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Optical absorption by aggregates of small particles

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The optical absorption of a medium containing aggregates of small particles is calculated in the quasistatic limit using a diffuse-cluster model in which each aggregate is considered to be a sphere with a radially dependent filling factor. For metallic particles, aggregation broadens the Fröhlich resonance and increases the low-frequency absorption by about a factor of 100.

I. INTRODUCTION

There have been two general approaches for calculating the optical properties of an aggregate containing from 2 to 1000 or more small spherical particles. One approach is to do the calculation for selected aggregates containing a few (2 to 10) particles, and to assume that the results are representative for larger numbers of particles.[1-4] To facilitate such calculations, several approximations or assumptions are often made. These include, for example, the quasistatic approximation, the neglect of high-L multipolar polarizabilities, restriction to highly symmetric geometrical arrangements of spherical particles, and the use of a local dielectric function. An accurate calculation for such systems is difficult and time consuming. In fact, even a pair of touching spheres is a formidable system for which only limited progress has been made.[5,6]

The second approach is to consider the particle aggregate as a single homogeneous sphere with a suitably chosen average dielectric function $\bar{\epsilon}(\omega)$. Curtin and Ashcroft[7] have used a renormalization-group technique to find $\bar{\epsilon}(f,\omega)$, where f is the filling factor for particles in the aggregate, followed by averaging over f using a distribution function $N(f)$, to take account of the fact that different aggregates in a large sample should have different values of f. Hui and Stroud[8] have used a fractal model to obtain $\bar{\epsilon}(R,a,d_f,\omega)$ as a function of R, the radius of the spherical aggregate, a, the particle radius, and d_f, the fractal dimension. A primary objective of these theories is to explain the enhancement of the far-infrared absorption for metallic particles.[9,10] The theories can give reasonable results in the far-infrared region, but the high-frequency region has either not been investigated[7] or one finds what appears to be extraneous structure that has not been seen experimentally.[8] A satisfactory model should give enhanced far-infrared absorption and a structureless, broadened Fröhlich resonance at higher frequencies.[11]

Models which represent an aggregate by an equivalent homogeneous sphere have major deficiencies. Aggregates actually have irregular shapes and their "surfaces" are extremely rough. Furthermore, the distribution of particles is inhomogeneous and correlated in such a way that the validity of an average dielectric function is questionable. For example, the particles are generally touching, so the average dielectric constant should be close to the percolation threshold in the sense that the distribution of depolarization factors $g(n)$ should have appreciable weight near $n=0$.[12]

In this paper we examine a "diffuse cluster" model which corrects some of the deficiencies of the homogeneous sphere models discussed above. Spherical symmetry is assumed, but the filling factor of particles in the aggregate is assumed to fall off smoothly from the maximum value f_0 at the center to zero at the outer radius R. The filling factor $f(r)$ at a given distance r from the center determines an average dielectric function $\bar{\epsilon}(f)$, giving a radially dependent dielectric function $\bar{\epsilon}(r)$. The resulting "diffuse cluster" can be considered as a statistical average over a large number of aggregates with irregular shapes, and it takes into account the fact that an average cluster has a greater density of particles at the center than near the edge. We shall calculate the optical absorption of a medium containing a small filling factor of diffuse clusters of metallic particles. The spectral distribution of depolarization factors, $g(n)$, will also be determined in order to allow a material-independent comparison with other theories.

II. THEORY AND DISCUSSION

The first step is to find the radially dependent average dielectric function $\bar{\epsilon}(r)$ for the diffuse cluster. We take a simple functional form for the filling factor of particles in the cluster,

$$f(r)=f_0[1-(r/R)^u]\ , \tag{1}$$

where f_0, the filling factor at $r=0$, and the exponent u are adjustable parameters, and R is the radius of the cluster. At each radius r, the Bruggeman effective-medium theory[13] is used to find the average dielectric function $\bar{\epsilon}(r)$,

$$\frac{\epsilon-\bar{\epsilon}(r)}{\epsilon+2\bar{\epsilon}(r)}f(r)+\frac{\epsilon_h-\bar{\epsilon}(r)}{\epsilon_h+2\bar{\epsilon}(r)}[1-f(r)]=0\ , \tag{2}$$

where ϵ is the dielectric function of the particles and ϵ_h is the dielectric function of the surrounding medium.

