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OPTICAL PROPERTIES OF SMALL-PARTICLE COMPOSITES

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ABSTRACT

A new theory for the effective dielectric constant of a small-particle composite system includes broadening of single-particle resonances by dipolar interactions and percolation at high particle density. Comparisons are made with effective medium theory, Maxwell-Garnett theory, resistor network models, and with optical measurements on metallic and dielectric composites.

INTRODUCTION

Both the Maxwell-Garnett theory (MGT)¹ and the effective medium theory (EMT)² have been used to calculate the effective dielectric constant and optical absorption of small-particle composite systems. However, neither theory is adequate. The infrared absorption spectrum of powders of ionic crystal cubes has a broad peak between the T₀ and L₀ frequencies.³ The MGT (for cubes) agrees roughly with experiment, but the experimental peak width is much greater than the theoretical width, and the predicted absorption peaks associated with the individual cube modes are not observed. An absorption peak often appears at the T₀ frequency; this is a mode with depolarization factor $n=0$, and it is not contained in the MGT. A system of metallic spheres (Ag in a SiO₂ matrix) has an absorption peak much broader than predicted by the MGT.⁴

The EMT theory for spheres has a mode with depolarization factor $n=0$ if the particle filling fraction $f > 1/3$; however, the sphere mode with $n \sim 1/3$ is absent for these f values. This theory therefore does not explain how absorption peaks corresponding to $n=0$ and $n \sim 1/3$ can appear simultaneously in ionic-crystal powders, and it also does not give the observed absorption peak for Ag spheres when $f=0.39$.

The new theory of the effective dielectric constant is an extension of the MGT which can treat particles of arbitrary shape. It includes both broadening effects of dipolar interactions between particles and a $n=0$ mode arising from percolation or clustering.

GENERAL THEORY

The electric dipole moment of a system of small particles in vacuum, with a uniform applied field E_0 , can be written⁵

$$M = v \langle \chi \rangle E_0, \quad (1)$$

where

$$\langle \chi \rangle = \sum_m \frac{C_m}{\chi^{-1} + 4\pi n_m}. \quad (2)$$

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Here v is the volume of the particles, which are composed of a material with dielectric susceptibility χ , while C_m and n_m are the strengths and depolarization factors of the dipole modes labeled by the index m . Imagine that the particle system forms a needle-shaped sample with the long axis in the direction of E_0 . If the sample has a homogenous effective susceptibility χ_{eff} , then one also has

$$M = V \chi_{\text{eff}} E_0, \quad (3)$$

where V is the volume of the needle. From Eqs. (1)-(3) one finds

$$\chi_{\text{eff}} = f \sum_m \frac{C_m}{\chi^{-1} + 4\pi n_m}, \quad (4)$$

where $f=v/V$ is the particle filling fraction.

The depolarization factors n_m lie in the range $0 \leq n_m \leq 1$ and are densely distributed for a many-particle system, so it is convenient to replace the sum over the discrete mode index m by an integral over the continuous variable n : $\sum_m C_m \rightarrow \int C(n)D(n)dn = \int g(n)dn$,

where $D(n)$ is the density of modes and $g(n) = C(n)D(n)$. Eq. (4) then becomes

$$\chi_{\text{eff}} = f \left[C_0 \chi + \int_0^1 \frac{g(n)dn}{\chi^{-1} + 4\pi n} \right]. \quad (5)$$

The separately written term $C_0 \chi$ comes from the mode with $n_m=0$; all other modes, with $n_m>0$, are included in the integral. The function $g(n)$ contains the dipole strength and density of the particle resonance modes, whereas C_0 is the strength of the percolation mode. The quantities $g(n)$ and C_0 depend only on the structure of the composite system, including the filling fraction f (they are independent of the material χ), and they obey the sum rule

$$C_0 + \int_0^1 g(n)dn = 1. \quad (6)$$

GAUSSIAN BROADENING MODEL

Every valid theory of the effective susceptibility can be cast into the form of Eq. (5), and different theories will yield different results for C_0 and $g(n)$. An extension of the MGT will be described; it includes random dipolar interactions which cause a Gaussian broadening function to appear in the theory.

