Optical absorption by clusters of small metallic spheres

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An ansatz for the distribution of depolarization factors, based on a theory of the optical response of nearly touching spheres, is used to calculate the optical absorption of a medium containing isolated clusters of small metallic spheres. The calculated absorption agrees qualitatively with experiments over the entire frequency range. In the far-infrared region we find enhanced absorption and predict a small deviation from an ω^2 frequency dependence.

I. INTRODUCTION

The anomalously large far-infrared absorption of small metallic particles has been the subject of numerous experimental and theoretical studies.[1-6] The particles are generally spherical, with radii on the order of 100 Å and are contained in an insulating host. Far-infrared measurements can be summarized by writing the absorption coefficient as

$$\alpha = Kf\omega^2 , \tag{1.1}$$

where f is the volume fraction of the particles, ω is the photon frequency, and K depends only weakly on frequency ω, particle material, and radius a. The weak dependence on particle size suggests that (i) magnetic dipole absorption is not involved in the enhanced absorption, (ii) the electron mean free path, which enters into the electric dipole absorption, is determined by scattering within the particle rather than scattering from the surface.

Recent experiments and theories[5,6] suggest that particular clustering is responsible for the enhancement. Sen and Tanner[5] have attempted to model particle clusters by randomly oriented needles. By making the length/width ratio of the needles large, the depolarization factor L along the needle axis is small, leading to a low-frequency electric dipole resonance. This resonance can give low-frequency absorption many orders of magnitude larger than predicted for spherical particles, but one does not find even an approximate ω^2 dependence as in Eq. (1.1). They conclude that clusters cannot be considered as needle-shaped particles.

Curtin and Ashcroft[6] consider three models of fairly compact, roughly spherical clusters of radii $R \sim 2000$ Å, much larger than the individual particle radii a. In their first model, a fused cluster model, the particles are connected by conducting paths. The magnetic dipole absorption, which is proportional to the square of the particle size, is thereby greatly enhanced, as it contains the factor R^2 in place of a^2. In this model $\alpha \propto \omega^2$. Their second model, the cluster percolation model, considers clusters as spheres with a distribution of filling fraction f of particles within each sphere. Each spherical cluster has a dielectric function $\epsilon(f,\omega)$. By choosing a reasonable distribution of filling fractions f, they find that the Fröhlich resonance factor $[\epsilon(f,\omega)+\epsilon_h]^{-1}$, ϵ_h being the dielectric function of the host material, leads to enhanced absorption. However, $\alpha(\omega) \propto \omega$ rather than ω^2. In their third model, the cluster tunnel function model, each particle in the cluster is considered to be joined to its neighbor by a resistor and capacitor in parallel. This model again gives enhanced absorption with $\alpha(\omega)=\omega^2$ as $\omega \to 0$, but there may be large deviations from an ω^2 behavior at frequencies that are somewhat higher but still in the far infrared.

With the exception of the fused cluster model, all of these models have some difficulty obtaining sufficient absorption together with an ω^2 dependence at low frequencies. None of the models gives a reasonable frequency dependence over the entire frequency range, from the far infrared to the ultraviolet. The clusters often observed experimentally have a loose, open appearance, and are neither needlelike nor compact.

In this work we propose an ansatz for the distribution of dipolarization factors which is suggested by calculations of optical absorption by pairs and chains of spherical particles. The absorption is calculated over the entire frequency range, from the far infrared to the plasma frequency; the results appear to be consistent with experiments, even though the low-frequency dependence differs slightly from ω^2.

II. OPTICAL ABSORPTION OF CLUSTERED SPHERICAL PARTICLES

A. Average dielectric constant

We take a system of clustered spherical metallic particles with a small volume filling fraction $f \ll 1$. The particles are assumed small enough that retardation can be neglected, and one has only electric dipole absorption.[7,8] The host material is taken to be vacuum ($\epsilon_h = 1$). A realistic dielectric constant ϵ_h for the host can easily be included, as will be discussed below, but the qualitative behavior of the optical absorption is not affected by the

value of ϵ_h. The sphere radius $a \gtrsim 50$ Å, and we neglect effects of band structure so we use a Drude dielectric function

$$\epsilon(\omega)=1-\omega_p^2/\omega(\omega+i/\tau) \tag{2.1}$$

for the sphere material.[9]