General methods have been developed to calculate the electromagnetic properties of a sphere with a radially dependent dielectric function.[14] For simplicity we shall use the quasistatic approximation, in which the sphere is much smaller than the wavelength of light, and electric dipole absorption is assumed to predominate. The sphere is imagined to consist of a large number of thin spherical shells, each with a different dielectric function. Using an impedance transfer method, the multipole polarizability α_l of the sphere can be determined, although only the dipole ($l=1$) polarizability is needed to calculate the absorption.

Consider a spherical shell of inner radius r_1 and outer radius r_2, with a constant dielectric function $\bar{\epsilon}(r')$, $r_1<r'<r_2$. The scalar potential $V(\mathbf{r})$ and radial displacement $D_r(\mathbf{r})$ in the shell are

$$V(\mathbf{r})=(C_1r^l+C_2r^{-l-1})Y_{lm}(\theta,\varphi)\ , \tag{3}$$

$$\begin{aligned} D_r(\mathbf{r})&=-\bar{\epsilon}\frac{\partial V}{\partial r} \\ &=\bar{\epsilon}[-lC_1r^{l-1}+(l+1)C_2r^{-l-2}]Y_{lm}(\theta,\varphi)\ . \end{aligned} \tag{4}$$

Define the admittance

$$W(r)=-\frac{r}{l}\frac{D_r(r)}{V(r)}\ , \tag{5}$$

which is continuous across the interface between adjacent shells. Suppose that $W(r_1)$ is known; then Eqs. (3)–(5) can be used to solve for C_1/C_2 in terms of $W(r_1)$. Then using the same equations at $r=r_2$ one finds

$$W(r_2)=\frac{\bar{\epsilon}\left[\left[\rho+\frac{l+1}{l}\right]W(r_1)+\frac{l+1}{l}(\rho-1)\bar{\epsilon}\right]}{(\rho-1)W(r_1)+\left[\frac{l+1}{l}\rho+1\right]\bar{\epsilon}}\ , \tag{6}$$

where $\rho=(r_2/r_1)^{2l+1}$. The admittance at the surface of a small central sphere of radius r_0 and dielectric function $\bar{\epsilon}(0)$ is

$$W(r_0)=\bar{\epsilon}(0)\ . \tag{7}$$

Starting with Eq. (7) and using Eq. (6) repeatedly, one can determine $W(R)$ at the outer radius $r=R$.

In the region $r>R$ the scalar potential is the sum of an externally applied potential and the induced potential,

$$V(\mathbf{r})=C(r^l-\alpha_l r^{-l-1})Y_{lm}(\theta,\varphi)\ , \tag{8}$$

where α_l is the unknown multipolar polarizability. Calculating $D_r(\mathbf{r})=-\epsilon_h(\partial V/\partial r)$, where ϵ_h is the spatially constant dielectric function of the surrounding medium and using Eq. (5) at $r=R$, we find the polarizability,

$$\alpha_l=\frac{W(R)-\epsilon_h}{W(R)+\frac{l+1}{l}\epsilon_h}R^{2l+1}\ . \tag{9}$$

Instead of determining $W(R)$ by repeated application of Eq. (6) for a larger number of thin spherical shells, one can also numerically integrate the differential form of Eq. (6),

$$\frac{dW}{dr}=r^{-1}\left[l+1+l\frac{W(r)}{\bar{\epsilon}(r)}\right][\bar{\epsilon}(r)-W(r)] \tag{10}$$

from $r=0$ to $r=R$ with the initial values $W(0)=\bar{\epsilon}(0)$ and $W'(0)=0$.

