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OPTICAL PROPERTIES OF FRACTAL CLUSTERS

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ABSTRACT

Optical scattering and absorption characteristics of fractal clusters are calculated with a self-consistent scheme in which the multiple scattering is explicitly taken into account. Our results indicate that for optical scattering the gold colloidal aggregates with fractal dimension D=1.75 behave essentially as low dimensional objects and therefore can be accurately described by the single scattering Born approximation. However, the absorption spectrum of the clusters is shown to be significantly affected by the proximity of the gold particles to their nearest neighbors in the aggregate structure.

INTRODUCTION

Fractal is a term which denotes objects with dilatational symmetry. The density-density correlation function of a fractal structure is generally given by $C(r) \sim r^{d-D}$, which insures that the Fourier transform of C(r), denoted as the structure factor S(q), will also have a power-law behavior, i.e. $S(q) \sim q^{-D}$, where D is the fractal dimension and d is the Euclidean dimension of the embedding space. Within the single-scattering Born approximation, the intensity of the scattered wave is proportional to the structure factor. Within the past few years, this fact was employed extensively in light-scattering experiments to extract intrinsic structural information, such as the fractal-dimension, from fractal objects [1]. However, this approach is based on the assumption that the effects of multiple scattering are negligible. In this short note we examine the legitimacy of this assumption and report the main results of our study on optical scattering and absorption characteristics of gold colloidal aggregates.

CALCULATION AND RESULTS

Our calculation is based on Ewald's self-consistent field method [2] in which the local exciting field at each particle site, including multiple-scattering effects to all orders, is obtained exactly. The scattered field outside the cluster is then the sum of radiation emitted by all particles in the cluster; and the absorption spectrum is similarly obtained by summing the energy

absorbed by each particle. Implicit in our approach is that the polarizability of each gold particle is not given by the expression for a sphere in vacuum. Rather, due to the proximity of each gold particle to its neighbors, the polarizability is calculated by taking into account all the near-field effects arising from higher-order-multipole interactions. The effect of this near-field interaction will be commented on later.

Calculation is performed on fractal clusters generated by an off-lattice cluster-cluster aggregation algorithm. Its structure closely resembles the gold colloidal aggregates obtained in the laboratory. Fig. 1 shows the log-log plot of the q-dependence of the polarized scattering intensity at λ=488 nm. The solid line is obtained by averaging over different clusters and over different incident directions for each cluster. In the small q region, the wave cannot resolve the detailed structure of the cluster and the curve is therefore flat. In the region $R_G^{-1}<q<a^{-1}$, where R_G is the cluster radius and a the particle radius, an excellent linear behavior is obtained as would have been expected for fractal clusters. A Born approximation calculation gives an almost identical curve (although the magnitude is somewhat shifted). The coincidence of the two sets of results indicates that the multiple-scattering effect is not important for gold aggregates with fractal dimension D=1.75.

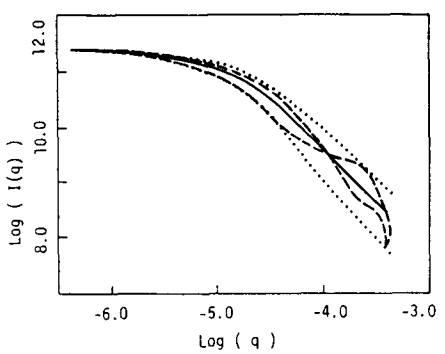

Fig. 1. Log-lot plots of the scattering intensity versus wave-vector q. Solid line is obtained by averaging over different clusters and over different directions of the same cluster; dashed lines are examples of the behavior of two individual clusters averaged over different directions; dotted lines indicate the standard deviation.

What is also shown in Fig. 1 is the scattering behavior of individual clusters averaged over different incident directions as denoted by dashed curves. It is clear that they are not fractal-like at all. The power-law behavior emerges only after averaging, and the standard deviation is indicated by the dotted curves.

While multiple scattering does not bring a measurable difference to the optical scattering, the absorption spectrum is greatly affected by the proximity of the gold particles to their neighbors (in spite of the low average density of the clusters). Since in an aggregate a particle always touches its neighbor(s), it could be asked whether the particle-particle interaction is resistive or capacitive in nature. We performed order-of-magnitude estimates of the RC time constant between the touching particles and found that, at optical frequencies, $\omega>>1/RC$ by at least an order of magnitude. Therefore, the near-field coupling is basically capacitive and has the same physics as that underlying the

dielectric anomaly in the Maxwell-Garnett theory [3]. An exact calculation for a periodic chain of particles has been performed [4]. It is shown that the effective polarizability of a particle, renormalized by all the higher-order-multipole interaction with its neighbors, has a red-shifted resonance peak as compared with that of a Mie-resonance for a single particle in vacuum. Since the particles in fractal clusters basically form chain-like structures, the shift in the resonance peak of the polarizability is indeed manifested experimentally as seen in Fig. 2. Two absorption peaks are shown. The smaller one at left is centered at the Mie-resonance frequency and arises from (1) the single particles in the solution that are not part of the aggregated cluster and (2) particles situated at the peripheral of a cluster. The larger one at right is red-shifted and arises from the particles inside the clusters. As a verification for the origin of these peaks, experiments have been performed on an aggregate cluster whose distribution is much more biased towards the single-particle end. As expected, the relative weight of the two peaks is shifted as a result.

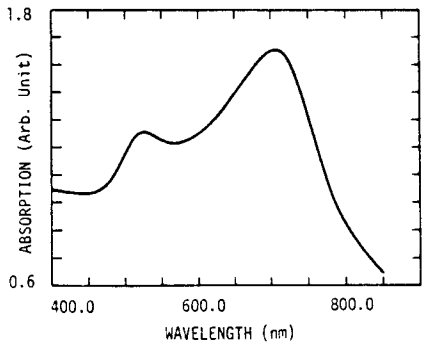

Fig. 2. Experimental absorption spectrum.

SUMMARY

To summarize, we have shown that (1) multiple-scattering will not bring any measurable difference to the Born-approximation description of scattering intensity; (2) the power-law behavior in scattering intensity is an average behavior; and (3) the polarizability of each gold particle is significantly renormalized by its near-field interaction with its neighbors, resulting in the red-shift of the absorption (resonance) peak. A more detailed presentation of these results will be published elsewhere.

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