The average dielectric constant of the medium can be written in the form

$$\epsilon_{\rm av}\approx 1+4\pi f\langle\chi\rangle\ , \tag{2.2}$$

where

$$\langle\chi\rangle=\frac{1}{4\pi V}\sum_i \frac{v^i}{3}\sum_{\alpha=1}^{3}\sum_m \frac{C^i_{\alpha\alpha}(m)}{[\epsilon(\omega)-1]^{-1}+n^i_m} \tag{2.3}$$

is the average electric susceptibility of the clusters.[10] The susceptibility of a given cluster, denoted by the index i, is expressed as a sum over modes labeled by the index m, with depolarization factors n^i_m and dipole strengths $C^i_{\alpha\alpha}(m)$, where α is a Cartesian index. An average over orientation is given by $\frac{1}{3}\sum_\alpha$; v^i is the volume of the particles in cluster i and V is the total volume of the particles included in the average. The depolarization factors n^i_m are a set of numbers lying in the range $0<n^i_m<1$. When the above averages are performed, the values of n^i_m will become continuously distributed, leading to the result[11,12]

$$\epsilon_{\rm av}=1+f\int_0^1 \frac{g(n)}{[\epsilon(\omega)-1]^{-1}+n}dn\ , \tag{2.4}$$

where $g(n)dn$ is the average number of depolarization factors lying in the range $(n, n+dn)$, multiplied by their average dipole strengths. The depolarization factor is often denoted by the symbol L; in this work we use n in order to avoid confusion with L, which labels the multipolar polarizability of a sphere.

The dipole strengths $C^i_{\alpha\alpha}(m)$ and depolarization factors n^i_m which appear in Eq. (2.3) satisfy the sum rules

$$\sum_m C^i_{\alpha\alpha}(m)=1\ , \tag{2.5}$$

which is equivalent to the oscillator strength sum rule, and

$$\sum_{\alpha=1}^{3}\sum_m C^i_{\alpha\alpha}(m)n^i_m=1\ , \tag{2.6}$$

which states that the average depolarization factor of an arbitrary cluster is the same as that of a sphere.[13] As an example, for an ellipsoid, where there is only one mode, with dipole strength 1, along each axis, this sum rule gives $n_1+n_2+n_3=1$, where n_1, n_2, and n_3 are the depolarization factors along the three axes.[14] For the trivial case of a sphere, $n_1=n_2=n_3=\frac{1}{3}$. The function $g(n)$ in Eq. (2.4) satisfies the corresponding sum rules

$$\int_0^1 g(n)dn=1\ , \tag{2.7}$$

and

$$\int_0^1 ng(n)dn=\tfrac{1}{3}\ , \tag{2.8}$$

which is valid for $f\ll 1$.[15]

The optical absorption coefficient is calculated from the expression

$$\alpha=\frac{2\omega}{c}{\rm Im}[(\epsilon_{\rm av})^{1/2}] \tag{2.9}$$

$$\approx\frac{\omega}{c}f\,{\rm Im}\left[\int_0^\infty \frac{g(n)}{(\epsilon-1)^{-1}+n}dn\right]\ . \tag{2.10}$$

If the host has a dielectric constant $\epsilon_h\neq 1$, Eq. (2.10) must be multiplied by $(\epsilon_h)^{1/2}$, and the ϵ which appears in the integrand must be replaced by ϵ/ϵ_h.

B. Ansatz for $g(n)$

We cannot actually calculate $g(n)$ starting with Eqs. (2.2) and (2.3), since we would need information about the sphere configurations in all clusters as well as the depolarization factors n^i_m and dipole strengths $C^i_{\alpha\alpha}(m)$ for each cluster. Instead, we use calculations for simple clusters and make an ansatz for $g(n)$ which appears consistent with these calculations. Although there have been many calculations of the polarizability of sphere clusters of various kinds, no calculation has been able to obtain accurate results in the limit of touching spheres.

The dipole polarizability of a cluster involves infinitely many multipolar polarizabilities of the individual spheres in the cluster. As the spheres approach each other, the high-L multipoles become increasingly important. Calculations by Clippe *et al.*[16] and by Gérardy and Ausloos[17] for several kinds of clusters are generally restricted to dipolar ($L=1$) terms, although some calculations keep up to octupolar ($L=3$) terms. Ruppin[18] has treated a cluster of two spheres by introducing bipolar coordinates; this method also becomes inaccurate for nearly touching spheres.

