Dielectric constant of a composite inhomogeneous medium

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We derive an expression for the effective dielectric constant of a composite medium considering the contributions from both the electric and the magnetic dipole terms. We show that the form of the size distribution of small metallic particles determines the value of the volume fraction at which a sharp increase in ac absorption of a composite material occurs. Depending on the width and mode radius of the size distribution, the effective dielectric constant of a composite medium can be increased by several orders of magnitude.

I. INTRODUCTION

The electromagnetic properties of inhomogeneous composite materials have been of considerable interest for a long time because of the great variety of situations in which these materials occur. Recent increases in activity in the field are at least partially caused by the interest in selective absorbers of solar and infrared radiation,[1] by an increasing number of applications in astronomy and atmospheric physics,[2] and by the indications that the electromagnetic behavior of the composite system may be very different from the behavior of individual components.[3]

Propagation of electromagnetic waves in such inhomogeneous composite media is often treated by assigning an effective dielectric constant to the composite medium. The best known examples of effective-medium theories are the Maxwell-Garnett[4] theory and the Bruggeman[5] theory. It has been shown[1,6,7] that the effective dielectric constant can be invoked by requiring the forward scattering amplitude to be equal to zero for the case of scattering of electromagnetic waves of given frequency on small particles forming a composite material, when placed in an effective medium. If particles of one material are dispersed in a continuous host of another material, we talk about a *separated-grain structure* which can be approximated by a layered sphere model. This case leads to the Maxwell-Garnett rule[4] and its generalizations. If the space is filled by a random mixture of two or more constituents, we talk about an *aggregate structure*. This aggregate structure is modeled by a random mixture of homogeneous spheres of individual materials, and it leads to the well-known Bruggeman rule[5] and its generalizations.

Until now the results of the scattering approach to the effective-medium theory have been derived assuming either a discrete size distribution of individual grains, or assuming all grains of the same size. We present the generalization of the scattering approach to the effective-medium theory by (a) considering a continuous size distribution of grains, (b) considering an arbitrary number of components of a composite material, and (c) taking into account both the contribution of electric and magnetic dipole terms.

In Sec. II we present a generalization of the Bruggeman-type effective-medium theory, including magnetic dipole and size distribution effects in an aggregate structure model. In Sec. III general equations of an aggregate structure model are reduced to a form suitable for numerical calculations considering a γ-type and log-normal size distributions. Numerical calculations demonstrate an increase in the imaginary part of a dielectric constant of a composite medium due to magnetic dipole and size distribution effects. In Sec. IV we present a generalization of Maxwell-Garnett-type arguments, including magnetic dipole and size-distribution effects in a separated-grain model. Results are summarized in Sec. V.

II. AGGREGATE STRUCTURE MODEL

Consider a medium composed of a random mixture of several small particle constituents with bulk dielectric constants ϵ_j. Such an aggregate structure can be modeled by a random mixture of homogeneous spheres of individual materials. Let $n_j(r)$ be the size distribution of grains of the jth components. Then the forward scattering amplitude $S(0)$ has the form[8,9]

$$S(0)=\frac{1}{2}\sum_j \sum_n (2n+1)\int n_j(r)[a_n(r,\epsilon_j)+b_n(r,\epsilon_j)]dr\ , \qquad (1)$$

where the sum over j runs over all components of a composite medium, the sum over n runs over all contributing partial waves, and a_n and b_n are the corresponding partial-wave scattering amplitudes (Mie scattering functions). We assume that all particles are much smaller than the wavelength λ of the considered electromagnetic radiation. In this case only $n=1$ partial wave will contribute to the scattering amplitude. Expanding a_1 and b_1 in the power series of the sphere's radius r, and keeping the leading term of each expansion, we obtain (in Ref. 9 an incorrect minus sign in the b_1 term is given)

$$(a_1)_j = \tfrac{2}{3} i x_j^3 \frac{\epsilon_j - 1}{\epsilon_j + 2} , \quad (2)$$

$$(b_1)_j = \tfrac{1}{45} i x_j^5 (\epsilon_j - 1) , \quad (3)$$

where $x = 2\pi r/\lambda$ is the size parameter of a spherical particle of radius r. The partial-wave scattering amplitudes a_1 and b_1 represent the electric and magnetic dipole contribution to the scattering amplitude. They are also referred to as surface-phonon and surface-plasmon modes.[10,11] Since $a_1 \sim x^3$ and $b_1 \sim x^5$, b_1 is usually neglected. However, in the regions of large dielectric constant, the b_1 term can become important. Therefore, we retain the magnetic dipole term b_1, and only when we want to obtain simple formulas which can be compared with the Bruggeman rule will we neglect the b_1 contribution to the scattering amplitude.

