EFFECTIVE DIELECTRIC FUNCTION OF COMPOSITE MEDIA

Ping Sheng

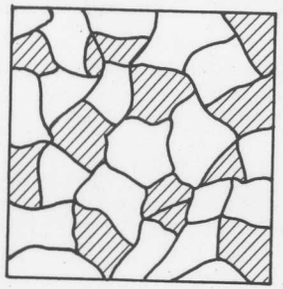
Theoretical Sciences Group
Corporate Research Science Laboratories
Exxon Research and Engineering Co.
P. O. Box 45
Linden, N.J. 07036

Abstract

This article reviews the relationship between the microstructure of a composite, i.e. geometric shapes as well as topological arrangements of the different components, and two unique characteristics of metal-insulation composites -- the percolation threshold and the optical dielectric anomaly. It is demonstrated that the effective medium approach to the calculation of effective dielectric constant $\bar{\varepsilon}$ can yield realistic results provided that the microstructural information is properly taken into account.

It is well known that the electromagnetic response of a single-component, homogeneous system can be completely characterized by a complex dielectric function[1] $\varepsilon(\omega) = \varepsilon_R(\omega) + i(4\pi\sigma(\omega)/\omega)$, where ε_R is the dielectric constant, σ is the conductivity, and ω is the angular frequency of the electromagnetic wave. In the case of a random inhomogeneous composite, however, the task of characterizing the electromagnetic response is generally much more involved due to the random scatterings of the probing wave by the inhomogeneities. Yet in the limit of $\lambda >> \xi$, where λ is the wavelength and ξ the typical scale of inhomogeneities, a great conceptual simplification occurs because the waves cannot resolve the individual scattering centers. Therefore, the medium would appear uniform, characterized by an effective dielectric function $\bar{\varepsilon}(\omega)$.

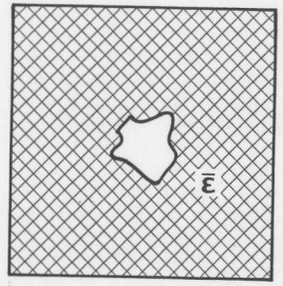
In the literature there are two prevalent approaches for the calculation of the effective dielectric constant $\bar{\varepsilon}$. One is Bruggeman's effective medium theory[2]. The main idea of this theory can be described as follows. Consider a random composite consisting of two components, with dielectric constants ε_1 and ε_2, as schematically illustrated in Fig. 1(a).



(a)

Fig. 1 (a) Schematic picture of a random composite.

Since an exact calculation of the electric field distribution for the random, infinite system is impossible, the Bruggeman approach is to focus attention on one of the grains (say a grain of component 1) and regard the rest of the composite as a homogeneous medium characterized by a yet undetermined effective dielectric constant $\bar{\varepsilon}$. This is shown in Fig. 1(b).



(b)

Fig. 1 (b) The rest of the medium is treated as homogeneous for the calculation of depolarization field of a single grain.

In the presence of an applied electric field, the single inclusion in the uniform medium $\bar{\varepsilon}$ will give rise to a dipole depolarization field which, in the spherical grain approximation, is proportional to $(\bar{\varepsilon} - \varepsilon_1)/(\bar{\varepsilon} + 2\varepsilon_1)$. Repeating the same problems with a grain of component 2 results in another dipole moment proportional to $(\bar{\varepsilon} - \varepsilon_2)/(\bar{\varepsilon} + 2\varepsilon_2)$. In order to be consistent with the initial assumption that the medium should appear homogeneous to the probing wave, the average depolarization field must vanish. That is,

$$p\,\frac{\bar{\varepsilon} - \varepsilon_1}{\varepsilon_1 + 2\bar{\varepsilon}} + (1-p)\,\frac{\bar{\varepsilon} - \varepsilon_2}{\varepsilon_2 + 2\bar{\varepsilon}} = 0, \qquad (1)$$

where p is the volume fraction of component 1. It should be mentioned that Eq. (1) has been shown to be equivalent to the coherent potential approximation in the multiple-scattering formulism[3].