We shall consider in detail the calculations for a pair of spheres described in Refs. 19 and 20. The spheres have equal radii a, and their centers lie on the z axis and are separated by a distance D. A spacing parameter $\sigma=D/2a$ is equal to 1 if the spheres touch. These calculations are more accurate than those of Refs. 16–18 because multipolar polarizabilities up to order $L=50$ are kept; this allows good results to be found for nearly touching spheres ($\sigma\gtrsim 1.01$). Since the modes evolve continuously from those of an isolated sphere as the spheres are brought together from an infinite separation, each mode can be labeled by the index l, equal to the order L of the multipolar polarizability of an isolated sphere. Different symbols l and L are used because at a *finite* separation between spheres a mode with a given index l involves infinitely many multipole orders L.

The susceptibility of the pair of spheres, for an electric field in the z direction, is

$$\chi_{||}=\frac{1}{4\pi}\sum_{l=1}^{\infty}\frac{C_{||}(l)}{(\epsilon-1)^{-1}+n_{||}(l)}\ , \tag{2.11}$$

and for an electric field in the x or y directions,

$$\chi_{\perp}=\frac{1}{4\pi}\sum_{l=1}^{\infty}\frac{C_{\perp}(l)}{(\epsilon-1)^{-1}+n_{\perp}(l)}\ . \tag{2.12}$$

Here $C_{||}(l)$, $n_{||}(l)$, $C_{\perp}(l)$, and $n_{\perp}(l)$ depend only on the spacing σ. For spheres with an infinite separation ($\sigma \to \infty$), the depolarization factors are $n_{||}(l)=n_{\perp}(l)=l/(2l+1)$, and all of the strength is in the $l=1$ (dipole) mode: $C_{||}(1)=C_{\perp}(1)=1$, $C_{||}(l)=C_{\perp}(l)=0$ for $l>1$.

How do these modes change as the spheres are moved into contact? Consider first the $\perp$ modes, for which the solution converges rapidly even for touching spheres.[20] As σ decreases, all of the $n_{\perp}(l)$ increase. For example, as σ goes from ∞ to 1, $n_{\perp}(1)$ changes from 0.33 to 0.36, $n_{\perp}(2)$ from 0.40 to 0.42, $n_{\perp}(3)$ from 0.43 to 0.44; the values of all $n_{\perp}(l)$ remain less than $\frac{1}{2}$. We see that the shift in positions is small. There is some transfer of strength from the $l=1$ mode into higher-l modes. At $\sigma=1$ the average depolarization factor is

$$\langle n_{\perp} \rangle = \sum_{l=1}^{\infty} C_{\perp}(l) n_{\perp}(l) = 0.375 , \tag{2.13}$$

which is a moderate change from $\langle n_{\perp} \rangle = \frac{1}{3}$ at $\sigma=\infty$.

For the $||$ modes, a solution was found only for $\sigma > 1.01$, but this gives us important insight into what happens when the spheres touch at $\sigma=1.0$. There is a remarkable shift of the depolarization factors: as $\sigma \to 1$ every $n_{||}(l) \to 0$ for a fixed value of l. The modes continue to leave the accumulation point $n=\frac{1}{2}$ and move down to $n=0$, so at $\sigma=1$ there must be a continuous distribution of modes between $n=0$ and $n=\frac{1}{2}$. This behavior is similar to that which occurs for two touching cylinders, where there is an exact solution.[21] The small-l modes carry significant strength with them as they move to smaller n values, as is evident from Fig. 8 of Ref. 20. Of course, any given mode eventually loses its strength as it approaches $n=0$. Rewriting the sum rule (2.6) in the present notation, we have

$$\sum_{l=1}^{\infty} C_{||}(l) n_{||}(l) + 2 \sum_{l=1}^{\infty} C_{\perp}(l) n_{\perp}(l) = 1 \tag{2.14}$$

or

$$\langle n_{||} \rangle + 2 \langle n_{\perp} \rangle = 1 . \tag{2.15}$$

Using the value of $\langle n_{\perp} \rangle$ given in Eq. (2.13), we find $\langle n_{||} \rangle = 0.25$ when $\sigma=1$, which is a downward shift from the value $\langle n_{||} \rangle = \frac{1}{3}$ at $\sigma=\infty$. The modes for other configurations of spheres, such as a linear chain, a square lattice, or a cubic lattice, behave in a similar way qualitatively as the spheres approach each other if the applied electric field has a component along the lines joining sphere centers,[20] and we assume that this is true also for irregular clusters.

