Giant Fluctuations of Local Optical Fields in Fractal Clusters

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Giant fluctuations of the intensities of local optical fields in fractal clusters are established, dependent on a high Q factor (low dissipation) of an optical resonance. We have shown that the nonlinear-optical enhancement by fractals is due to these fluctuations and not to a high mean magnitude of the local field. We have calculated the distribution function $P(G)$ of a relative local-field intensity G and found a new scaling dependence, $P(G) \propto G^{-\varepsilon}$, with the index ε independent of an excitation frequency and dissipation rate.

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The optics of fractal clusters (called simply "fractals" below) have attracted recently considerable attention (e.g., Refs. [1–7]). Fractals have been predicted [4,5] and observed (e.g., Ref. [7]) to possess strongly enhanced nonlinear optical responses, which are attributed to the presence of very large local optical fields. A prerequisite of the enhancement is penetration of an optical field into a system, shown [1] for fractals with the dimension $D \leq 2$. The nonlinear polarizabilities studied provide only a few average characteristics of enhanced local fields. No direct information on the statistics of the fluctuations of these fields is available. In this research we have directly calculated the distribution function of local optical-field intensities in fractals. This function is the most complete local (one-point) characteristic of the local optical field.

A known approach to the fluctuation statistics in fractals is based on the concept of multifractality [8], which entails the analysis of the scaling of physical quantities (fractal measures) averaged over some radius l. This technique has never been used for the optical-field intensity as a measure, although its application to the vibrations of fractals has revealed a multifractal behavior [9]. However, optical responses in most cases can be considered as local. This is our rationale for considering in this Letter the statistics of the local fields nonaveraged over l. We have obtained a simple relation [see below Eq. (5) and Fig. 1] between different moments of the local intensity in the scaling region of frequencies, which suggests the absence of multifractality for the *local* intensity as a measure. However, this does not allow one to exclude the possibility that, *averaged* over some radius l, the intensity can be multifractal. This is due to the fact that the calculation of an nth moment of the averaged intensity invokes nth-order correlations for intensities at different monomers.

We consider a cluster as a fractal set of N particles (monomers) with dipolar interaction between them determined by the complex linear polarizability χ_0 of the isolated monomer. We define $Z \equiv \chi_0^{-1}$, $X \equiv -\mathrm{Re}Z$, and $\delta \equiv -\mathrm{Im}Z$. In the theory, X plays the role of a natural spectral variable ($X=0$ corresponds to the surface plasmon resonance of the monomers), and $\delta > 0$ describes the dielectric losses. A typical distance between monomers (~size of a monomer) $R_0 \sim 50$–100 Å is much less than the radiation wavelength λ (see, e.g., Refs. [6] and [7]). As for the total radius R_c of a cluster, we assume that $R_0 \ll R_c \ll \lambda$, so that the amplitude $\mathbf{E}^{(0)}$ of the exciting wave is the same on all the monomers. Experimentally [6,7], the radius R_c ranges from hundreds of angstroms to a few microns. Even if $R_c \gtrsim \lambda$, only the interaction of monomers within a sphere much smaller than λ is important [10], so that the above assumption about $\mathbf{E}^{(0)}$ is still valid for all monomers interacting with a given one. For simplicity of presentation, we set below $R_0 = 1$.

The amplitude $E_{i\alpha}$ ($i = 1, \ldots, N$, and $\alpha = x, y, z$) of the local optical field is a random vector function of the monomer number i due to the spatial inhomogeneity intrinsic to fractals. We introduce a $3N$-dimensional vector

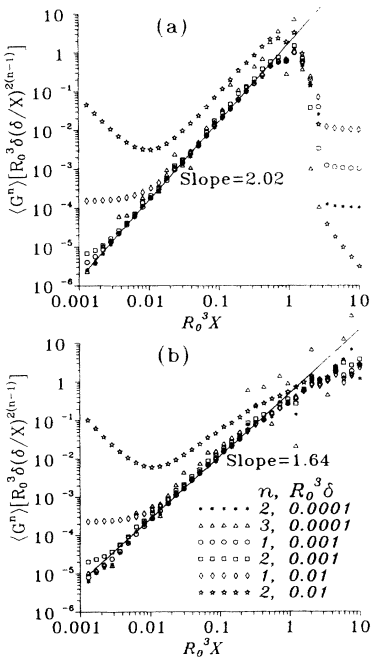

FIG. 1. Normalized moments $\langle G^n \rangle \delta Q^{-2(n-1)}$ as functions of X for CCA (a) and DCCA (b) for the values of n and δ shown.