If the two components of the composite are metal and insulator, that is, $\varepsilon_1 = 1$ and $\varepsilon_2 = 0$, then it is easy to verify that the Bruggeman theory predicts an effective conductivity that vanishes at $p_c = 1/3$. This behavior, known as the percolation threshold, is physically related to the fact that below the threshold, there is no possibility for metal grains to form a connected network of infinite extent. In granular films[4-6], the percolation threshold behavior is reflected in the transmission electronmicroscope pictures of the microstructure as shown in Fig. 2.

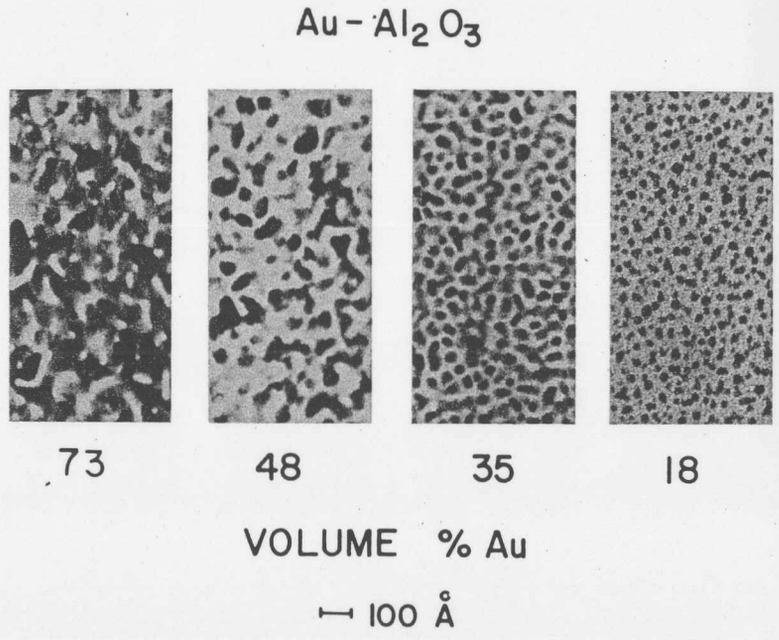


Fig. 2 Transmission electron micrographs of the granular cermets Au-Al_2O_3 for four different compositions.

It is seen that at p = 0.73, the Al_2O_3 (white) are disconnected inclusions in the metallic Au matrix (black). As p is decreased, a matrix inversion occurs until at p = 0.35 the metal particles are the inclusions in the insulator matrix. Between p = 0.48 and p = 0.35 we have a labyrinth structure, and somewhere between these two composition values it is clear that the last infinite metallic network must be broken and the dc conductivity vanishes. Therefore, Bruggeman's theory is qualitatively correct in predicting a percolation threshold. However, quantitatively the agreement is poor as shown in Fig. 3.

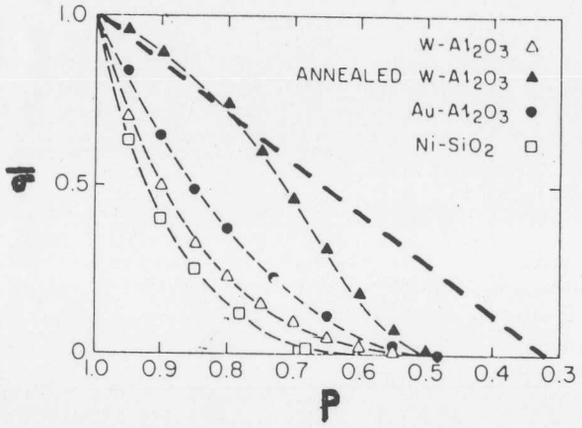


Fig. 3 Normalized dc conductivity of granular metals. The straight dashed line is the Bruggeman theory. After Abeles [1].

