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Giant high-order field moments in metal–dielectric composites

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Abstract

A scaling theory describing the local field distribution and high-order field moments in metal–dielectric percolating composites is developed. It is shown that the field distribution is extremely inhomogeneous and consists of small spatially separated clusters of very sharp peaks, "hot" spots, where the local fields are much greater than the applied field. The theory predicts that the high-order field moments that characterize the average enhancement of nonlinear optical processes are very large and frequency independent in a wide spectral range. The local nonlinear signals from the "hot" spots exceed the average surface-enhanced signal by many orders of magnitude, a fact that opens a fascinating possibility of the nonlinear spectroscopy of single molecules and nanoparticles.

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The local electric field fluctuations can be strongly enhanced in the optical and infrared spectral ranges for a percolating nanocomposite containing metal particles that are characterized by the dielectric constant ε_m with negative real $\varepsilon'_m < 0$ and small imaginary parts $\kappa = \varepsilon''_m/|\varepsilon'_m| \ll 1$ [1,2]. Since the metal–insulator transition associated with percolation represents a dynamic phase transition one might anticipate that the current and field fluctuations are scale-invariant and large. In percolating composites, however, the fluctuation pattern appears to be quite different from that for a second-order transition, where the fluctuations are characterized by a long-range correlation and their relative magnitudes are of the order of unity at any point. In contrast, for the DC percolation, for example, the local electric fields are concentrated at the edges of large metal clusters so that the field maximums (large fluctuations) are separated by distances of the order of the percolation correlation length, ξ_p, which diverges when the

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metal volume concentration p approaches the percolation threshold p_c [3–5,20]. Below we show that the difference in fluctuations becomes even more striking in the optical spectral range where the local field peaks have a resonance nature and, therefore, their relative magnitudes can be up to 10^5, for the linear response, and up to 10^{20}, for nonlinear responses (e.g., for third-order optical nonlinearity), with distances between the peaks much larger than ξ_p.

When wavelength λ of an incident beam is much larger than the particle size a_0 we can introduce a potential $\phi(\boldsymbol{r})$ for the local electric field, and the field distribution problem reduces to a solution of the equation representing the current conservation law, $\nabla \cdot (\sigma(\boldsymbol{r})[-\nabla\phi(\boldsymbol{r}) + \boldsymbol{E}_0(\boldsymbol{r})]) = 0$, where $\boldsymbol{E}_0$ is the applied field and $\sigma(\boldsymbol{r})$ is the local conductivity that takes σ_m and σ_d values, for the metal and dielectric bonds, respectively. In the discretized form this relation acquires the form of Kirchhoff's equations defined on a cubic lattice [1]. The Kirchhoff's equations, in turn, can be written in the matrix form with the "interaction matrix" defined in terms of the local dielectric constants, $\varepsilon(\boldsymbol{r}) = (4\pi i/\omega)\sigma(\boldsymbol{r})$. Then, the Kirchhoff's equations map the Anderson's transition problem with the Hamiltonian (which we refer hereafter as to Kirchhoff's Hamiltonian, KH) built from the local dielectric constants. The off-diagonal elements of the KH are $H_{ij} = -\varepsilon_{ij}$ and the diagonal elements are defined as $H_{ii} = \sum_j \varepsilon_{ij}$, where j refers to the nearest neighbors of i. The dielectric constants ε_{ij} take values ε_m and ε_d with probabilities p and $(1-p)$, respectively. Thus, the KH is of Anderson's type, with both on- and off-diagonal correlated disorder. Since $\varepsilon'_m < 0$ and $\varepsilon_d > 0$ the manifold of the KH eigenvalues Λ_i contains the eigenvalues which have the real parts equal (or close) to zero, with very small imaginary parts ($\kappa \ll 1$). Then the eigenstates that correspond to the eigenvalues $|\Lambda_i/\varepsilon_m| \ll 1$ are strongly excited by the external field and seen as giant field fluctuations representing the non-uniform plasmon resonances.

