

Optical properties of fractal clusters (susceptibility, surface enhanced Raman scattering by impurities)

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A theory is developed which describes, for the first time, the optical properties of fractal clusters (i.e., aggregates having nontrivial Hausdorff dimensionality and consisting of interacting monomer particles). It is shown with respect to these properties the fractal clusters differ substantially from both gases and condensed media. A dipole-dipole interaction between the monomers is assumed. The theory is based on the self-consistent-field equations. It takes into account the fluctuating character of the fractal cluster (the fact that the probability of mutual approach of the monomers is not small while the integral probability density tends asymptotically to zero). An expression for the linear susceptibility is obtained. The spectra of individual monomers joined into a cluster are subject to splitting, shift, and broadening, which depend strongly on the fractal (Hausdorff) dimensionality of the cluster, but are independent of the number of monomers in it (if the cluster has a nontrivial dimensionality). At the same time, the monomers preserve partially their individuality, and the susceptibility remains quasisonant. The broadening, just as the imaginary part of the susceptibility, is independent of the dissipation in an individual monomer. Surface enhanced Raman scattering (SERS) is predicted from an impurity particle fixed near one of the monomers of the cluster if the latter is excited in its absorption band. The gain of the SERS is also determined by the fractal dimensionality.

1. INTRODUCTION

Fractals, objects of non-integer (in the case of general position) dimensionality imbedded in three-dimensional space,^{1,2} are attracting ever increasing interest. Their physical realization are, in particular, fractal clusters. These are aggregates of particles, called monomers, joined by bonds. The number of monomers in a certain radius r inside a fractal is given asymptotically (as $r \rightarrow \infty$) by

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

where R_0 is a constant of the dimension of length, and D is an index, called the fractal (Hausdorff) dimensionality. D is in general a noninteger, and a fractal is called nontrivial when D is less than the dimensionality of the space.

The bonds specify the long-range paired correlation between the monomers, corresponding to a density-density correlation function

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

where r is the distance between the monomers, R_c is the total dimension of the fractal, and the exponent ($D - 3$) in the function g is also determined by the fractal dimensionality (a consequence of gauge invariance).

Fractal clusters are formed, in particular, in diffusion-limited aggregation processes (polymerization).³⁻⁵ Accordingly, fractals are particles having different physical properties in colloidal solutions and in suspensions (see, e.g., Refs. 6-9). A solidifying surface that grows under diffusion-limited conditions with insufficient surface relaxation, or is formed when the material is sprayed-on, is also an aggregate

of fractal clusters.^{5,10} Most macromolecules (polymers) are fractals.¹¹ Fractals include also the so-called percolation clusters (see, e.g., Ref. 12) formed when bonds are randomly produced between centers and are models of fluctuations in phase transitions, and also structures of binary solutions and polymers.

It is shown in the present paper that fractals have unique optical properties that differ radically from those of either gases or condensed media. When a fractal is formed, the lines of monomers broaden and split into doublets, but the latter remain centered near the initial positions, in which the minimum absorption of the fractal takes place. Thus, the individuality (the resonant character of the lines) of monomers is partially conserved. This property is due to the fact that the integral density of the particles of the fractal tend to zero with increase of its radius, in proportion to R_c^{D-3} . Simultaneous interaction of many monomers has therefore low probability, but their binary interaction can be quite strong in view of the presence of the pair correlation (2). As $D \rightarrow 3$, i.e., on going to a trivial fractal, the lines broaden strongly (in the "thermodynamic" limit $N \rightarrow \infty$, $R_c \rightarrow \infty$, $R_0 = \text{const}$), owing to the long-range character of the dipole-dipole interaction. This is evidence that the monomers have a tendency to lose their individuality (formation of a broad level band) in a condensed medium.

It will be shown below that fractals have also another important property—they are subject to surface-enhanced Raman scattering (SERS) by impurity centers. It is customary to assume (see Refs. 13 and 14) that SERS is produced when an impurity is bound to a rough surface of a polarizable body. In this respect, the entire fractal is an extremely rough

"surface" (with dimensionality D). The results of the present paper explain a fact hitherto not understood,¹⁴ that the strongest SERS signal of impurity molecules is observed from aggregated metallic particles in colloidal solutions (such particles are now known to be fractal clusters).