Another widely-used approach to the calculation of $\bar{\varepsilon}$ was the Maxwell-Garnett theory [7]. Its tranditional derivation relies on the analogy of metal-insulator composite as a polarizable medium in which the metal grains play the role of "atoms".

By using the familiar Clausius-Mosotti equation[8], one obtains a relationship between the dielectric constant of the composite and the polarizability of the metal particles:

$$\frac{\bar{\varepsilon} - \bar{\varepsilon}_2}{\varepsilon + 2\varepsilon_2} \quad \frac{4\pi n\alpha_1}{3\varepsilon_2} \quad . \tag{2}$$

Here n is the volume density of the metal particles, and α_1 is the polarizability of a metal grain. By substituting for α_1 the expression for polarizability of an isolated metal sphere immersed in a uniform medium of dielectric constant ε_2, we get the Maxwell-Garnett equation

$$\frac{\bar{\varepsilon} - \varepsilon_2}{\varepsilon_2 + 2\bar{\varepsilon}} = p\,\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \quad . \tag{3}$$

Equation (3) is equivalent to the averaged T-matrix approximation in the multiple scattering formalism[3].

The Maxwell-Garnett theory can be easily shown not to yield a percolation threshold at any finite values of p. However, it does predict another peculiar property of the composite, the dielectric anomaly[9], which is absent in Bruggeman's theory.

To describe this effect, let us consider the frequency dependence for the real and imaginary parts of the metal dielectric function shown schematically in Fig. 4(a), where ω_p denotes the plasma frequency. If now we have a metal-insulator composite with insulator being the matrix component, the real and imaginary parts of the effective dielectric constant would look like Fig. 4(b) according to the Maxwell-Garnett theory.

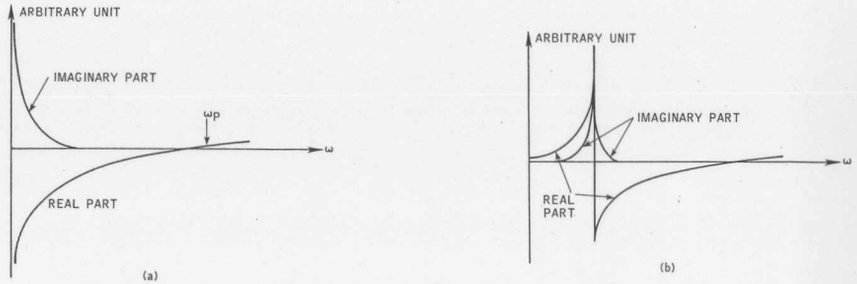


Fig. 4 Schematic illustration of the frequency dependence of the dielectric constant for (a) an ideal metal and (b) a metal-insulator composite according to the Maxwell-Garnett theory.

It is to be noted that there is a frequency ω_p above which the effective dielectric function behaves exactly like a metal. However, at $\omega \ll \omega_p$ the composite is more like an insulator. Therefore, ω_p is essentially a frequency threshold for the metal-insulator transition. At ω_R, there is an absorption peak arising from increased penetration of electromagnetic field into the metal grains.

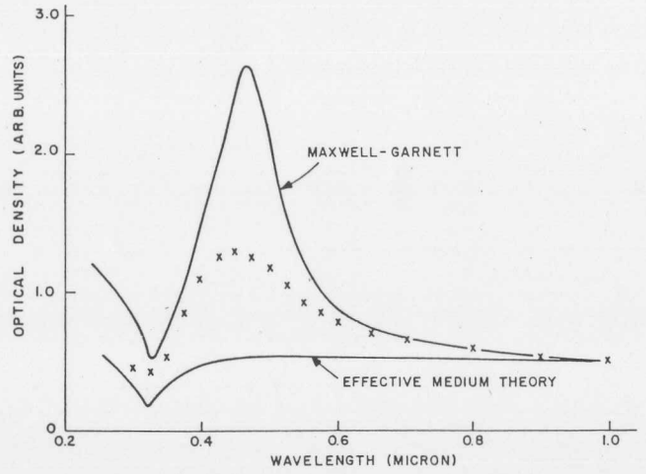


Fig. 5 Comparison of experimental results on the dielectric anomaly with both the Bruggeman and the Maxwell-Garnett theories. The sample is Ag-SiO_2 film containing 0.39 volume fraction Ag. After Ref. [10].

