Surface modes of big clusters and resonances in generalized LC–model of metal-dielectric nanocomposites

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Abstract. Random impedance networks with inductive L and capacitive C bonds have been widely addressed in a literature to describe properties of disordered metal-dielectric nanocomposites. In this paper we show that networks with single bonds in the form of parallel oscillatory LC–circuits and capacitances C are more appropriate model for metal-dielectric composite in optical frequency range. Resonant spectrum of such networks demonstrates absence of resonances at frequencies higher than the plasma frequency of metal \( \omega_p \). Eigenmodes of big ordered clusters are studied. Their resonances are shown to be surface modes having the form of multipoles of various order. It is in agreement with theory of surface plasmons in metallic nanowires. The idea for metal-metal and metal-semiconductor nanocomposites with different plasma frequencies is put forward.

1. Introduction
Disordered nanocomposites consisting of small (\( \leq 30 \) nm) granules of noble metal (Ag, Au) incorporated into dielectric matrix attracting considerable attention due to their interesting optical properties. First of all, it is giant fluctuations of local electric fields in composite which lead to Surface-Enhanced Raman scattering (SERS) [1]. This behavior is caused by surface plasmon resonances in metallic grains which allow to concentrate the energy of electromagnetic wave in volumes much smaller than \( \lambda^3 \), where \( \lambda \) is a wavelength of incident radiation. The main feature for SERS is the presence of “hot spots” – regions in composite, where local electric field is much higher than those in the other parts of the composite. Another interesting properties are anomalous optical absorption, higher harmonic generation and other nonlinear effects.

Optical properties of disordered nanocomposites can be adequately modeled by electric networks consisting of inductances L and capacitances C, randomly distributed in a lattice [2]. Inductive bonds L here model metallic grains, while capacitances C model dielectric bridges between them. This representation follows from discretization of Maxwell equations for given composite in quasistatic approximation.

Random LC–networks have a wide resonant spectrum with complicated structure [3]. Local electric fields in such networks exhibit giant fluctuations which have multifractal structure [3]. Multifractality is a result of dipole–dipole interaction between resonant clusters which can be considered as harmonic oscillators [2, 4, 5].
2. Approximation of metal-dielectric nanocomposites by random LC-networks

Maxwell equations for a composite have a form

\[
\text{rot } \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \tag{1}
\]

\[
\text{rot } \mathbf{H} = \frac{4\pi}{c} \mathbf{j} + \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t}, \tag{2}
\]

\[
\text{div } \mathbf{D} = 4\pi \rho, \tag{3}
\]

\[
\text{div } \mathbf{B} = 0. \tag{4}
\]

For a non-magnetic composite permeability \( \mu = 1 \) and \( \mathbf{B} = \mathbf{H} \). Let us assume that there are no exterior local charges in the composite, so \( \rho = 0 \) and \( \text{div } \mathbf{D} = 0 \). In the quasistatic approximation the magnetic field vanishes, hence \( \text{rot } \mathbf{E} = 0 \) and we can introduce an electric potential \( \mathbf{E} = -\nabla \varphi \). Also from \( \text{rot } \mathbf{H} = 0 \) we get the equation

\[
\mathbf{j} = -\frac{1}{4\pi} \frac{\partial \mathbf{D}}{\partial t}, \tag{5}
\]

where \( \mathbf{D} = \mathbf{D}_0 \exp(-i\omega t) \). The electric induction \( \mathbf{D} \) is related with the electric field \( \mathbf{E} \) by the equation \( \mathbf{D} = \varepsilon(\omega)\mathbf{E} \). The permittivity of dielectric \( \varepsilon_d \) can be considered as a constant \( \varepsilon \) in the optical range of frequencies. The permittivity of metal \( \varepsilon_m \) in Drude model without dissipation reads

\[
\varepsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega^2}. \tag{6}
\]

This relation is valid for metals where \( \omega_p \tau \gg 1 \) in the frequency range \( \omega \tau \gg 1 \).