Using Eqs. (1)–(3), the forward scattering amplitude can be written as

$$S(0) = i \left[\frac{2\pi}{\lambda} \right]^3 \sum_j \int r^3 n_j(r) \left[\frac{\epsilon_j - 1}{\epsilon_j + 2} + \frac{1}{30} \left[\frac{2\pi}{\lambda} \right]^2 r^2 (\epsilon_j - 1) \right] dr . \quad (4)$$

From the condition that the forward scattering amplitude $S(0)$ vanishes when scatterers are placed in an effective medium characterized by an effective dielectric constant ϵ, follows the equation for ϵ in the form

$$\sum_j \int r^3 n_j(r) \left[\frac{\epsilon_j - \epsilon}{\epsilon_j + 2\epsilon} + \frac{1}{30} \left[\frac{\omega}{c} \right]^2 (\epsilon_j - \epsilon) r^2 \right] dr = 0 , \quad (5)$$

where the circular frequency ω and c are used instead of λ.

The third moment of the size distribution $n_j(r)$ is proportional to the volume V_j occupied by the particles of dielectric constant ϵ_j by the relation

$$\frac{4\pi}{3} \int r^3 n_j(r) dr = V_j . \quad (6)$$

The fifth moment of the size distribution $\int r^5 n_j(r) dr$ has no obvious direct physical meaning and in general it cannot be expressed as a function of only the bulk characteristics (that is, the volume V_j and the bulk dielectric constant ϵ_j) of components forming a composite inhomogeneous medium.

Thus the basic equation for an effective dielectric constant ϵ, for the case of a separated-grain structure, is

$$\sum_j \left[V_j \frac{\epsilon_j - \epsilon}{\epsilon_j + 2\epsilon} + \frac{2\pi}{45} \left[\frac{\omega}{c} \right]^2 (\epsilon_j - \epsilon) \int r^5 n_j(r) dr \right] = 0 , \quad (7)$$

where $n_j(r)$ is the size distribution and V_j is the volume fraction occupied by particles of dielectric constant ϵ_j.

We conclude that the size distribution of the grains $n_j(r)$ enters the equation for a dielectric constant ϵ of a composite medium only through the magnetic dipole term b_1 in the form of the fifth moment $\int r^5 n(r) dr$ of the size distribution. Numerical examples of how the grains' size distribution can affect the dielectric constant of a composite medium are treated in the following section.

If magnetic dipole terms in Eq. (7) are neglected, we have

$$\sum_j V_j \frac{\epsilon_j - \epsilon}{\epsilon_j + 2\epsilon} = 0 , \quad (8)$$

which is the usual result well known as the Bruggeman mixing rule.[6]

If all grains of the material characterized by a dielectric constant ϵ_j are of the same size, the size-distribution function $n_j(r)$ has the form of a δ function

$$n_j(r) = N_j \delta(r - r_j) , \quad (9)$$

where N_j is the number of grains of the jth type per unit volume. In this case the basic equation (7) for a dielectric constant of a composite medium reduces to

$$\sum_j V_j \left[\frac{\epsilon_j - \epsilon}{\epsilon_j + 2\epsilon} + \frac{1}{30} \left[\frac{\omega r_j}{c} \right]^2 (\epsilon_j - \epsilon) \right] = 0 , \quad (10)$$

which is identical with the equation (3.2) of Stroud and Pan.[6]

Consider a two-component composite material, where one of the components is a dielectric ϵ_1 (formally there is no distinction between the treatment of metals and insulators; by dielectric we mean the case when magnetic dipole term is small and can be neglected) and the other component is a metal characterized by a dielectric constant ϵ_2. Then general equation (7) for the effective dielectric constant ϵ has the form

$$V_1\frac{\epsilon_1-\epsilon}{\epsilon_1+2\epsilon}+V_2\frac{\epsilon_2-\epsilon}{\epsilon_2+2\epsilon}+\frac{2\pi}{45}\left[\frac{\omega}{c}\right]^2(\epsilon_2-\epsilon)\times\int r^5 n(r)dr=0\ , \qquad (11)$$

where V_1 and $V_2=1-V_1$ are the volume fractions of considered components and $n(r)$ is the grains' size distribution of a metallic component.

For completeness of our discussion we notice that if some of the components forming a composite medium contain grains for which the size is comparable to the wavelength λ of the considered electromagnetic radiation, then higher partial waves in the scattering amplitude have to be considered. In this case, the effective dielectric constant ϵ can be obtained by solving numerically the equation

$$S(0)=i\left[\frac{\omega}{c}\right]^3\epsilon^{3/2}\sum_j\left[\frac{3}{4\pi}V_j\frac{\epsilon_j-\epsilon}{\epsilon_j+2\epsilon}+\frac{1}{30}\left[\frac{\omega}{c}\right]^2(\epsilon_j-\epsilon)\int r^5 n_j(r)dr\right]$$
$$+\tfrac{1}{2}\sum_k\sum_n(2n+1)\int n_k(r)[a_n(r,\epsilon_k;\epsilon)+b_n(r,\epsilon_k;\epsilon)]dr=0\ , \qquad (12)$$

where the sum over j runs over all components contributing to the scattering amplitude only through the $n=1$ partial wave, the sum over k runs over the components for which higher partial waves cannot be neglected, and the sum over n runs over all contributing partial waves. Standard expressions for the partial-wave scattering amplitudes a_n and b_n for a case of a homogeneous spherical particle can be found in several available monographs.[8,9]