Evidence for the dielectric anomaly has been observed in granular Ag - SiO_2 and Au - SiO_2 films [9]. Figure 5 [10] compares the experimental result with both the Maxwell Garnett and the Bruggeman theories. It is seen that whereas the Maxwell-Garnett theory does produce the absorption peak at about the right frequency, the Bruggeman theory exhibits no peak at all.

Such comparisons raise the obvious question: what is the underlying physics responsible for this difference in behavior? The answer to this question is facilitated by the recognition in the last few years that the Maxwell-Garnett theory can be alternatively derived by using the effective - medium approach[11]. That is, if we consider the embedding of a coated sphere in an effective medium, then the condition of vanishing depolarization field would yield Eq. (3) provided that the sphere is of component 1 and the coating is of component 2 with a thickness determined directly by the relative volume fraction of the two components. This derivation of the Maxwell-Garnett formula immediately tells us that the difference between the two theories lies in the consideration of two types of microstructures. Whereas the Bruggeman theory treats the two components in an equivalent manner, the basic structural unit of a coated sphere in the Maxwell-Garnett case implies an asymmetrical consideration of the two components. It is clear that if we make up a composite by the random placement of coated spheres, then the coating component would always remain the matrix constituent regardless of the composition. Therefore, it is not surprising that there is no percolation threshold in the Maxwell-Garnett theory. A schematic illustration of the microstructures implicity treated by the Bruggeman and the Maxwell-Garnett theories are shown in Fig. 6.

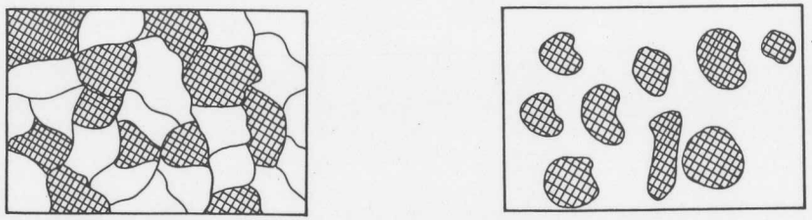


Fig. 6 Schematic illustration of the two types of microstructure treated by the Bruggeman theory (a) and the Maxwell-Garnett theory (b).

The elucidation of the difference between the two theories shows that there is only one underlying approach--the effective medium theory--to the approximate calculation of the effective dielectric constant. However, it also confronts the users of the effective medium theory with the following unresolved problems:

(1) Is the absence of the dielectric anomaly in the Bruggeman theory the physical consequence of its implicit microstructure or the result of the approximation used in its derivation?

(2) Does the fact that both theories cannot even qualitatively describe all the experimental results of granular metals signify (a) the need for carrying the effective medium approach to higher orders of approximation, or (b) the need for better modelling of the granular metal microstructure?

Consideration of the two problems shows that in both cases the question revolves around the role of microstructure in the calculation of effective dielectric constant. In this article, we wish to use the concept of "structural units" as a means for incorporating the microstructural information, i.e. geometric shapes as well as topological arrangement of the grains, in a statistical manner. For example, the structural unit in the Maxwell-Garnett case is a coated sphere, but the basic unit in the Bruggeman theory is a grain of either component. An alternative choice of structural unit for (the microstructure of) the Bruggeman case is a two-grain combination[12] in which each grain can be either component 1 or component 2, denoted here as a pair-cluster. The possible advantages of using a two-grain pair-cluster unit rather than the usual

one-grain unit lies in the explicit presence of the two-component interface in the basic structural units. As we may recall, in the derivation of the Bruggeman theory the only interfaces explicitly considered are those between the individual grain and the effective medium. Therefore, any phenomenon intrinsically associated with the interfaces between the two components, such as the dielectric anomaly, are not expected to be adequately accounted for. The use of the pair-cluster units thus holds promise to answer the first problem posed above.