2. LINEAR SUSCEPTIBILITY OF A FRACTAL

Consider a fractal consisting of N monomers located at points $\{r^i\}$ and interacting via dipole-dipole forces. We obtain the linear response of the dipole moment within the framework of the equations of the time-dependent self-consistent field. Let the light-wave intensity be $\mathbf{E}(t) = \mathbf{E}_\omega e^{-i\omega t} + \text{c.c.}$ The quantum-mechanical mean value of the dipole moment induced by the wave field at the i th monomer is similarly expressed: $\mathbf{d}^i(t) = \mathbf{d}_\omega^i e^{-i\omega t} + \text{c.c.}$ We leave out hereafter the indices ω of the amplitudes. We assume for simplicity that the monomers are identical and are isotropically polarized (by assuming the latter property we lose effects connected with the light-wave polarization). The equations for the response amplitudes are

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

here \mathbf{E} is the external field, \mathbf{E}^i is the field due to the remaining monomers at the location of the given one, and $\chi_0 = \chi_0(\omega)$ is the polarizability of an isolated monomer; a (Latin) superscript stands everywhere for the number of the particle, and a (Greek) subscript for a tensor component;

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

where \mathbf{n}^{ij} is a unit vector in the direction of $r^{ij} \equiv r^j - r^i$; the prime on the summation sign means that the sum extends over all monomers but the i th. For simplicity we assume everywhere that the light wavelength λ exceeds considerably the cluster dimension R_c .

A property of a dipole interaction (and in general of a multiple interaction with nonzero moment) is that the self-consistent field vanishes on averaging over a spherically symmetric distribution. Contributions are therefore made in (4) only by anisotropic fluctuations of the particle density. By virtue of the rarefaction (asymptotically zero average density, see the Introduction) of a nontrivial fractal, almost all monomers are located at large ($\gg R_0$) distances from the given one and form an approximately isotropic cloud that makes a small contribution to (4).

Starting from the properties described above, we separate from the self-consistent field \mathbf{E}^i the contribution of the few closest monomers (the fluctuating component). We represent the field of the large number of remote monomers in the usual fashion, as a sum of a depolarizing field and a Lorentz field \mathbf{E}^L . We combine the first of them with the external field \mathbf{E} . After this renormalization, \mathbf{E} in (3) no longer stands for the external field but for the average macroscopic field, the response to which is to be determined. The self-consistent (local) field acquires 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 Σ'' denotes summation over the monomers located inside the sphere of a certain sufficiently small radius R_L constructed around the given (i th) monomer (Lorentz sphere).

The Lorentz field can be easily calculated in the case of a fractal as the field produced by the charges on the surface of the selected sphere of radius R_L , or by using integral relation (e.g., in analogy with Ref. 15). Using (2) for the monomer density around the fixed i th monomer, we get

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

where d is the average (in the sense of the response amplitude) dipole moment of the monomer. In contrast to the case $D = 3$, the Lorentz field (6) depends on R_L .

It can be seen from (5) and (6) that \mathbf{E}^L does not exceed the field of one monomer brought to within a distance $r \lesssim R_0$ to the given one. This approach is probable, notwithstanding the asymptotically zero integral density of the nontrivial fractal: it follows from (1) and (2) that the average number of monomers within the radius R_0 around the given one is equal to unity.

Starting with the indicated properties, we retain in the sum Σ of (5) only one term corresponding to the nearest monomer numbered, say, j (binary approximation). For self-consistency it is necessary that the Lorentz sphere contain (on the average) one monomer. In accordance with (1) and (2), this choice means that $R_L = R_0$.

In view of the symmetry of the dipole-dipole interaction relative to particle exchange [to reversal of the sign of \mathbf{n}^{ij} in (5)], and since the nearby monomers are located in the same field of the remote monomers, we conclude that $\mathbf{d}^j = \mathbf{d}^i$. The self-consistent field (5) takes then the form

$$E_\alpha^i = -d_\beta^i (\delta_{\alpha\beta} - 3n_\alpha^{ij}n_\beta^{ij}) (r^{ij})^{-3} + E_\alpha^L, \quad \mathbf{E}^L = Dd/3R_0^3. \quad (7)$$

Even though the two contributions to (7) are of the same order (it must be recognized that $r^{ij} \lesssim R_0$), they manifest themselves differently, as will be shown below. The field proportional to \mathbf{d}^i (binary) and describing the fluctuation in the nearest environment of the monomer causes, besides a shift of the spectrum, a broadening not connected with the initial relaxation (dissipation) in the monomer. In addition, the analytic properties of the susceptibility are changed: the poles in the complex frequency plane are replaced by branch points. In contrast to the binary contribution, the second term (the Lorentz field) in (7) is not random and therefore, as is clear beforehand, does not change the analytic properties of the response and leads only to a certain renormalization of the latter (the meromorphism of the response function is not violated if only the Lorentz field is taken into account).

To prevent details from obscuring the results of the fluctuating character of a nontrivial fractal (whose binary-interaction probability not small at zero average density), we develop the theory first in a purely binary approximation, neglecting the Lorentz field \mathbf{E}^L . We next (see Sec. 4) take \mathbf{E}^L into account exactly and confirm the arguments advanced above.