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$|E)$ with components $(i\alpha|E)=E_{i\alpha}$, and similarly for other vectors. Then the equation for $|E)$ acquires the form [2]

$$|E)=|E^{(0)})-Z^{-1}W|E)\,, \tag{1}$$

$$(i\alpha|W|j\beta)=\begin{cases}[r_{ij}^2\delta_{\alpha\beta}-3(\mathbf{r}_{ij})_\alpha(\mathbf{r}_{ij})_\beta]r_{ij}^{-5}, & i\neq j\,,\\ 0, & i=j\,,\end{cases}$$

where W is the dipole-dipole interaction operator and $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. For both analytical and computational purposes, it is convenient to express the solution of Eq. (1) in terms of the eigenvectors $|m)$ of W and the corresponding eigenvalues w_m $(m=1,\ldots,3N)$. Having done so, we obtain [2] the local field at the ith monomer, $\mathbf{E}_i$, and the polarizability tensor of this monomer, $\chi^{(i)}$, as

$$E_{i\alpha}=Z\chi^{(i)}_{\alpha\beta}E^{(0)}_\beta\,, \tag{2}$$

$$\chi^{(i)}_{\alpha\beta}=\sum_{m,j}(i\alpha|m)(j\beta|m)(w_m-X-i\delta)^{-1}\,.$$

The linear polarizability of the cluster per monomer, $\chi=(3N)^{-1}\langle\sum_i\chi^{(i)}_{\alpha\alpha}\rangle$, scales as $\mathrm{Im}\chi\sim|X|^{1-d_0}$ in the collective spectral region [2],

$$\delta, N^{-(3/D-1)/(1-d_0)}\ll|X|\ll 1\,, \tag{3}$$

where D is the fractal dimension and d_0 is the optical spectral dimension, $0<d_0<1$.

We introduce the relative intensity of the local field at the ith monomer, G_i, and its distribution function, $P(G)$, as

$$G_i=|E_i|^2/|\mathbf{E}^{(0)}|^2,\quad P(G)=\left\langle N^{-1}\sum_{i=1}^{N}\delta(G-G_i)\right\rangle, \tag{4}$$

where the averaging is taken over the ensemble of all clusters. We note that $P(G)$ depends on X as a parameter. We will show that there exists a region of G where $P(G)$ scales, and that the moments of $P(G)$ are determined by the large-G tails of this function outside this scaling region.

The moment $\langle G^n\rangle=\int P(G)G^n dG$ $(n=1,\ldots)$ is the enhancement factor of incoherent nth-order optical excitation. As shown in Ref. [2], an exact result ("optical theorem") is valid, $\langle G\rangle=(X^2+\delta^2)\delta^{-1}\mathrm{Im}\chi$. Very similar to the derivation of the enhancement coefficient G^{RS} of the Raman scattering [6], one can show that in the region of Eq. (3) $\langle G^2\rangle\sim X^4\delta^{-3}\mathrm{Im}\chi$. Comparing $\langle G\rangle$ and $\langle G^2\rangle$, we conjecture for an arbitrary n that

$$\langle G^n\rangle\sim Q^{2(n-1)}\langle G\rangle\sim Q^{2n}\delta\,\mathrm{Im}\chi\,, \tag{5}$$

where $Q\equiv|X|/\delta$ is the quality factor of the optical resonance in the monomer, which is large, in particular, for many metals in the visible-ir region.

