Surface plasmon excitation and correlation-induced localization-delocalization transition in semicontinuous metal films

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(Received 29 April 2005; published 6 September 2005)

By solving the surface plasmon (SP) eigenproblem, a scaling theory is developed for the electromagnetic response of semicontinuous metal films. It is shown that short-range correlations in the governing Kirchhoff Hamiltonian result in delocalization of the SP eigenmodes in the center of the spectrum. The subset of those modes has a zero measure so that their relative weight in the spectrum becomes asymptotically small for large systems. Still, the singularity caused by the delocalized states results in modification of the critical indices for the high-order field moments and thus affects the optical properties of the composite. Comparison between the developed theory and exact numerical calculations reveals excellent agreement.

DOI: 10.1103/PhysRevB.72.113102 PACS number(s): 73.20.Mf, 71.30.+h, 73.22.Lp, 78.67.Bf

The localization of the electron wave function, which occurs in random media and was first described by Anderson,[1] is one of the most important concepts in the contemporary theory of disordered systems. Development of the scaling theory[2] improved and made possible more intuitive understanding of the phenomena governing the motion of the elementary particles in such media. It is now well established that in one-dimensional (1D) and two-dimensional (2D) systems described by noncorrelated random potential distributions, all electron states are exponentially localized.[3,4] This is valid for various levels of disorder and in the limit of large systems. The localization of the electron wave function implies that each electron is bound in a particular region of space, and thus transport through the media is impeded. It is also believed that in the three-dimensional (3D) case and for a certain strength of the disorder, extended states exist and accordingly, a metal-dielectric transition can take place.[5] Similar to the quantum-mechanical problem, localization is also observed for classical wave propagation in disordered media.[4] In both cases, disorder prevents the establishment of extended solutions (Bloch states) due to the absence of translation symmetry.

Recently, short-range correlations between elements of the quantum-mechanical Hamiltonians have been shown to result in delocalization of the electron wave function in the 1D case.[6,7] In these studies, the correlations are enforced separately for diagonal and off-diagonal matrix elements, while mixed cross correlations between the elements are not considered. In this paper we argue that the electromagnetic response of a broad class of physical systems can be described by random Hamiltonians that are characterized by cross-correlated diagonal and off-diagonal elements. Specifically, we investigate the excitation of collective electronic states, surface plasmons (SP), in a random metal-dielectric film. Our study presents theoretical evidence of a zero measure delocalization for the SP eigenmodes and their manifestation in the optical response of the system.

The random metal-dielectric composites are simple binary media which are usually fabricated by deposition of nanosized metal particles on dielectric substrate. In the visible and infrared spectral ranges, the metal conductivity σ_m is a complex number with a positive imaginary part σ_m'', and a small real part σ_m' (representing losses in metal). Therefore, a metal particle can be viewed as an inductance L connected in series to a resistance R, while the dielectric host is modeled as a capacitance C. Relying on this model, one may think of the inhomogeneous metal film as a random network of *RLC* circuits.[8,9] The geometrical disorder in such systems leads to a broad range of SP resonances (corresponding to equivalent *RLC* resonances) and strong enhancement of the local electric fields.[9,10]

To investigate the SP modes that are excited on the film surfaces, we restrict our study to composites of metal particles with sizes much smaller than the wavelength of illumination, $a \ll \lambda$. Under this condition one can neglect retardation effects and seek a solution for the local potential in the quasistatic approximation. The resulting "generalized" current conservation has the form

$$\nabla \cdot [\sigma(\mathbf{r})(-\nabla \varphi(\mathbf{r}) + \mathbf{E}_0)] = 0, \tag{1}$$

where $\sigma(\mathbf{r})$ is the spatially dependent local conductivity, $\varphi(\mathbf{r})$ describes the local potential, and $\mathbf{E}_0$ is the external field. In our model we assign to $\sigma(\mathbf{r})$ a metal conductivity σ_m with probability p or a dielectric conductivity σ_d with probability $1-p$. Discretization of Eq. (1) on a square lattice with size L leads to a system of L^2 linear equations $\hat{\mathbf{H}} \cdot \mathbf{\Phi} = \mathbf{F}$, where the matrix $\hat{\mathbf{H}}$ is the Kirchhoff Hamiltonian (KH), while the vectors $\mathbf{\Phi}$ and $\mathbf{F}$ are the local potentials and externally induced currents, respectively. The KH is a symmetric random matrix with diagonal elements given by the sum $H_{ii} = \Sigma_j \sigma_{ij}$ of all bond conductivities σ_{ij}, that connect the ith site with it nearest neighbors and off-diagonal elements $H_{ij} = -\sigma_{ij}$. Due to the random nature of the conductivities σ_{ij} the KH is thus mathematically similar to the Anderson Hamiltonian (AH) that is studied in quantum mechanics.[3,9] However, unlike the AH,

the diagonal and off-diagonal elements of the KH are not independent. The correlations are due to the local current conservation, and as we will show later they result in dramatic changes in the nature of the SP localization as compared to the discrete noncorrelated Anderson analog.