From Eq. (5), we get the expression for the displacement current density in dielectric

\[
\mathbf{j} = -i\omega \frac{\varepsilon_d}{4\pi} \nabla \varphi. \tag{7}
\]

It is equivalent to the relation \( I = YU \) between the current \( I = ja^2 \) and the voltage \( U = \varphi_1 - \varphi_2 \) in a cubic lattice of capacitances with small lattice constant \( a \). Here \( Y = -i\omega C_d \) is the admittance of the capacitor with the capacitance \( C_d = \varepsilon a/4\pi \). On the other hand, in metals making use of Eq. (6) we have

\[
\mathbf{j} = -\left( i\omega \frac{1}{4\pi} + \frac{\omega_p^2}{i\omega 4\pi} \right) \nabla \varphi \tag{8}
\]

which corresponds to a cubic lattice of parallel \( LC \)-circuits which has the admittance \( Y = -i\omega C_m - 1/i\omega L_m \) with the inductance \( L_m = 4\pi c^2/(a\omega_p^2) \) and the capacitance \( C_m = a/4\pi \). The resonant frequency \( c/\sqrt{L_mC_m} \) of this circuits is the plasma frequency \( \omega_p \). In the low-frequency range \( \omega \ll \omega_p \) the parallel \( LC \)-bonds can be replaced by a single inductances \( L \) because \( i\omega C_m \ll ic^2/\omega L_m \).

As shown in our previous work [6], Kirchhoff equations for \( LC \)-network can be reduced to a generalized eigenvalue problem

\[
\sum_j K_{ij} \varphi_j - \omega^2 \sum_j C_{ij} \varphi_j = 0. \tag{9}
\]

Here \( \varphi_i \) are potentials at the lattice sites enumerated by index \( i \), \( K_{ij} \) is the matrix of inverse inductances \( 1/L_{ij} \) and \( C_{ij} \) is the matrix of capacitances between sites \( i \) and \( j \). If sites \( i \) and \( j \)
are not connected by inductance or capacitor, corresponding matrix elements $K_{ij}$ or $C_{ij}$ is zero. Diagonal elements of both matrices are

$$K_{ii} = -\sum_{j \neq i} K_{ij}, \quad C_{ii} = -\sum_{j \neq i} C_{ij}.$$  \hspace{1cm} (10)

The resonant frequencies $\omega$ of the system can be calculated from the equation

$$\det (K - \omega^2 C) = 0.$$ \hspace{1cm} (11)

3. Generalizations of LC–model

Disordered nanocomposites can be adequately modeled by electric lattice with randomly distributed inductances $L$ and capacitances $C$ [2, 3, 9]. The inductances and the capacitances qualitatively correspond to randomly positioned metal grains and dielectric bridges between them. We will consider an LC–network with topology of two-dimensional square lattice, whose sites are connected with bonds which are randomly chosen to be inductances $L$ or capacitances $C$ with probabilities $p$ and $1 - p$ respectively. We will refer these probabilities as concentrations of $L$– and $C$–entries. Such planar networks correspond to a composite consisting from long metallic rods, randomly positioned in dielectric but parallel to each other.

As was mentioned above, networks with purely $L$– and $C$–bonds can be used to model metal-dielectric composites in the low-frequency range $\omega \ll \omega_p$. However this model gives a significant number of resonant frequencies $\omega \approx \omega_p$ and even $\omega \gg \omega_p$ (Figure 1). Therefore it is necessary to study generalized networks with randomly positioned bonds in the form of parallel LC–circuits and capacitances $C$.

![Figure 1](image)

**Figure 1.** Spectral density of resonances $\rho(\lambda)$ for 2d LC–networks with various concentration $p$ of $L$–bonds (a,b,c) and LC–$C$–networks with various concentration of parallel LC–circuits (d,e,f). Numerical computation for networks of size 20 x 20 sites with averaging over 20 000 realizations.

Let us introduce the reduced resonant frequencies [2, 3]

$$\lambda = \frac{(\omega/\omega_0)^2}{1 + (\omega/\omega_0)^2},$$ \hspace{1cm} (12)
which maps the frequency spectrum $0 < \omega < \infty$ to the interval $[0, 1]$ for $\lambda$. It is convenient and allows to investigate some special types of symmetry.

