

# Fractals: Optical susceptibility and giant raman scattering

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A theory is developed which describes the optical properties of fractal clusters (i.e. of aggregates of non-trivial Hausdorff dimension consisting of interacting monomer particles). It is shown that with respect to these properties fractal clusters differ significantly from both gases and condensed media. The interaction between the monomers is assumed to be dipole-dipole. The theory is based on the self-consistent field equations; it takes into account the fluctuation nature of the fractal cluster (considerable probability for approach of monomers to each other despite an asymptotically zero integral density). An expression is obtained for the linear susceptibility. Combination of the monomers with the formation of a cluster entails the splitting, shift and broadening of the monomer spectra. These changes depend strongly on the fractal (Hausdorff) dimension of the cluster but do not depend on the number of monomers in it (for a cluster of non-trivial dimension). On the other hand, the monomers partially retain their individuality and the susceptibility – its quasi-resonance nature. Broadening, like the imaginary part of the susceptibility, does not depend on dissipation in an individual monomer. It is predicted that giant Raman scattering may occur at an impurity particle fixed near one of the cluster monomers when excitation takes place in the absorption band of the cluster. The enhancement factor for the scattering is also determined by the fractal dimension.

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## 1. Introduction

Interest has recently been grown to the so-called fractals – objects of fractional dimension, immersed into a three-dimensional space [1, 2]. Their physical counterparts are in particular fractal clusters which are aggregates of particles (called monomers) bound to each other. The number of monomers within a sphere of radius  $R$  inside a fractal is asymptotically (at  $R \rightarrow \infty$ ) defined as the ratio

$$N = (R/R_0)^D \quad (1)$$

where  $R_0$  is the length scale constant,  $D$  is the index called the fractal (Hausdorff) dimension. Generally speaking,  $D$  is non-integer; a fractal is called non-trivial when  $D$  is smaller than the space dimension.

Due to the bonds, there arises a long-range pair

correlation between the monomers, the respective density-density correlation function being

$$g(r) \propto r^{D-3}, \quad R_0 \lesssim r \lesssim R_c, \quad (2)$$

where  $r$  is the distance between the monomers,  $R_c$  is the entire fractal size, the function  $g$  is also dependent on the fractal dimension (as a consequence of scale invariance).

Fractal clusters are produced in particular by diffusion-limited aggregation [3–5]. Henceforth, particles of different physical origin in colloids and suspensions are also fractals (see e.g. [6–9]). Another example of fractal aggregates can be the solid surface grown under diffusion-limited conditions and insufficient surface relaxation or sputter-deposited [5, 10]. Most macromolecules (polymers) are fractals [11] as well as percolation clusters formed by random cou-

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pling of monomers which are a good approximation for polymerization processes and phase transitions. Reference [12] gives a comprehensive description of linear optical properties of metal clusters, which when growing under nonequilibrium conditions may form fractal structures.

Reference [13] treats the light scattering by fractals in terms of the mean-field theory. In [14] the dielectric response is calculated within a model of the effective medium. It should be noted that both papers ignore such a decisive property of the fractal as its fluctuation behavior [15]. In this paper it will be shown that fractals possess the unique optical properties essentially different from those of both gases and condensed media. The monomers lines in a fractal are broadened and split into doublets: the latter however remain centered close to the initial position where the fractal absorption is minimum. Thus the individuality of monomers (resonant line profiles) is partially retained. This is due to the fact that the integral density of the particles in a fractal tends to zero as its radius grows  $\propto R_c^{D-3}$ . For this reason, a simultaneous interaction of many monomers is not likely to occur, while the binary interaction becomes highly probable because of the pair correlation (2). The strong binary interaction at an asymptotically zero density is the consequence of the fluctuation nature of a fractal. At  $D \rightarrow 3$ , i.e. in a trivial fractal, the lines are very much broadened (in the "thermodynamic" limit  $N \rightarrow \infty$ ,  $R_c \rightarrow \infty$ ,  $R_0 = \text{const.}$ ) which is associated with the long-range dipole-dipole interaction. This indicates that the monomers tend to lose their individuality (i.e. they tend to form a wide range of levels) in a condensed medium.

Another important property of fractals, as will be shown below, is the appearance of giant Raman scattering (GRS) from the impurity centers. As is conventionally thought (see reviews [16, 17]), GRS occurs when an impurity attaches to the rough surface of a polarized solid. In this regard a fractal represents an extremely rough "surface" (with  $D$  dimension). The results obtained allow us to account for the earlier obscure fact [17] that the strongest GRS signal from impurity molecules is observed on metal colloidal aggregates (which are known to be fractal clusters).

## 2. Linear susceptibility of a fractal

Consider a fractal consisting of  $N$  monomers located in  $\{\mathbf{r}^i\}$  sites and coupled via dipole-dipole interaction. We seek to calculate the linear response of the dipole moment in terms of time-dependent self-consistent field equations. Let the field have the form  $\mathbf{E}(t) = \mathbf{E}_\omega e^{-i\omega t} + \text{c.c.}$  The quantum mechanical average of the dipole moment of the  $i$ -th monomer is written

likewise as  $\mathbf{d}^i(t) = \mathbf{d}_\omega e^{-i\omega t} + \text{c.c.}$  Indices  $\omega$  by the amplitudes will be omitted in further treatment. For the sake of simplicity, the monomers are assumed to be identical and isotropically polarized. Then the response amplitudes will have the form

$$d_\alpha^i = \chi_0 (\mathbf{E} + \mathbf{E}^i)_\alpha; \quad (3)$$

where  $\mathbf{E}$  is the external field,  $\mathbf{E}^i$  is the field of other monomers in the point of location of the given one;  $\chi_0 = \chi_0(\omega)$  is the polarizability of an isolated monomer, the Latin superscript hereafter labels the number of the particle and the subscripts refer to the tensor components;

$$E_\alpha^i = - \sum_j' (\delta_{\alpha\beta} - 3n_\alpha^{ij} n_\beta^{ij}) (r^{ij})^{-3} d_\beta^j, \quad (4)$$

where  $\mathbf{n}^{ij}$  is the unit vector in the direction  $\mathbf{r}^{ij} \equiv \mathbf{r}^i - \mathbf{r}^j$ ; a prime at  $\sum$  shows that the summation extends over all monomers, except the  $i$ -th one. Our further simplifying assumption is that the light wavelength  $\lambda$  exceeds the cluster size  $R_c$ .