In order to simplify the treatment of the SP excitation in metal-dielectric films, we first work in the regime of single-particle resonance, $\varepsilon_m'=-\varepsilon_d$, where the dielectric constants $\varepsilon_s=4\pi i\sigma_s/\omega_r$ depend on the complex conductivities σ_s (s stands for the metal or the dielectric components) and the resonance frequency ω_r. Next, we normalize Eq. (1) by σ_d and use a new set of nondimensional permittivities $\varepsilon_d^*=1$ and $\varepsilon_m^*=-1+i\kappa$, where for noble metals and visible light the losses are small $\kappa=\varepsilon_m''/|\varepsilon_m'|\ll 1$. Following the scaling theory,[9] we seek a general solution of Eq. (1) as an expansion over the eigenstates Ψ_n of the SP eigenproblem

$$\nabla\cdot[\theta(\mathbf{r})\nabla\Psi_n(\mathbf{r})]=\Lambda_n\Psi_n(\mathbf{r}), \tag{2}$$

where the topology function $\theta(\mathbf{r})=\pm 1$ maps the real part of the nondimensional dielectric constant $\varepsilon^*(\mathbf{r})$ and thus corresponds only to geometrical characteristics of the film. The reduction of Eq. (2) on a square lattice results in a matrix equation $\hat{\mathbf{H}}'\cdot\boldsymbol{\Psi}_n=\Lambda_n\boldsymbol{\Psi}_n$, where $\hat{\mathbf{H}}'$ is the real part of the normalized KH and has the same correlation properties. We solve the SP eigenproblem by applying Neumann-type boundary conditions, thus assuring the conservation of the local currents at the film boundaries. For example, we use $\theta(\mathbf{r})[\mathbf{n}\cdot\nabla\Psi_n(\mathbf{r})]|_{x=0}=\theta(\mathbf{r})[\mathbf{n}\cdot\nabla\Psi_n(\mathbf{r})]|_{x=L}$ at the left and right boundaries of the film.

To begin our analysis of the SP eigenproblem we first examine some specific eigenmodes. For metal-dielectric films at the percolation threshold, we distinguish two limiting cases. In the first case presented in Fig. 1(a), the SP eigenmode situated at the band edge is strongly localized. However, the nature of the eigenstates at the band center [see Fig. 1(b)] is completely different. Those states are extended and according to our studies (not presented here) they exhibit multifractal properties. In Fig. 1(c) we also show a particular SP mode that is manifested in the periodic case. The periodic structure is modeled as a square lattice of metal particles with metal coverage equal to 2/3. The important feature to be recognized here is the presence of two length scales, one corresponding to the macroscopically extended Bloch states and the second to local oscillations on the scale of a single particle. We believe that the microscopic SP eigenmode fluctuations correspond to a strong inhomogeneity of the electromagnetic fields observed even for perfectly ordered metal-dielectric films.[11]

The statistical properties of the SP eigenproblem are investigated in terms of the density of states $\rho(\Lambda)$ and SP localization lengths $\xi(\Lambda)$. Both characteristics are studied for the KH and for the corresponding discrete, noncorrelated AH. To simulate the AH we rely on the fact that for each metal concentration p the elements of matrix $\hat{\mathbf{H}}'$ take discrete values with a specific probability. Those probability distributions are then used to build up the AH without enforcing correlations between its elements.

