Optical properties of aggregate clusters

Zhe Chen,* Ping Sheng, D. A. Weitz, H. M. Lindsay, and M. Y. Lin*
Exxon Research and Engineering Company, Route 22E, Annandale, New Jersey 08801

P. Meakin
Central Research and Development Department, E.I. DuPont de Nemours Company, Wilmington, Delaware 19898
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We examine the optical properties of aggregate clusters and consider the effects of multiple scattering. The long-range fractal correlations can modify the mean index of refraction of the clusters, but multiple scattering has no effect on the wave-vector dependence of the scattering. By contrast, the short-range correlations inherent in a connected cluster lead to high-order multipole interactions which cannot be treated with a mean-field approach. These are shown to determine the wavelength dependence of the absorption and depolarized scattering from metallic clusters in good accord with experiment.

An understanding of the optical properties of particulate aggregates is of great importance in many diverse areas of science and technology. Examples of current interest include the absorption and scattering of light by interplanetary and interstellar dust,[1,2] the optical effects of air and water pollution, radiative transport of energy in fires,[3] the nuclear-winter scenario,[4] and industrial processes.[5] Of essential importance in determining the optical properties of such aggregates is a detailed knowledge of their structure. Considerable progress has been achieved recently, with the realization that aggregates often possess scale-invariant structures.[6] Indeed, light scattering has been widely used to determine the fractal dimension, d_f, of aggregates,[7] since the structure factor $S(q)\sim q^{-d_f}$, where q is the scattering vector. However, the detailed optical properties of fractal structures have not as yet been addressed. In particular, there has been no investigation of the effects of both the short-range nearest-neighbor, and the long-range fractal correlations of the particles that comprise the aggregate to determine the possible consequences of multiple scattering within a single cluster. This could not only have a significant effect on the absorption of the aggregates, but could also lead to serious problems determining d_f from $S(q)$.

In this paper we study the optical properties of fractal aggregates using computer-generated clusters whose structure is known.[8] We show that the dominant effect of multiple scattering is reflected in the mean-field index of refraction of the clusters. By contrast, and contrary to, intuitive expectation, multiple-scattering effects do not mask the q dependence of the scattering, even when the polarizability of each particle is large, and when $d_f>2$, so that the cluster is geometrically opaque. In addition, we show that, in spite of the aggregates' generally low density, the connected structure necessarily imposes significant high-order multipole interactions between each particle and its nearest neighbors. For metal particles, this results in both the appearance of a second, red-shifted absorption peak as distinct from the single-particle Mie resonance, as well as strong depolarized scattering. We estimate these effects for colloidal gold aggregates and compare our predictions to experimental results.

To examine the consequences of the fractal correlations, we use Ewald's self-consistent field method[9] in which the local exciting field at each particle site, including multiple scattering to all orders, is obtained exactly. Thus, if $\mathbf{E}(\mathbf{x}_i)$ denotes the local field at site $\mathbf{x}_i$,

$$\mathbf{E}(\mathbf{x}_i)=\mathbf{E}_0(\mathbf{x}_i)+\sum_{j\neq i}^{N}\vec{\alpha}(j)\{C^1(i,j)\mathbf{E}(\mathbf{x}_j)+C^2(i,j)[\mathbf{E}(\mathbf{x}_j)\cdot\mathbf{x}_{ij}]\mathbf{x}_{ij}\}\frac{e^{ik_0|\mathbf{x}_{ij}|}}{|\mathbf{x}_{ij}|}\ , \tag{1}$$

where

$$C^1(i,j)=(k_0^2+ik_0/|\mathbf{x}_{ij}|-1/|\mathbf{x}_{ij}|^2)\ ,$$

and

$$C^2(i,j)=(3/|\mathbf{x}_{ij}|^2-3ik_0/|\mathbf{x}_{ij}|-k_0^2)/|\mathbf{x}_{ij}|^2\ .$$

Here $\mathbf{x}_{ij}=\mathbf{x}_i-\mathbf{x}_j$, $\mathbf{E}_0(\mathbf{x})=\hat{e}\exp(i\mathbf{k}_0\cdot\mathbf{x})$ is the electric vector of the incident wave, $\mathbf{k}_0$ is the incident wave vector, $\hat{e}$ the unit vector, and $\vec{\alpha}(j)$ is the polarizability tensor of the jth particle. Equation (1) constitutes a set of $3N$ linear simultaneous equations whose solution yields the local fields at each particle position. Since all $|\mathbf{x}_{ij}|^{-1}$, $|\mathbf{x}_{ij}|^{-2}$, and $|\mathbf{x}_{ij}|^{-3}$ terms are included, retardation

effects are fully taken into account. The cluster density is assumed to be sufficiently dilute so that scattering from other clusters can be neglected. Experimentally, this can be achieved by dilution, whereas the structure within a single cluster cannot be modified.

