Giant enhancement of electric field between two close metallic grains due to plasmonic resonance

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We theoretically examine plasmonic resonance between two close metallic grains separated by a gap of width much less than the length of the incident electromagnetic wave. Resonance conditions are established and the electric field enhancement is found. Our general arguments are confirmed by analytic solution of the problem for simplest geometries. We discuss an extension of our results to more complex cases.

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Interaction of electromagnetic field with metallic dimers recently became a focus of intensive research due to extraordinary potentials for various applications ranging from nanophotonics to bio/chemical sensing. A key feature of such nanostructures utilized in these applications is a significant field enhancement in the dimer's gap. This enhancement is primarily studied experimentally or using computer modeling, which does not allow us to uncover the relation between the characteristics of the near field enhancement and the physical properties and geometry of the dimer and host material. In this Letter, we present an analytical description of the characteristics of the field enhancement between two metallic nanogranules embedded into the host dielectric.

Resent progress in nanofabrication have led to thriving activity in the actual design of composite materials with plasmonic subwavelength dimensions for applications in photonics and chemical sensing. They can be realized as surface grain structures on a dielectric substrate [1]. The giant electric field enhancement is observed in narrow gaps between metallic grains. Strongly amplified electromagnetic fields can be generated both in a broad spectral range for disordered metal-dielectric composites and at selected frequency ranges for periodically ordered nanostructures. The literature devoted to the problem is immense; for introduction to the research region a reader can use the monograph [2], and for brief examination of the disordered composites see [3].

The plasmonic resonances can be excited at propagation of an electromagnetic wave through a composite material where metal grains are inserted into a dielectric matrix. It is known [4] that the plasmonic resonance in a single metallic grain is excited at a frequency near the plasma one lying in the ultraviolet spectral region for "good" metals (Ag, Au, etc.). To reach the resonance in the optical or near-IR diapason, one should use a special geometry where metallic grains are separated by distances much smaller than their size. Then giant electric field enhancement occurs in the gap between the grains at resonance conditions implying, particularly, large negative permittivity of the grains. Here, we theoretically investigate the phenomenon. The resonance conditions are related mainly to the local geometrical characteristics of the gap. The field enhancement, on the contrary, is determined by a variety of geometrical factors controlling the energy flow to the gap. We present general arguments that enable us to estimate both the resonance frequencies and the electric field enhancement for grain dimers. The arguments are confirmed by analytic solution of the problem for two identical metallic spheres. Then we extend our consideration to more complicated cases.

We consider the case of a monochromatic electromagnetic wave of frequency ω, then the electric field strength is written as $\mathrm{Re}[\boldsymbol{E}\exp(-i\omega t)]$. The permittivity of the matrix, $\varepsilon_{\mathrm{d}}(\omega)$, is assumed to be of order unity, with small imaginary part. We accept a local relation between the electric field strength and the electric displacement field $\boldsymbol{D}$, $\boldsymbol{D}=\varepsilon_{\mathrm{m}}(\omega)\boldsymbol{E}$, in the metal grains. Here, ε_{m} is the permittivity of the metal. In optical and near-IR spectral regions the permittivity of a "good" metal can be described by Drude–Lorentz formula

$$\varepsilon_{\mathrm{m}} \sim -(\omega_{\mathrm{p}}/\omega)^2[1-i/(\omega\tau)], \qquad (1)$$

where ω_{p} is the plasma frequency and τ is the electron relaxation time. Therefore, in the frequency interval $\omega_{\mathrm{p}} \gg \omega \gg \tau^{-1}$, the permittivity ε_{m} has negative real part, large by its absolute value, and relatively small imaginary part. The same is true for the dielectric contrast $\varepsilon=\varepsilon_{\mathrm{m}}/\varepsilon_{\mathrm{d}}$. Thus, we arrive at the condition necessary for the giant electric field enhancement.

We examine mainly the case where two close metallic grains are surrounded by an unbounded dielectric medium. The grains are assumed to be small that is their sizes are much less than the wavelength λ of the electromagnetic wave (in the dielectric medium). We are looking for the electromagnetic field profile near the grains, especially in the gap between the grains, where one expects an essential enhancement of the field. The problem belongs to the so-called

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near-field optics. The electric field near small metallic grains can be examined in quasi-electrostatic approximation [2].