To calculate the effective dielectric constant in the pair-cluster theory, we will approximate the geometry of the two-grain pair by a sphere in which each half can be either one of the two components. By embedding this sphere in an effective medium and calculating the resulting depolarization field, we obtain an equation for the effective dielectric constant $\bar{\varepsilon}$ after averaging over all two-hemisphere combinations and all orientations of the applied field relative to the plane separating the two hemispheres:

$$p^2 \frac{\bar{\varepsilon} - \varepsilon_1}{2\bar{\varepsilon} + \varepsilon_1} + (1-p)^2 \frac{\bar{\varepsilon} - \varepsilon_1}{2\bar{\varepsilon} + \varepsilon_2} \frac{4}{9} p(1-p) \frac{2\bar{\varepsilon} - \varepsilon_1 - \varepsilon_2}{K\bar{\varepsilon}(\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_1 + \varepsilon_2 + 4\bar{\varepsilon})/3}$$

$$+ \frac{2}{9} p(1-p) \frac{\bar{\varepsilon}(\varepsilon_1 + \varepsilon_2) - 2\varepsilon_1\varepsilon_2}{H\bar{\varepsilon}(\varepsilon_1 - \varepsilon_2)^2 + 2(\varepsilon_1\varepsilon_2 + \varepsilon_1\bar{\varepsilon} + \varepsilon_2\bar{\varepsilon})/3} = 0, \quad (4)$$

where

$$H = \frac{1}{4} \sum_{m=1}^{\infty} \frac{I_m}{[m(\varepsilon_1 + \varepsilon_2) + (2m+1)\bar{\varepsilon}]}, \quad (5)$$

$$K = \frac{1}{4} \sum_{m=1}^{\infty} \frac{I_m}{[2m\varepsilon_1\varepsilon_2 + (n + 1/2)(\varepsilon_1 + \varepsilon_2)\bar{\varepsilon}]}, \quad (6)$$

$$I_m = \frac{m(4m+1)[(2m+1)!]^2}{4^{2m}(m!)^4(2m-1)^2(m+1)^2(2m+1)} \quad (7)$$

Details of the derivation can be found in Ref. (12). To compare the results of the pair-cluster theory with the Bruggeman theory, we show in Fig. 7 the calculated optical transmission spectrum for a series of 500-A-thick Ag-SiO_2 films using realistic Ag and SiO_2 dielectric constant values. The optical dielectric constant of the composite is then evaluated by using both the pair-cluster theory (solid line) and the Bruggeman theory (dashed line). It is easily seen that the pair-cluster theory displays an extra absorption peak (or transmission dip) near $\lambda \simeq 0.37$ μm, the dielectric anomaly, which the Bruggeman theory does not have. The peak disappears, however, in the composition regime of $0.4 < p < 0.7$ where a matrix inversion occurs. Since in this particular composition range the two components is expected to exhibit a labyrinth structure, the disappearance of the absorption peak indicates that the dielectric anomaly may be associated with the particular microstructure of isolated inclusions embedded in a continuous matrix.