The strong fluctuations of the local electric field lead to enhancement of various optical nonlinear effects. For example, four-wave mixing and generation of higher harmonics can be enhanced in percolating composites, and the bistable behavior of the effective conductivity can take place when the conductivity switches between two stable values [6,21,22]. Nonlinear percolating composites are potentially of great practical importance as media with intensity-dependent dielectric functions and, in particular, as nonlinear filters and optical bistable elements. The large field fluctuations reveal themselves, e.g., in the enhanced Raman scattering observed in percolating systems [7,23]. The local field enhancement was previously studied in fractal aggregates of metal particles [8,9,24–26].

For the most interesting spectral range where $\varepsilon'_m(\omega) < 0$, the local field distribution and enhancement for optical nonlinearities are poorly known for metal–dielectric composites. When p is small, the field and nonlinearities are large at the particle positions and the largest enhancement occurs at the frequency ω_r corresponding to the plasmon resonance of an individual metal grain [1,6,21,22]. The effective medium theory was developed to describe the nonlinear response of percolating composites [10,27]. For linear problems, predictions of the effective medium theory usually offer a quick insight into a problem. This theory, however, has disadvantages typical for all mean-field

theories, namely, it diminishes fluctuations in a system [1] that can be very large for $\varepsilon'_m(\omega) < 0$ and $\kappa \ll 1$ and play a crucial role in nonlinear optical responses [2].

Below, we develop a scaling theory for the spatial distribution of the local fields and their high-order field moments that characterize enhancements of nonlinear optical effects in percolating metal–dielectric composites. For estimations, we assume that metal grains have the Drude dielectric function $\varepsilon_m(\omega) = \varepsilon_b - (\omega_p/\omega)^2/(1 + i\omega_\tau/\omega)$, where ε_b is a contribution to ε_m due to the interband transitions, ω_p is the plasma frequency, and $\omega_\tau = 1/\tau \ll \omega_p$ is the relaxation rate. In the high-frequency range considered here, losses in metal grains are small, $\omega_\tau \ll \omega$, and the real part of the metal dielectric function ε'_m is negative and much larger in modulus than the imaginary part ε''_m, for the frequencies ω less than the renormalized plasma frequency $\omega_p^* = \omega_p/\sqrt{\varepsilon_b}$. The metal grains are placed in a dielectric substrate characterized by ε_d.

Using the numerical technique described in detail in [7,11,28], we calculated spatial distributions of the local fields. In Fig. 1, we show the calculated field distributions $I(\boldsymbol{r}) = I(x, y) = |\boldsymbol{E}(\boldsymbol{r})/E_0|^2$ in a 2d silver-on-glass film ($\omega_p = 9.1$ eV, $\omega_\tau = 0.021$ eV, $\varepsilon_d = 2.2$) at $p = p_c$; $E_0 = 1$ is the amplitude of the incident wave; the wavelength λ is assumed to be much larger than the metal grain size, $\lambda \gg a_0$. For simplicity, all distances are given in the a_0 units. For individual silver particles, the resonance condition $Re(\varepsilon_m(\omega_r)) \simeq -\varepsilon_d$ [6,21,22] is fulfilled at $\lambda \approx 0.4\,\mu$m (see Fig. 1a). In Fig. 1b and 1c, we also show $I(\boldsymbol{r})$ for $\lambda = 1.5$ and $12\,\mu$m that correspond to $\varepsilon_m \approx -118 + i3.2$ and $\varepsilon_m \approx -7.6 \times 10^3 + i1.5 \times 10^3$, respectively. As seen in the figure, the local fields form a set of peaks with the magnitudes about 10^4 for $\omega = \omega_r$; the peaks become larger with increasing λ.

We consider first the case when $\omega \simeq \omega_r$ corresponding to $\varepsilon_d \simeq -\varepsilon'_m \sim 1$ and the loss factor $\kappa \ll 1$. We express the fluctuating potential $\phi(\boldsymbol{r})$ in terms of the eigenvalues Λ'_n and eigenstates Ψ'_n of the real (Hermitian) part, H', of the non-Hermitian KH, $H = H' + iH''$, where $H'' \propto \kappa$ is small since $\kappa \ll 1$. The local potentials can be represented as $\phi(\boldsymbol{r}) = \sum_n \mathscr{E}_n \Psi'_n(\boldsymbol{r})/(\Lambda'_n + ib_n\kappa)$, where $\mathscr{E}_n$ is proportional to the projection of the external field E_0 potential on the eigenstate $\Psi'_n(\mathscr{E}_n \propto E_0)$, and $ib_n\kappa$ is a small correction to the eigenvalue Λ'_n due to $\kappa \neq 0$ ($b_n \sim b \sim 1$). The introduction of the term $ib_n\kappa$ in the denominator of the expression for $\phi(\boldsymbol{r})$ is equivalent to introducing complex energies in the standard response theory.