Implicit in our approach is that the polarizability of each particle is *not* given by the expression for an isolated sphere. Rather, due to the very strong short-range correlations[10] caused by the connectivity of the cluster, the effective polarizability, $\vec{\alpha}$, must be evaluated for each particle embedded in its local chainlike environment of nearest neighbors. The resulting anisotropic $\vec{\alpha}(\omega,\mathbf{q})$ is characterized by uniaxial symmetry with $\alpha_{zz}=\alpha_1$, $\alpha_{xx}=\alpha_{yy}=\alpha_2$, $\alpha_{xy}=\alpha_{xz}=\alpha_{yz}=0$ in the coordinate system where the z axis coincides with the local chain axis. Thus the short-range high-order multipole interactions between a particle and its neighbors, which are of particular importance for metallic clusters,[11] are included in the $\vec{\alpha}(\omega,\mathbf{q})$ used, and only the dipole component of the radiated fields is included in Eq. (1).

We use clusters generated by computer simulation through an off-lattice cluster-cluster diffusion-limited aggregation algorithm,[8] for which $d_f \approx 1.8$. For comparison to experiment, we consider colloidal gold aggregates,[6] and use an effective anisotropic polarizability for particles of diameter $d=15$ nm. Equation (1) is solved numerically to obtain the local fields for different cluster configurations and for different orientations of each cluster relative to the incident wave. From the local fields, we calculate the differential scattering cross sections for a single cluster

$$\left\langle \left[\frac{d\sigma}{d\Omega} \right]_{1,2} \right\rangle = |\alpha|^2 k_0^4 N \int g_{1,2}(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d^3r \ , \tag{2}$$

where Ω denotes the solid angle $|\alpha|^2=(\alpha_1^2+2\alpha_2^2)/3$, the angular brackets denote configurational averaging, subscripts 1,2 denote polarized and depolarized scattering, respectively, N is the number of particles in the cluster and

$$g_1(r)=N^{-1}\left\langle \sum_{i,j}^{N} \delta(\mathbf{r}-\mathbf{x}_{ij}) \tilde{E}_x(\mathbf{r}+\mathbf{x}_j) \tilde{E}_x^*(\mathbf{x}_j) \right\rangle , \tag{3a}$$

$$g_2(r)=N^{-1}\left\langle \sum_{i,j}^{N} \delta(\mathbf{r}-\mathbf{x}_{ij}) \times [\tilde{E}_y(\mathbf{r}+\mathbf{x}_j)\cos\theta - \tilde{E}_z(\mathbf{r}+\mathbf{x}_j)\sin\theta] \times [\tilde{E}_y^*(\mathbf{x}_j)\cos\theta - \tilde{E}_z^*(\mathbf{x}_j)\sin\theta] \right\rangle . \tag{3b}$$

In Eq. (3) we have assumed the incident wave $\mathbf{E}_0$ to be polarized in the x direction and the scattering plane to be the yz plane, with θ the scattering angle. The quantities $\tilde{E}_{x,y,z}(\mathbf{x})$ are defined as the components of the polarization vector $\mathbf{p}$ divided by $|\alpha|$ as well as by the phase factor of the incident wave, $\tilde{E}(\mathbf{x})=\mathbf{E}(\mathbf{x})\exp(-i\mathbf{k}_0\cdot\mathbf{x})$. When the polarizability of the particle is isotropic (α is a scalar quantity), $|\tilde{E}|$ may be identified as the magnitude of the local field.

For the single-scattering Born approximation and isotropic polarizability, we have $\tilde{E}_x=1$ and $\tilde{E}_{y,z}=0$, which immediately leads to the familiar results of $g_1(r)=C(r)$, the density-density correlation function, and $g_2(r)=0$. For comparison, we write $\tilde{E}(\mathbf{x})=m_x+\Delta_x(\mathbf{x})$, where $m_x=\langle \tilde{E}_x(\mathbf{x})\rangle$ is the mean of $\tilde{E}_x$ and $\Delta_x(\mathbf{x})$ is the fluctuation of $\tilde{E}_x$ at $\mathbf{x}$ about the mean. Then,

$$g_1(r)=|m_x|^2 C(r)+F_1(r) \ , \tag{4a}$$

with

$$F_1(r)=N^{-1}\left\langle \sum_{i,j}^{N} \delta(\mathbf{r}-\mathbf{x}_{ij}) \Delta_x(\mathbf{r}+\mathbf{x}_j) \Delta_x^*(\mathbf{x}_j) \right\rangle . \tag{4b}$$