Omitting the field \mathbf{E}^L from (7), we obtain the solution (3), (7) in the form

$$d_\alpha^i = M_{\alpha\beta}^{-1} E_\beta, \quad M_{\alpha\beta} = (\chi_0^{-1} + \Phi) \delta_{\alpha\beta} - 3n_\alpha^{ij}n_\beta^{ij} \Phi, \quad (8)$$

where $\Phi = (r^{ij})^{-3}$. The response matrix M^{-1} is given by

$$M_{\alpha\beta}^{-1} = A \delta_{\alpha\beta} + B n_\alpha^{ij}n_\beta^{ij}, \quad A = (\chi_0^{-1} + \Phi)^{-1}, \quad (9)$$

$$B = (\chi_0^{-1} - 2\Phi)^{-1} - A.$$

We recognize now that the given monomer can be approached by any of the monomers of the fractal. We must therefore express Φ in the form

$$\Phi = \sum_j (r^{ij})^{-1}. \quad (10)$$

If the binary approximation (8)–(10) is used self-consistently, averaging over the configurations $\{r^i\}$ should yield only the paired correlator (2).

Taking into account the isotropy of the particle distribution, we obtain for the average amplitude of the dipole-moment response

$$d = \chi_1 E, \quad \chi_1 = \langle \chi_i \rangle, \quad \text{Sp} \langle M^{-1} \rangle, \quad (11)$$

where $\langle \dots \rangle$ is an average over the ensemble of clusters, i.e., over the sets $\{r^i\}$; the trace is taken over the tensor indices; χ_1 is the average susceptibility of the monomer in the fractal. The value of χ_1 , obviously, no longer depends on the number of the particle. Therefore the dipole susceptibility of the cluster is

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

The physical meaning of this result is lucid. The first term in the angle brackets corresponds to dipoles that are perpendicular to the vector r^{ij} that joins them; the statistical weight of such an arrangement is equal to 2. The second term corresponds to the case of a collinear arrangement of the dipoles [the field reverses direction in this case and is doubled in intensity, cf. (4)]. The additive character of the averaging of the indicated configurations, which follows from (12), is due to the binary approximation.

To calculate χ_1 we must find averages of quantities of the type $(z + \Phi)^{-1}$, where z is a complex parameter [cf. (12)]. We use for this purpose the Laplace transform

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

where $\text{Im } z < 0$; we obtain the result for $\text{Im } z < 0$ by analytic continuation;

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

As a consequence of the binary approximation, the averaging over all monomer pairs i, j in (14) is carried out independently; this yields

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

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

Substituting the correlator (2), we obtain from (16) asymptotically as $R_c \rightarrow \infty$ (the actual requirement is $R_c \gg |\chi_0|^{1/3}$)

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

where $\Gamma(x)$ is the gamma function, and the branch of the power-law function is fixed by choosing the phase: $i = e^{i\pi/2}$. The procedure used above to calculate the function (14) is similar (accurate to the use of the "imaginary time") to that

known in the theory of static quenching of incoherent excitations.¹⁶ It can be seen from (17) that $f(t) \rightarrow 0$ are $R_c \rightarrow \infty$. Therefore, taking (1) into account, we obtain from (13), (15) and (17) in the thermodynamic limit (as $N \rightarrow \infty$, $R_c \rightarrow \infty$, $R_0 = \text{const}$)

$$\langle (z + \Phi)^{-1} \rangle = R_0^3 S_\alpha(-R_0^3 z), \quad (18)$$

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

where $\alpha = D/3$, and S_α is a special function of the complex variable z , determined from (18) with $\text{Im } z > 0$; its analytic continuation into the lower half-plane is defined by the relation

$$S_\alpha(z^*) = S_\alpha^*(z). \quad (19)$$

It can be shown that $S_\alpha(z)$ is analytic in the complex plane, with a cut from 0 to ∞ along the real axis; $z = 0$ is a branch point. At $\alpha = 1/2$ the function $S_\alpha(z)$ is expressed in terms of standard functions [17]

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

It follows from (12) and (19) that the dipole susceptibility of the fractal is of the form

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

It can be seen from this expression that the form of the functional dependence of the cluster on the monomer susceptibility is determined by the fractal dimensionality, whereas the scales of this dependence are set by the dimensional parameter R_0 of the fractal.