According to the one-parameter scaling theory the eigenstates Ψ'_n are thought to be all localized for the 2d case (see discussion in [12,29]). On the other hand, it was shown that there is a transition from chaotic eigenstates [13,14] to localized eigenstates in the 2d Anderson problem [15] with intermediate crossover region [16]. For $\varepsilon_d = -\varepsilon_m = 1$ and $p = p_c = \frac{1}{2}$ the on-diagonal disorder in the KH with $H \approx H'$ is characterized by $\langle H'^2_{ii} \rangle = 4$ that corresponds to the chaos-localization transition [15]. The KH has also strong off-diagonal disorder, $\langle H'_{ij} \rangle = 0$ ($i \neq j$). Our conjecture is that the eigenstates Ψ'_i are localized for all Λ' (see Fig. 1). (We cannot, however, rule out a possibility of the inhomogeneous localization similar to that obtained for fractals [9,25,26].) Since only the κ fraction of the eigenstates are effectively excited by the external field the "distance" between them, the local-field correlation length ξ^*_e, is $\xi^*_e \sim \kappa^{-\nu_e} \gg 1$, where

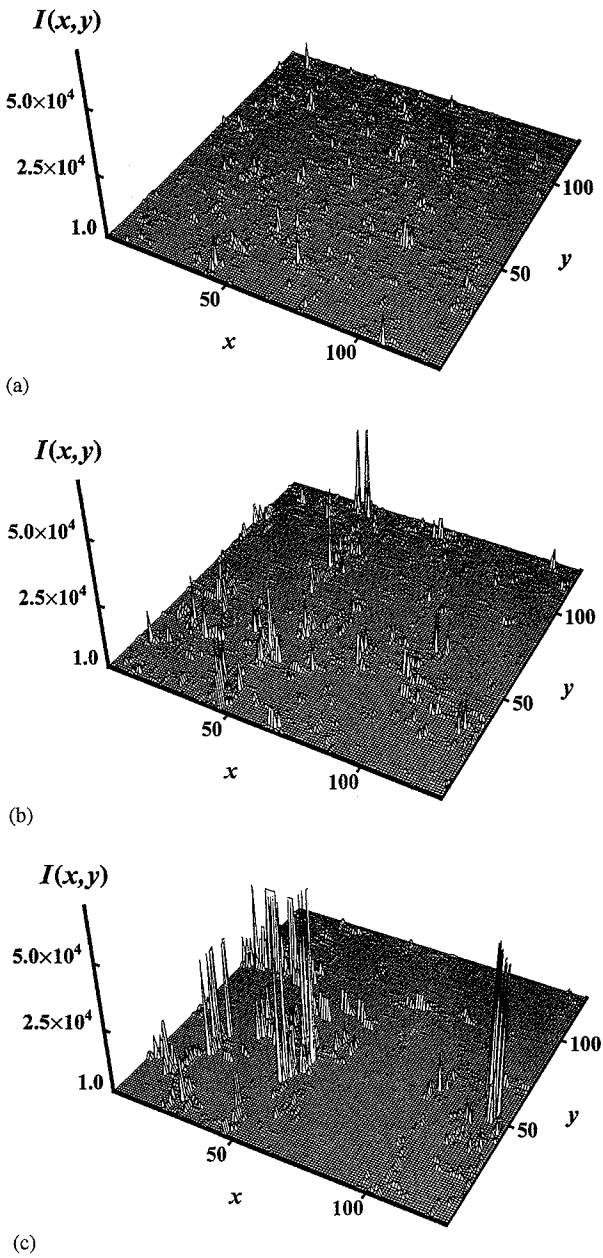

Fig. 1. Distribution of the local field intensities in a semicontinuous silver film at $p = p_c$ for different wavelengths; (a) $\lambda = 0.4$ μm; (b) $\lambda = 1.5$ μm; (c) $\lambda = 12$ μm. [The coordinates x and y are given in the lattice period (a_0) units.]