From Eq. (4) it is clear that the effect of multiple scattering is twofold. First, the magnitude of the local field is altered on average by a factor $|m_x|^2$, from which the mean-field index of refraction of the cluster can be determined. Second, the correlations of the fluctuating part of the local fields produces an additive term, $F_1(r)$. In Fig. 1 $C(r)$ and $F_1(r)$, calculated for a typical set of clusters, are plotted as a function of r/d. $C(r)$ displays a power-law falloff, $(r/d)^{d_f-3}$ as expected. By contrast, $F_1(r)$ is both small in magnitude (even though $|\Delta|$ is non-negligible) and short range in nature, with a width comparable to d. Thus the Fourier transform of $F_1(r)$ produces only a very small constant in $S(q)$ for $q \lesssim 1/d$. This is demonstrated by the points in Fig. 1, which is the Fourier transform of $S(q)$ calculated directly using Eq. (2) and the local fields. It is in excellent accord with $C(r)$, with an indiscernable contribution from $F_1(r)$. Thus we arrive at the very important result that, despite the fractal correlations of the particles, the effects of *multiple scattering only alter the magnitude of the scattering, but not its form* when $S(q)\sim q^{-d_f}$.

This conclusion is, in fact, quite general. In addition to the diffusion-limited cluster-cluster aggregates, we have also investigated both clusters simulated using reaction-limited kinetics,[12] which have $d_f \approx 2.1$, as well as those simulated using single-particle diffusion-limited aggrega-

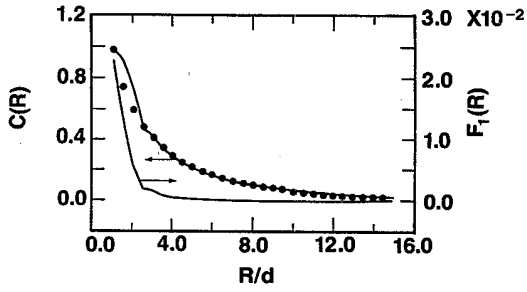

FIG. 1. The average $[C(R)]$ and fluctuating $[F_1(R)]$ contributions to the correlation of the local fields, averaged for 36 random orientations of 39 different clusters of 300 particles with $d_f=1.8$. The same anisotropic $\vec{\alpha}$ was used for each particle, as calculated for a gold particle of $d=15$ nm in a chainlike nearest-neighbor environment, with $\lambda=488$ nm. The solid circles are the Fourier transform of the q-dependent scattering from the clusters calculated using the exact local fields.

tion,[13] which have $d_f \approx 2.5$. In both cases, the clusters are geometrically opaque since $d_f > 2$. Nonetheless, $F_1(r)$ is small in magnitude and short range in its extent, so that, again, multiple scattering does not affect the q dependence of the scattering in the fractal regime. The physical origin of this conclusion presumably arises from the fact that multiple scattering completely scrambles any structural information in $S(q)$, as evidenced by the lack of correlations in $\Delta(x)$, and therefore only affects the mean field. Finally, we note that $F_1(r)$ is independent of cluster size, a fact which can immediately be deduced from the short-range nature of $F_1(r)$. Thus, in our calculations, we have already reached the large-cluster size limit for $F_1(r)$, and further increase in cluster size will have no effect on either the spatial extent, or the magnitude of $F_1(r)$ compared to $C(r)$. By contrast, m_x, and therefore the effective index of refraction of the cluster, does vary as a function of the fractal dimension and cluster size as can be shown from mean-field calculations.[4] Our results on this aspect of the problem will be reported separately.

While the fluctuating part of the local field will have no discernable effect in any experimental measure of the polarized scattering from fractal clusters, the depolarized scattering will directly reflect the consequences of the fluctuating term. This can be seen using the same analysis for $g_2(r)$, where we find that $m_{yz} \approx 0$ while $F_2(r)$ has behavior similar to $F_1(r)$. Thus the depolarized scattering is dominated by the $F_2(r)$ term, leading directly to the prediction that it should be independent of q for $q \leq 1/d$, in accord with experiment.[14]

In all cases investigated, we find $F_1(0) \ll |m_x|^2 C(0)$, so that the effect of the long-range fractal correlations on the absorption of the clusters is reflected in m_x. While this is an average quantity, the traditional mean-field treatments, such as the Maxwell-Garnett theory,[15] will *not* adequately describe the absorption of the clusters, since they are based on a random distribution of neighboring spheres, and thus ignore the strong short-range correlations inherent in a connected cluster. Thus for metallic clusters, a mean-field approach will not be able to account for the experimental observations such as the appearance of a second red-shifted absorption peak, or the large degree of depolarized scattering.[14] Our results here suggest that a more appropriate approach for these properties is through the calculation of the effective polarizability of a random distribution of dimers[11] or other small chainlike structures, subjected to an average field determined by the mean-field index of refraction, through m_x.