To determine the dependence of χ (21) on the radiation frequency, we specify the form of the susceptibility χ_0 of a single monomer. For systems having an isolated resonance we have near this resonance

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

where Ω is the deviation from resonance, Γ is the relaxation constant (the width of the resonance), and ω_m and R_m are respectively the characteristic excitation frequency and the geometric dimension of the system. In the two-level-system model

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

where d_{12} is the dipole moment of the transition (we use a system of units in which $\hbar = 1$). For the important case of a monomer in the form of a macroscopic sphere of radius R_m and dielectric constant ϵ , the known expression

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

reduces in the vicinity of the isolated resonance to the form (22), with parameters

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

The values of ϵ'' , $\partial\epsilon'/\partial\omega$ in (25) are taken at a point at which $\epsilon' = -2$. For plasmon resonance in a metallic sphere

$$\varepsilon = \varepsilon_0 - (\omega_p/\omega)^2, \quad \omega_m = \frac{3}{2}\omega_p(\varepsilon_0+2)^{-1/2}, \quad \omega_0 = \omega_p(\varepsilon_0+2)^{-1/2}, \quad (26)$$

where ε_0 is the constant contribution made to ε by the interband transitions, ω_p is the plasma frequency, and ω_0 is the resonant frequency corresponding to the point $\Omega = 0$.

When account is taken of (22), it can be seen from (21) that inclusion of a monomer in a fractal broadens and shifts the spectral lines of the latter by amounts of the order of the characteristic fractal frequency

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

As indicated above, the broadening of the spectra is due to the large density fluctuations in the nontrivial fractal.

The existence of a thermodynamic limit (or of a gauge invariance—independent of the susceptibility per monomer of the cluster radius R_c) is an exclusive feature of a nontrivial fractal ($D < 3$); this feature vanishes at $D = 3$. In the latter case, as can be seen from the initial relation (16), a logarithmic divergence appears and the estimate of the broadening (shift) of the monomer lines takes the form

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

We point out that the logarithm is never too large here, since $R_c \lesssim \lambda$. The fact that in the theory there are no divergences of a nontrivial fractal means also that the form (2) of the correlation function, which is valid strictly speaking only at $R_0 \lesssim r \lesssim R_c$, can be used in calculations [in Eq. (16)] in the entire range of r .

If the fractal broadening Ω_f (27) exceeds considerably the initial width Γ , the latter can be made to approach zero in (21). In that case, however, the imaginary part of the function S_α does not tend to zero; it is finite and its sign is determined by that of the imaginary part of Γ . In this case the susceptibility is determined by a complex function of a real pure argument

$$s_\alpha(x) \equiv S_\alpha(x+i0). \quad (29)$$

This function satisfies the following sum rule for the imaginary part and the requirement that the real part be conserved:

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

At $x < 0$ the function s_α is pure real and takes the form

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

The imaginary part $\text{Im } s_\alpha(x)$ is positive at $x > 0$ and vanishes at $x = 0$ together with all its derivatives. These properties can be easily tracked using as an example a fractal cluster of dimensionality 1.5, for which it follows from (20) that

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

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

The function $s_\alpha(x)$, which determines the line contour in the case of large fractal broadening, is shown in Fig. 1 for $D = 1.5$ and 2.5, which span the values of the Hausdorff dimensionality of most known fractals. We point out that in the case of fractals on a plane and of an electric field E per-

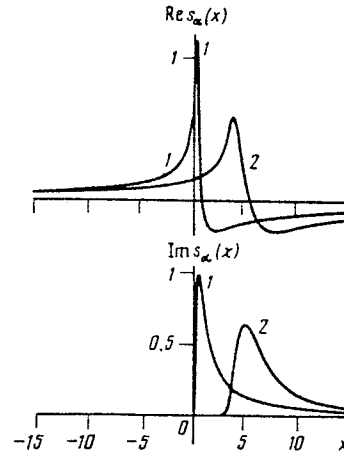


FIG. 1. Real and imaginary parts of the function (18). Curves: 1— $\alpha = 0.5, D = 1.5$; 2— $\alpha = 0.83, D = 2.5$.

pendicular to the plane, the susceptibility is determined by one function s_α :

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

where the approximate value of X was obtained with allowance for (22).

The vanishing of the imaginary part of χ_1 at negative detunings, which can be tracked in Fig. 1, is due to the fact that the excited levels of all the monomers are shifted in this case upward from the initial positions (the interaction energy is positive). The resonance, and with it also the absorption described by $\text{Im } \chi$, is therefore possible only for positive detuning from lines of isolated monomers. Of course, absorption at negative detunings is in fact strictly nonzero, but it is small in the parameter $(\Gamma/\max(\Omega, \Omega_f))^2$.