For the case of a two-component insulator-metal composite with metallic grains' size comparable to the wavelength λ, a simple iteration scheme for a dielectric constant ϵ of a composite medium can be developed. If ϵ_1 and ϵ_2 are dielectric constants of dielectric and metallic components, respectively, and V and $n(r)$ are a volume fraction and the size distribution of metallic components, the effective dielectric constants ϵ of a composite may be obtained from the equation

$$\epsilon=\epsilon_1\frac{A(1-V)+B(\epsilon)}{A(1-V)-2B(\epsilon)}\ , \qquad (13)$$

where

$$A=i\frac{12\pi^2}{\lambda^3}\ ,$$

and

$$B(\epsilon)=\int\sum_n(2n+1)[a_n(r,\epsilon_2/\epsilon)+b_n(r,\epsilon_2/\epsilon)]n(r)dr\ .$$

The first estimate of ϵ can be obtained from Eq. (11), assuming particles much smaller than the wavelength. This estimate is used to calculate $B(\epsilon)$ and a new value of ϵ is obtained from Eq. (13).

III. NUMERICAL EXAMPLES

The effect of a magnetic dipole term in Eq. (10) on the effective dielectric constant has been discussed at length by Stroud and Pan.[6] They found that inclusion of this term can increase the far-infrared attenuation constant by a factor of 10^2–10^3. The purpose of our numerical study will be to show that in addition to the above-mentioned increase the form of the size distribution can further increase the effective dielectric constant of a composite medium by several orders of magnitude, even if the mode radius of the size distribution and the volume fraction of metallic components are kept at the same value. Our numerical example has been chosen purely to illustrate the magnitude of the size-distribution effect. Application to high infrared absorption in metal-dielectric composites will be attempted later.

Log-normal and γ-type size distributions have been generally used for describing size distribution of small particles growing by coalescence.[12,13] A γ-type size distribution is given by

$$n(r)=ar^{\alpha}e^{-br}\ , \qquad (14)$$

where a, b, and α are constants characterizing the size distribution.

For the kth moment m_k we obtain

$$m_k\equiv\int_0^\infty r^k n(r)dr=a\frac{\Gamma(\alpha+k+1)}{b^{\alpha+k+1}}\ . \qquad (15)$$

Obviously, the zeroth-order moment is related to the total number of grains N per unit volume

$$N=m_0\equiv\int n(r)dr=a\frac{\Gamma(\alpha+1)}{b^{\alpha+1}}\ , \qquad (16)$$

and the third-order moment m_3 is related to the volume fraction V of the considered component

$$\frac{3}{4\pi}V = m_3 \equiv \int r^3 n(r)dr = a\frac{\Gamma(\alpha+4)}{b^{\alpha+4}} . \quad (17)$$

The fifth moment of the size distribution then can be expressed in the form of the third moment or of the volume fraction V as

$$m_5 \equiv \int r^5 n(r)dr = a\frac{\Gamma(\alpha+6)}{b^{\alpha+6}} = \frac{3}{4\pi}V\frac{\Gamma(\alpha+6)}{b^2\Gamma(\alpha+4)} . \quad (18)$$

Furthermore, the parameter b of the size distribution is related to the mode r_M of the size distribution by the relation

$$b = \frac{\alpha}{r_M} . \quad (19)$$

Consequently, the fifth moment of the γ-type distribution (14) can be written as a function of the mode r_M and parameter α in the form

$$m_5 = \frac{3}{4\pi}Vr_M^2\frac{\Gamma(\alpha+6)}{\alpha^2\Gamma(\alpha+4)} . \quad (20)$$

Thus from Eqs. (13) and (20) follows

$$V_1\frac{\epsilon_1-\epsilon}{\epsilon_1+2\epsilon}+V_2\frac{\epsilon_2-\epsilon}{\epsilon_2+2\epsilon} + V_2\frac{1}{30}\left[\frac{\omega}{c}\right]^2 r_M^2\frac{\Gamma(\alpha+6)}{\alpha^2\Gamma(\alpha+4)}(\epsilon_2-\epsilon)=0 , \quad (21)$$

which is a cubic equation for an effective dielectric constant ϵ.