We now imagine carrying out the average in Eq. (2.3) which leads to the function $g(n)$ in Eq. (2.4). If the system contained only identical touching sphere pairs, $g(n)$ would consist of a continuous function in the range $0<n<\frac{1}{2}$, originating from the $||$ modes, and a series of spikes in the range $0.36 \le n \le \frac{1}{2}$, originating from the $\perp$ modes. If the spheres have unequal sizes, $g(n)$ is qualitatively similar, but is more closely centered at $n=\frac{1}{3}$. More complicated clusters can also contribute to $g(n)$ in the range $\frac{1}{2}<n<1$. We assume that the final result of averaging is the function $g(n)$ shown in Fig. 1, a Gaussian function centered at $n=\frac{1}{3}$. The true $g(n)$ will depend on the nature of the system; however, the most important feature of $g(n)$ is that it is quite broad and has a value considerably different from zero near $n=0$.[22]

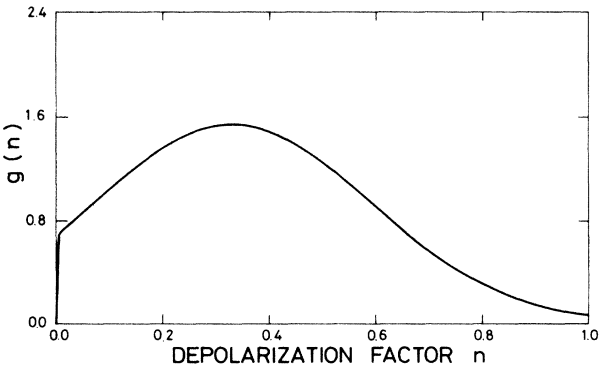

FIG. 1. The distribution of depolarization factors, $g(n)$.

The most speculative part of our ansatz for $g(n)$ is the behavior near $n=0$, where the existing calculations for finite clusters give us no clear guide. If the system contains finite, isolated clusters, we must have $g(0)=0$; otherwise $\mathrm{Re}(\epsilon_{\mathrm{av}})$ would diverge as $\ln(1/\omega)$ in the limit $\omega \to 0$, as can be shown from Eqs. (2.1) and (2.4). We assume that near $n=0$, $g(n) \propto n$, and propose the function

$$g(n) = C \tanh(Bn) \exp[-w(n-\tfrac{1}{3})^2] , \tag{2.16}$$

where w is a parameter which controls the width of $g(n)$, B controls the slope at $n \to 0$, and C is a normalizing constant.[23] B is a large constant which increases as the average cluster size increases, approaching infinity for an infinite cluster size. This behavior is consistent with calculations for an *infinite* cubic lattice of touching spheres, which give $g(0) \neq 0$.[24,25] We have taken $w=7.4$ and $B=10^4$ in Eq. (2.16).

C. Calculation of absorption coefficient and discussion

The absorption coefficient has been calculated using Eqs. (2.4), (2.10), and (2.16), with parameters in the Drude dielectric function appropriate for Sn: $\hbar\omega_p = 7.7$ eV and a Fermi velocity $v_F = 1.24 \times 10^8$ cm/s. The scattering rate is $\tau^{-1} = v_F/l$ where $l=25$ Å is a mean free path arising from scattering by impurities within the spheres rather than by the surface. We introduce the reduced frequency $\Omega = \omega/\omega_p$ and scattering rate $\gamma = 1/\omega_p \tau$, and plot the absorption coefficient (in arbitrary units) as a function of Ω for both clustered spheres and separated spheres $[g(n) = \delta(n-\frac{1}{3})]$.