First consider a randomly oriented single particle of volume v_p , in a field E . Its dipole moment is

$$\mu = v_p \langle \chi_p \rangle E, \quad (7)$$

where $\langle \chi_p \rangle$ is the single particle susceptibility, expressible in the form of Eq. (2). For a sphere, $\langle \chi_p \rangle = (\chi^{-1} + 4\pi/3)^{-1}$; for a cube,

see references 5 and 6. Imagine applying an electric field to a powder consisting of identical particles, and draw a large sphere with one of the particles at its center. The dipole moment of the central particle is

$$\mu_i = v_p \langle \chi_p \rangle (E_o + h_i \mu_i / v_p), \quad (8)$$

where E_o is the field at the central particle arising from the system outside the sphere, and $h_i \mu_i / v_p$ is the sum of the dipolar fields of the particles inside the sphere. The index i labels a given particle configuration, and h_i is a geometrical factor containing the dipolar sum. One can solve Eq. (8) for μ_i and take a configuration average by introducing the probability P_i of a configuration i . The average susceptibility of an interacting particle can then be written

$$\langle \chi_I \rangle = (v_p E_o)^{-1} \sum_i P_i \mu_i \quad (9)$$

The configuration average can be found by assuming that the particles other than the central particle are independently and randomly distributed in the large sphere, excluding a small spherical volume of radius r_{min} containing the central particle. That is, correlation between the "other" particles is neglected, and this allows the central limit theorem to be used, with the result

$$\langle \chi_I \rangle = \int_{-\infty}^{\infty} \frac{P(h) dh}{\langle \chi_p \rangle^{-1} - h} \quad (10)$$

where $P(h)$ is a Gaussian broadening function,

$$P(h) = (w \sqrt{2\pi})^{-1} \exp(-\frac{1}{2} h^2 / w^2), \quad (11)$$

with

$$w^2 = \frac{16}{15} \pi f v_p (r_{min})^{-3}. \quad (12)$$

Finally the Maxwell-Garnett theory is applied to these interacting particles with susceptibility $\langle \chi_I \rangle$, and one finds that the effective susceptibility of the composite system is

$$\chi_{eff} = \left[\frac{1}{\chi} + \frac{1-f}{f \langle \chi_I \rangle} \right]^{-1}. \quad (13)$$

If χ_{eff} is written in the form of Eq. (5), the percolation mode C_o does not appear explicitly, and a tail of the broadened single-particle resonance function $g(n)$ appears in the unphysical region $n < 0$. The percolation mode is introduced by taking its strength to

be equal to the total strength of the unphysical tail,

$$C_0 = \int_{-\infty}^0 g(n) dn, \quad (14)$$

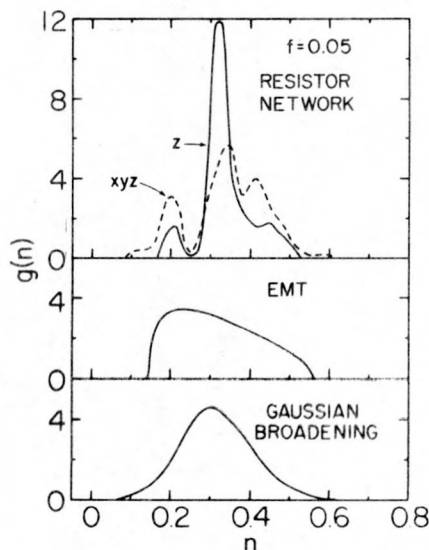
and thereafter setting $g(n) = 0$ for $n < 0$.