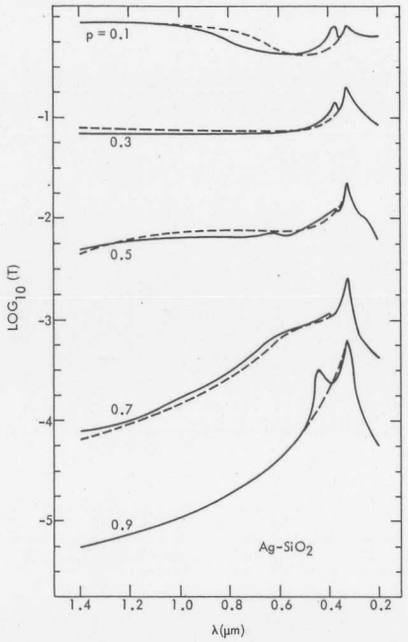


Fig. 7 Calculated optical transmission as a function of wavelength for a series of 500-A Ag-SiO_2 films. (-) pair-cluster theory, (---) Bruggeman theory. For clarity, the curves are displaced vertically with respect to each other.

To further accentuate the effect of microstructure, we show in Fig. 8 the transmission spectrum for the same Ag-SiO_2 films calculated in the Maxwell-Garnett theory. By comparing Figs. 7 and 8, it becomes clear that the position and the magnitude of the dielectric anomaly are drastically different. Therefore, although the complete absence of the dielectric anomaly in the Bruggeman theory can be ascribed to the neglect of two-component interfaces in its derivation, the microstructure, nevertheless, does govern the manifestation of the phenonemon.

Let us now consider the problem of constructing a realistic theory for the effective dielectric function of granular metals[6]. We will hypothesize at this stage that the discrepancies between the experimental results and the predictions of both the Bruggeman and the Maxwell-Garnett theories stem from the inadequacy of their structural units in modelling the cermet microstructure. To search for new structural units appropriate for these granular composites, we observe that the cermet is formed by the two-step process of surface diffusion and coalescence. That is, the molecules that land on the substrate (of the film) usually have excess energy and, therefore, tend to move about before they stick with other molecules of the same component and form the grain. The average distance of this surface motion is usually denoted as the surface diffusion length, which is the basic scale of inhomogeneity. Suppose now let us consider a spherical region with the dimension of a diffusion length. Inside such a region there can be a large number of molecules of either component. Therefore, statistically the relative volume fraction occupied by the two components should be close to the macroscopic average value. If a grain is formed inside this region through surface diffusion and coalescence, there are two possible outcomes as shown in Fig. 9. That is, component 1 may form the grain and component 2 the coating, which we denote as a type 1 structural unit, or component 2 may form the grain and

component 1 the coating, which we denote as a type 2 structural unit. At a given composition p, the relative probability of occurrence for the two types of structural unit can be estimated by counting the number of equally probable final configurations corresponding to different positions of the grain inside the region.

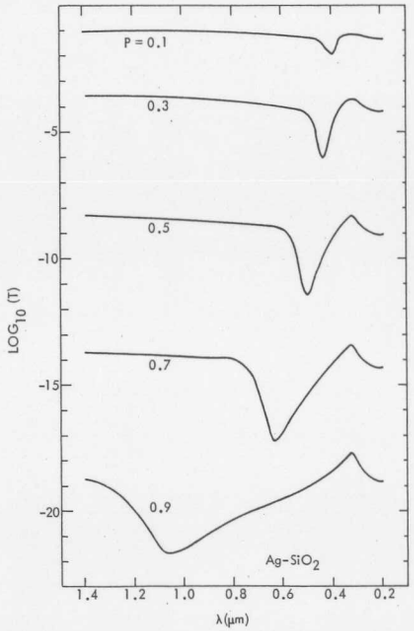


Fig. 8 Optical transmission as a function of wavelength for a series of 500-Å Ag-SiO_2 films, calculated by the Maxwell-Garnett theory. For clarity, the curves are vertically displaced with respect to each other.

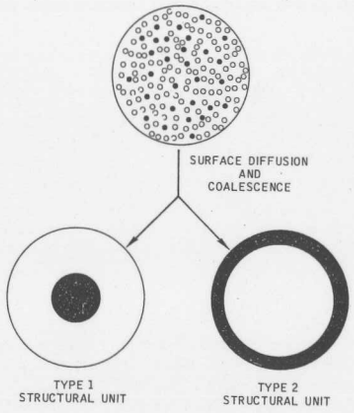


Fig. 9 Schematic illustration of the grain formation process in granular metal films.