Substituting $|X|\sim 1$, the maximum enhancement factors can be estimated from Eq. (5) as $\langle G^n\rangle_{\max}\sim Q^{2n-1}$, and $\langle G^n\rangle_{\max}\gg 1$ for $n\geq 1$. *This estimate implies that most of the nonlinear enhancement stems from very large fluctuations of the local-field intensities and not from their high mean magnitude.* In fact, if there were no fluctuations, then it would be $\langle G^n\rangle_{\max}\sim\langle G\rangle^n_{\max}\sim Q^n$ and $\langle G^n\rangle_{\max}\ll Q^{2n-1}$ for $n>1$.

We have carried out numerical simulations using four types of fractal clusters: random walk (RW), diluted random walk (DRW), cluster-cluster aggregates (CCA) [11,12], and diluted CCA (DCCA). Diluted clusters have been generated from the original RW and CCA clusters by the decimation algorithm [2]. Briefly, each monomer of the original cluster is removed from the cluster with the probability $1-\beta$, where $\beta\ll 1$ is the fraction of monomers left. Finally, all clusters are rescaled to obtain $R_0=1$. A diluted cluster models a collection of monomers obtained by a random doping of a fractal network, say, a fractal polymer. The dilution (decimation) does not change the fractal dimension of the cluster, D (thus, $D=2$ for RW and DRW, and $D\approx 1.75$ for CCA and DCCA), but does simplify its structure at the minimum scale. Numerical calculations include 1000 clusters of each of the four types, with each cluster containing $N=100$ monomers (control calculations with $N=75$ give practically the same results).

The scaled enhancement factors $\langle G^n\rangle\delta Q^{-2(n-1)}$ $(n=1,2,3)$ for CCA and DCCA are shown in Fig. 1. In the collective (scaling) region (3), these quantities should be equal to $X^2\mathrm{Im}\chi(X)$ and, consequently, should have a universal dependence on X and should not depend on either n or δ, provided Eq. (5) is valid. Supporting Eq. (5), in this region the curves for different n and δ coincide, except for the case of $n=2$ and $\delta=0.01$, where the curve is parallel to the rest of curves. The latter is attributed to $\delta=0.01$ not being small enough for the given $n=2$. Outside the region (3), Eq. (5) fails dramatically.

In accord with Eq. (5), the universal behavior of curves in the collective region (3) of Fig. 1 should be scaling with an index equal to $1+d_0$. From this we find $d_0=-0.02$ for CCA and $d_0=0.64$ for DCCA. Independently, we find from our computations of $\mathrm{Im}\chi$ (data not shown) that $d_0=0\pm 0.02$ for CCA and $d_0=0.71\pm 0.02$ for DCCA, in reasonable agreement with the above values. The fact that the curves in Fig. 1 for all moments are close implies strong enhancement for higher moments and, consequently, for higher-order nonlinear photoexcitation. For example, for silver in the red region [6], $Q\sim 30$. Therefore, $\langle G^{n+1}\rangle/\langle G^n\rangle\sim Q^2\sim 10^3$, i.e., there are 3 orders of magnitude of the enhancement for each successive power n of nonlinearity.

We now consider the form of the distribution function $P(G)$ of Eq. (4). The scaling behavior of Eq. (5) and Fig. 1 implies that the moments of G for $n\geq 1$ are principally determined by the far right wing of $P(G)$. The structure of Eq. (5) suggests that in this wing $G\gtrsim Q^2$ and $P(G)$ and $P(G)\lesssim\delta\,\mathrm{Im}\chi$. Another characteristic point is $G=1$, in whose vicinity the intensity of the local field is close to that of the external field. In the intermediate region, $1\ll G\ll Q^2$, there is no characteristic field to compare to the local field. Therefore, $P(G)$ is likely to have

the scaling form, $P(G) \propto G^{-\varepsilon}$, where ε=const is a positive index. The fact that the moments (5) are determined by $G \gtrsim Q^2$ brings about the requirement $\varepsilon < 2$. The power-law form of $P(G)$ is related to the scale invariance of the system. The structure of Eq. (1) is such that the spatial scale enters the problem only in the product with $Z^{1/3}$. Therefore, the index ε, being scale invariant, should not depend on X and δ either.