The Figure 1 shows the comparison of the spectral density of resonances (SDR) $\rho(\lambda)$ for random networks with $L-$ and $LC-$bonds in a lattice of capacitances $C$ for various values of the probability $p$. The spectral density of resonances for networks with $L-$ bonds is taken from [3]. The spectral density of resonances $\rho(\lambda)$ for various concentrations of $LC-$bonds $p$ is shown in Figure 1d-f. In the case of low concentrations $p$ (Figure 1d) the shape of $\rho(\lambda)$ resembles that for networks with $L-$ and $C-$bonds. The redshift of the central frequency from $\lambda = 1/2$ to $\lambda = 1/3$ arises because the frequency of a single ”metallic” bond with $L, C = 1$ in capacitive lattice $C = 1$ is now

$$\omega_{0}^{LC} = \frac{c}{\sqrt{2LC}} = \frac{\omega_{0}^{L}}{\sqrt{2}}$$

instead of $\omega_{0}^{L} = c/\sqrt{LC} = 1$ for $LC-$networks. When concentration $p$ is high, the spectrum looks completely different (Figure 1f).

One can note that there are no resonant frequencies higher than $\omega_{p}$ ($\lambda = 0.5$) in such random networks with parallel $LC$ circuits. It is in agreement with the fact that metal in the Drude model becomes transparent to incident radiation in frequency range $\omega > \omega_{p}$ and thus has no absorption. Experimental observations of metal-dielectric nanocomposites show presence of weak absorption peaks with frequencies $\omega > \omega_{p}$, but since it is a result of nonlinear effects they cannot appear in our linear model. High peak at $\lambda = 0.5$ ($\omega = \omega_{p}$) which arise near the percolation threshold corresponds to a volume plasmon in metal and is formed by eigenfrequencies of parallel $LC-$circuits.

![Figure 2](image-url)

**Figure 2.** Example of random 2d network with two types of parallel $LC$ circuits and corresponding spectral density of resonances $\rho(\lambda)$ for network at the percolation threshold $p_{LC1} = p_{LC2} = 0.5$. Eigenfrequency of parallel $LC-$bonds of the first type $\omega_{p1} = 1/\sqrt{L_{1}C_{1}} = 0.5$ ($\lambda = 0.2$), for the second type $\omega_{p2} = 1/\sqrt{L_{2}C_{2}} = 2$ ($\lambda = 0.8$). Numerical computation for networks of size 20 x 20 sites with averaging over 20 000 realizations.

We can introduce more general model in the form of random network consisting from two types of parallel $LC-$circuits with two different resonant frequencies $\omega_{01} = c/\sqrt{L_{1}C_{1}}$ and $\omega_{02} = 1/\sqrt{L_{2}C_{2}}$ (see Figure 2a). Such a network corresponds to a mixture of two metals with different plasma frequencies $\omega_{p1}$ and $\omega_{p2}$ or to a composite consisting of metallic grains in the matrix of n–type degenerate semiconductor, which plasma frequency

$$\omega_{p}^{sc} = \sqrt{\frac{4\pi ne^2}{m}}$$

(14)
which depends on the concentration of free carriers \( n \) and can be much smaller than those of metal.

It is well seen from the figure that all resonances are positioned in the band between \( \omega_{p1} \) and \( \omega_{p2} \) and there are no higher and lower frequencies (Figure 2b). It is in a full agreement with surface plasmon resonance condition, which requires the permittivity of grains \( \varepsilon_g \) and permittivity of background medium \( \varepsilon_b \) to be of the opposite signs. In the frequency range \( \omega < \omega_{p1} \) both permittivities are negative, while for \( \omega > \omega_{p2} \) both \( \varepsilon_g, \varepsilon_b > 0 \) and we have a non-resonant mixture of two dielectrics.

One can see presence of two peaks at the edges of the resonant spectrum (Figure 2a). They have a form of \( \delta \)-function like singularities and arise close to the percolation threshold. In 2d square networks with two types of parallel LC circuits it is obvious that at least one of the singularities exists for any \( p \) since percolation threshold \( p_C = 0.5 \).