At $\Omega_f \gg \Gamma$, with allowance for (19) and (22), the spectral dependence of the susceptibility (21) of a fractal imbedded in a three-dimensional space takes the form

$$\chi_1 = N \chi_1 = \frac{1}{3} N R_0^3 [2s_\alpha(X) - \frac{1}{2} s_\alpha^2(-\frac{1}{2}X)], \quad (34)$$

where X is defined in (33). This dependence is illustrated in Fig. 2. It can be seen that when the fractal dimensionality is

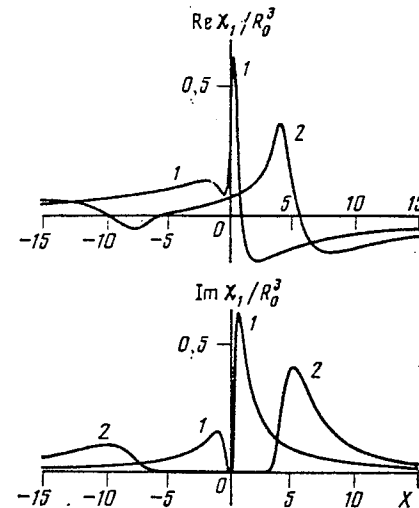


FIG. 2. Real and imaginary parts of the susceptibility (34) (per monomer), calculated in the binary approximation, vs the variable $X = -R_0^3 \text{Re } \chi_0^{-1} \approx \Omega/\Omega_f$. Curves: 1— $D = 1.5$; 2— $D = 2.5$.

decreased the resonance becomes more peaked, and the peaks shift towards the $\Omega = 0$ axis, i.e., the monomers preserve their individuality to a greater degree. The real part of the susceptibility is no longer proportional to the derivative of the imaginary part. The splitting of the contour into doublets is determined by the contribution of the various configurations of the dipoles [see the discussion that follows Eq. (12)]. At negative detunings the resonance is due to contributions of collinear dipole pairs whose excited level is shifted downward (negative interaction energy). At detunings considerably larger than the fractal width, the susceptibility (34) is independent of the fractal dimensionality and tends to the susceptibility of an isolated monomer.

The width of the resonance and the imaginary part of the susceptibility (34) are finite and are independent (at $\Omega \gg \Gamma$) of the initial width Γ . They are due to dephasing phenomena. Different pairs of monomers, whose mutual approach is probable in view of the fractal correlation (2), have randomly shifted levels and resonate at different frequencies, and this leads to rapid relaxation of the induced dipole moment (polarization). This effect is similar to Landau damping in the sense that the finite line width and the imaginary part of the susceptibility are not connected with dissipation in individual monomers, a dissipation that limits the lifetime of the populations.

3. SURFACE ENHANCED RAMAN SCATTERING (SERS) BY IMPURITIES IN FRACTALS

We consider the enhancement of Raman scattering by an impurity particle, due to the excess of the local field in the fractal over the mean value. Let the Raman-scattering particle be at a short distance from a certain (i th) monomer of the fractal, and let the particle radius vector drawn from the point r be designated \mathbf{R} . The field \mathbf{E}^c acting on this impurity particle consists of the average field, the self-consistent field of the fractal at the particle location, and the field of the nearest (i th) monomer regarded as an induced dipole:

$$E_a^c = \chi_0 \Pi_{\alpha\beta} (E + E^i)_\beta, \quad (35)$$

$$\Pi_{\alpha\beta} = a \delta_{\alpha\beta} + b n_\alpha n_\beta; \quad a = \chi_0^{-1} - R^{-3}, \quad b = 3R^{-3},$$

where \mathbf{n}^c is a unit vector in the direction of \mathbf{R} . In the Lorentz-field approximation we can obtain from (3) and (8) the following expression for the sum of the average and self-consistent fields:

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

To keep the details from obscuring the physical principles, we shall neglect the enhancement of the Raman scattering by the interaction of the impurity particle with the fractal at the scattered-radiation frequency. This, at any rate, is valid for sufficiently large frequency shifts due to scattering.

The SERS gain G is determined by the ratio of the mean squared field acting on the impurity to the square of the field E . From (35) and (36), with allowance for the spherical symmetry we obtain for the gain

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

Assuming a random orientation of the impurity particle relative to the bonds of the fractal, we represent G (37) as a contraction of two fourth-rank tensors:

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

Using the form (9) of the response matrix and averaging over the orientations, we get

$$\langle M_{\alpha\beta}^{-1} M_{\gamma\delta}^{-1} \rangle = \delta_{\alpha\gamma} \delta_{\beta\delta} \langle |A|^2 + \frac{2}{3} \text{Re}(AB^*) + \frac{1}{3} |B|^2 \rangle + \frac{1}{15} (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \langle |B|^2 \rangle. \quad (39)$$

The expression for $\langle \Pi_{\alpha\beta} \Pi_{\gamma\delta}^* \rangle$ takes the form, with the substitutions $A \rightarrow a$ and $B \rightarrow b$. As a result, expression (37) for the gain becomes

$$G = \left[\frac{2}{3} |\chi_0|^{-2} + \frac{4}{15} R^{-6} \right] \langle |\chi_0^{-1} + \Phi|^{-2} \rangle + \left[\frac{1}{3} |\chi_0|^{-2} + \frac{4}{15} R^{-6} \right] \langle |\chi_0^{-1} - 2\Phi|^{-2} \rangle + \frac{1}{3} R^{-6} \text{Re} \langle (\chi_0^{-1} + \Phi)^{-1} (\chi_0^{-1} - 2\Phi)^{-1} \rangle. \quad (40)$$

