A theory of spectral properties of disordered metal-semiconductor nanocomposites

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Abstract. Random LC-networks are widely used to describe optical properties of disordered metal-dielectric nanocomposites. In such networks inductive bonds correspond to metal regions, while capacitive bonds represent dielectric. We show that parallel LC-circuits better describe metallic regions where values of $L$ and $C$ depend on a network lattice parameter and plasma frequency of metal. Spectral properties of disordered metal-dielectric and metal-heavily doped semiconductor composites are studied in a framework of this generalized LC-model. We derive analytical expressions for dependence of eigenfrequencies of metal-dielectric composites on permittivity of dielectric and relation between eigenfrequencies of metal-semiconductor composites before and after metal-dielectric transition in semiconductor. Obtained results are illustrated by numerical simulations.

1. Introduction
Disordered composites consisting of nanosize grains of noble metals placed into a dielectric matrix attract considerable attention because of their interesting optical properties associated with plasmon resonances, including second harmonic generation, enhanced optical absorption and surface-enhanced Raman scattering \cite{1}.

Discretized Maxwell equations in quasistatic approximation of metal regions with Drude-permittivity $\varepsilon_m(\omega) = 1 - \omega_p^2/\omega^2$ correspond to a cubic lattice of parallel LC-circuits with $L_m = 4\pi c^2/(a\omega_p^2)$ and $C_m = a/(4\pi)$, where $\omega_p$ is a plasma frequency of metal, $a$ is a lattice parameter of discretization network and $c$ is the speed of light. In the following we consider the units where $c = 1$. Dielectric regions correspond to a cubic lattice of capacitors $C_d = a\varepsilon_d/(4\pi)$ if permittivity $\varepsilon_d$ is approximately constant in optical region. Thus, continuous heterogeneous medium is replaced by a discrete network with LC- and C-bonds. In literature the approximation when LC-bonds are replaced to L-bonds is extensively studied \cite{1, 2, 3}. However, it is valid only for a low frequencies $\omega \ll \omega_p$ and the properties of the general case remain unclear.

Resonances in such networks can be studied in terms of generalized eigenvalue problem \cite{4}

$$\sum_j K_{ij}\varphi_j - \omega^2 \sum_j C_{ij}\varphi_j = 0, \quad (1)$$

where indices $i$ and $j$ enumerate sites of a network. Eigenvalues $\omega^2$ are squared resonant frequencies of a system and eigenvectors $\varphi$ describe distribution of potential at the sites of
network for eigenmodes. $K$ is a matrix of inverse inductances between sites of network: $K_{ij} = 1/L_{ij}$ if sites $i$ and $j$ are directly connected by inductance $L_{ij}$, otherwise $K_{ij} = 0$. Diagonal elements are defined by a sum rule $K_{ii} = -\sum_{j \neq i} K_{ij}$. $C$ is a matrix of capacitances: $C_{ij} = \varepsilon_d a/\pi$ if sites $i$ and $j$ are connected by a capacitor, otherwise $C_{ij} = 0$. Diagonal elements $C_{ii} = -\sum_{j \neq i} C_{ij}$. These properties directly follow from Kirchhoff’s rules for a network. Matrices $K$ and $C$ are symmetric, sparse and of size $N \times N$, where $N$ is a number of sites in a network. Resonant spectrum of network is given by characteristic equation

$$
|K - \omega^2 C| = 0. \tag{2}
$$

2. Resonances in metal-dielectric nanocomposites

Resonant spectrum of $LC-C$–network, corresponding to metal-dielectric composite, depends on permittivity of a dielectric $\varepsilon_d$ since elements of matrix $C$ involve capacitances $\varepsilon_d a/\pi$. In this section we will show that initial generalized eigenvalue problem (2) can be transformed to a form, which does not depend on $\varepsilon_d$.

The total matrix of capacitances $C$ is a sum $C = C_d + C_m$, where $C_d$ is a matrix of capacitances of dielectric and $C_m$ is a matrix of capacitances of metal. Matrices $K$, $C_m$ and $C_d$ have the following structure

$$
K = \frac{a \omega_p^2}{4 \pi} K^*, \quad C_d = \frac{\varepsilon_d a}{4 \pi} C_d^*, \quad C_m = \frac{a}{4 \pi} C_m^*, \tag{3}
$$

where matrices with the asterisk (*) are dimensionless matrices with unit non-zero elements. These matrices are adjacency matrices with the additional sum rule for the diagonal elements: $K_{ii}^* = -\sum_{j \neq i} K_{ij}^*$ etc. Therefore, from Eq. (2) we obtain

$$
\left| K^* - \omega_p^2 \frac{\varepsilon_d C_d^* + C_m^*}{\omega_p^2} \right| = 0. \tag{4}
$$