By assuming the grain to be spherical, it is clear, that, in case of type 1, the number of configurations is proportional to $u_1 = (1-p^{1/3})^3$. By the same reasoning, the number of configurations for the type 2 unit is proportioned to $u_2 = [1 - (1-p)^{1/3}]^3$. It follows that the relative probability of occurrence for the type 1 unit is $f = u_1/(u_1 + u_2)$, and that for the type 2 unit is 1-f.

If we now build up a random composite from these two structural units according to their assigned statistical weights, the system will be dominated by type 1 structural units in the range $0.35 > p > 0$, since f only varies between 1 and 0.92. That is, the structural would essentially look like isolated grains of component 1 embedded in the continuous matrix of component 2. On the other hand, in the range of $1 > p > 0.65$ we expect the reverse structure in which component 2 becomes isolated and component 1 constitutes the continuous phase. Therefore, there is a matrix inversion occuring in the range $0.65 > p > 0.35$, where we can expect a labyrinth structure. Comparing the above structural description with Fig. 2, we see that the model composite is in reasonable accord with the reality. Now the construction of a theory for the effective dielectric function proceeds along the following three steps: (1) embedding the structural units in a uniform effective medium, (2) calculating the dipole moments of the structural units when they are polarized by a uniform applied field, and (3) requiring the average dipole moments to vanish. By approximating the dipole moment of a structural unit (in arbitrary configuration) by the dipole moment of the concentric configuration, $D_{1,2}$, we get the effective medium condition as

$$f D_1 + (1 - f) D_2 = 0 \qquad (8)$$

Since the arguments leading to the value of f remains unchanged if one relaxes the condition of spherical geometry and considers a speroidal particle enclosed in a similar-shaped region, Eq. (8) remains valid for spheroidal structural units. In that case $D_{1,2}$ stands for the orientationally averaged dipole moment of confocal spheroidal particles embedded in an effective medium $\bar{\varepsilon}$:

$$D_1 = \frac{2}{3} D[\bar{\varepsilon}, \varepsilon_1, \varepsilon_2, p, A(\alpha, u), B(\alpha)] + \frac{1}{3} D[\bar{\varepsilon}, \varepsilon_1, \varepsilon_2, p, 3-2A(\alpha,u), 3-2B(\alpha)] \quad 9(a)$$

$$D_2 = \frac{2}{3} D[\bar{\varepsilon}, \varepsilon_2, \varepsilon_1, 1-p, A(\beta, v), B(\beta)] + \frac{1}{3} D[\bar{\varepsilon}, \varepsilon_2, \varepsilon_1, 1-p, B-2A(\beta,v), 3-2B(\beta)] \quad 9(b)$$

Where α is the ratio between the minor (major) and major (minor) axes of the elliptic cross section for the type - 1 oblated (prolate) spheroidal unit, β is the similar quantity for the type - 2 unit, $u = (p/\alpha)^{1/2}$ and $v = ((1-p)/\beta)^{1/2}$. The functions D, A, and B have the following forms:

$$D(\bar{\varepsilon},x,y,\mu,A,B) = \frac{[A\bar{\varepsilon} + (3-A)y]\,[y-x]\mu + [Bx+(3-B)y]\,[\bar{\varepsilon}-y]}{A\,(3-A)\,(\bar{\varepsilon}-y)\,(y-x)\mu + [Bx + (3-B)y]\,[Ay + (3-A)\,\bar{\varepsilon}]} \qquad (10)$$

$$A(\gamma, w) = \frac{3}{2} \frac{1}{w^3(1-\gamma^2)} \left[\frac{1}{\sqrt{1-\gamma^2}} \tan^{-1} \frac{w\sqrt{1-\gamma^2}}{\sqrt{s^2+\gamma^2w^2}} - w(s^2+\gamma^2w^2)\right], \qquad (11)$$