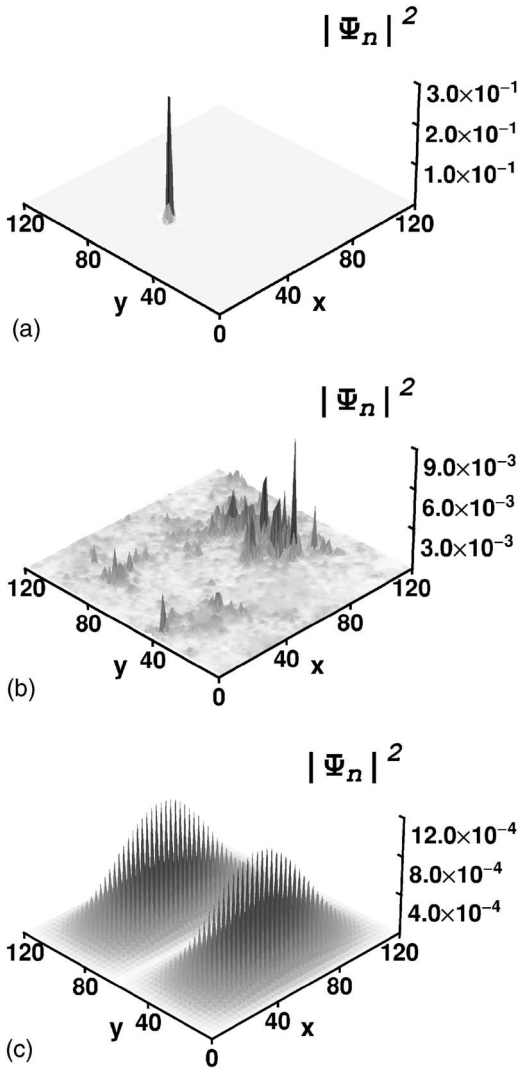

FIG. 1. Surface plasmon eigenmodes in random (a), (b) and periodic (c) metal-dielectric films. The corresponding eigenvalues are: (a) $\Lambda=-5.6945$ (localized), (b) $\Lambda=0.0044$ (delocalized), (c) $\Lambda=-5.9974$ (periodic).

In Fig. 2(a) we show that both correlated and noncorrelated eigenproblems have quite similar densities of states for most of the spectrum. However, at the band center we observe a singularity in the case of the KH. To better understand this important peculiarity, we plot [see the inset of Fig. 2(a)] the region of very small eigenvalues ($\Lambda\ll 1$) on a log-log scale. In the first approximation the density of states seems to diverge as a power law $\rho(\Lambda)\simeq A|\Lambda|^{-\gamma}$, where A is a normalization constant and $\gamma=0.14\pm 0.01$ is a critical exponent. However, a logarithmic singularity $\rho(\Lambda)\simeq A[1+\ln(|\Lambda|^{-\gamma})]$ also fits the result. Those two functions are virtually identical in broad range of the arguments $e^{1/\gamma}\gg|\Lambda|\gg e^{-1/\gamma}$, and therefore for simplicity, in the scaling theory that follows, we use the power-law relationship. In Fig. 2(a) we have also included the result for the noncorrelated AH case, where the density of states is relatively uniform throughout the spectra and does not show any singularities, which matches our expectations.

The role of the cross correlations presented in the KH

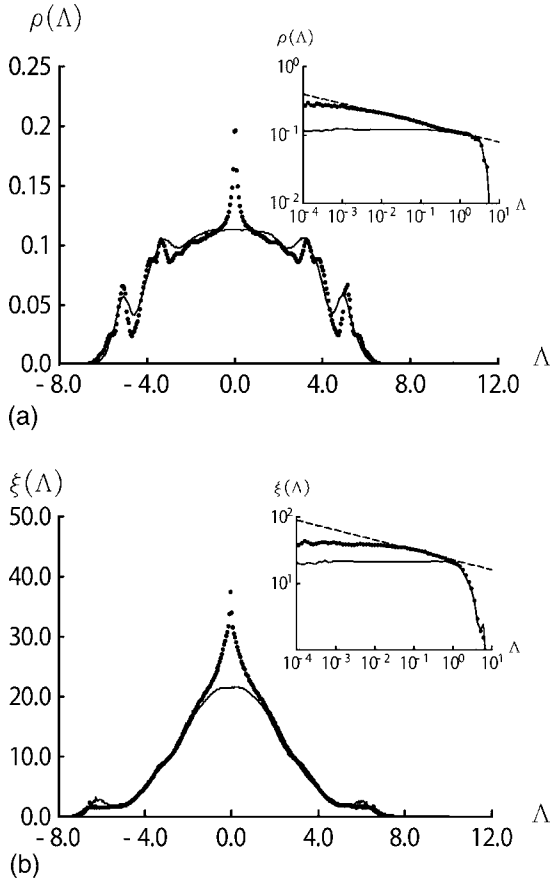

FIG. 2. The density of states $\rho(\Lambda)$ (a), and the SP localization lengths $\xi(\Lambda)$ (b) for the KH (dots) and for the corresponding Anderson problem (solid line), calculated at the resonant condition $\varepsilon_d^*=-\varepsilon_m^*=1$. The band-center singularity is shown in the log-log insets where a power-law fit (dashed line) with exponent $\gamma=\alpha=0.14$ is applied. The data is averaged over 100 different realizations of percolation samples each with size $L=120$.