Our approach to the calculation of the effective $\overleftrightarrow{\alpha}$ for colloidal gold aggregates is based on the nature of the electromagnetic coupling between adjacent particles which can be determined by estimating the effective RC time constant. Transmission electron micrographs show that the width, w, of the metal bond between spheres is at most a few angstroms. Since this constriction is substantially less than the bulk mean free path of the electrons, l_b, we expect the effective resistivity to be increased substantially.[16] If we account for this by $\rho = \rho_0(1 + l_b/w)$ where ρ_0 is the bulk resistivity, a simple integration gives the resistance between two spheres, $R \sim \rho l_b / w^2$. To estimate the capacitance, we note that the charging energy of two spheres that are touching is roughly one-third that of two spheres widely separated.[1] Thus since $C = d/2$ for a single sphere, the effective capacitance for the pair of spheres is $C \sim 3d$. Using $w \sim 0.03d$ (~ 5 Å), we have $\omega RC \sim 10^2 \gg 1$ for optical frequencies, and the coupling between the spheres is therefore predominantly capacitive.

To estimate the effective polarizability for the gold particles in their local chainlike environment, we choose a model that is tractable but, nonetheless, reflects the essential physics of the capacitive coupling between the spheres. We obtain the rigorous solution[18] for the scattering from a periodic chain of gold particles. We consider cylindrical, rather than spherical, particles for ease of calculation. The width and diameter are both set to 15 nm, and their separation is fixed at a value (2.8 nm) so as to yield the experimentally observed position of the red-shifted peak in the absorption. To determine the wavelength dependence of the absorption of the clusters, orientationally averaged results are used. We observe two peaks, one at 520 nm due to α_2 and excitation normal to the chain axis, and the second at 720 nm due to α_1 and excitation along the axis. The calculated absorption is in good agreement with that measured experimentally, giving us confidence that the calculated $\overleftrightarrow{\alpha}$ appropriately describes the anisotropic polarizability of the gold particles in their local environment.

Another directly observable manifestation of $\overleftrightarrow{\alpha}$ is the magnitude of the depolarized scattering, which can be characterized by means of the ratio of the depolarized scattering, $R = I_{VH}/I_{VV}$. In Fig. 2 we compare the calculated R with experiment. The magnitude of the calculated polarized scattering has been normalized to the value measured at 488 nm, and, since the polarized scattering is highly q dependent, the experimental data are all measured at the same $q = 0.01$ nm^{-1}. The agreement is very good, correctly accounting for the rise in R as λ increases, due to the increased anisotropy in $\overleftrightarrow{\alpha}$ associated with the collective plasmon excitation. The nar-

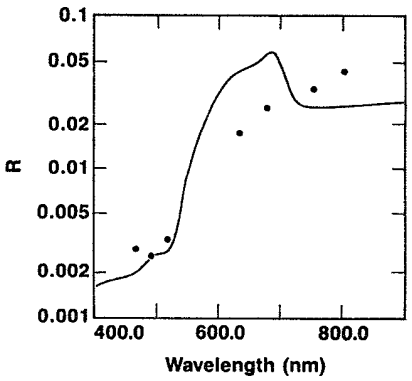

FIG. 2. The wavelength dependence of the depolarization ratio calculated using the anisotropic $\overleftrightarrow{\alpha}$ determined for a gold particle in a chain. The solid circles are the values measured for colloidal gold clusters. The calculated and measured values of the polarized scattering were normalized at $\lambda = 488$ nm.

row resonance around 700 nm is not observed in experiment, presumably because it is broadened by the many different local configurations actually present in a cluster.

In summary, we have shown that multiple scattering primarily modifies the mean optical properties of the clusters, but does not significantly effect the q dependence of the scattering as long as $q \lesssim 1/d$. Therefore, it is still valid to regard the optical scattering intensity from aggregates as proportional to the product of the structure factor and the form factor, with $S(q) \sim q^{-d_f}$. However, inherent to the aggregate structure is the renormalization of the form factor for metal clusters that results in a red-shifted absorption peak with enhanced depolarized scattering. We note, in conclusion, that these results confirm that the claims made by Schaefer *et al.*[19] that multiple scattering precludes the measurement of d_f for gold colloid aggregates, are incorrect and were based on a misinterpretation of their data.

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*Also at Department of Physics, City College of CUNY, New York, NY 10031.

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