The final step is to find the absorption coefficient of a medium containing these diffuse-cluster particle aggregates and to compare it with the absorption coefficient if the particles are separated. The average dielectric function of a medium containing spherical particles with dipole polarizability α_1, volume v and filling factor $f \ll 1$ is

$$\epsilon_{\mathrm{av}}=1+4\pi f\alpha_1/v\ , \tag{11}$$

and the absorption coefficient is

$$\mathscr{A}=(2\omega/c)\mathrm{Im}(\epsilon_{\mathrm{av}})^{1/2}\ , \tag{12}$$

where for simplicity we have taken $\epsilon_h=1$ for the surrounding medium. For the separated spheres, each of radius a, the polarizability is $\alpha_1=a^3(\epsilon-1)/(\epsilon+2)$, and the filling factor is $f=f_1$. If the same amount of material is in spherical aggregates of radius R, one can show, using Eq. (1), that the filling factor of these larger spheres is $f=(u+3)f_1/uf_0$. The polarizability α_1 of these spheres is given by Eq. (9). It is convenient to calculate a dimensionless absorption coefficient $A=\mathscr{A}c(f_1\omega_p)^{-1}$ where ω_p is the plasma frequency of the metallic particles. We find, for the separated spheres,

$$A_S=3\frac{\omega}{\omega_p}\mathrm{Im}\left[\frac{\epsilon-1}{\epsilon+2}\right] \tag{13}$$

and for the aggregated spheres,

$$A_C=3\frac{\omega}{\omega_p}\left[\frac{u+3}{uf_0}\right]\mathrm{Im}\left[\frac{W(R)-1}{W(R)+2}\right]\ . \tag{14}$$

The absorption coefficients A_S and A_C have been calculated using a free-electron dielectric function $\epsilon=1-\omega_p^2/\omega(\omega+i\gamma)$ with parameters representing Sn: $\omega_p=1.15\times10^{15}\ \mathrm{s}^{-1}$, $v_F=1.24\times10^{8}$ cm/s. The electron mean free path is taken to be $L=25$ Å, giving $\gamma=v_F/L\omega_p=0.043$. In Eq. (1) the central filling factor is $f_0=0.5$ and the exponent is $u=1$. Figure 1 shows A_C and A_S as functions of the frequency ratio ω/ω_p. It is

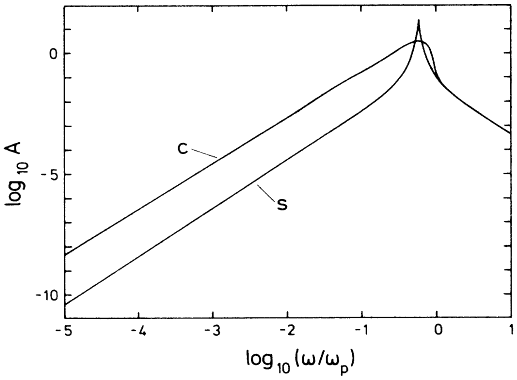

FIG. 1. The dimensionless absorption coefficient of a medium containing aggregated metallic spheres (A_C) and separated spheres (A_S) as a function of the frequency ratio ω/ω_p. The values of the parameters in the cluster model are $f_0=0.5$ and $u=1$. The sphere material is Sn (see the text).

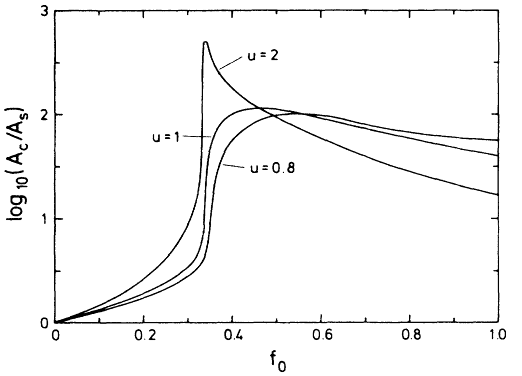

FIG. 2. The ratio of the absorption of aggregated spheres to that of separated spheres (A_C/A_S) at the frequency $\omega=10^{-5}\omega_p$, as a function of the central filling fraction f_0, for various values of the exponent u.

evident that clustering broadens the dipole absorption peak and gives a low-frequency enhancement by a factor of about 100. There are no spurious peaks at any frequency, and the absorption is similar qualitatively to that found by Bohren and Huffman using a continuous distribution of depolarization factors.[11] The results are independent of the cluster radius R, apart from the breakdown of the quasistatic approximation for R greater than a few hundred Å. The electron mean free path $L=25$ Å implies particle radius $a \gtrsim 25$ Å.