In general, if a composite medium consists of several dielectric and several metallic components and if each metallic component is characterized by a γ-type size distribution, we obtain a more general form of Eq. (21),

$$\sum_j V_j\frac{\epsilon_j-\epsilon}{\epsilon_j+2\epsilon}+\frac{1}{30}\left[\frac{\omega}{c}\right]^2\sum_m V_m r_{Mm}^2\frac{\Gamma(\alpha_m+6)}{\alpha_m^2\Gamma(\alpha_m+4)} \times(\epsilon_m-\epsilon)=0 , \quad (22)$$

where the summation over j runs over all components and the summation over m runs over all metallic components (over components with non-negligible magnetic dipole contribution). The γ-type size distribution $n_m(r)$ of the metallic components are characterized by the mode radius r_{Mm} and a constant α_m.

If a log-normal size distribution

$$n(r)=\frac{1}{r\sqrt{2\pi}\ln\sigma_g}\exp\left[-\left[\frac{\ln(r/r_g)}{\sqrt{2}\ln\sigma_g}\right]^2\right]$$

with a geometric mean radius r_g and standard deviation σ_g is used instead of a considered γ-type size distribution, a slight change in the equations for numerical calculations is needed. The mode radius r_M and the factor $\Gamma(\alpha+6)/\alpha^2\Gamma(\alpha+4)$ of the γ-type size distribution have to be replaced by a geometric mean radius r_g and a factor of $\exp[8(\ln\sigma_g)^2]$, respectively.

To demonstrate the effect of the metallic grains' size distribution on the effective dielectric constant ϵ of a composite medium, we consider a two-component composite with dielectric constants $\epsilon_1=1$ and $\epsilon_2=\epsilon_D$, where Drude dielectric function ϵ_D is given by

$$\epsilon_D = 1-\frac{\omega_p^2}{\omega(\omega+i/\tau)} .$$

Plasma frequency ω_p and the relaxation time τ are chosen in such a way that $\omega_p\tau=100$. Considered frequency ω is determined by $\omega/\omega_p=10^{-2}$.

Given the size distribution $n(r)$, Eq. (21) can be used to calculate the effective dielectric constant ϵ as a function of the metallic component filling factor (volume fraction). The width of the size distribution (14) is determined by the constant α. The larger α is, the narrower is the size distribution. In Fig. 1 we have plotted $n(r)/n(r_M)$ where r_M is a mode radius for $\alpha=1$, 3, 10, and 100.

The effect of the mode radius on the effective dielectric constant ϵ of a two-component composite medium is shown in Fig. 2 for the case of a size distribution with $\alpha=1.0$ and with the mode radius r_M

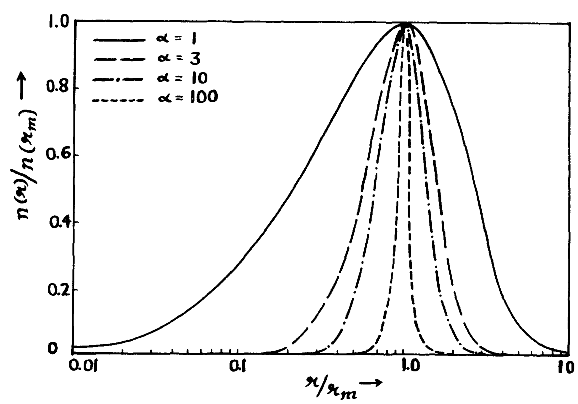

FIG. 1. With increasing parameter α, the size distribution, $n(r)/(n(r_m)$, changes from broad (with $\alpha=1$) to narrow, close to being a δ-function distribution (with $\alpha=100$).

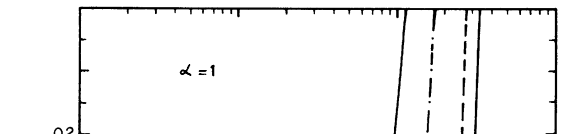

FIG. 2. Imaginary part of the dielectric constant of a composite material, Im(ϵ), as a function of volume fraction V of the metalliclike component. The calculations are performed for a size distribution with $\alpha=1$; $\omega_p\tau=100$ and $\omega/\omega_p=10^{-2}$. The values of the scaled mode radius $\omega_p r_M/c=0.1$, 0.5, and 1. For comparison, Im(ϵ) calculated from the Bruggeman mixing rule is also shown (curve B). The increasing mode radius r_M shifts the percolation threshold (which occurs at $V=0.33$ in the Bruggeman case), toward the smaller volume fractions.

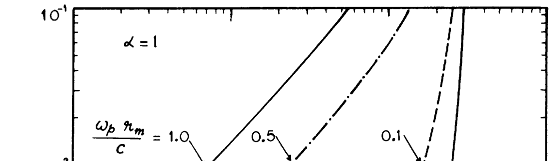

FIG. 3. Imaginary part of the dielectric constant of a composite medium, Im(ϵ), for the Bruggeman case (B) and for three different values of the mode radius r_M. In these cases $\alpha=1$, $\omega_p\tau=100$, and $\omega/\omega_p=10^{-2}$.

given by $\omega_p r_M/c=0.1$, 0.5, and 1.0. For comparison, also the effective dielectric constant ϵ calculated from a simple Bruggeman mixing rule (8) is shown. The dielectric-to-metal transition (percolation threshold) occurs in the Bruggeman case around the value of the filling factor $V=0.33$ as expected. If we generalize the percolation threshold for nonzero frequencies the effect of magnetic dipole term is to shift the percolation threshold towards small values of the filling factor. The amount of shift is a function of the mode radius. With $\omega_p r_M/c=1$, the percolation threshold is shifted to about $V=0.1$ at $\omega/\omega_p=10^{-2}$.