A distinctive feature of the dipole-dipole interaction (and, in general, of multipole interaction with a non-zero moment) is that the self-consistent field (4) turns to zero when averaged over spherically symmetric distribution. Hence only (anisotropic) fluctuations of the particle density contribute to (4). Because of the rarefied structure (asymptotically zero mean density; cf. Introduction) of a non-trivial fractal, nearly all the monomers are a long distance from the given one and form approximately isotropic cloud negligibly contributing to (4).

Proceeding from the above consideration, we extract from the self-consistent field  $\mathbf{E}^i$  the contribution from few nearest monomers (the fluctuating component). The field of the rest (distant) monomers can be taken into account in a usual way (see e.g. [18]), if one implies that  $\mathbf{E}$  (3) is the mean (instead of external) field and adds the Lorentz field  $\mathbf{E}^L$ . As a result, the self-consistent (local) field has the form

$$E_\alpha^i = - \sum_j'' (\delta_{\alpha\beta} - 3n_\alpha^{ij} n_\beta^{ij}) (r^{ij})^{-3} d_\beta^j + E_\alpha^L. \quad (5)$$

Here  $\sum''$  means summation over the monomers contained within a sphere of some, sufficiently small, radius  $R_L$ .

The Lorentz field can also be calculated for fractals. It is reasonably done by using the integral relations (similar to e.g. [19]). Making use of (2), for the monomer density around a fixed  $i$ -th monomer, we obtain

$$\mathbf{E}^L = \frac{D}{3R_0^3} \left( \frac{R_L}{R_0} \right)^{D-3}, \quad (6)$$

where  $\mathbf{d}$  is the mean (with respect to the response amplitude) dipole moment of the monomer. In contrast to the three-dimensional limit, the Lorentz field (6) depends on the radius of the "cut out" sphere.

As seen from (5) and (6), the total contribution to  $\mathbf{E}^i$  from all monomers that are outside the sphere of  $R_L$  radius does not exceed the contribution from a single monomer at a  $r \lesssim R_0$  distance from the given one. Such approach of the monomers is quite probable inspite of the asymptotically zero integral density of the non-trivial fractal. From (1), (2) it follows that the average number of monomers within a sphere of radius  $R_0$  around the given one is unity.

Proceeding from the above indicated properties, in the sum  $\sum''$  in (5) we shall only keep one term corresponding to the nearest, say  $j$ -th, monomer (binary approximation). The requirement for that is that within the Lorentz sphere there should be only one (on the average) monomer. According to (1), (2), this means that  $R_L = R_0$ .

Taking into account the dipole-dipole interaction symmetry with respect to the particles exchange (change of the sign of  $\mathbf{n}^{ij}$  in (5)) and the fact that the approached monomers appear to be in identical fields of the distant monomers, we conclude that  $\mathbf{d}^j = \mathbf{d}^i$ . Then the self-consistent field (5) is rewritten as

$$\mathbf{E}_x^i = -d_\beta^i (\delta_{x\beta} - 3n_x^{ij} n_\beta^{ij}) (r^{ij})^{-3} + \mathbf{E}_x^L; \quad \mathbf{E}^L = D\mathbf{d}/3R_0^3. \quad (7)$$

Although both contributions to (7) are of the same order of magnitude (it should be taken into account that  $r^{ij} \lesssim R_0$ ), they differ basically in their effects. The field proportional to  $\mathbf{d}^i$  (binary) and describing fluctuations in close vicinity of the monomer leads to the spectral shift and broadening, independent of the initial relaxation (dissipation) in the monomer. Moreover, analytical properties of the susceptibility are modified: instead of the poles in the complex frequency plane there appear points of branching. Unlike the binary contribution, the second term (Lorentz field) in (7) is not of a random origin and hence, as is obvious, does not affect the analytical behavior of the response, only leading to some renormalization of the latter (with the account of the Lorentz field only the response function remains meromorphic).

Therefore, not to obscure with details the results associated with the fluctuation nature of a non-trivial fractal (high probability of binary interaction at zero mean density), first we adopt pure binary interaction, neglecting the Lorentz field  $\mathbf{E}^L$ . Next (see Sect. 4)  $\mathbf{E}^L$  will be taken into account precisely to confirm the above suggestions.

So, omitting  $\mathbf{E}^L$  in (7) gives a solution for (3), (7) in the form:

$$d_x^i = M_{x\beta}^{-1} E_\beta; \quad M_{x\beta} = (\chi_0^{-1} + \varphi) \delta_{x\beta} - 3n_x^{ij} n_\beta^{ij} \varphi, \quad (8)$$

where  $\varphi = (r^{ij})^{-3}$ . The response matrix  $M^{-1}$  is defined as

$$M_{x\beta}^{-1} = A \delta_{x\beta} + B n_x^{ij} n_\beta^{ij}, \quad A = (\chi_0^{-1} + \varphi)^{-1}; \\ B = (\chi_0^{-1} - 2\varphi)^{-1} - A. \quad (9)$$

Now, we take into account the probability for any of the fractal's monomers to approach the given one. Then,  $\varphi$  should be written as

$$\varphi = \sum_j' (r^{ij})^{-3}. \quad (10)$$

A self-consistent use of the binary approximation (8)–(10) should only yield, when averaged over the configurations  $\{\mathbf{r}^i\}$ , the pair correlator (2).