We are interested in the electric field strength enhancement, characterized by the ratio E_c/E_0, where E_c is the electric field strength in the central segment of the gap between the grains, and E_0 is the electric field strength in the incident electromagnetic wave. An essential enhancement has to be observed near resonance frequencies, then there are two principal contributions to the ratio,

$$E_c/E_0 = G/(\varepsilon - \varepsilon_{\mathrm{res}}) + G_{\mathrm{bg}}, \qquad (2)$$

that can be called resonance and background terms. Form of expression (2) follows from the general properties of Maxwell equations solutions when all materials have linear electric response. The quantity $\varepsilon_{\mathrm{res}}$, as well as the factors G and G_{bg}, are determined by geometry of the grains and by the gap thickness. The resonance frequency can be evaluated now from the expression (1), $\omega_{\mathrm{res}} \sim \omega_{\mathrm{p}}/\sqrt{|\varepsilon_{\mathrm{res}}|}$.

In the case of close grains the electric field of the resonance mode is localized in the central segment of the gap between the grains where it can be regarded as flat [gray region in Fig. 1(a)]. An electromagnetic wave can propagate along a narrow flat gap between two metallic bodies separated by a dielectric medium provided $\varepsilon = -2/(\beta\delta)$ in the case $|\varepsilon| \gg 1$ where β is the propagation constant [5]. Standing waves are determined by the conditions $\beta L \approx \pi n$ where n is an integer number and L is the longitudinal size of the gap. For two close smooth grains L can be estimated as $\sqrt{a\delta}$, where a is characteristic grain curvature radius, see Fig. 1(a). Thus, we obtain the following estimation for the resonance values of the permittivity

$$\varepsilon_{\mathrm{res}} \sim -\sqrt{a/\delta}/(n + \delta n), \qquad (3)$$

where n is an integer number and $\delta n \sim 1$. The estimation is valid at $n \ll \sqrt{a/\delta}$.

Let us consider the first resonance corresponding to $n=1$. The electric field inside the gap is approximately homogeneous at distances $\rho \lesssim \sqrt{a\delta}$ from the gap center where the gap can be regarded as flat. Outside the region, at distances $a \gg \rho \gg \sqrt{a\delta}$ from the gap center, the gap thickness is estimated as ρ^2/a; it is much larger than in the center. The potential difference $\Delta\Phi \sim E_c\delta$ between the grain boundaries is ρ independent in the main approximation at the distances, since ε is effectively infinite at the scales. Thus, we arrive at $E \sim \Delta\Phi a/\rho^2 \sim E_c a\delta/\rho^2$. The field strength determines the charge density at the grain boundaries that scales $\propto \rho^{-2}$ as well. Therefore the dipole moment d of the grains is determined by the distances $\sim a$ and can be estimated as $d \sim E(a)a^3 \sim E_c\delta a^2$.

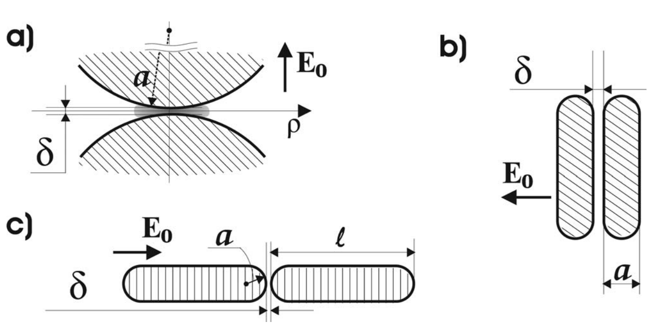

Fig. 1. Narrow gaps between (a) two metallic grains, (b) two parallel elongated grains, (c) two coaxial elongated grains.

The geometrical factor G in Eq. (2) can be evaluated from the balance between the Ohmic dissipation rate Q and the energy flux to the system from the incident wave. At the resonance frequency, Q is estimated as

$$Q \sim \omega\varepsilon''(E_c/\varepsilon')^2(a\delta)^{3/2}, \qquad (4)$$

where the last factor represents the metal volume where the dissipation occurs and E_c/ε' is the estimate for the electric field amplitude in this volume. The energy flux is determined by the work per unit time done by the external field on the system and is estimated as $\omega d E_0 \sim \omega E_c a^2 \delta E_0$. Comparing the expressions one finds $G \sim (a/\delta)^{3/2}$, that is $G \gg 1$ at our conditions. One can also evaluate the dipole radiation intensity

$$I \sim \omega E_c^2 \delta^2 a^4/\lambda^3. \qquad (5)$$

The radiation leads to additional energy losses, our scheme is correct provided $I \ll Q$.