Even below the value of the percolation threshold, the metallic grains' size distribution has a considerable effect on the value of the effective dielectric constant ϵ. In Fig. 3 we have plotted Im(ϵ) as a function of the volume fraction V for the case of $\alpha=1$ and $\omega_p r_M/c=0.1$, 0.5, and 1.0 on a log-log scale. For comparison the Bruggeman case is also shown. We see that the increase of a mode radius by a factor of 10 (keeping the volume fraction V constant) can increase the imaginary part of the effective dielectric constant of a composite medium by a factor of 10^3.

Figures 4 and 5 similarly show the effect of the width of the size distribution on the percolation threshold and the imaginary part of effective dielectric constant ϵ. Depending on the width of the size distribution, the imaginary part of dielectric constant can be increased up to a factor of 10^3 compared to the value given by the Bruggeman mixing rule.

We conclude that the finite width of the grains' size distribution and the distribution's mode radius can produce a shift of percolation threshold towards smaller values of volume fraction of metallic components. Also, the value of the effective dielectric constant of a composite medium can be increased by

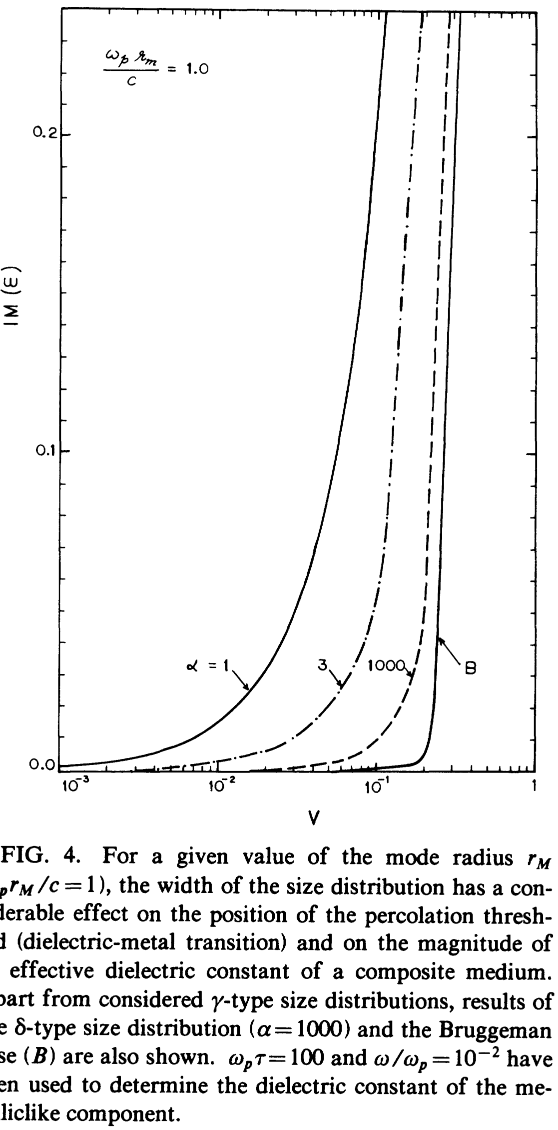

FIG. 4. For a given value of the mode radius r_M ($\omega_p r_M/c=1$), the width of the size distribution has a considerable effect on the position of the percolation threshold (dielectric-metal transition) and on the magnitude of an effective dielectric constant of a composite medium. Apart from considered γ-type size distributions, results of the δ-type size distribution ($\alpha=1000$) and the Bruggeman case (B) are also shown. $\omega_p\tau=100$ and $\omega/\omega_p=10^{-2}$ have been used to determine the dielectric constant of the metalliclike component.