$B(\gamma) = A(\gamma, 1/\gamma^{1/3})$ evaluated at s=0, where s is the solution of the equation $(s^2 + w^2)^2 (s^2 + \gamma^2 w^2) = 1$. A and B assumes the special value of 1 for spherical geometry. It is noted that if f is set equal to 1, Eq. (8) becomes the generalized Maxwell-Garnett equation which specializes to Eq. (3) in the spherical case.

A comparison of the calculated optical transmissions spectrum for a series of thin Au-SiO_2 films with the experimental results are shown in Fig. 10. The theoretical inputs are the realistic dielectric constants of Au and SiO_2, $\alpha = 1$, $\beta = 2$, the p values marked to the right of each curve, and the film thickness marked above each curve. It is seen that the new theory reproduces all the characteristics features of the data. In particular, the position and magnitude of the dielectric anomaly, and its eventual disappearance for $p \geq 0.8$ are all in good agreement. For effective dc conductivity

$\bar{\sigma}$ and its variation with p, we show in Fig. 11 two sets of experimental data corresponding to the same sample before and after the annealing treatment and their best theoretical fits. The theory curves are obtained by using $\varepsilon_1 = 1$, $\varepsilon_2 = 0$, $\alpha = 1$, and the β values marked in the figure. The strikingly good agreement, especially the reproduction of the opposite curvatures in the two sets of experimental data, shows that the insulator inclusions before annealing are mostly in the form of oblate platelets, which becomes rounded upon annealing. The increase in the effective conductivity can be intuitively understood by recognizing that the platelets are more effective than spheres in impeding the current flow.

The success of the new theory in explaining both the optical and dc response of granular films brings us to the essential point of this article. Namely, the effective medium approach to the calculation of effective material parameters can indeed yield realistic results provided that the microstructure of the random composite is properly taken into account. This conclusion, which may seem natural in hindsight, nevertheless does emphasize the need for future research in quantifying the different types of microstructure in random inhomogeneous systems.

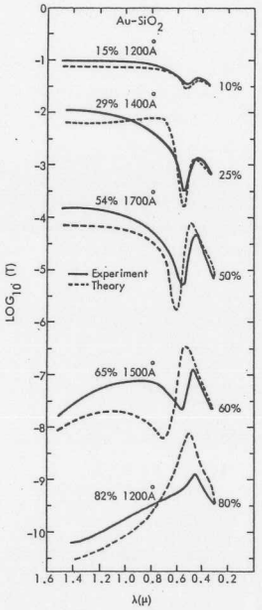


Fig. 10 Optical transmission as a function of light wavelength for a series of Au-SiO_2 samples. The metal volume fraction and the film thickness are labeled above each curve. Theoretical curves are normalized to the experimental values at 0.3 μm. For clarity, the curves are displaced with respect to one another.

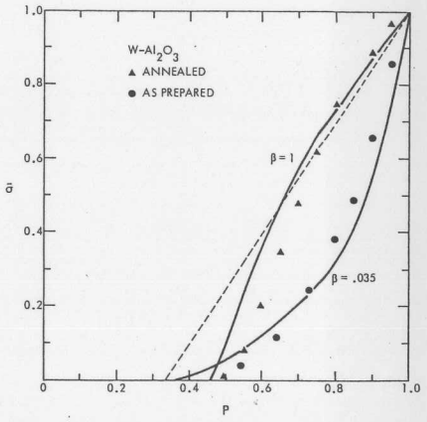


Fig. 11 Effective conductivity as a function of metal volume fraction p for samples of W-Al_2O_3 films. The solid lines are calculated from the theory. Dashed lines denote the Bruggeman result. The data are from Ref. [4].

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