Matrices $K^*$ and $C_m^*$ both represent the same structure of metallic bonds, so $C_m^* = K^*$ and Eq. (4) can be rewritten as

$$
\left| (1 + (\varepsilon_d - 1) \omega_p^2 / \omega_d^2) K^* - \varepsilon_d \omega_p^2 / \omega_d^2 (C_d^* + K^*) \right| = 0. \tag{5}
$$

It is a generalized eigenvalue problem

$$
|K^* - \mu (C_d^* + K^*)| = 0 \tag{6}
$$

with eigenvalues

$$
\mu = \frac{\varepsilon_d \omega_p^2 / \omega_d^2}{1 + (\varepsilon_d - 1) \omega_d^2 / \omega_p^2}. \tag{7}
$$

Eigenvalues $\mu$ do not depend on permittivity of dielectric $\varepsilon_d$ and can be computed only for one value of $\varepsilon_d$. Therefore each eigenfrequency $\omega$ can be expressed in the permittivity $\varepsilon_d$ and eigenvalue $\mu$

$$
\omega = \frac{\omega_p}{\sqrt{\varepsilon_d (1 - \mu) / \mu + 1}}. \tag{8}
$$

For example, surface plasmon in spherical granule with frequency $\omega_p/\sqrt{3}$ has $\mu = 1/3$ and Eq. (8) gives the well-known result $\omega = \omega_p/\sqrt{2 \varepsilon_d + 1}$. Another example is volume plasmon in metal: it has frequency $\omega_p$, which does not depend on the permittivity $\varepsilon_d$. 
The spectral density of resonances in two-dimensional LC–C–networks for different values of \( \varepsilon_d \) is shown in Figure 1. We can see that the number of peaks of the spectral density does not depend on \( \varepsilon_d \) (Figures 1a and 1b). Both spectra are coincide up to statistical fluctuations in terms of spectral variable \( \mu \) (Figure 1c).

Matrices \( K^* \) and \( C_d^* \) are both negative semidefinite because they are diagonally dominant matrices with negative diagonal entries due to sum rule. We can rewrite Eq. (6) in the following form

\[
|K^* - \frac{\mu}{1 - \mu}C_d^*| = 0. \tag{9}
\]

The generalized eigenvalue problem with negative semidefinite matrices has non-negative eigenvalues \( \mu/(1 - \mu) \geq 0 \) so \( 0 \leq \mu \leq 1 \). Therefore, all spectra have no resonant frequencies higher than \( \omega_p \), which is clearly seen in Figure 1.

![Figure 1](image)

**Figure 1.** Spectral density of resonances \( \rho(\omega) \) for random LC–C–networks with concentration of parallel circuits \( p_{LC} = 0.1 \), \( \omega_p = 1 \) and permittivity of dielectric \( \varepsilon_d = 1 \) (a) and \( \varepsilon_d = 5 \) (b). In picture (c) both spectra are shown in terms of spectral variable \( \mu \) and coincide up to statistical fluctuations. The results were calculated numerically for ensemble of \( 10^5 \) networks of size \( 20 \times 20 \) sites with periodic boundary conditions in both directions.

### 3. Resonances in metal-semiconductor nanocomposites

Composite of metal and highly doped semiconductor can be considered as a mixture of two Drude-metals [5, 6] with different plasma frequencies \( \omega_{p1} \) and \( \omega_{p2} \). Usually \( \omega_{p1} \) lies in ultraviolet or visible range, while \( \omega_{p2} \) lies in THz or infrared range. Such a system corresponds to a network with two types of LC – bonds with different resonant frequencies.

In this case matrices \( K \) and \( C \) in Eq. (2) are a sum of matrices for two metals \( K = K_1 + K_2 \), \( C = C_{m1} + C_{m2} \) where

\[
K_1 = \frac{a\omega_{p1}^2}{4\pi}K_1^*, \quad K_2 = \frac{a\omega_{p2}^2}{4\pi}K_2^*, \quad C_{m1} = \frac{a}{4\pi}C_{m1}^*, \quad C_{m2} = \frac{a}{4\pi}C_{m2}^*. \tag{10}
\]

Thus, we come to the equation

\[
|(\omega_{p1}^2 K_1^* + \omega_{p2}^2 K_2^*) - \omega^2(C_{m1}^* + C_{m2}^*)| = 0. \tag{11}
\]