The index ε could not be found analytically in the general case. We estimate it in the binary approximation [2], which is directly applicable to the diluted fractals. In this approximation, the nearest neighbor gives the major contribution to the local field around any given monomer. The local G factor is found as

$$G_i = (\delta \sin\theta)^2[(X - r^{-3})^2 + \delta^2]^{-1} + (\delta\cos\theta)^2[(X + 2r^{-3})^2 + \delta^2]^{-1}, \quad (6)$$

where $\mathbf{r}$ is the radius connecting the pair of nearest neighbors and θ is the angle between $\mathbf{r}$ and $\mathbf{E}^{(0)}$. In this approximation, we obtain $P(G) = \int \delta(G - G_i(r,\cos\theta)) \times \rho(r) d^3 r$, where $\rho(r)$ is the distribution density for the nearest neighbor. Recalling that $G \gg 1$, we conclude from Eq. (6) that for a given X the maximum contribution to $P(G)$ is given by $r \sim |X|^{-1/3}$. Assuming that $\rho(r)$ does not vanish, we arrive at the requirement $|X| \lesssim 1$ for original fractals and a much more relaxed condition $|X| \lesssim \beta^{-3/D}$ for diluted fractals. With such conditions in mind, we obtain $P(G) \propto G^{-3/2}$, i.e., the *universal* index $\varepsilon = 1.5$.

The distributions $P(G)$ have been computed numerically using Eqs. (2) and (4) and employing the known Lanczos algorithms of the large-matrix diagonalization. For the CCA fractals the results are given in Fig. 2 and for DCCA in Fig. 3. The distributions for RW and DRW (not shown) are similar to those of Fig. 3. For all X, except $X=0$, there exists a wide wing of $G \gg 1$, manifesting the giant fluctuations of the local fields in fractals. For $\delta = 0.001$, the function $P(G)$ scales for $G \gg 1$ with the indices $\varepsilon \approx 1.45$ (CCA, Fig. 2) and $\varepsilon \approx 1.43$ (DCCA, Fig. 3). These indices are close to each other and rather close to, albeit different from, the binary-approximation value of 1.5. For both RW and DRW, we obtain $\varepsilon \approx 1.39$. As we see from Figs. 2 and 3, with the increase of δ to 0.01, the scaling region of $G \gg 1$ shrinks. The smaller the X, the smaller the G at which the deviation from scaling (seen as a cutoff) takes place. This cutoff occurs at $G \sim Q^2$, in accord with the scaling condition $G \ll Q^2$, and is necessary to yield the correct moments [Eq. (5) and Fig. 1].

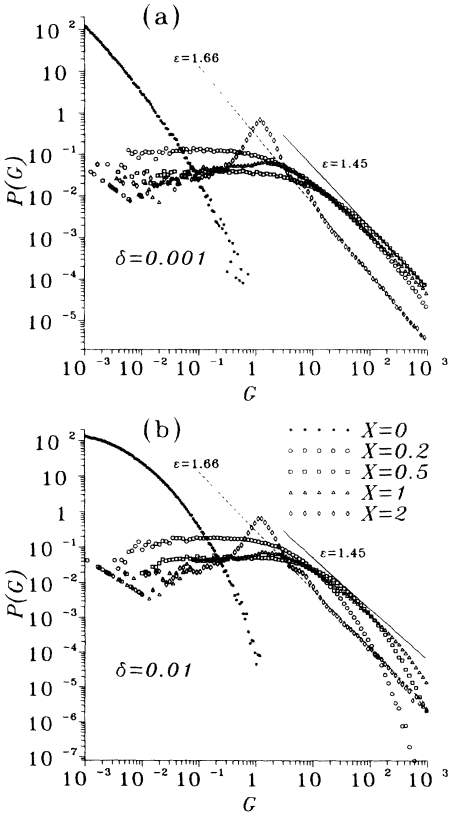

FIG. 2. Distribution function $P(G)$ of the local-field intensities for CCA obtained for $\delta = 0.001$ (a) and 0.01 (b) for the values of X indicated.