If f is very small or if interactions between particles are neglected, $P(h) \rightarrow \delta(h)$ and $\langle \chi_1 \rangle \rightarrow \langle \chi_p \rangle$. Eq. (13) then reduces to the usual Maxwell-Garnett theory for particles of arbitrary shape.⁵

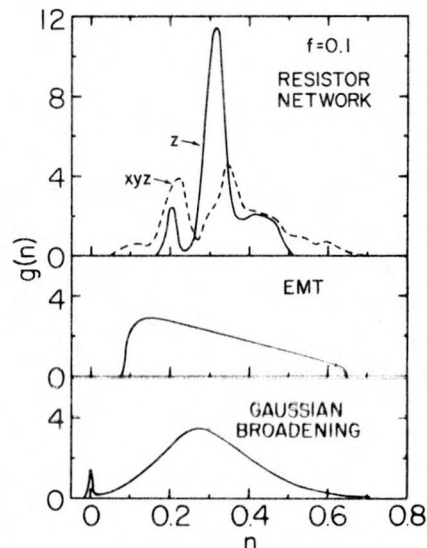
RESULTS

The particle resonance function $g(n)$ has been calculated for interacting spheres using the Gaussian broadening model, and it is shown in Fig. 1 using four values of f . The percolation mode C_0 is simulated by a peak at $n=0$. As f increases, the sphere mode broadens and its center shifts from $n=1/3$ to smaller values of n , while the percolation mode grows stronger. Fig. 1 also shows the EMT theory for spheres, written in the form of Eq. (5). The function $g(n)$ broadens asymmetrically as f increases, and for $f > 1/3$, the critical concentration for the onset of percolation, there is no remnant of a particle resonance peak.

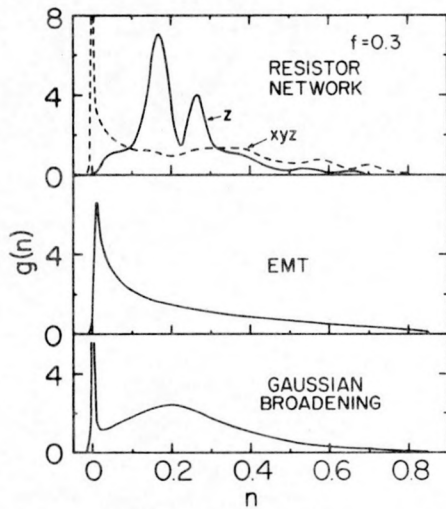
A random resistor network also has been used to simulate a composite system. An electric field is applied in the z direction to a cubic resistor network with host resistors of unit conductivity containing randomly located defect resistors with conductivity $1 + 4\pi\chi$. Each defect resistor in the z direction contributes $\chi \cdot \Delta V$ to the dipole moment, ΔV being the potential difference across the resistor. The dipole moment of a single defect resistor in the z direction becomes infinite if $\chi^{-1} = -4\pi/3$ and thus the defect simulates a sphere with depolarization factor $n=1/3$. Several defects simulate a group of interacting spheres. Defects in the x and y directions do not contribute to the dipole moment in the z



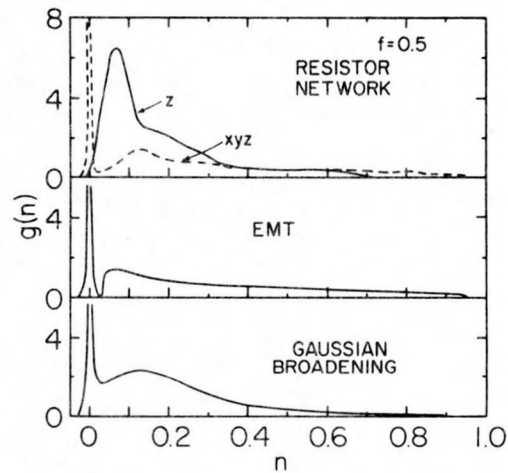
(a) $f=0.05$



(b) $f=0.1$



(c) $f=0.3$



(d) $f=0.5$

Fig. 1. Mode strength $g(n)$ as a function of depolarization factor n , with four values of the filling fraction f . Calculations using the Gaussian broadening model, the effective medium theory, and resistor network models are compared.

direction, but they broaden resonance structure arising from nearby z -directed defects. A calculation of the total dipole moment of the network gives an effective susceptibility in the form of Eq. (5). Fig. (1) shows the function $g(n)$ for networks with defects in only the z direction (solid curve) and with equal defect concentrations in the x , y , and z directions (dashed curve). Percolation occurs only in the xyz model.