With the account of isotropic particles distribution, for the mean dipole moment one obtains

$$\mathbf{d} = \chi_1 \mathbf{E}, \quad \chi_1 = 1/3 S p \langle M^{-1} \rangle, \quad (11)$$

where  $\langle \dots \rangle$  is the average over the  $\{\mathbf{r}^i\}$  ensemble; the trace is taken by tensor indices;  $\chi_1$  is the mean monomer susceptibility in a fractal. The value of  $\chi_1$  is, obviously, independent of the number of the particle. Hence the dipole susceptibility of the fractal is

$$\chi = N \chi_1 = N \frac{1}{3} \left\langle \frac{2}{\chi_0^{-1} + \varphi} + \frac{1}{\chi_0^{-1} - 2\varphi} \right\rangle. \quad (12)$$

Physical meaning of the result obtained is apparent. The first term in angular brackets refers to the dipoles direction normal to the vector  $\mathbf{r}^{ij}$ . Statistical weight of such disposition equals 2. The second term describes collinear geometry of dipoles (when the field reverses its direction and becomes twice as high; cf. (4)). The statistical weight is 1. The additive character of averaging over the configurations, following from (12), is associated with the binary approximation.

To calculate  $\chi_1$  it is necessary to find the average of the quantities  $(z + \varphi)^{-1}$ , where  $z$  is the complex parameter (cf. (12)). For this purpose we make use of the Laplas transformation

$$\left\langle \frac{1}{z + \varphi} \right\rangle = i \int_0^\infty dt \exp(-izt) F(t), \quad (13)$$

where  $\text{Im } z < 0$ . The result for  $\text{Im } z > 0$  can be found by analytical extension;

$$F(t) = \langle \exp(-it\varphi) \rangle \\ \equiv \left\langle \prod_j \{1 - [1 - \exp[-it(r^{ij})^{-3}]]\} \right\rangle. \quad (14)$$

As a consequence of the binary approximation, averaging over all pairs of monomers in (14) is done independently to yield

$$F(t) = [1 - f(t)]^N, \quad (15)$$

$$f(t) = \left\{ \int_0^{R_c} \left[ 1 - \exp\left(-\frac{it}{r^3}\right) g(r) d^3r \right] \right\} \left\{ \int_0^{R_c} g(r) d^3r \right\}^{-1}. \quad (16)$$

Substituting correlator (2), from (16) one obtains in the limit  $R_c \rightarrow \infty$  (actually it is required that  $R_c \gg |\chi_0|^{1/3}$ ) an asymptotical expression

$$f(t) = R_c^{-D} (it)^{D/3} \Gamma(1 - D/3); \quad (17)$$

where the branch of the power-law function is fixed by the choice of the phase:  $i = e^{i\pi/2}$ . The averaging procedure employed is analogous to the one used in the theory of static damping of incoherent excitations [20]. From (17) it is evident that  $f(t) \rightarrow 0$  at  $R_c \rightarrow \infty$ . Therefore, with the account of (1), from (13), (15), (17) in the "thermodynamic" limit (at  $N \rightarrow \infty$ ,  $R_c \rightarrow \infty$ ,  $R_0 = \text{const.}$ ) one finds

$$\langle (z + \varphi)^{-1} \rangle = R_0^3 S_z(-R_0^3 z),$$

$$S_z(z) = i \int_0^\infty \exp[izt - (it)^2 \Gamma(1 - \alpha)], \quad (18)$$

where  $\alpha = D/3$ ,  $\Gamma(\dots)$  is the Gamma-function,  $S_z$  is the function of the complex variable  $z$ , determined from (18) at  $\text{Im } z > 0$ . Its analytical extension to the lower semiplane is fulfilled through the relation

$$S_z(z^*) = S_z^*(z). \quad (19)$$

As can be shown, the function  $S_z(z)$  is analytical in the complex plane with a cut along the real axis from 0 to  $\infty$ ;  $z=0$  is the point of branching. At  $\alpha=1/2$  the function  $S_z(z)$  is represented as the standard functions [21]

$$S_{1/2}(z) = -\frac{1}{z} \cdot \left\{ 1 - \left(-\frac{\pi^2}{4z}\right)^{1/2} \exp\left(-\frac{\pi}{4z}\right) \text{Erfc}\left[\left(-\frac{\pi}{4z}\right)^{1/2}\right] \right\}. \quad (20)$$

The dipole susceptibility of the fractal, as follows from (12), (19), has the form:

$$\chi = N \chi_1, \quad \chi_1 = 1/3 R_0^3 [2S_z(-R_0^3 \chi_0^{-1}) - 1/2 S_z(1/2 R_0^3 \chi_0^{-1})]. \quad (21)$$

From this expression it can be seen that the cluster susceptibility, as a function of the monomer susceptibility, is determined by the fractal dimension, while the dependence scale is fixed by the parameter  $R_0$  of the fractal.