$\nu_e = \frac{1}{2}$ (in a d-dimensional space, $\nu_e = 1/d$). Based on the above reasoning we neglect the overlapping of the eigenstates Ψ' in calculating the moments $G_n \equiv \langle |\boldsymbol{E}(\boldsymbol{r})/E_0|^n \rangle$ of the local field and thus obtain $G_n = \int c_n(\Lambda')/|\Lambda' + ib\kappa|^n d\Lambda'$, where $c_n = \sum_k |\mathscr{E}_k/E_0|^n \langle |\nabla \Psi'_k|^n \rangle \delta(\Lambda' - \Lambda'_k)$ and ρ is the density of states. Assuming that c_n is smooth functions of Λ' in the vicinity of zero and taking into account that all parameters of H' for the considered case $\varepsilon_d \simeq -\varepsilon'_m \sim 1$ are about unity we immediately obtain $G_n \sim \kappa^{-n+1}$ for $n \geqslant 2$.

We note that the above results are in good agreement with comprehensive numerical calculations performed in [11,28] for a 2d system with $\varepsilon_m/\varepsilon_d \approx -1$ and $p = p_c$; for a particular case of $n = 2$, it was shown there that $G_2 \sim \kappa^{-\gamma}$ and $\xi^*_e \sim \kappa^{-\nu_e}$, with $\gamma \approx 1.0$ and $\nu_e \approx 0.5$, as the above speculations predict. Also, we note that in accordance with the above consideration, the field distribution can be thought of as a set of peaks with amplitude $E^*_m \simeq E_0 \kappa^{-1} \gg E_0$ separated by distances ξ^*_e, so that $G_n \sim (E^*_m/E_0)^n / \xi^{*d}_e \sim \kappa^{-n+1}$.

In the infrared part of the spectrum ($\omega \ll \omega_r$), the parameters associated with ε_m in the KH can be much larger than unity and the above consideration cannot be directly applied, in this case. To understand the structure of giant optical field fluctuations for the large contrast, $|\varepsilon_m|/\varepsilon_d \gg 1$, and calculate the high-order field moments we further develop the scaling arguments of the percolation theory [3,17,18,30]. We divide a system into cubes of size l and consider each cube as a new renormalized element. All such cubes can be classified into two types. A cube that contains a continuous path of metallic particles is considered as a "conducting" element. A cube without such an "infinite" cluster is considered as a non-conducting, "dielectric" element. Following the finite size arguments, the effective dielectric constant of the "conducting" cube $\varepsilon^*_m(l)$ decreases on increasing its size l as $\varepsilon^*_m(l) \cong l^{-t/\nu_p} \varepsilon_m$, whereas the effective dielectric constant of the "dielectric" cube $\varepsilon^*_d(l)$ increases with l as $\varepsilon^*_d(l) \cong l^{s/\nu_p} \varepsilon_d$ (t and s are the percolation critical exponents for the static conductivity and dielectric constant, respectively, and ν_p is the critical index for the percolation correlation length: $\xi_p \cong |p - p_c|^{-\nu_p}$ [1]). We set now the cube size l to be equal to l^*:

$$l^* = (|\varepsilon'_m|/\varepsilon_d)^{\nu_p/(t+s)} . \tag{1}$$

Then, in the renormalized system, where each cube of the size l^* is considered as a single element, the ratio of the dielectric constants of these new elements is equal to $\varepsilon^*_m(l^*)/\varepsilon^*_d(l^*) \cong \varepsilon_m/|\varepsilon'_m| = -1 + i\kappa$, where the loss-factor $\kappa \approx \omega_\tau/\omega \ll 1$. The average distance between the field maxima in the renormalized system is equal to ξ^*_e, and the average distance ξ_e between the field maxima in the original system, as follows from (1), is

$$\xi_e \cong \xi^*_e l^* \cong (|\varepsilon'_m|/\varepsilon''_m)^{\nu_e} (|\varepsilon'_m|/\varepsilon_d)^{\nu_p/(t+s)} . \tag{2}$$