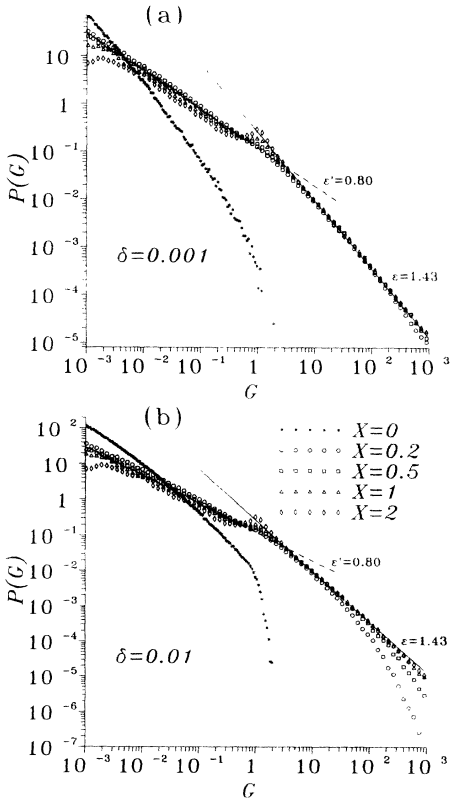

FIG. 3. Same as Fig. 2, but for DCCA.

For $X \gtrsim 1$ the eigenmodes are strongly localized mainly on pairs of monomers, and one may not expect the scaling of $P(G)$. However, for diluted clusters (DCCA) in the case $1 \lesssim |X| \lesssim \beta^{-3/D}$, the binary approximation is applicable, yielding the scaling of $P(G)$ with $\varepsilon = 1.5$. This explains why the scaling behavior of $P(G)$ for diluted fractals persists with the same index up to X as large as 3 (Fig. 3), while for nondiluted fractals for $X = 3$ we obtain $\varepsilon = 1.66$, different from $\varepsilon = 1.45$ for $|X| \lesssim 1$ (Fig. 2).

We note also that for $X \ll 1$, another scaling region is seen with the index $\varepsilon' \approx 0.8$ for DCCA (Fig. 3) and a small, if not zero, index for CCA (Fig. 2). We have also found $\varepsilon' \approx 0.60$ for RW and $\varepsilon' \approx 0.76$ for DRW. This region does not give rise to the optical hyperpolarizabilities, but may manifest itself by the persistence of the quasilinear response even for high light intensities.

The strong fluctuations of local optical fields described by the distribution function $P(G)$ may play important roles in a variety of nonlinear photophysical-photochemical effects in random clusters and on rough surfaces. Among those are parametric wave mixing, laser-induced electron emission, laser heating, melting, evaporation, and ionization, nonlinear selective photomodification of metal clusters [7], radiative desorption of atoms and molecules, radiation pressure at rough surfaces, nonlinear photochemistry of surfaces and adsorbates, and laser generation of plasmas with concurrent emission of x rays at rough surfaces [13], to indicate some.

An important application of the present theory could be hot-plasma generation on rough surfaces by femtosecond laser pulses observed recently [13]. Gold blacks, known to consist of fractal clusters of gold, were shown [13] to couple effectively to the laser radiation. In such a medium, an ultrashort laser pulse creates a dense electron plasma which does not expand considerably during the pulse time, occupying the volume of the former solid. Hence, the light pulse interacts with the plasma possessing the fractal geometry. The distribution of the temperature on the subwavelength scale reflects the distribution of the local-field intensity, $P(G)$. Because of the long tail of $P(G)$ for $G \gg 1$, there will be spots of high temperature with sizes $\sim R_0 \sim 100$ Å at the monomers, where G is high. We can speculate that such hot spots may contribute significantly to hyperpolarizabilities and the x-ray production by the plasma. The radiation spectrum of such plasmas for short times after the excitation would reflect the inhomogeneity of the temperature.

To summarize briefly, we have shown for fractal clusters that the relative intensity G [Eq. (4)] of the local optical fields fluctuates in a wide interval, $1 \lesssim G \lesssim Q^2$. The distribution function (Figs. 2 and 3) of these fluctuations contains the broad scaling region ($1 \ll G \ll Q^2$) and the cutoff tail ($G \gtrsim Q^2$). The latter determines the enhancement factors $\langle G^n \rangle$ for the n-photon excitation, shown to be very large [see Eq. (5) and Fig. 1].

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