4. Resonances of big clusters
Resonances in disordered LC–networks and resonances in ordered linear [2], staircase [9] and fractal [2] inductive clusters in capacitive lattice have been studied in the literature. However resonances in closed dense inductive clusters in the form of different geometrical figures (squares, rectangles, circles etc.) with big sizes have not been studied yet. Such configurations in two-dimensional networks correspond to metal nanowires of different cross-section placed into a dielectric medium (or vacuum). We will examine such a configurations in the framework of the generalized model with parallel LC–circuits and C–bonds considering square clusters from parallel LC–circuits as an example. Such cluster of size \( l \times l \) (for \( l = 2 \)) is shown on Figure 3a.

As can be seen from eigenmode potential distribution, which is given by coresponding eigenvector in generalized eigenvalue problem (9), some of the modes have a form of surface oscillations (Figure 3b-d). Number of these surface modes \( n_s \) is equal to the number of LC–bonds at the border between cluster and capacitive lattice, i.e. \( 4l \). Other modes have a structure of volume oscillations at plasma frequency. Therefore the total number of resonances is equal to the total number of oscillatory LC–bonds in the cluster.

![Figure 3](image)

Figure 3. Example of square LC–cluster of size \( l=2 \) in lattice of capacitors \( C \) (a) and surface modes in square cluster of size \( l=20 \) in form of multipoles of various order with corresponding resonant frequencies (b,c,d)

In a 2d lattice the surface modes have a form of planar multipoles of the order \( m \) beginning with \( m = 1 \) (dipole) and higher. The resonant frequency increases with the order of the multipole (Figure 3). It is in a good agreement with classical theory of surface plasmons in metallic nanowires [7]. Some of these surface modes (for example, dipole mode) are two times degenerated due to their symmetry.

It is interesting to note that in the case of purely-inductive clusters (made only from \( L \) bonds) all resonant modes have a form of similar surface modes (see Figure 3b-d) with different
frequencies. But there are no volume modes in the cluster, hence the total number of resonances in this case $n_{res} = 4l$.

![Images of collective eigenmodes](image_url)

**Figure 4.** Symmetric (a) and antisymmetric (b) collective eigenmodes in system with two square $LC$-clusters of size $l=10$, positioned at distance 9 bonds between them and corresponding potential signatures (c,d)

In the system of two identical dense clusters, placed at some distance from each other the initial multipole modes split on symmetric (Figure 4a) and antisymmetric one (Figure 4b) with different frequencies $\omega_S$ and $\omega_{AS}$ and thus became non-degenerate due to their interaction. One can see that frequency of the symmetric mode $\omega_S$ is higher than of the antisymmetric one $\omega_{AS}$, while usually we have $\omega_{AS} > \omega_S$. This can be understood from signatures of the potential distribution in far field (Figure 4c,d). One can see that the symmetric collective eigenmode has a form of multipole of the higher order than the antisymmetric one and therefore has higher eigenfrequency.

5. Conclusion

More general network description of metal-dielectric nanocomposites in the form of networks with $LC$- and $C$-bonds has been proposed. We have shown that spectral properties of such networks is more similar to the spectrum of metal-dielectric nanocomposites than that of networks with purely-inductive and capacitive bonds. Surface modes in dense clusters have a form of multipoles of various order, which is in agreement with theory of surface plasmon resonances in metallic nanowires. The model for metal-metal and metal-semiconductor composites with different plasma frequencies is also proposed.

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References

[1] Brouers F, Blacher S, Lagarkov A N, Sarychev A K, Gadenne P and Shalaev V M 1997 *Phys. Rev. B* **55** 13234
[2] Clerc J P, Giraud G, Luck J M and Robin Th 1996 *J. Phys. A* **29** 4781
[3] Jonckheere Th and Luck J M 1998 *J. Phys. A* **31** 3687
[4] Levitov L S 1989 *Europhys. Lett.* **9** 83
[5] Parshin D A and Schober H R 1998 *Phys. Rev. B* **57** 10232
[6] Olekhno N A, Beltukov Y M and Parshin D A 2014 *J. Phys. Conf. Ser.* **541** 012075
[7] Klimov V V, Nanoplasmonics, 2009
[8] Clerc J P, Giraud G, Laugier J M and Luck J M 1990 *Adv. Phys.* **39** 191
[9] Schafer S, Raymond L and Albinit G, 2005 *Eur. Phys. J. B* **43** 81