Let us consider two neighboring conducting clusters of size l. The clusters have inductive conductances $\Sigma_i = -i\omega\varepsilon^*_m(l) l/4\pi$; this is because the metal conductivity is inductive for $\omega < \omega^*_p$ ($\varepsilon'_m < 0$, $|\varepsilon'_m| \gg \varepsilon''_m$). The gap between the two conducting clusters has a capacitive conductance $\Sigma_c(l) \simeq -i\omega\varepsilon^*_d(l) l/4\pi$. We choose the size $l = l^*$

so that the capacitive and inductive conductances are equal to each other in modulus, $|\Sigma_c(l^*)| = |\Sigma_i(l^*)|$. Then there is a resonance in the system, and the electric field is strongly enhanced in the inter-cluster gap. Yet, the local field is mostly enhanced only for the part ξ_e^{*-d} of the clusters. The potential drop across the gap can be estimated as $U_{AB}^* \sim E_m^* l^*$, and the local field concentrates at the points of the closest approach, where the gap shrinks down to the period lattice, a_0. At these points of the original system, the local field acquires the largest values

$$E_m/E_0 \cong (E_m^*/E_0)l^* \sim (|\varepsilon_m'|/\varepsilon_m'')(|\varepsilon_m'|/\varepsilon_d)^{\nu_p/(t+s)} . \tag{3}$$

The points of the close approach determine the gap capacity conductance $\Sigma_c(l^*)$, that in turn depends on the cluster size l^*. Therefore, the number $n_c(l^*)$ of the close-approach points scales with the size l^* in the same way as the conductance Σ_c, i.e., $n_c(l^*) \sim \Sigma_c(l^*) \sim \varepsilon_d^*(l^*) l^{*d-2} \sim l^{*s/\nu_p+d-2}$.

The following pattern of the local field distribution emerges from the above speculations: The largest local fields are concentrated in the resonant clusters of the size l^* defined in (1); the high-local-field areas are separated in distance by the field correlation length $\xi_e \gg 1$ determined in Eq. (2). Within each resonant area there are $n_c(l^*)$ sharp peaks of the amplitude E_m given by (3). With increasing wavelength, the scale l^* increases, so do the amplitude E_m and the number of local field maxima $n_c(l^*)$ in each resonating cluster. The average distance ξ_e between the resonant sets of the field peaks also increases with λ. One can track this behavior for the field fluctuations in Fig. 1. Note that the cluster resonances are similar, in some respects, to the Lifschitz singularities [19] originally considered for the vibration spectrum of disordered alloys.

This pattern of the local field distribution results in the following estimate for the high-order moments of the local fields, $G_n \sim E_m^n n_c(l^*)/\xi_e^d$, which with the use of (1)–(3) gives

$$G_n \simeq (|\varepsilon_m'|/\varepsilon_d)^{((n-2)\nu_p+s)/(t+s)} (|\varepsilon_m'|/\varepsilon_m'')^{n-1} . \tag{4}$$

The quantity G_n characterizes enhancement of optical nonlinearities due to the high local fields in a percolating system. For $\varepsilon_d = -\varepsilon_m'$, Eq. (4) reduces to the above obtained result $G_n \sim \kappa^{-n+1}$. Since in the visible and infrared spectral ranges the real part of the dielectric constant of a typical metal is large, $|\varepsilon_m'| \gg \varepsilon_d$, whereas the losses are small, $\varepsilon_m'' \ll |\varepsilon_m'|$, the values of the field moments G_n are huge in magnitude. For a 2d system $t \approx s \approx \nu_p = \frac{4}{3}$, and Eq. (4) gives $G_n \simeq (|\varepsilon_m'|/\varepsilon_d)^{(n-1)/2}(|\varepsilon_m'|/\varepsilon_m'')^{n-1}$. For the Drude metal and $\omega \ll \omega_p$, we can simplify this expression as $G_n \simeq \varepsilon_d^{(1-n)/2}(\omega_p/\omega_\tau)^{n-1}$, i.e., the local field moments are large and frequency independent. In Fig. 2, results of our numerical calculations of the field moments for silver semicontinuous films on glass are compared with predictions of the scaling formula (4). We see that there is excellent agreement between the developed scaling theory and numerical simulations.

