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Resonant excitations and nonlinear optics of fractals

Vladimir M. Shalaev[a,1], Mark I. Stockman[b] and R. Botet[c]

[a]*Physikalisches Institut der Universität Heidelberg, Philosophenweg 12, W-6900 Heidelberg, Germany*
[b]*State University of New York at Buffalo, Amherst, NY 14260, USA*
[c]*Université Paris-Sud, 91405 Orsay, France*

A scale-invariant theory of nonlinear light scattering by fractal clusters is developed. Due to the presence of very high and strongly fluctuated local fields the scattering is hugely enhanced. The enhancement factor for coherent anti-Stokes Raman scattering (CARS) and optical phase conjugation (OPC) is found. Scaling properties of nonlinear light scattering by collective excitations of fractals are obtained. The corresponding exponent describing a dependence of the scattering enhancement factor on spectral variable is $2d_0 + 6$, where d_0 is the optical spectral dimension. Computer simulations dealing with cluster–cluster aggregates are presented. The numerical results fully confirm the theoretical predictions of the magnitude of the enhanced nonlinear scattering and its scaling behavior as well. The results obtained are in agreement with experimental data on four-wave light scattering by silver fractal clusters.

1. Scale self-similar objects – fractals, introduced by Mandelbrot [1] and their physical counterparts – like fractal clusters have recently been an area of active research. Such clusters possess very interesting physical and, in particular, unique optical properties, different from those of gases and "conventional" condensed media [2, 3]. This is due to the unusual combination of fractal properties: asymptotically zero integral density and together with this, strong correlation of particle locations. These properties, being mutually contradictory for a nonfractal medium, are a consequence of the power-law drop of the pair-correlation function (density–density) $g(r)$ with the intermonomer distance r and of the scaling dependence of the number of monomers in a fractal on its radius R_c,

$$g(r) = \frac{D}{4\pi} R_0^{-D} r^{D-3}, \qquad N = \left(\frac{R_c}{R_0}\right)^D, \tag{1}$$

[1] Present address: Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada.

where R_0 is the length dimension parameter denoting the typical distance between neighbor monomers. The exponent D is the fractal (Hausdorff) dimension. A fractal is called nontrivial, when $D<3$. If this is the case, the integral density $\propto R_c^{D-3}$ is asymptotically zero (at $R_c \to \infty$). This feature, together with strong pair correlation (1), is the reason for the great role that fluctuations play in a nontrivial fractal.

If monomers possess a high quality ("sharpness") of an optical resonance, for example, metal particles, strongly fluctuating local fields in a fractal can significantly exceed the external field. Nonlinearities, as usual, increase the effect fluctuations and related to this are the huge magnitudes of nonlinear polarizabilities of fractals predicted [4] on the base of simple binary model. This prediction was then confirmed experimentally [5, 6] for degenerated four-wave mixing processes in fractal silver clusters. It was obtained that aggregation of initially isolated silver particles into fractal clusters leads to the improvement of efficiency of the nonlinear four-wave process in 10^6 times.

The aim of this paper is to develop a theory of optical nonlinearities of fractals based on the scaling arguments.

2. Let us consider a cluster, consisting of N polarizable particles (monomers) located in the points $\{r_i\}$. Monomers are dipole-polarized (at optical frequencies ω) particles with the linear polarizability $\chi_0(\omega)$ and nonlinear polarizability $\chi^{(n)}$. The induced dipoles of different monomers interact via the dipole–dipole forces. Let us point out that the nonlinear polarizability $\chi^{(n)}$ may be either the own polarizability of a monomer or the polarizability of an impurity bound to the monomer. As an example we deal with anti-Stokes Raman scattering (CARS) and optical phase conjugation (OPC) – four-wave parametric processes during which two photons of ω_1 frequency transform into two photons with ω_2 and ω_s frequencies. Such processes are described by a third-order nonlinear polarizability $\chi^{(3)}_{\alpha\beta\gamma\delta}(-\omega_s; \omega_1, \omega_1, -\omega_2)$, where ω_s is the generated frequency, ω_1 and ω_2 are the frequencies of the interacted waves. For CARS $\omega_s = 2\omega_1 - \omega_2$. OPC is a completely degenerated process $\omega_s = \omega_1 = \omega_2$.

