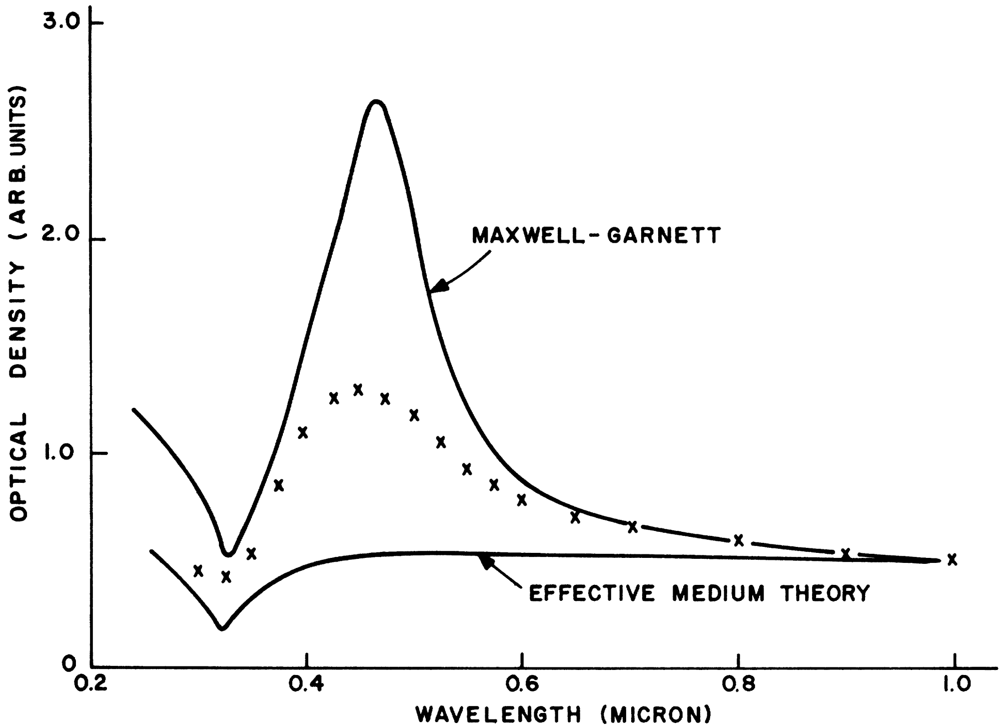

FIG. 3. Optical density of Ag-SiO_2 film containing 0.39 vol. fraction Ag. Theoretical curves computed from Eqs. (1) and (2); experimental data points (Ref. 5) are represented by crosses. The optical densities have been normalized at 1 μm.

plasmas resonance in granular metals,[6] i.e., a shift to longer wave lengths as the volume fraction of the metal is reduced. Similarly good agreement with the theory is obtained for other granular metals[4,7] in which the metal grains are isolated.

On the other hand, the EMT result is strikingly different from experiment in that it yields no distinctive absorption peak (see Fig. 3). Calculations using Eq. (1) show that for $x = 0.39$ the plasma wavelength is about 1 μm and is increasing very rapidly with decreasing x indicating approach to a metal-nonmetal transition. This variation of the plasma frequency is very different from experimental observation.[6] We therefore conclude that the EMT is not applicable to metal dispersions while the MGT provides a reasonably good description of the dielectric constant of such systems.

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