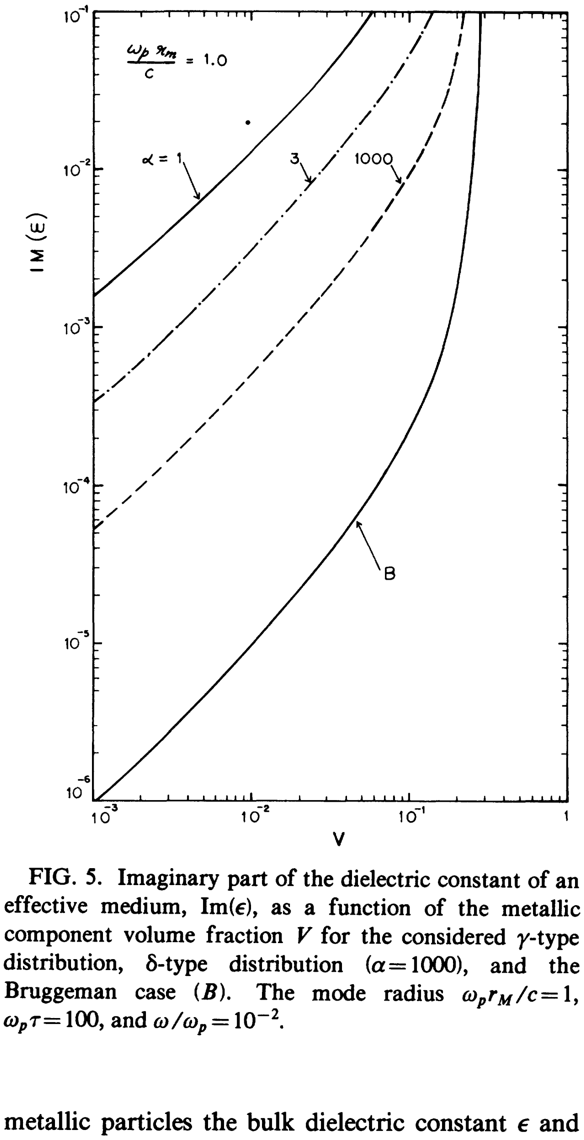

FIG. 5. Imaginary part of the dielectric constant of an effective medium, Im(ϵ), as a function of the metallic component volume fraction V for the considered γ-type distribution, δ-type distribution ($\alpha=1000$), and the Bruggeman case (B). The mode radius $\omega_p r_M/c=1$, $\omega_p\tau=100$, and $\omega/\omega_p=10^{-2}$.

several orders of magnitude not only from the value predicted by Bruggeman model, but also from the value predicted by δ-type function size distribution ($\alpha=1000$).

The anomalous far-infrared absorption of two-component small particle composites is a well-known fact.[3,14–16] Theoretical calculations are 1–3 orders of magnitude below the measured far-infrared absorption. We suggest that proper consideration of the metallic grains' size distribution may at least bring theoretical calculations closer to experimental results. The case of 1-μm palladium particles in the KCl matrix is treated by Chýlek *et al.*[17] It is possible that for considerably smaller metallic particles the bulk dielectric constant ϵ and plasma frequency ω_p will have to be modified due to boundary effects.

IV. SEPARATED GRAIN MODEL

Consider a case when several materials with dielectric constants ϵ_j are dispersed in a form of small grains in a host material of dielectric constant ϵ_J. A simplified model of this separated-grain structure consists of a spherical nucleus of dielectric constant ϵ_j surrounded by a spherical shell of the host medium with dielectric constant ϵ_J. The forward scattering amplitude $S(0)$ for the scattering of plane electromagnetic waves on an ensemble of such layered spheres can be written in the form

$$S(0)=\frac{1}{2}\sum_j\sum_n(2n+1)\int\int n_j(r,R)[a_n(r,R,\epsilon_j,\epsilon_J)+b_n(r,R,\epsilon_j,\epsilon_J)]dr\,dR \qquad (23)$$

where $n_j(r,R)$ is the size distribution of the layered spheres with the dielectric constant ϵ_j of the inner sphere of radius r and radius R of the outer sphere. The functions a_n and b_n are partial-wave scattering amplitudes[9,10] for the scattering of electromagnetic waves on a layered sphere. Summation over n runs over all contributing partial waves, and the summation over j runs over all components of the composite medium.

In the case where the size of the layered spheres is considerably smaller than the wavelength of the incoming radiation, and where dielectric constants of the components are not too large, we keep only the leading terms of a_1 and b_1,

$$a_1 = +ix^3\frac{2}{3}\frac{(\epsilon_J-1)(\epsilon_j+2\epsilon_J)+(r/R)^3(2\epsilon_J+1)(\epsilon_j-\epsilon_J)}{(\epsilon_J+2)(\epsilon_j+2\epsilon_J)+2(r/R)^3(\epsilon_J-1)(\epsilon_j-\epsilon_J)}, \tag{24}$$

$$b_1 = +ix^5\tfrac{1}{45}[(\epsilon_J-1)+(\epsilon_j-\epsilon_J)(r/R)^5], \tag{25}$$

where $x=2\pi R/\lambda$ is the size parameter of the outer spherical shell of radius R.