In order to find the dependence of  $\chi_1$  (21) on the radiation frequency, we have to specify the form of

the dependence for an isolated monomer  $\chi_0$ . For systems having an isolated resonance, in its vicinity

$$\chi_0 = -R_m^3 \omega_m (\Omega + i\Gamma)^{-1}, \quad (22)$$

where  $\Omega$  is the resonance detuning,  $\Gamma$  is the relaxation constant (resonance width);  $\omega_m$ ,  $R_m$  are, respectively, the typical excitation frequency and geometrical size of the system. In a two-level model

$$R_m^3 \omega_m = |d_{12}|^2 \quad (23)$$

where  $d_{12}$  is the dipole moment of the transition (we adopt the system of units where  $\hbar=1$ ). For the case of importance when a monomer has a shape of a macroscopic sphere of  $R_m$  radius with the dielectric permiability  $\varepsilon$ , the familiar expression

$$\chi_0 = R_m^3 (\varepsilon - 1) / (\varepsilon + 2) \quad (24)$$

in the vicinity of an isolated resonance is reduced to the form (22) with the parameters

$$\omega_m = 3(\partial \varepsilon' / \partial \omega)^{-1}, \quad \Gamma = 1/3 \omega_m \varepsilon''; \quad \varepsilon' \equiv \text{Re } \varepsilon; \quad \varepsilon'' \equiv \text{Im } \varepsilon. \quad (25)$$

In (25) the values of  $\varepsilon'$ ,  $\partial \varepsilon' / \partial \omega$  are taken in the point in which  $\varepsilon' = -2$ . Note that for a plasmon resonance in a metallic sphere

$$\varepsilon = \varepsilon_0 - (\omega_p / \omega)^2, \quad \omega_m = 3/2 \omega_p (\varepsilon_0 + 2)^{-3/2},$$

$$\omega_0 = \omega_p (\varepsilon_0 + 2)^{-1/2}, \quad (26)$$

where  $\varepsilon_0$  is the constant contribution to  $\varepsilon$  due to interzone transitions;  $\omega_p$  is the electron plasma frequency;  $\omega_0$  is the resonance frequency corresponding to  $\Omega=0$ .

From (21) with the account of (22) it is evident that incorporating a monomer into a fractal leads to broadening and shift of the monomer's spectral lines by the amount of order of characteristic "fractal" frequency

$$\Omega_f \equiv \omega_m (R_m / R_0)^3. \quad (27)$$

As has been mentioned, the spectral broadening is due to large density fluctuations in a non-trivial fractal.

Existence of the thermodynamic limit (or scale invariance, i.e. independence of the susceptibility per monomer of the cluster radius  $R_c$ ) is typical of a non-trivial fractal ( $D < 3$ ). For  $D=3$  this property vanishes. In the latter case, as can be seen from the initial relation (16), a logarithmic divergence appears and the line broadening (shift) of the monomer is estimated as

$$\Omega_f \sim \omega_m (R_m / R_0)^3 \ln(R_c / R_0). \quad (28)$$

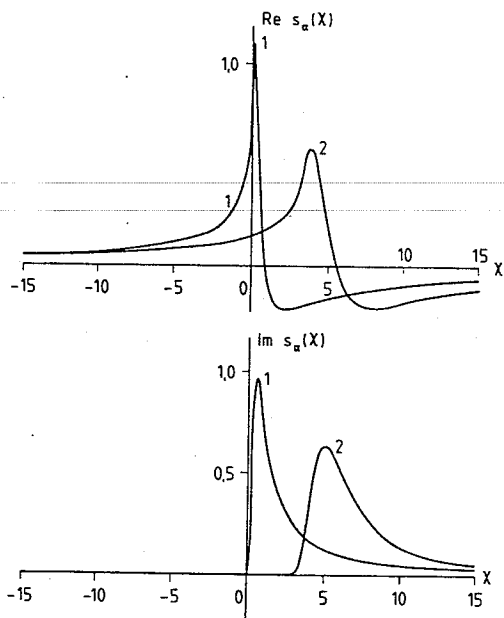


Fig. 1. Real and imaginary parts of function (18). Curves: 1 -  $\alpha=0.5$ ,  $D=1.5$ ; 2 -  $\alpha=0.83$ ,  $D=2.5$

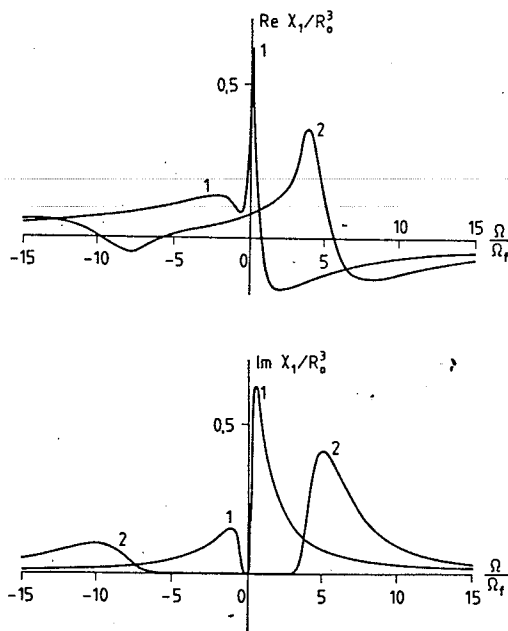


Fig. 2. Real and imaginary parts of susceptibility (34) (per monomer) calculated in the binary approximation as a function of the variable  $x = -R_0^3 \text{Re } \chi_0^{-1} \approx \Omega/\Omega_f$ . Curves: 1 -  $D=1.5$ , 2 -  $D=2.5$