Matrices \( K_1^* \), \( C_{m1}^* \) and \( K_2^* \), \( C_{m2}^* \) are the same so

\[
|(\omega_{p1}^2 - \omega^2)K_1^* + (\omega_{p2}^2 - \omega^2)K_2^*| = 0. \tag{12}
\]

Finally, we come to a generalized eigenvalue problem

\[
|K^* - \xi(K_1^* + K_2^*)| = 0 \tag{13}
\]
with eigenvalues
\[ \xi = \frac{1 - \omega^2/\omega_{p1}^2}{1 - \omega^2/\omega_{p2}^2}. \] (14)

One can note that the same expression for \( \xi \) can be obtained if permittivity of dielectric \( \varepsilon_d \) in Eq. (7) is replaced by the Drude-permittivity \( \varepsilon(\omega) = 1 - \omega^2/\omega_{p}^2 \). Resonant spectrum in terms of spectral variable \( \xi \) is a function of concentration \( p \) and does not depend on values of \( \omega_{p1} \) and \( \omega_{p2} \). One can note that the structure of problem (13) is equivalent to those of (6) so \( 0 \leq \xi \leq 1 \), and all resonant frequencies of such networks take values in the range \( \omega_{p2} \leq \omega \leq \omega_{p1} \). It is in agreement with results of numerical simulations shown in Figure 2. Physical interpretation is straightforward in the Drude-model: both permittivities are negative for \( \omega < \omega_{p2} \) and there are no resonances in the composite; in region \( \omega > \omega_{p1} \) both permittivities are positive and composite is transparent for incident radiation.

![Figure 2](image)

**Figure 2.** Spectral density of resonances \( \rho(\omega) \) for random \( LC-C \)–networks (a) and \( LC-LC \)–networks (b), corresponding to metal-dielectric and metal-metal nanocomposites. In both cases \( p = 0.5 \) and networks are percolating. Picture (c) shows both spectrums in terms of spectral variables \( \mu \) and \( \xi \) respectively. The results were calculated numerically for ensemble of \( 10^5 \) networks of size \( 20 \times 20 \) sites with periodic boundary conditions in both directions.

### 4. Mapping between different models

It is interesting to note that resonant spectrum of \( LC-C \)–model of metal-dielectric composite in terms of spectral variable \( \mu \) as well as spectrum of \( LC-LC \)–model of metal-semiconductor composite in terms of variable \( \xi \) are coincide with spectrum of \( L-C \)–networks in terms of variable

\[ \lambda = \frac{(\omega/\omega_p)^2}{1 + (\omega/\omega_p)^2}. \] (15)

Indeed, if every bond of network is a single inductance or a single capacitor, problem (2) can be reduced to

\[ |K^* - \lambda(K^* + C^*)| = 0, \] (16)

where \( C = C_d \) is a matrix of capacitances of dielectric. This formulation is directly maps with (6) because corresponding right and left matrices in these eigenvalue problems are equivalent. Detailed study of spectral properties of random \( L-C \)–networks is given in paper [3]. Thus, fundamental results of work [3], as well as results for networks with fluctuating entries [4] could be directly applied to a study of spectral properties of \( LC-C \)– and \( LC-LC \)–networks in terms of spectral variables \( \mu \) and \( \xi \).

Using mapping between problems (6) and (13) one can obtain the expression which connects the eigenfrequencies of a metal-semiconductor composite when semiconductor acts as dielectric...
and after it exhibits metal-dielectric transition (for example, after heating of an initial composite)

\[ \omega = \omega_p 2 \sqrt{1 - \mu (1 - \frac{\omega^2}{\omega_p^2})}, \]

(17)

where \( \omega \) are frequencies of eigenmodes of metal-semiconductor composite with semiconductor acting as metal and \( \mu \) is a spectrum of composite with semiconductor acting as dielectric.

5. Conclusion
In present article we analytically derived expressions which describe dependence of resonant spectrum of disordered metal-dielectric and metal-semiconductor composites on matrix permittivity as well as transformation of resonant spectrum in the case of metal-dielectric transition in one of the components. These equations have a common property: both of them do not include information about geometry of the system in explicit way. All information about geometry manifests itself in initial resonant spectrum of the composite, i.e. spectrum, corresponding to initial matrix permittivity. Obtained formula also leads to correct expressions for some well-known cases.

Mapping between several types of network problems have been established. It takes place when special spectral variables are introduced. This makes possible a straightforward generalization of some properties of well-studied random \( LC \)-networks to \( LC-C \)- and \( LC-LC \)-networks.

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