The presented qualitative picture is confirmed by rigorous analytical calculations for the case where the metallic grains are close identical spheres of radii a separated by a distance $\delta \ll a$. Our problem can be solved analytically by passing to the so-called bispherical reference system [6]. Here, we do not discuss details of the calculations (they will be published elsewhere) and present final results only. With logarithmic accuracy, one finds for the incident wave polarization parallel to the symmetry axis

$$\varepsilon_{\mathrm{res}} = -\frac{\sqrt{a/\delta}}{n - 1/2}, \qquad (6)$$

where $n = 1, 2, \ldots$. For $n=1$ the parameters in Eq. (2) are

$$G = \frac{8\pi^2}{3}\frac{(a/\delta)^{3/2}}{\ln(a/\delta)}, \quad G_{\mathrm{bg}} = -2\sqrt{a/\delta}. \qquad (7)$$

The expressions are in accordance with our general reasoning.

One can test more sophisticated grain geometries that are characterized by a number of scales. We examine strongly prolate grains of length l, their mutual arrangement can be either parallel or coaxial, Figs. 1(b) and 1(c) with a narrow gap δ between them. The resonance condition is determined by the smallest longitudinal gap dimension. Hence, one can use the same relation (3), where a is the smallest curvature radius of the grains characterizing the gap. It is the cylinder radius in the parallel case and curvature radius of the grain tips in the coaxial case. The field enhancement G in Eq. (2) should be found, as above, from the energy balance: in the case of parallel cylinders $G \sim a/\delta$, and in the case of elongated grains $G \sim l a^{1/2} \delta^{-3/2}$.

In our analysis, we used the quasistatic approximation that implies that all the characteristic sizes of the grains are much less than $\lambda/\sqrt{|\varepsilon|}$. Besides, we established that the resonance mode is localized between the grains, at distances $\rho \lesssim \sqrt{a\delta}$ from the gap center. And just the vicinity determines the resonance condition (3). Therefore the resonance condition survives if $\lambda/\sqrt{|\varepsilon|} \gg \sqrt{a\delta}$, which leads to the condition $\lambda^2 \gg a^{3/2}\delta^{1/2}$, justifying Eq. (3) even for large grains. However, the amplification factor in this case should be determined using complete geometry of the system and Maxwell equations.

Since the resonance mode is localized between the grains, a principal role in giant electric field enhancement for a random distribution of the grains is played by grain dimers with suitable separations, satisfying the resonance condition. Thus a number of sharp peaks in the space distribution of the electric field has to be observed in the disordered metal—dielectric composite in the external electromagnetic wave. Experimental data [7,8] qualitatively proves the conclusion, see, e.g., [9,10]. To determine the number of peaks at a given frequency one has to know a probability distribution of small separations δ (in comparison with the grain sizes) in grain dimers.

Recently considerable efforts are applied in designing periodic metal-dielectric composites, see, e.g., [11]. One could imagine a periodic structure of metallic grains separated by small distances. In this case resonance modes can be excited where the electric field has sharp maxima in central segments of the gaps between the grains. However, due to overlapping of the modes localized near the gaps, the resonance has to be transformed into a band of delocalized modes, like it occurs for electrons in a periodic potential (crystalline lattice). As our analysis shows, the structure of the electric field in the gap between the grains at distances smaller than the grain size is fixed by boundary conditions at the metal-dielectric interface. Therefore the resonance frequency has to be determined by matching conditions in the regions between the grains instead of the condition at infinity for two grains immersed in an unrestricted dielectric medium. Thus, we expect that the bandwidth is of the order of the separation between the resonance frequencies. Thus, relying on a power-like dependence like in Eq. (1), we conclude that for grains characterized by a single size a the bandwidth is of the order of the resonance frequency itself.

One of our assumptions was smoothness of the grain boundaries. If the boundaries are rough then a problem appears concerning an enhancement of energy losses observed in [12]. The giant electrical field enhancement lead to increasing nonlinear effects. The problems need a special investigation and are out of the scope of this work.

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