If the fractal broadening  $\Omega_f$  (27) appreciably exceeds the initial (relaxation constant) width  $\Gamma$ , the latter in (21) may tend to zero. In this case however the imaginary part of the function  $S_\alpha$  does not go to zero: it is finite and has the sign determined by the sign of the imaginary part  $\chi_0$ . The susceptibility in the case discussed is defined as a complex function of a purely real argument

$$s_x(x) \equiv S_x(x + i0). \quad (29)$$

This function satisfies the following rule of sums for the imaginary and the real parts:

$$\int_0^\infty \text{Im } s_x(x) dx = \pi, \quad \int_{-\infty}^\infty \text{Re } s_x(x) dx = 0. \quad (30)$$

For  $x \leq 0$ , the function  $s_x$  is real and acquires the form

$$s_x(x) = \int_0^\infty dt \exp[xt - t^\alpha \Gamma(1-\alpha)]. \quad (31)$$

The imaginary part  $\text{Im } s_x(x)$  is positive at  $x > 0$ ; in the point  $x=0$  it is zero with all its derivatives. The properties described can readily be illustrated by an example of a fractal cluster with the dimension 1.5, for which from (20) it follows

$$\text{Im } s_{1/2}(x) = 1/2 \pi x^{-3/2} \exp(-\pi/4x) \theta(x), \quad (32)$$

where  $\theta(x)$  is the Heavyside step function.

The function  $s_x(x)$  describing the spectral line in the case of large fractal broadening is shown in Fig. 1 for values  $D=1.5$ ;  $2.5$ . It is just in this interval that the values of Hausdorff dimension of most known fractals lie. Note that when fractals are on the surface and the electric field  $E$  is perpendicular to it, the susceptibility is solely determined by the function  $s_x$ :

$$\chi_1 = R_0^3 s_x(x), \quad x = -R_0^3 \text{Re } \chi_0^{-1} \approx \Omega/\Omega_f, \quad (33)$$

where the approximate value of  $x$  has been calculated with the account of (22).

Zero value of  $\text{Im } \tilde{S}_x$  observed in Fig. 1 at negative detunings is due to the displacement of the excited monomers levels upwards from their initial position (positive interaction energy). Thus, the resonance and consequently the absorption described by  $\text{Im } \chi$  are possible only for positive detunings from the monomers lines. Of course, the absorption at negative detunings is actually not exactly zero, but its parameter  $(\Gamma/\max(\Omega, \Omega_f))^2$  is negligibly small.

The spectral dependence of the fractal susceptibility (21) in a three-dimensional space at  $\Omega_f \gg \Gamma$  and with (19), (22) acquires the form:

$$\chi = N \chi_1 = 1/3 N R_0^3 [2s_x(x) - 1/2 s_x^*(-1/2x)], \quad (34)$$

where  $x$  is defined by (33). This dependence is plotted in Fig. 2. As seen from the figure, with decreasing fractal dimension the resonance becomes narrower and the peaks are shifted to the axis  $\Omega=0$ , i.e. the

monomers retain more of their individuality. Note that the real part of the susceptibility is no longer proportional to the imaginary part derivative. Splitting of the spectral contour into doublets is associated with contributions of different dipole configurations (see the discussion following formula (12)). Resonance at negative detunings is generated by contributions of collinear dipole pairs having a down-shifted excited level (negative interaction energy). At detunings larger than the fractal width, susceptibility (34) is independent of the fractal dimension and tends to approach the susceptibility of an isolated monomer.

The resonance width and the imaginary part of (34) are finite and independent (at  $\Omega_f \gg \Gamma$ ) of the width  $\Gamma$ . They are determined by the phase mismatch. Different pairs of monomers, which are probable to approach each other because of the fractal correlation (2), have randomly shifted levels and resonate at different frequencies, which results in a rapid relaxation of the dipole moment (polarization). This effect is similar to the Landau damping in that the finite width and the imaginary part of the susceptibility are independent of dissipation, limiting the lifetimes of populations.

### 3. Giant Raman scattering on impurities in a fractal

Consider the enhancement of Raman scattering on an impurity particle due to the local field in a fractal exceeding the mean one. Let the particles on which the Raman scattering occurs be a small distance from some ( $i$ -th) monomer. Its radius-vector from the point  $\mathbf{r}$  will be denoted as  $\mathbf{R}$ . The field  $\mathbf{E}^c$  acting on the particle is essentially a combination of the mean field, the self-consistent field of the fractal in the point of the particle location and the field of the nearest ( $i$ -th) monomer considered as an induced dipole:

$$\begin{aligned} E_\alpha^c &= \chi_0 \Pi_{\alpha\beta} (\mathbf{E} + \mathbf{E}^i)_\beta, \\ \Pi_{\alpha\beta} &= a \delta_{\alpha\beta} + b n_\alpha^c n_\beta^c; \quad a = \chi_0^{-1} - R^{-3}, \quad b = 3R^{-3} \end{aligned} \quad (35)$$

where  $n_\alpha^c$  is the unit vector in the  $\mathbf{R}$  direction. Neglecting the Lorentz field, from (3), (8) for the sum of the mean and self-consistent field one obtains

$$(\mathbf{E} + \mathbf{E}^i)_\alpha = \chi_0^{-1} M_{\alpha\beta}^{-1} E_\beta. \quad (36)$$

Not to shadow the main physical principles, at first we shall neglect the enhancement of Raman scattering due to the impurity interaction with the fractal at the scattered radiation frequency. Anyway, this holds true for fairly large frequency detunings.