It is easy to verify that

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

$$\text{Re} \langle (\chi_0^{-1} + \Phi)^{-1} (\chi_0^{-1} - 2\Phi)^{-1} \rangle = R_0^3 \text{Re} \{ (2\chi_0^{-1} + \chi_0^{-1})^{-1} [S_\alpha (-R_0^3 \chi_0^{-1}) - S_\alpha^* (\frac{1}{2} R_0^3 \chi_0^{-1})] \}. \quad (42)$$

It can be seen from a comparison of the widths of the corresponding structures that the interference term (42) is small in terms of the parameter $\Gamma/\Omega_f \ll 1$. Note that this term has a small spectral width (of order Γ).

It follows from the representation (22) that in G (40) the contribution proportional to $|\chi_0|^{-2}$ is small in the parameter $\Gamma^2/\omega_m^2 \ll 1$. Thus, from among the three fields accounted for [see the discussion of Eq. (30)], only that of the fractal monomer closest to the scattering particles is significant. Its dipole, however, is induced by the self-consistent field of the entire fractal and depends on the Hausdorff dimensionality D . Taking into account the ongoing estimates, we obtain for the gain from (40) and (41)

$$G = \frac{2}{15} \frac{R_0^3 R^{-6}}{-\text{Im} \chi_0^{-1}} \text{Im} \left[7S_\alpha (-R_0^3 \chi_0^{-1}) - S_\alpha \left(\frac{1}{2} R_0^3 \chi_0^{-1} \right) \right]. \quad (43)$$

The maximum gain, G_{\max} , is reached at $R \sim R_m$. For a dielectric-sphere monomer we can write rigorously $R = R_m$. It follows then from (43) for the case of large fractal broadening ($\Omega_f \gg \Gamma$), with allowance for the analytic-continuation formula (19), that

$$G_{\max} = \frac{2}{15} \frac{\omega_m^2}{\Omega_f \Gamma} \text{Im} \left[7s_\alpha(X) + s_\alpha \left(-\frac{1}{2} X \right) \right]; \quad (44)$$

with X as defined in (33). Since the two functions $\text{Im} s_\alpha$ in (44) never differ from zero simultaneously, the spectral form of the SERS gain agrees, at a given sign of the detuning, with the form of the absorption spectrum given by $\text{Im} \chi$ (34). This property is a consequence of the employed approximations—the binary one and $R_c \ll \lambda$. The connection between $(\text{Im} \chi)$ and the factor G_{\max} can be written in explicit form by rewriting (44) with the aid of (34):

$$G_{\max} = (\omega_m^2/\Omega_f \Gamma) [\frac{7}{3} - \frac{3}{5} \theta(-\Omega)] \text{Im} \chi_i / R_0^3. \quad (45)$$

It is expedient to compare the result (44) with the expression for the gain of SERS by an impurity particle fixed on the surface of a dielectric sphere¹⁴:

$$G_{\max} = 4 \left[\frac{\epsilon - 1}{\epsilon + 2} \right]^2 = 4 \omega_m^2 \Gamma^2, \quad (46)$$

where the second equality was obtained for the susceptibility, in the form (22), of the sphere, while $\bar{\Gamma}$ is the width of the resonance. It is customary to use for $\bar{\Gamma}$ the observed resonance width, while the frequency shift due to the interaction of different spheres with one another is calculated by using the theory of the averaged Lorentz field (see, e.g., Ref. 13). We point out that both the observed broadening and the shift of the resonance are large. Thus, the phenomenological parameter $\bar{\Gamma}$ agrees with the value Ω of the present theory. This shows that the use of (46) for a fractal cluster underestimates G_{\max} by a factor $\Omega_f/\Gamma \gg 1$ compared with Eq. (44), which is the result of a consistent theory in which both the shifts and the broadenings of monomer resonances are obtained in a self-consistent fashion.

The appearance of the factor $(\Omega_f \Gamma)^{-1}$ in the SERS gain (44) is not accidental and is not connected with specific approximations. The point is that spontaneous Raman scattering is an incoherent effect. Therefore the quantity to be averaged over the ensemble of fractals is the squared modulus of the field acting on the impurity [cf. (37)]. On the other hand the phase of this field, which is important for coherent effect, is immaterial in this case. Consequently, the impurity emission is determined by the local field of the nearest monomer. If the latter is at resonance with the external field, the gain is proportional to Γ^{-2} in accordance with (46). Furthermore, the probability that the monomer nearest to the impurity is resonant is estimated to be the spectral width Γ/Ω_f . It is the product to these factors which leads (apart from a factor of the order of unity) to the predicted Eq. (44).