eigenproblem is next studied in terms of the SP localization lengths $\xi(\Lambda)$. The localization length for each eigenmode is calculated using the gyration radius $\xi^2(\Lambda_n)=\int(\mathbf{r}-\langle\mathbf{r}\rangle_n)^2|\Psi_n(\mathbf{r})|^2d\mathbf{r}$, where $\langle\mathbf{r}\rangle_n=\int\mathbf{r}|\Psi_n(\mathbf{r})|^2d\mathbf{r}$ is the "mass center" of the nth mode and the integration is performed over the film surface. Our results for $\xi(\Lambda)$ are presented in Fig. 2(b). Similar to what we have observed for the density of states [see Fig. 2(a)], there is a singularity at the band center for the KH. The localization length diverges logarithmically for $\Lambda\to 0$, but also can be fitted with a power law $\xi(\Lambda)\sim|\Lambda|^{-\alpha}$, where $\alpha=0.15\pm0.02$. The size effect is clearly visible for the extended states with $\xi(\Lambda)\geqslant L$.

The existence of delocalized states has been recently predicted for somewhat similar (but not the same) SP eigenproblem in Ref. 12, where it was concluded that those modes play a dominant role in the interaction with light. Here, we show that the role of the delocalized modes ($\xi(\Lambda)\geqslant L$) is more subtle. In the limit of large systems $L\to\infty$ the measure of those states in the spectrum rapidly falls as $\mu\sim e^{-L/\gamma}\ln(L)$, where we have assumed logarithmic singularities for $\xi(\Lambda)$ and $\rho(\Lambda)$ with $\alpha=\gamma$. However, despite the zero measure the delocalized states still affect the optical properties of the composite as shown below.

Relying on the SP eigenproblem, we develop a scaling theory for the high-order moments $M_{n,m}=\langle|\mathbf{E}(\mathbf{r})|^n[\mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})]^{m/2}\rangle/(|\mathbf{E}_0|^n[\mathbf{E}_0\cdot\mathbf{E}_0]^{m/2})$ of the local electric fields $\mathbf{E}(\mathbf{r})=-\nabla\varphi(\mathbf{r})$, averaged over the film surface. To accomplish this, we expand the local potential $\varphi(\mathbf{r})$ over the SP eigenstates and assuming a power-law singularity for both density of states $\rho(\Lambda)$ and the SP localization length $\xi(\Lambda)$ we obtain a simple scaling relationship for the field moments

$$M_{n,m}\simeq\int_{-\infty}^{\infty}\frac{\rho(\Lambda)[a/\xi(\Lambda)]^{2(n+m-1)}}{(\Lambda^2+\kappa^2)^{(n+m)/2}}e^{im\phi(\kappa,\Lambda)}d\Lambda\simeq\kappa^{-\varkappa_{n,m}}, \tag{3}$$

where $\varkappa_{n,m}=(n+m-1)(1-2\gamma)+\gamma$ is a positive scaling exponent ($n+m\geqslant 1$), and $\phi(\kappa,\Lambda)=\tan^{-1}(\kappa/\Lambda)$ is a phase factor. In the derivation of Eq. (3) we use $\alpha=\gamma$, which agrees with our numerical results. Note that the singularity's critical index γ affects the high-order field moments through its contribution to the index $\varkappa_{n,m}$. The previously reported result,[9] which was obtained based on the assumption that all modes are localized, can be retrieved from the formula above by setting $\gamma=0$. Thus formula Eq. (3) corrects the former theory,[9] by taking into account the delocalized states.