The enhanced low-frequency absorption can be understood qualitatively by noting that the Bruggeman average dielectric function $\bar{\epsilon}$ gives very large low-frequency absorption if f is near the percolation threshold $f_c=\frac{1}{3}$. Therefore the low-frequency absorption occurs primarily at the radius r such that $f(r)=f_c$. This interpretation is supported by Fig. 2, which shows the ratio A_C/A_S plotted as a function of f_0 for several values of u. If $f_0<\frac{1}{3}$ there is no value of r for which $f(r)=f_c$, and A_C/A_S is not large. For $u=2$ there is an especially high peak in A_C/A_S at $f_0\sim\frac{1}{3}$, since in this case there is a large central region where $f(r)\sim f_c$.

The spectral distribution of depolarization factors $g(n)$, which is defined by writing the average dielectric function in the form[15,16]

$$\epsilon_{\text{av}}=1+f_1\int_0^1 \frac{g(n')dn'}{(\epsilon-1)^{-1}+n'} \tag{15}$$

can be calculated by letting $(\epsilon-1)^{-1}=-(n+is)$, where s is a small positive constant. Using the relation

$$\lim_{s\to 0}\text{Im}(x-is)^{-1}=\pi\delta(x)\ ,$$

we find

$$\begin{aligned} g(n)&=\lim_{s\to 0}(\pi f_1)^{-1}\text{Im}\epsilon_{\text{av}} \\ &=\lim_{s\to 0}\frac{3(u+3)}{\pi u f_0}\text{Im}\left[\frac{W(R)-1}{W(R)+2}\right] . \end{aligned} \tag{16}$$

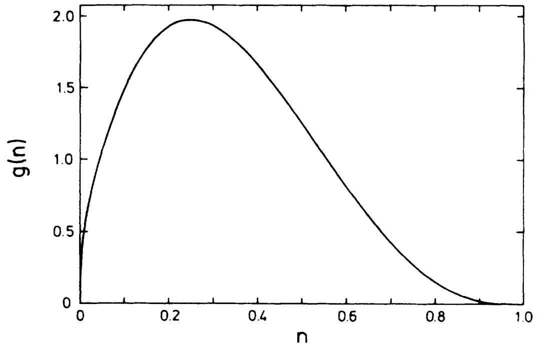

FIG. 3. The spectral distribution of depolarization factors for aggregated spheres, $g(n)$, as a function of n, with $f_0=0.5$ and $u=1$.

Figure 3 shows the spectral distribution $g(n)$ for aggregated spheres as a function of n;[17] this can be contrasted with $g(n)=\delta(n-\frac{1}{3})$ for separated spheres. The width of $g(n)$ is responsible for the broad absorption peak in aggregates, and the large value of $g(n)$ near $n=0$ is responsible for the enhanced low-frequency absorption. This spectral distribution is qualitatively similar to an ansatz for $g(n)$ which was proposed in Ref. 12; however the ansatz had even larger values near $n=0$, giving a low-frequency absorption enhancement factor of about 10^4. For $n<10^{-3}$ we find $g(n)\propto n^{1.2}$, whereas for the ansatz of Ref. 6, $g(n)\propto n$. At high frequencies ($\omega \gtrsim \gamma$) the absorption for aggregates is approximately independent of the damping parameter γ in the dielectric function, since here the large width of $g(n)$ is the dominant factor in determining the absorption. However, at low frequencies ($\omega \lesssim \gamma$) A_C and A_S are both proportional to γ and the ratio A_C/A_S is independent of γ. Both A_C and A_S are independent of the particle size, apart from the possible size dependence of the mean free path L.

As mentioned in the introduction, one should take into account the proximity effects of the touching particles in the aggregate, and the Bruggeman theory for $\bar{\epsilon}$ does not do this correctly. Using the qualitative arguments presented in Ref. 12, we would expect that the inclusion of proximity effects would increase the low-frequency enhancement of A_C and cause the enhancement to be less dependent on the choice of the central density f_0. Other refinements of the theory would be to include magnetic dipole absorption and absorption due to an oxide layer on the particles.[18]

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