4. ALLOWANCE FOR THE LORENTZ FIELD

Let us consider the influence of the Lorentz field. With E^L taken into account, the solution of Eqs. (3) and (7) is of the form [cf. (8)]

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

From this, for the susceptibility of fractals, we have

$$\tilde{\chi} = N \tilde{\chi}_1, \quad \tilde{\chi}_1 = R_0^3 \{ R_0^3 \chi_1^{-1} - \alpha \}^{-1}, \quad (48)$$

where χ_1 is given by (21); here and henceforth the tilde labels a renormalized quantity, i.e., calculated with allowance for the Lorentz field. The spectral dependence of the susceptibility (34) is now replaced by

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

We point out that in contrast to (34) the susceptibility (49) has a pole. Since, however, the real and imaginary parts of χ_1 are of the same order, this pole is located far in the complex plane and does not influence greatly the behavior at physical values of the frequency.

Relation (49) is illustrated in Fig. 3. Comparison with Fig. 2 shows that, as expected [see the discussion following Eq. (6)], renormalization of the susceptibility does not alter the qualitative feature of its behavior. Indeed, the spectrum remains split into a doublet, each component of which is shifted and broadened by amounts of the same order. Quantitatively, the renormalization in the "blue" region ($\Omega > 0$) is noticeable: the peaks are approximately 30% higher and are shifted somewhat towards the $\Omega = 0$ axis compared with Fig. 2. In the region $\Omega < 0$ the renormalization is negligibly

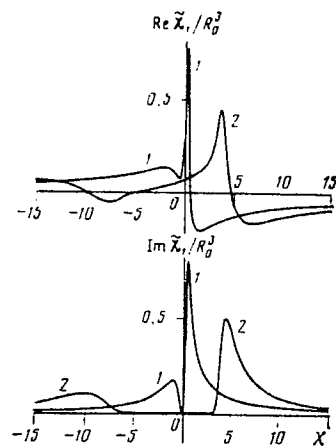


FIG. 3. The same as Fig. 2, but for the susceptibility (7) renormalized by taking the Lorentz field into account.

small. The linear susceptibility of the fractal is thus determined mainly by fluctuations in the nearest environment of the monomer. The Lorentz field leads only to some renormalization which is small in the "red"-shift region that is of greatest interest for observation of the SERS effect.

In analogy with the foregoing, allowance for the Lorentz field renormalizes the SERS gain. We have in place of (36)

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

which leads to the renormalized value

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

where G is given by (43). With allowance for (48), we get therefore in place of (44)

$$\tilde{G}_{\max} = (\omega_m^2 / \Omega_f \Gamma) [7/5 - 3/5 \theta(-\Omega)] \text{Im } \tilde{\chi}_1 / R_0^3. \quad (52)$$

Thus, the connection (44) between the SERS gain and absorption factor (the value of $\text{Im } \tilde{\chi}_1$) does not change at all when the Lorentz field is taken into account.

5. CONCLUDING DISCUSSION

We summarize briefly the general principles and the result of this paper. A theory for the optical properties of fractal clusters (called here fractals for short) has been formulated for the first time. The linear susceptibility has been obtained [see (21), (34), and also (48), (49), and Figs. 2 and 3]. The existence of surface-enhanced Raman scattering by impurity centers embedded in a fractal has been predicted [the gain is given by (43) and (51)].

Fractals differ in their optical properties from both gases and condensed media. The point is that nontrivial fractals have low (asymptotically, zero) average density (in this respect they are similar to gases). The reason is the presence of the power-law pair correlation (2). The very same correlation, however, makes for a sizable probability of pairwise mutual approach of the monomers that make up the fractal, and hence for a strong interaction between them (as in the condensed phase). These properties have made it possible to construct for the linear response of a nontrivial fractal a theory based on subdivision of the self-consistent field into contributions of the nearest neighbor (binary approximation)

and of the Lorentz field. The fluctuating field of a nearest neighbor turns out to be the most important [see the discussions following Eqs. (7), (9), and (52)].

The cause of SERS by a fractal is that an impurity particle at a fixed location near some monomer is subjected to the influence of the local field of only this monomer. This field is strong, because the monomers in a fractal preserve in part their individuality (because of the rarefaction and disorder of the fractal). The gain G , obtained in the binary approximation, is given by Eq. (43), and its spectral dependence by (44). The latter duplicates approximately the form of the absorption spectrum [see (45)]. Allowance for the Lorentz field, while renormalizing the gain, does not change its connection with the absorption of the fractal [see (52)].