It is possible to recover Eq. (3) by considering the local field as a set of peaks with characteristic size $l_p^*\simeq\xi(\kappa)$, magnitude $E_m^*\sim E_0\kappa^{-1+2\gamma}$, and separation distance between them proportional to $\xi_e^*\sim l_p^*\kappa^{(-1+3\gamma)/2}$. Based on this similarity the theory can be extended to frequencies that are away from the single-particle resonance ($\varepsilon_m'=-\varepsilon_d$). This is accomplished through renormalization of the system by dividing it in segments with size $l_r=a(|\varepsilon_m'|/\varepsilon_d)^{\nu/(t+s)}$, where t, s, and ν are the critical exponents for the static conductivity, dielectric constant, and percolation correlation length, respectively. At the new length scale, the effective dielectric constants of the segments $\varepsilon_m(l_r)$ and $\varepsilon_d(l_r)$ possess the same resonance properties $\varepsilon_m(l_r)/\varepsilon_d(l_r)\simeq-1+i\kappa$ as the original SP eigenproblem. Taking into consideration that the electric field is renormalized as $E_m\sim(l_r/a)E_m^*$ and the new field separation length is $\xi_e\sim(l_r/a)\xi_e^*$, the field moments are estimated as

$$M_{n,m}\simeq\left(\frac{|\varepsilon_m'|}{\varepsilon_m''}\right)^{\varkappa_{n,m}}\left(\frac{|\varepsilon_m'|}{\varepsilon_d}\right)^{(\nu(n+m-2)+s)/(s+t)}, \tag{4}$$

where we have used the scaling relationship $n(l_r)\propto(l_r/a)^{s/\nu}$ for the number of peaks in each segment. Note, that at the single-particle resonance $\varepsilon_m'=-\varepsilon_d$, formula Eq. (4) is reduced to the previous result Eq. (3).

To examine the frequency dependence of the moments $M_{n,m}$ we consider noble metals and use the Drude model for the dielectric constant $\varepsilon_m(\omega)\simeq\varepsilon_b-(\omega_p/\omega)^2/(1+i\omega_\tau/\omega)$, where ε_b is the interband transition term, ω_p is the plasma frequency, and $\omega_\tau\ll\omega_p$ is the relaxation rate.[13] Applying the exact block elimination method[14] we check Eq. (4) for Ag composites in the high-frequency range $\omega_p>\omega>\omega_\tau$. The results are shown in Fig. 3. Clearly, there is an excellent correlation between the numerical simulations and theoretical

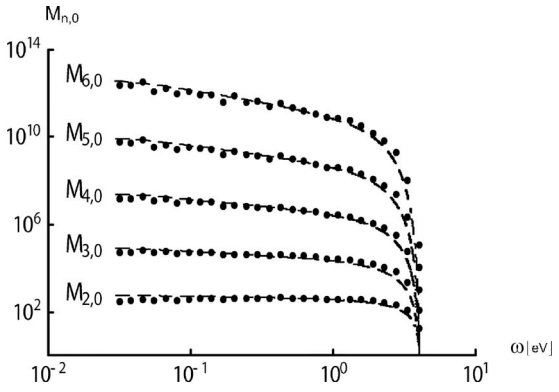

FIG. 3. The local-field moments $M_{n,0}$ (dots) are calculated with the exact numerical method and compared to the analytical results with exponent $\gamma=0.14$ (dashed lines). The numerical data are averaged over 20 realizations of percolation systems with size $L=250$. In the analytical estimates we use $t \simeq s \simeq \nu \simeq 4/3$ (Ref. 9).

results. In both cases the field moments gradually decrease with the increase of the frequency and converge toward unity for $\omega=\omega_p/\sqrt{\varepsilon_b}$. It is important to note that the enhancement of the local electric field, manifested through the high-order field moments, is directly measured in various linear and nonlinear optical processes. For example, surface-enhanced Raman scattering has been shown to be proportional to $M_{4,0}$, while the enhancement of Kerr optical nonlinearity is given by $M_{2,2}$ (Refs. 9 and 15). Thus, experimental investigation of these processes and their spectral dependencies can result in further insight into the localization properties of the SP eigenmodes.

In summary, we have investigated the surface plasmon excitation in random metal-dielectric films. The KH describing the system exhibits unique short-range correlations between the diagonal and off-diagonal elements. These correlations, occurring because of the local current conservation, result in a localization-delocalization transition for the electromagnetic response of the composite. This transition is manifested as a singularity in the center of the spectrum and corresponds to a zero measure subset of delocalized SP eigenstates. Such type of delocalization is inherent only of the correlated KH and is not present in the noncorrelated discrete Anderson analog. The scaling theory that is developed accounts for both localized and delocalized SP eigenmodes and describes the high-order field moments responsible for the nonlinear optical response of the system. Despite the zero measure of the SP delocalization, it is found that it still affects the optical properties of the composite by modifying the critical indices in the field moments. The developed theory is shown to be in excellent agreement with our numerical calculations.

This work was supported in part by NSF Grants No. ECS-0210445 and HRD-0317722 and by NASA Grant No. NCC-1035.

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