The GRS enhancement factor  $G$  is defined as the

ratio of the average square of the field influencing the particle to the square of the mean field. From (35), (36) in the limit of spherical symmetry it is estimated to be

$$G = \langle |\mathbf{E}^c|^2 \rangle / |\mathbf{E}|^2 = 1/3 S_p \langle TT^+ \rangle, \quad T = \Pi M^{-1}. \quad (37)$$

Supposing random orientation of the particle with respect to the fractal bonds,  $G$  (37) can be represented as a convergence of two tensors:

$$G = \frac{1}{3} \langle \Pi_{\alpha\beta}^* \Pi_{\beta\gamma} \rangle \langle M_{\gamma\delta}^{-1} M_{\delta\alpha}^{-1*} \rangle. \quad (38)$$

Using the response matrix in the form (9) and averaging over orientations, one finds

$$\langle M_{\alpha\beta}^{-1} M_{\beta\gamma}^{-1*} \rangle = \delta_{\alpha\gamma} \langle |A|^2 + \frac{1}{3} |B|^2 + \frac{2}{3} \text{Re}(AB^*) \rangle. \quad (39)$$

The expression for  $\langle \Pi_{\alpha\beta} \Pi_{\beta\gamma}^* \rangle$  has the same form, with the substitution  $A \rightarrow a$  and  $B \rightarrow b$ . Then (37) will have the form:

$$G = \frac{2}{3} R^{-6} \{ \mathbf{z} \langle |\chi_0^{-1} + \varphi|^{-2} \rangle + \langle |\chi_0^{-1} - 2\varphi|^{-2} \rangle \}. \quad (40)$$

One can readily see that

$$\langle |\chi_0^{-1} + \varphi|^{-2} \rangle = -R_0^3 \text{Im} S_x(-R_0^3 \chi_0^{-1}) / \text{Im} \chi_0^{-1}, \quad (41)$$

$$\langle |\chi_0^{-1} - 2\varphi|^{-2} \rangle = \frac{1}{2} R_0^3 \text{Im} S_x(\frac{1}{2} R_0^3 \chi_0^{-1}) / \text{Im} \chi_0^{-1}. \quad (42)$$

Of the three fields considered (see discussion of (35)) the essential contribution is given only by the field of the monomer nearest to the scattering particle. Its dipole however is generated by the self-consistent field of the entire fractal and depends on the Hausdorff dimension  $D$ . With the account of the above estimates, from (40), (41) the enhancement factor is evaluated as

$$G = -\frac{1}{3} \frac{R_0^3 R^{-6}}{\text{Im} \chi_0^{-1}} \text{Im} \left[ 4S_x(-R_0^3 \chi_0^{-1}) - S_x\left(\frac{1}{2} R_0^3 \chi_0^{-1}\right) \right]. \quad (43)$$

The enhancement factor reaches its maximum  $G_{\max}$  at  $R \sim R_m$ . For dielectric sphere we may put exactly  $R = R_m$ . Then from (43) or large fractal broadening ( $\Omega_f \gg \Gamma$ ) with the account of analytical extension (19) it follows that

$$G_{\max} = \frac{1}{3} \frac{\omega_m^2}{\Omega_f \Gamma} \text{Im} [4s_x(x) + s_x(-x/2)], \quad (44)$$

where  $x$  is defined by (33). It is interesting to note that, the spectral profile of the enhanced GRS, as seen from (44), reproduces the spectral form of absorption given by  $\text{Im} \chi_1$  (34). Relation between the absorption ( $\text{Im} \chi_1$ ) and the factor  $G_{\max}$  can be written in an explicit form, provided (44) is expressed in terms of (34)

$$G_{\max} = 2 \frac{\omega_m^2}{\Omega_f \Gamma} R_0^{-3} \text{Im } \chi_1. \quad (45)$$

It is worth comparing (44) with the expression for enhanced GRS on the impurity particle located on the dielectric sphere surface [17]

$$G_{\max} = 4 |(\varepsilon - 1)/(\varepsilon + 2)|^2 = 4 \omega_m^2 / \bar{\Gamma}^2, \quad (46)$$

where the latter equality has been obtained for the sphere susceptibility in the form (22),  $\bar{\Gamma}$  being the resonance width. For  $\bar{\Gamma}$  the observed resonance width is conventionally used while the frequency shift due to the interaction of various spheres is calculated from the theory of mean Lorentz field (see e.g. [16]). Note that both the resonance broadening and the resonance shift are large. Hence the phenomenological parameter  $\bar{\Gamma}$  corresponds to the value  $\Omega_f$  in the theory under discussion. From this one can see that (46), being used for a fractal cluster, underestimates  $G_{\max}$  by a factor of  $\Omega_f / \Gamma \gg 1$  as compared to the estimate (44), derived from the consistent theory which evaluates the shift and broadening of the monomers resonance jointly.

Appearance of the factor  $(\Omega_f \Gamma)^{-1}$  in the GRS enhancement coefficient is not accidental and is independent of the particular approximations. The point is that spontaneous Raman scattering is a noncoherent effect. Therefore it is the square of the absolute value of the field influencing the particle that should be averaged over the ensemble of fractals (cf. (37)). The phase of the field, which is essential for coherent effects, is of no importance here. As a consequence, emission from the impurity is determined by the local field of the nearest monomer. If the latter is resonant to the applied field, then, according to (46), the enhancement factor  $G$  is proportional to  $\Gamma^{-2}$ . The probability of this event is estimated as the relative spectral width  $\Gamma / \Omega_f$ . The product of these factors is responsible for the predicted dependence (44) (within a unit factor).