The main quantity that we are going to calculate below is the enhancement factor $G^{(3)}$ for the 3rd-order nonlinear process such as CARS and OPC. $G^{(3)}$ is defined as the ratio of the radiation intensity generated at the monomers in a cluster to the analogous intensity for the free (isolated) particles. The enhancement coefficient $G^{(3)}$ for the CARS (or OPC) process has the form

$$G^{(3)} = \left| \frac{\langle \chi^{(3F)}_{\alpha\beta\gamma\delta} \rangle e^{(1)}_\beta e'^{(1)}_\gamma e^{(2)*}_\delta}{\chi^{(3)}_{\alpha\beta\gamma\delta} e^{(1)}_\beta e'^{(1)}_\gamma e^{(2)*}_\delta} \right|^2, \tag{2}$$

where $e^{(1)}$, $e'^{(1)}$, $e^{(2)}$ are the polarization unit vectors of the incident waves, $\chi^{(3F)}_{\alpha\beta\gamma\delta}$ is the polarizability of the cluster (per monomer), and the angle brackets $\langle \ldots \rangle$ denote averaging over an ensemble of clusters. We seek to calculate the ensemble averages of the nonlinear polarizability $\chi^{(3F)}$. When the monomers are the constituents of a cluster, the field acting upon them is the local field E_i rather than the external field $E^{(0)}$. Also the dipole interaction of the monomers at the generated frequency ω_s should be included. Taking these arguments into account, we can write the following system of the equations for nonlinear light-induced dipole moments ($R_c \ll \omega/c$):

$$d^{NL}_{i,\alpha} = \chi^{(3)}_{\alpha\beta\gamma\delta} E^{(1)}_{i,\beta} E'^{(1)}_{i,\gamma} E^{(2)*}_{i,\delta} - \chi_0(\omega_s) \sum_j (i\alpha|W|j\beta) d^{NL}_{j,\beta} , \tag{3}$$

$$(i\alpha|W|j\beta) = \begin{cases} (\delta_{\alpha\beta} - 3n^{ij}_\alpha n^{ij}_\beta) r^{-3}_{ij} , & i \neq j , \\ 0 , & i = j , \end{cases} \tag{4}$$

where $r_{ij} = r_i - r_j$, $n^{ij} = r_{ij}/r_{ij}$. Local fields E_i can be found from the system of equations for linear dipole momenta d_i,

$$\chi_0^{-1} d_{i,\alpha} = E^{(0)}_\alpha - \sum_{j=1}^{N} (i\alpha|W|j\beta) d_{j,\beta} . \tag{5}$$

Let us introduce eigenvectors $|n)$ of the W-operator and corresponding eigenvalues w_n: $(n|W|m) = w_n \delta_{nm}$. Solving (5) in terms of eigenvectors of W, we find [3]

$$E_{i,\alpha} = \chi_0^{-1} d_{i,\alpha} = \chi_0^{-1} \chi_{i,\alpha\beta} E^{(0)}_\beta , \qquad \chi_{i,\alpha\beta} = \sum_{nj} \Lambda_n (i\alpha|n)(n|j\beta) , \tag{6}$$

where $\Lambda_n = (w_n - X - i\delta)^{-1}$, $X \equiv -\mathrm{Re}\, \chi_0^{-1}$, $\delta \equiv -\mathrm{Im}\, \chi_0^{-1}$. From (3) and (6) follows the expression for nonlinear polarizability of a fractal:

$$\langle \chi^{(3F)}_{\alpha\beta\gamma\delta} \rangle = (\chi_0^{-1})^3 \chi_0^{-1*} \langle \chi^{(3)}_{\alpha'\beta'\gamma'\delta'} \chi_{j,\alpha'\alpha} \chi_{j,\beta'\beta} \chi_{j,\gamma'\gamma} \chi^*_{j,\delta'\delta} \rangle . \tag{7}$$

Substituting (6) into (7) and expanding the product of factors Λ in simple factors,

$$\Lambda_n \Lambda_m \Lambda_l \Lambda^*_k = R_{lk} [\Lambda_n \Lambda_m \Lambda_l - R_{mk} \Lambda_n \Lambda_m + R_{nk} R^*_{mk} (\Lambda_n - \Lambda^*_k)] , \tag{8}$$

$$R_{nm} \equiv \frac{i}{2\,\mathrm{Im}\, \chi_0^{-1} - (w_n - w_m)} , \tag{9}$$

for high-quality resonances ($R_0^3 \delta \ll 1$) and identical linear wave polarizations in (2), we find after averaging over the orientations

$$G^{(3)} = \left(\frac{\pi}{20}\right)^2 \frac{X^8}{|\mathrm{Im}\ \chi_0^{-1}|^6}\, \Phi^2(X, R_0)\,, \tag{10}$$

$$\Phi = \Big\langle \sum_{\substack{n \\ ii'j'j''}} \delta(X - \omega_n) \times (i\alpha|n)(n|j\beta)(j\beta|n)(n|i'\delta)(j'\alpha|n)(n|j\gamma)(j\gamma|n)(n|j''\delta) \Big\rangle\,. \tag{11}$$