Figure 2 contrasts the gradual increase of the percolation constant C_0 in the Gaussian broadening theory as f increases, with the sudden increase of C_0 in the EMT at the critical concentration $f=1/3$.

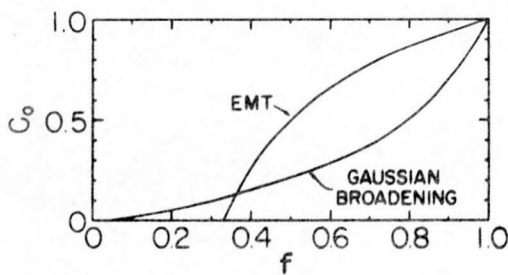


Fig. 2. Strength of the percolation mode C_0 as a function of f for the Gaussian broadening model and the effective medium theory.

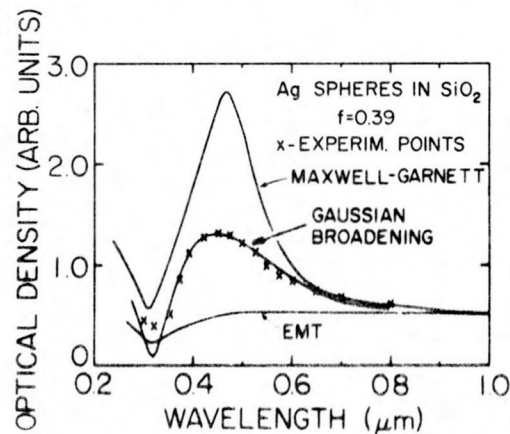


Fig. 3. Calculations of optical absorption of Ag spheres in SiO_2 using three theories, and a comparison with experiment.

Eq. (5) can be adapted easily to find the effective dielectric constant ϵ_{eff} of a system of particles with dielectric constant ϵ in a host with dielectric constant ϵ_h by writing $\chi = (\epsilon/\epsilon_h - 1)/4\pi$ and $\chi_{\text{eff}} = (\epsilon_{\text{eff}}/\epsilon_h - 1)/4\pi$. The Gaussian broadening theory has been used to calculate the optical absorption of Ag spheres in a SiO_2 host⁴, with a filling fraction $f=0.39$. It is evident from Fig. 3 that the new theory is in better agreement with experiment than either the MGT or the EMT. The theory has also been used to calculate the infrared absorption spectrum of ionic crystal powders. It reproduces qualitatively both the broad peak between ω_{TO} and ω_{LO} arising from particle modes and the narrow peak at ω_{TO} arising from clustering.

CONCLUSION

The Gaussian broadening model gives robust particle modes and describes powders in which the particles retain their identity for relatively large f values, but it becomes incorrect for f close to 1. It is qualitatively similar to the z-directed resistor network. In the EMT, just as in the xyz resistor network, the particles lose their identity as f increases, a behavior consistent with the particle-host symmetry.

The absence of a sharp percolation threshold in the Gaussian broadening model may be physically reasonable for samples consisting of a thin powder layer, in which particle clustering and deviations from randomness occur. It is a phenomenological model, in the sense that the cutoff radius, r_{min} in Eq. (12) was somewhat arbitrarily chosen as $r_{\text{min}} = \frac{1}{2}(v_p)^{\frac{1}{3}}$, a value for which the mode broadening agrees qualitatively with the resistor network calculations. The percolation strength C_0 arises in an unnatural manner, and it is inaccurate to neglect higher multipole interactions between particles. A combination of Gaussian broadening with the EMT might give a better theory for the effective dielectric constant.

ACKNOWLEDGEMENT

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