The general expression (23) for the forward scattering amplitude $S(0)$ contains the layered spheres' size-distribution function $n_j(r,R)$, which gives the number of layered spheres per unit volume with the inner radius between r and $r+dr$ and the outer radius between R and $R+dR$. While the radius r of the inner sphere is given by the size distribution $n_j(r)$ of the grains of material with the dielectric constant ϵ_j, the radius R of the outer spherical shell of the host material with dielectric constant ϵ_J is subjected to our choice within definite limits. To simplify the mathematical treatment of the model, we choose the ratio r/R to be the same for all layered spheres with the same material of an inner sphere. Therefore, for each j we can write

$$\left[\frac{r}{R}\right]_j = V_j^{1/3}, \tag{26}$$

with V_j being the fractional volume of a component with dielectric constant ϵ_j. Using Eqs. (23)–(26), the forward scattering amplitude can be written as

$$S(0)=i\left[\frac{2\pi}{\lambda}\right]^3\sum_j\int\frac{1}{V_j}r^3n_j(r)\left[\frac{(\epsilon_J-1)(\epsilon_j+2\epsilon_J)+V_j(2\epsilon_J+1)(\epsilon_j-\epsilon_J)}{(\epsilon_J+2)(\epsilon_j+2\epsilon_J)+2V_j(\epsilon_J-1)(\epsilon_j-\epsilon_J)}+\frac{1}{30}\left[\frac{2\pi}{\lambda}\right]^2\frac{1}{V_j^{2/3}}r^2[(\epsilon_J-1)+V_j^{5/3}(\epsilon_j-\epsilon_J)\right]dr\ . \tag{27}$$

From the consideration that the forward scattering amplitude $S(0)$ vanishes when scatterers are placed in an effective medium characterized by an effective dielectric constant ϵ, the basic equation for ϵ follows in the form

$$\sum_j\left[\frac{(\epsilon_J-\epsilon)(\epsilon_j+2\epsilon_J)+V_j(2\epsilon_J+\epsilon)(\epsilon_j-\epsilon_J)}{(\epsilon_J+2\epsilon)(\epsilon_j+2\epsilon_J)+2V_j(\epsilon_J-\epsilon)(\epsilon_j-\epsilon_J)}+\frac{2\pi}{45}\left[\frac{\omega}{c}\right]^2\left[\frac{\epsilon_J-\epsilon}{V_j^{5/3}}+\epsilon_j-\epsilon_J\right]\int r^5n_j(r)dr\right]=0\ . \tag{28}$$

We see again that the grains' size distribution $n_j(r)$ enters the equation for an effective dielectric constant ϵ through the magnetic dipole term in the form of the fifth moment of the size distribution.

By setting $\epsilon_J=\epsilon$ in Eq. (28) we obtain the case of homogeneous spheres considered earlier. In this case Eq. (28) reduces to Eq. (7) as expected.

If magnetic dipole terms in Eq. (28) can be neglected, the equation for the effective dielectric constant ϵ of a composite medium simplifies into

$$\sum_j\frac{(\epsilon_J-\epsilon)(\epsilon_j+2\epsilon_J)+V_j(2\epsilon_J+\epsilon)(\epsilon_j-\epsilon_J)}{(\epsilon_J+2\epsilon)(\epsilon_j+2\epsilon_J)+2V_j(\epsilon_J-\epsilon)(\epsilon_j-\epsilon_J)}=0\ , \tag{29}$$

which represents the generalization of the Maxwell-Garnett mixing rule following from the "no-scattering" condition.

In the simplest case of a two-component composite with dielectric constants ϵ_j and ϵ_J, Eq. (29) leads to

$$\epsilon=\epsilon_J\frac{(\epsilon_j+2\epsilon_J)+2V_j(\epsilon_j-\epsilon_J)}{(\epsilon_j+2\epsilon_J)-V_j(\epsilon_j-\epsilon_J)}\ , \tag{30}$$

which is just the Maxwell-Garnett mixing rule.

If the $2V_j(\epsilon_J-\epsilon)(\epsilon_j-\epsilon_J)$ terms are neglected with respect to the $(\epsilon_J+2\epsilon)(\epsilon_j+2\epsilon_J)$ terms in denominators of Eq. (29), we obtain

$$\epsilon=\epsilon_J\frac{1+2\sum_j V_j(\epsilon_j-\epsilon_J)/(\epsilon_j+2\epsilon_J)}{1-\sum_j V_j(\epsilon_j-\epsilon_J)/(\epsilon_j+2\epsilon_J)}\ , \tag{31}$$

which is a form of generalized Maxwell-Garnett rule for the case of a multicomponent system obtained by Wood and Ashcroft.[18]

Instead of neglecting terms $2V_j(\epsilon_J-\epsilon)(\epsilon_j-\epsilon_J)$ in (29) we may use the binomial expansion for denominators in Eq. (29) and keep only terms proportional up to V_j. We obtain a new simple algebraic expression for an effective dielectric constant ϵ of a composite medium

$$\epsilon=\frac{\epsilon_J}{4}\left\{1+9\sum_j V_j\frac{\epsilon_j-\epsilon_J}{\epsilon_j+2\epsilon_J}+\left[\left[1+9\sum_j V_j\frac{\epsilon_j-\epsilon_J}{\epsilon_j+2\epsilon_J}\right]^2+8\right]^{1/2}\right\}. \quad (32)$$

Since the last equation is the result of an approximation to Eq. (29) for the case of more than two components, it should not be used for the case of a two-component composite medium, which can be solved exactly and which leads to the Maxwell-Garnett relation (30).