The giant field moments can be observed, for example, in enhancement of Raman scattering $G_{RS} \simeq G_4$ resulting from placing the Raman-active molecules on a percolating film [7,23]. In general, the nonlinear optical processes are phase dependent and proportional to a factor $|E|^n E^k$, i.e., they depend on the phase through the term E^k and

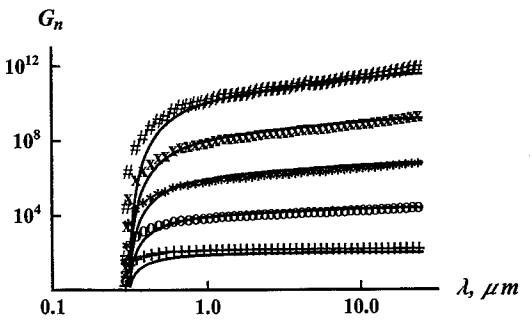

Fig. 2. The average enhancement of the high-order field moments G_n in a semicontinuous silver film ($d=2$) as a function of the frequency at $p = p_c$. Results of the numerical calculations for $n = 2,3,4,5$ and 6 are represented by +, 0, *, x, and #, respectively. The solid lines describe G_n found from the scaling formula (4).

their enhancement is estimated as $G_n^k = \langle |E/E_0|^n (E/E_0)^k \rangle$. Repeating the above consideration, we obtain $G_n^k \sim G_{n+k}$, for $n \geqslant 1$, and $G_0^k \simeq (\varepsilon_m''/|\varepsilon_m|)(|\varepsilon_m'|/\varepsilon_d)^{((k-2)\nu_p+s)/(t+s)}$, for $n=0$. For example, the Kerr-type nonlinear refraction and absorption $G_K \sim G_2^2$ [2] and it is estimated as $G_K \sim \varepsilon_d^{-3/2}(\omega_p/\omega_\tau)^3 \sim 10^7$, for an Ag semicontinuous film on glass. For parametric nonlinear processes, such as degenerate four-wave mixing (FWM), which is used to restore the wavefront in random media, the resultant enhancement is given by $G_{FWM} \sim |G_2^2|^2 \sim 10^{14}$. The enhancement for kth harmonic generation for $k\omega > \omega_p^*$ and $d = 2$ is estimated as $|G_0^k|^2 \sim (\omega_\tau/\omega)(\omega_p/\omega)^{2(k-1)} \gg 1$, i.e., in contrast to the processes with "photon subtraction" it does depend on the frequency.

Note that the local enhancements in the "hot" spots can be much larger than the average enhancements considered above. As follows from Fig. 1, the local field intensities are enhanced up to $|E/E_0|^2 \sim 10^5$ which gives for the local enhancements in the "hot" peaks 10^{10} and 10^{20}, for the Kerr-process and four-wave mixing, respectively. Similar estimations for 2d harmonic generation, taking into account the additional field enhancement at the generated 2ω frequency, give for the local enhancements 10^{15}. With such level of local enhancements, the nonlinear optical signals from single molecules and nanoparticles can be detected, using, for instance, the near-field scanning optical microscopy. This opens a fascinating possibility of the local nonlinear spectroscopy with nanometer spatial resolution.

Note, the fact that the problem considered here maps the Anderson transition problem, brings about new experimental means to study the problem by taking advantage of the high intensity and coherence of laser light and subwavelength resolution provided by recently developed near-field optical microscopy. In particular, by studying the high-order field moments associated with various nonlinear optical processes and spatial distribution of the nonlinear signal one can obtain unique information on the Anderson's eigenfunction distribution.

To summarize, large field fluctuations in random metal–dielectric composites near the percolation result in enormous enhancement of nonlinear optical processes. The

developed scaling theory describes well the high-order field moments characterizing the enhancement.

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