We conclude by examining qualitatively the application of the theory to real fractal clusters. These, as noted in the Introduction, are quite prevalent. It should be pointed out in this connection that in the development of the theory [see the transition from (14) to (15)] we have taken into account only pair correlations, whose function (2) is governed by fractal properties, and have neglected multiparticle correlations. If, to the contrary, the latter are large, a group of strongly correlated monomers can be regarded as a single monomer, but having already a renormalized susceptibility. As a result of this renormalization procedure, similar to the one used in the theory of phase transitions, we can return to the case of weak multiparticle correlation and obtain from (14) Eq. (18) and all the following ones.

For example, flexible linear macromolecules are fractals with dimensionality $D \approx 5/3$ (Ref. 11). A renormalized monomer in such a macromolecule is a segment of a chain within the limits of a line called persistent. This line is a region of monomers strongly correlated in position, on which a polymer can be regarded a rectilinear. The persistent length can include from several (e.g., in RNA) to several hundred (in a two-string DNA) monomers.

Let us examine applications of the theory to the SERS effect. We consider for the sake of argument small spherical silver particles, in which plasma oscillations have a wavelength $\lambda_p = 2\pi c/\omega_p = 140$ nm. It is customarily assumed that the SERS excitation spectra in such systems are grouped around the plasma resonance frequency ω_0 , which corresponds in silver, according to (26), to a wavelength $\lambda_0 = 340$ nm. In experiment, however (see, e.g., Fig 13 of Ref. 14), the SERS excitation spectra of the same impurity molecules can, depending on the method used to prepare the metallic matrix, have maxima both in the near UV (which corresponds approximately to λ_0) and in a region of longer wavelengths, up to the "red," of the spectrum. Attempts to explain such large spectral shifts to interaction of the monomers, which are assumed to be uncorrelated in space (trivial fractal structure), by resorting to the Lorentz theory, meet with certain difficulties. For example, to obtain an absorption peak at 650 nm it must be assumed that $\approx 86\%$ of the volume is occupied by the metal.¹³ Actually, however, experiments on aggregated metallic colloids, in which the maximum SERS signal was observed, the volume occupied by the metal was smaller by orders of magnitude (cf. Ref. 6).

We shall show below that whether or not a cluster consisting of metallic microspheres has an absorption band far in the long-wave region depends on its fractal dimensionality. To be specific, we assume the cluster to be maximally

dense (the spheres are close packed), i.e., we put $R_0 \approx R_m$. It follows then from (26) and (27) that the characteristic fractal frequency Ω_f is approximately 20% of ω_0 . The widths of the fractal spectra can exceed Ω_f by several times (cf. Fig. 3), i.e., be of the order of ω_0 .

The estimates show how large the spectral shifts of fractals can be. In the case of such large detunings, however, the linearized expression (22) for the susceptibility is, strictly speaking, no longer valid. It is then necessary to use in all the expressions the exact values $X = -R_0^3 \text{Re } \chi_0^{-1}$, (33), where χ_0 is given by (24) with ε given by (26). The quantity X as a function of ω behaves as follows: in the low frequency region ($\omega_0 \leq \omega \leq \omega_0 [(\varepsilon_0 + 2)/(\varepsilon_0 - 1)]^{1/2}$) X takes on values from 0 to ∞ , while in the long-wave region (as ω is decreased from ω_0 to 0), X runs through the finite segment of values from 0 to -1 . It is easily seen from Fig. 3 that $\text{Im } \tilde{\chi}_1$ is close to zero for X in the range from zero to a certain limiting value $-X_m$ that depends on the fractal dimensionality.

On the basis of the properties listed above, we conclude that absorption of fractals from metallic microspheres in the long-wave region (at $\omega < \omega_0$) is significant only when $X_m < 1$. The values (at half-maximum of $\text{Im } \tilde{\chi}_1$) for different fractal dimensionalities are the following (cf. 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 hence also the SERS effect, in the long-wave region is appreciable in the considered clusters only at $D \leq 1.75$. Note that $D \approx 1.75$ is expected for a cluster aggregation⁴; approximately the same value of D was obtained in experiments with colloidal gold.⁶ The proximity of the observed fractal dimensionality to the limit ($D = 1.75$) explains the observed¹⁴ variability of the appearance of a long-wave band in SERS excitation spectra.

The value of G obtained for fractals can be substantially larger than predicted by the customarily employed expression [see the discussion that follows Eq. (46)]. The point is that the interaction of the monomers in a fractal is taken into account consistently in the present theory. On the contrary, the shift of the absorption bands is usually (see, e.g., Ref. 13) described in accordance with the Lorentz theory, and their width is taken equal to the observed value. This last procedure underestimates G_{max} for fractals by a factor Ω_f/Γ . This circumstance can explain the heretofore not fully understood fact¹⁴ that the largest SERS effect was observed precisely for colloidal metallic aggregates, which are known (see, e.g., Ref. 6) to be of fractal nature.

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