The function Φ (11) coincides with the corresponding function Φ determining Raman scattering of light by clusters and has for collective excitations of the fractal the following scaling form [7]:

$$\Phi(R_0, X) \sim R_0^3 |R_0^3 X|^{d_0 - 1}\,, \tag{12}$$

where the exponent d_0 is the optical spectral dimension [3]. Note that the absorption, resonant Rayleigh scattering and the density of eigenstates of the fractal in the spectral region corresponding to the collective fractal excitations. are described by the same power-law dependence [3, 8, 9] (12). It follows from (10) and (12) that

$$G^{(3)} \sim \frac{|R_0^3 X|^{2d_0+6}}{|R_0^3\, \mathrm{Im}\ \chi_0^{-1}|^6}\,. \tag{13}$$

According to (13) $G^{(3)}$ has the scaling dependence on $|X|$ with the exponent $2d_0 + 6$ and is proportional to the huge factor: sixth power of the quality of resonance Q^6 ($Q \sim |R_0^3\, \mathrm{Im}\ \chi_0^{-1}|^{-1}$). The external field excites eigenmodes of the fractal with eigenvalues $w_n = X(\omega)$. Local fields E_ℓ of the resonant modes significantly exceed the external one E^0: $E_\ell / E^0 \sim Q \gg 1$. Since $G^{(3)} \sim |\langle \chi^{(3F)} / \chi^{(3)} \rangle|^2 \sim |(E_\ell / E^0)^3|^2$, we find that $G^{(3)} \propto Q^6$ in agreement with (13).

3. To complement the theory we carried out a numerical simulation of the enhancement factor $G^{(3)}$ on the base of the general expressions (2), (7). We used a model of a diluted fractal [3] for cluster–cluster aggregation with fractal dimension $D = 1.78$. In fig. 1 the plot of the $G^{(3)}$-factor multiplied by δ^6 ($R_0 = 1$) as a function of X for $\delta \equiv -\mathrm{Im}\ \chi_0^{-1} = 0.005$ is presented. The scaling behavior is observed in our simulations with the slope 6.7 ± 0.2 (the slope 6.78 is shown in the figure). This is in a good agreement with the theory giving for the exponent value $2d_0 + 6$ ($d_0 \simeq 0.3$ for the cluster–cluster aggregation [8]). The enhancement factor $G^{(3)}$ increases with increasing X in accordance with theory reaching at $X \sim 1$ the maximum value $G^{(3)} \sim (2\delta)^{-6}$ also in agreement with theoretically predicted value.

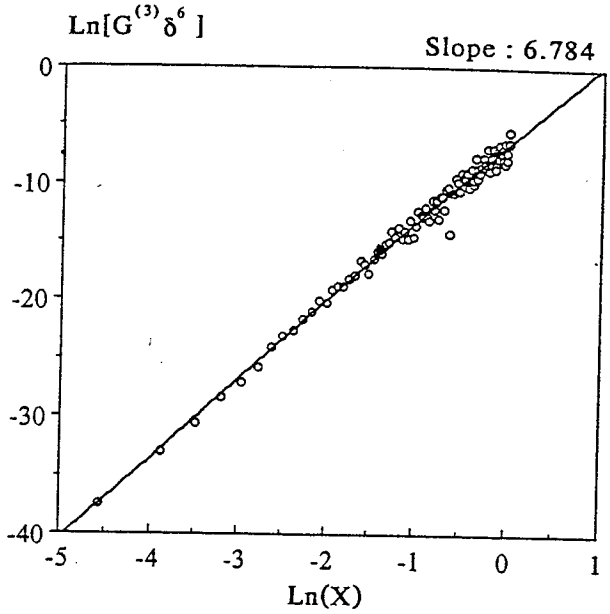

Fig. 1. ln–ln plot of the enhancement factor $G^{(3)}$ multiplied by δ^6 as a function of X.

In the case of fractal clusters consisting of small metallic balls, the monomer's polarizability is $\chi_0 = R_m^3(\epsilon - 1)/(\epsilon + 2)$ (where R_m is the radius of monomer and $\epsilon \equiv \epsilon' + i\epsilon''$ is a permeability of metal) and the corresponding quality of resonance $Q = R_m^{-3}\delta^{-1} = R_m^{-3}|\mathrm{Im}\ \chi_0^{-1}|^{-1} = (\epsilon' - 1)^2/3\epsilon'' \gg 1$ for the visible and infrared regions of the spectrum. Using the value of permeability ϵ for silver at the wavelength of the field $\lambda = 540$ nm used in our experiment [5, 6] and substituting the corresponding values for X and δ to the theoretical formula (13), we find $G^{(3)} \sim 10^6$ in agreement with experimental results obtained.

Thus, due to the aggregation of initially isolated particles into fractal clusters the efficiency of nonlinear optical processes of the third order such as CARS and OPC are greatly enhanced (proportionally to the sixth power of the quality of resonance). The corresponding enhancement factor has the scaling dependence on the spectral variable X with the exponent $2d_0 + 6$.

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