If the frequency shift due to Raman scattering is small ( $\Delta\omega \ll \Gamma$ ), the impurity-scattered radiation also interacts with the fractal monomers improving the efficiency of the process. The resultant form of the GRS enhancement factor is (cf. (37))

$$G = \frac{1}{3} \langle R_{\alpha\beta} T_{\beta\gamma} \cdot R_{\alpha\delta}^* T_{\delta\gamma}^* \rangle, \quad (47)$$

$$R \equiv M^{-1} \Psi; \quad \Psi_{\alpha\beta} \equiv R^{-3} (\delta_{\alpha\beta} - 3 n_\alpha^c n_\beta^c).$$

By the familiar procedure, from (47) one obtains for the enhancement factor  $G_{\max}$  in the main order

$$G_{\max} = \frac{\omega_m^4}{\Omega_f \Gamma^3} \left[ \frac{27}{10} - \frac{3}{10} \theta(-\Omega) \right] \text{Im } \chi_1 / R_0^3. \quad (48)$$

Comparison of (48) and (44) shows that the account of the additional enhancement due to scattering on the low-frequency impurity vibration leads to a rapid increase of  $G$ , since  $\omega_m / \Gamma \gg 1$ .

#### 4. Account of the Lorentz field

Consider the influence of the Lorentz field. With the account of  $\mathbf{E}^L$ , solutions (3) and (7) will have the form (cf. (8)):

$$d_\alpha^i = M_{\alpha\beta}^{-1} (\mathbf{E} + \mathbf{E}^L)_\beta.$$

For the fractal susceptibility one finds

$$\tilde{\chi} = N \tilde{\chi}_1, \quad \tilde{\chi}_1 = R_0^3 [R_0^3 \chi_1^{-1} - \alpha]^{-1}, \quad (49)$$

where  $\chi_1$  is defined by (21). Hereafter the tilda marks a renormalized value, i.e. the one calculated with the account of the Lorentz field. Then the spectral dependence of the susceptibility will be given not by (34), but by

$$\tilde{\chi} = N \tilde{\chi}_1 = N R_0^3 \{ 3 [2s_x(x) - 1/2s_x^*(-1/2x)]^{-1} - \alpha \}^{-1} \quad (49')$$

It should be noted that unlike (34), susceptibility (49') has a pole. However, since the real and imaginary parts of  $\chi_1$  are of the same order of magnitude, the pole occurs far away in the complex plane and does not appreciably affect the spectral behavior at physical values of frequency.

Figure 3 illustrates dependence (49'). From com-

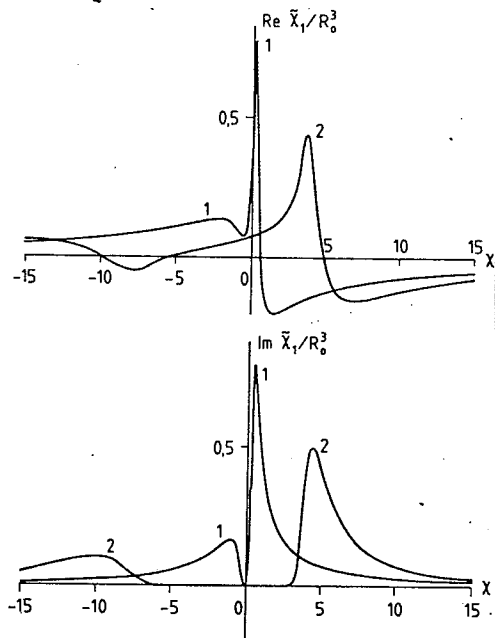


Fig. 3. The same as in Fig. 2, but for susceptibility (49') renormalized with the account of the Lorentz field

parison with Fig. 2 one can see that, as has been expected (see discussion after (6)), the susceptibility renormalization does not affect its qualitative behavior. Indeed, the spectrum remains splitted into a doublet with the components being shifted and broadened by the same order of magnitude. Quantitatively the renormalization in the "blue" range ( $\Omega > 0$ ) is noticeable: the peaks are by about 30% higher and a little shifted to the  $\Omega = 0$  axis as compared to Fig. 2. In the  $\Omega < 0$  limit the renormalization is negligibly small. Thus the linear fractal susceptibility depends mainly on the fluctuations in the close vicinity of the monomer. The effect of the Lorentz field is only to somewhat renormalize  $\chi_1$ , the renormalization being small in the "red" region of shifts where GRS is of most interest.

Similar to the above considerations, the account of the Lorentz field renormalizes the GRS enhancement factor. Instead of (36) we obtain:

$$(\mathbf{E} + \mathbf{E}^i)_\alpha = \chi_0^{-1} M_{\alpha\beta}^{-1} (\mathbf{E} + \mathbf{E}^L)_\beta, \quad (50)$$

which also results in the renormalized value

$$\tilde{G} = G |1 + \alpha \tilde{\chi}_1 / R_0^3|^2, \quad (51)$$

where  $G$  is defined by (44) if  $\Delta\omega \gg \Omega_f$ , or by (48) if  $\Delta\omega \gtrsim \Gamma$ . Then, instead of (48) one has

$$\tilde{G}_{\max} = \frac{\omega_m^4}{\Omega_f \Gamma^3} R_0^{-3} \left[ \frac{27}{10} - \frac{3}{10} \theta(-\Omega) \right] \text{Im } \tilde{\chi}_1. \quad (52)$$

Thus, the Lorentz field introduces no changes in (48) that relates the GRS enhancement factor to the absorption.

## 5. Final discussion

We summarize in short the basic principles used and the main results obtained. A theory of optical properties of fractal clusters (for shortness referred to as "fractals") has been developed. The linear susceptibility has been calculated (see (21), (34), and (49) and also Figs. 2 and 3). Giant Raman scattering has been predicted on the impurity centers bound to a fractal (the enhancement factor is given by (43), (51)).