It is evident from Fig. 2 that clustering broadens and lowers the height of the Fröhlich resonance peak at $\Omega = 1/\sqrt{3}$ and enhances the low-frequency absorption by a factor of 2×10^3 to 4×10^3. Whereas the low-frequency absorption α_s for separated spheres is proportional to Ω^2, it can be shown that for clustered spheres α_c is proportional to $\Omega^2 \ln(\Omega^{-1})$. The $\ln(\Omega^{-1})$ factor originates from the linear dependence $g(n) \propto n$ near $n=0$. If $g(n)$ were

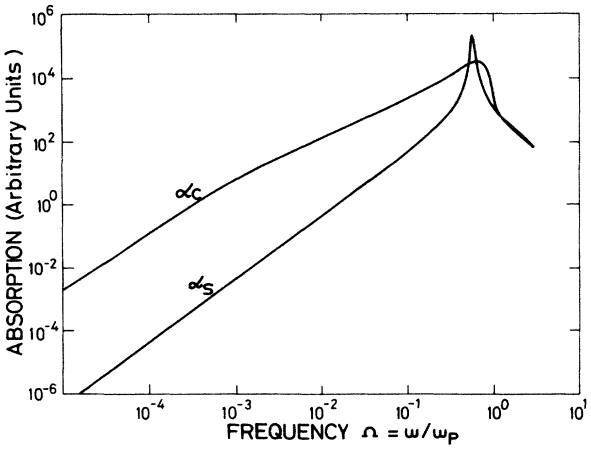

FIG. 2. Optical absorption coefficient, in arbitrary units, of a medium containing small metallic spheres, as a function of reduced frequency $\Omega=\omega/\omega_p$. The curves labeled α_c and α_s refer to a system of clustered spheres and separated spheres, respectively.

equal to zero between $n=0$ and some higher value of n, the limiting low-frequency dependence would be exactly Ω^2. The $\ln(\Omega^{-1})$ factor causes only a slight deviation from a straight line on the log-log plot in Fig. 2, so the departure from an Ω^2 dependence would not be easily detected experimentally.

We have used a filling factor $f=0.03$ and a host dielectric constant $\epsilon_h=4.84$, corresponding to KCl, to calculate the actual absorption coefficient of Sn spheres (in cm^{-1}) at the frequency $\tilde{\nu}=10\ \text{cm}^{-1}$ or $\Omega=1.6\times10^{-4}$. For separated spheres, $\alpha_s=3.1\times10^{-3}\ \text{cm}^{-1}$, and for clustered spheres, $\alpha_c=8.1\ \text{cm}^{-1}$, which is close to the measured value of $6\ \text{cm}^{-1}$.[2,26] The calculated values of both α_s and α_c are proportional to γ or τ^{-1}, so they depend strongly on the assumed electron mean free path. The low-frequency enhancement α_c/α_s decreases if $g(n)$ is made narrower by increasing the width parameter w in Eq. (2.16), and it increases if the slope parameter B increases. For example, if $B=10^5$, the enhancement is approximately 10^4, but the deviation from an Ω^2 dependence is more noticeable. Because of the somewhat arbitrary choices τ, w, and B, the close agreement between the calculated and experimental values of α_c is fortuitous. It is clear, however, that the required low-frequency enhancement can be achieved while maintaining an approximate Ω^2 frequency dependence.

III. CONCLUSION

Previous work on clustering models indicates that it is impossible to obtain sufficient enhancement of the far-infrared electric dipole absorption while maintaining an ω^2 dependence over a frequency range where such a dependence is, in fact, observed. We have constructed a function $g(n)$, a continuous distribution of depolarization factors, which can achieve the necessary enhancement. The frequency dependence of the absorption differs from Ω^2 by a slowly varying $\ln(\Omega^{-1})$ factor; although this is a small effect it would be of interest to confirm this predicted frequency dependence experimentally. Our ansatz for $g(n)$ is based on extrapolated results of calculations for nearly touching spheres, and hopefully it will be confirmed by more accurate theories. It is not clear that the standard model, based on spheres with sharp boundaries and a local dielectric constant $\epsilon(\omega)$, can successfully treat the problem of two spheres moving into contact, as one wonders how it can make any difference if the "surfaces" of two spheres 100 Å in radius are separated by 1 Å, 0.1 Å, or 0.01 Å. In this limit one may have to use a nonlocal theory, in which the cause of the low-frequency absorption is the generation of electron-hole pairs by the rapidly-varying electric field near the point of contact.

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