If all grains of the jth medium are of the same size, the size distribution function $n_j(r)$ can be taken in the form of the δ function (9), and the basic equation (28) for the effective dielectric constant ϵ reduces to

$$\sum_j\left[\frac{(\epsilon_J-\epsilon)(\epsilon_j+2\epsilon_J)+V_j(2\epsilon_J+\epsilon)(\epsilon_j-\epsilon_J)}{(\epsilon_J+2\epsilon)(\epsilon_j+2\epsilon_J)+2V_j(\epsilon_J-\epsilon)(\epsilon_j-\epsilon_J)}+\frac{1}{30}\left[\frac{\omega r_j}{c}\right]^2\left[\frac{\epsilon_J-\epsilon}{V_j^{5/3}}+\epsilon_j-\epsilon_J\right]V_j\right]=0\,, \quad (33)$$

which is an analogy of Eq. (10) for the case of layered spheres. Similarly an analogy of Eq. (12) can be written for the considered case of the separated-grain model.

Finally, the use of γ-type size distribution functions of the form (14) allows us to replace the fifth moments of the size distributions in Eq. (28), by the volume fractions V_j, and Eq. (28) reduces to

$$\sum_j\left[\frac{(\epsilon_J-\epsilon)(\epsilon_j+2\epsilon_J)+V_j(2\epsilon_J+\epsilon)(\epsilon_j-\epsilon_J)}{(\epsilon_J+2\epsilon)(\epsilon_j+2\epsilon_J)+2V_j(\epsilon_J-\epsilon)(\epsilon_j-\epsilon_J)}+\frac{1}{30}\left[\frac{\omega r_{Mj}}{c}\right]^2\left[\frac{\epsilon_J-\epsilon}{V_j^{5/3}}+\epsilon_j-\epsilon_J\right]V_j\frac{\Gamma(\alpha_j+6)}{\alpha_j^2\Gamma(\alpha_j+4)}\right]=0\,, \quad (34)$$

where r_{Mj} is the mode radius and α_j is a parameter of the size distribution function (14).

For the case of log-normal size distributions the mode radius r_{Mj} and the factor $\Gamma(\alpha_j+6)/\alpha_j^2\Gamma(\alpha_j+4)$ has to be replaced by a geometric mean radius r_{gj} and a factor of $\exp[8(\ln\sigma_{gj})^2]$, respectively, but the form of the equation remains the same.

An explicit form of an equation for an effective dielectric constant of a composite medium in a separated-grain model depends on considered geometry. We have assumed $(r/R)_j=\text{const}$ for all grains of the jth kind (the same assumption is made by Hashin and Shtrikman[19] in their variational approach). Different geometry may lead to a different form of an expression for the dielectric constant of a composite medium. This has been found earlier for the case of electric dipole interaction.[20] Regardless of assumed geometry the inclusion of magnetic dipole interaction brings additional terms proportional to the fifth moment of the size distribution.

V. CONCLUSION

Assuming the no-scattering condition in the form of vanishing forward scattering amplitude and considering continuous size distribution of grains, arbitrary number of components, and contributions from both the electric and the magnetic dipole terms, we have derived Eqs. (7) and (28) for the effective dielectric constant ϵ of a composite medium using an aggregate structure model and separated-grain structure, respectively. We have found that in both cases the electric dipole contribution is dependent only on the bulk characteristics of components, namely on the volume fractions V_j and dielectric constants ϵ_j. On the other hand, the magnetic dipole contribution to the forward scattering amplitude depends on the microstructure of grains through the fifth moment of the size distribution $\int r^5 n_j(r)dr$. Consequently, the effective dielectric constant of a composite system depends on the form of the size distribution of metallic grains.

For the case of two dielectric components composites, our Eqs. (7) and (28) reduce to usual Bruggeman and Maxwell-Garnett mixing rules. For the case of multicomponent dielectric composites, Eq. (7) is identical to the generalized form of the Bruggeman mixing rule as derived by many researchers before. On the other hand, Eq. (28) reduces to a form given by Eq. (29), which represents the generalized form of the Maxwell-

Garnett mixing rule for a multicomponent system, as it follows from the "no-scattering" assumption.

Numerical examples demonstrating the effect of the size distribution were calculated for the case of aggregate structure model using a γ-type size distribution function. Numerical results suggest that the width and mode radius of the metallic grains' size distribution can shift the percolation threshold toward smaller values of the volume fraction of metallic component, and it can increase the effective dielectric constant of a composite material by several orders of magnitude.

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