It has been shown that fractals possess unique optical properties different from those of gas-phase and condensed media. The point is that non-trivial fractals have a small (asymptotically zero) mean density (in this respect resembling gases). This is due to the power-law pair correlation (2). The same correlation however may cause the monomers to approach each other and hence to be involved into a strong interaction (as is the case in condensed phase).

These properties allowed us to construct a theory of non-linear response of the non-trivial fractal by representing the self-consistent field as the sum of the nearest neighbour field (binary approximation) and the Lorentz field. The former appears to be the decisive one (see the discussion following formulas (7), (49) and (52)).

Giant Raman scattering from a fractal occurs because the impurity particle fixed at some monomer is subject to a strong local field of this monomer only. This field is strong because all fractal monomers retain their individuality (as a consequence of rarified structure and disordering of the fractal). The enhancement factor  $G$ , estimated in binary approximation, is given by (48). Account of the Lorentz field, renormalizing the enhancement factor, does not affect its relation to the fractal absorption (see (52)).

Finally, let us consider qualitatively application of the theory to real clusters, which, as has been mentioned in Introduction, are widely spread. In this connection it should be noted that when developing the theory (see the transition from (14) to (15)) we took into account only the pair correlations whose function (2) is determined by the fractal properties, and ignored many-particles correlations. If still the latter are strong, then a group of strongly correlated particles may be considered as one monomer with a renormalized susceptibility. By the procedure of renormalization, analogous to the one used in the theory of phase transitions, it is possible to return back to weak many-particles correlation and to derive from (14) formula (18) and all the subsequent expressions.

For example, flexible linear macromolecules of polymers are fractal clusters with  $D \simeq 5/3$  dimension [11]. A renormalized monomer in such macromolecules may be considered to be the part of the chain limited by the so called persistent length. The latter is a range of strongly correlated monomers where the polymer may be considered to be rectilinear. The persistent length may range from some units (e.g. in RNA) up to hundreds (in two-chain DNA) of monomers.

Let us see how the theory can be applied to the effect of GRS. Consider small spherical particles of argentum whose plasma oscillations correspond to the wavelength  $\lambda_p = 2\pi c/\omega_p = 140$  nm. The excited GRS spectra in such systems are normally thought to group around the plasmon resonance frequency. According to (26), it corresponds to the wavelength  $\lambda_0 = 380$  nm. The experiments (see e.g. Fig. 13 in [17]) show that the excited GRS spectra of one and the same impurity, depending on the technique of preparation of metal matrices, appear to have maxima both in the near UV (which corresponds approximately to  $\lambda_0$ ) and in the longwave, up to the red, spectral



ranges. Explanations of the large spectral shifts by the account of monomers interaction which are considered to be noncorrelatedly spaced (trivial fractal structure) in terms of the Lorentz theory encounters difficulties. For example, in order to obtain the absorption peak at 650 nm, one has to assume that the metal takes up 86% of the bulk volume [16]. While in fact the experiments on aggregated metal colloids, in which maximum GRS signal was observed, yield an order of magnitude smaller value (cf. [6]).

Below we shall show that the presence or absence of a fairly longwave absorption band in a cluster depends on its fractal dimension. For definiteness we shall assume maximum density of the cluster (the spheres are in close contact with each other), i.e. we put  $R_0 \simeq R_m$ . Then from (26), (27) the typical fractal frequency  $\Omega_f$  is estimated to be about 20% of the  $\omega_0$ . The spectral width of fractals may several times exceed  $\Omega_f$  (cf. Fig. 3), i.e. it may be of order  $\omega_0$ .

The above estimate implies a large magnitude of the spectral shifts for fractals. For the detunings as large as that, however, the linearized susceptibility expression (22), strictly speaking, is no longer valid. Therefore it is necessary to introduce into all expressions  $x = -R_0^3 \text{Re } \chi_0^{-1}$  (33) instead of  $\Omega/\Omega_f$ , where  $\chi_0$  is fixed by (24) with  $\varepsilon$  in the form (26). The quantity  $x$  depends on  $\omega$  as follows. In the high-frequency region ( $\omega_0 \leq \omega \leq \omega_0 [(\varepsilon_0 + 2)/(\varepsilon_0 - 1)]^{1/2}$ )  $x$  values range from 0 to  $\infty$ ; in the longwave region  $x$  runs a finite interval of values from 0 to  $-1$ . In Fig. 3 it is seen that for  $x$  ranging from 0 to some limiting value  $-x_m$ , dependent on the fractal dimension,  $\text{Im } \tilde{\chi}_1$  is close to zero. Proceeding from the discussed properties, we conclude that the fractal absorption from metallic monospheres in the longwave range (at  $\omega < \omega_0$ ) is essential only for  $x_m < 1$ . The  $x_m$  values (at half-maximum  $\text{Im } \tilde{\chi}_1$ ) for various dimensions are as follows (see Fig. 3):  $D = 1.5$ ,  $x_m = 0.5$ ;  $D = 1.75$ ;  $x_m = 1.0$ ;  $D = 2.5$ ,  $x_m = 8.0$ . Thus, absorption, and consequently the effect of GRS, in the longwave range for the clusters under discussion are substantial only at  $D \lesssim 1.75$ . Note that for cluster aggregation it is expected that  $D \simeq 1.75$  [4]; a close value of  $D$  was obtained in the experiments with Au colloids [6]. The fractal dimension close to the boundary ( $D = 1.75$ ) is associated

with the variability of occurrence of the longwave band in the GRS excitation spectra. To conclude the discussion, we note that the dependence of  $G$  considered above (see (46) and thereafter) may account for the earlier obscure fact [17] that the maximum GRS was observed just on the metallic colloidal aggregates, being, as is known, (see e.g. [6]) of fractal nature.

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