Localized mode transfer and optical response in three-component composites

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We investigate the eigenmode transfer of local field and optical response in three-component composites with varying the difference admittance ratio \( h = (e_2 - e_0)/(e_1 - e_0) \). It is shown that at \( h = 0 \) or \( h = 1 \), i.e., a binary composite, the local-field distribution at resonances transfers from one form to another in the two-bond clusters, as well as in disordered composites. Numerical calculations also indicate that at the avoiding crossing region of dielectric resonances \( \eta \in (0, 2) \), the effective optical responses are very sensitive to \( \eta \) due to the competition among eigenmodes. For \( h = 0 \), the absorption peaks are blue-shifted with decreasing \( \eta \), while, for \( h > 2 \), the absorption peaks red-shifted with increasing \( \eta \). Moreover, in a three-component square network, the relation between the summation of dielectric resonances and \( \eta \) is numerically proved: \( \sum_{i=1}^{n} s_i = (n/2) \eta + (n/2) \) with the total impurity bonds \( n = n_1 + n_2 \).

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I. INTRODUCTION

Recently, resonant properties of binary composites have been widely studied.1–7 When dielectric resonance takes place, the system exhibits various eigenmode localizations of local field,8–10 including surface-plasmon modes in the disordered nanosystems,11,12 localized dipolar excitations on the roughly nanostructured surfaces,13 and selective photomodification in the fractal aggregates of colloidal particles.14 The fluctuations of local field are reported to enhance strongly the effective linear and nonlinear optical responses in composites.1,3,6,15 For a multi-component composite, local field distribution near resonances and the corresponding optical responses should show more complicated properties than what found in binary composite. In this connection, by introducing a difference admittance ratio \( \eta = (e_2 - e_0)/(e_1 - e_0) \) with \( e_i \) a complex admittance and frequency dependent, we have developed Green’s-function formalism (GFF) for a three-component composite.16 Using the GFF, for a cluster with arbitrary geometry, the resonance spectrum and local-field distribution at resonance can be analytically obtained. In a three-component network, at the region of difference admittance ratio \( \eta \in (0, 2) \), dielectric resonances avoid to cross each other due to the competition among them.16 When \( \eta \) is varied, one will ask the following two questions: for each eigenmode what kind of changes local-field distribution will experience? What about its effective linear and nonlinear optical responses? To answer them, in the present, we investigate the eigenmode transfer of local field and the effective optical response in three-component composites.

In a binary composite, \( n \) impurity bonds with admittance \( e_1 \) are embedded in an otherwise inhomogeneous network with admittance \( e_0 \). There exists a sum rule of dielectric resonance \( s = 1/[1 - (e_1/e_0)] \).\(^{2-5} \) \( \sum_{i=1}^{n} s_i = n/2 \). While, in a three-component square network, there are \( n_1 \) impurity bonds with admittance \( e_1 \) and \( n_2 \) impurity bonds with admittance \( e_2 \) embedded in an otherwise inhomogeneous network with admittance \( e_0 \). Then, in Sec. II, we report a relation between the summation of dielectric resonances and \( \eta \) in a three-component composite: \( \sum_{i=1}^{n} s_i = (n/2) \eta + (n/2) \) with the total bond \( n = n_1 + n_2 \). In Sec. III, we investigate the eigenmode transfer of local field near resonance for a linear two-bond cluster with varying \( \eta \). At \( \eta = 0 \), the local field in one resonance branch transfers from one form to another due to the admittance jump, while at \( \eta = 1 \) we find that the eigenmode transfer occurs at the second branch due to the competition between two admittance. In Sec. IV, we focus on the effective optical responses in three-component composites. Numerical results indicate that in the region \( \eta \in (0, 2) \), the optical responses are very sensitive to \( \eta \) in the two-bond clusters, as well as in the percolating composites. For \( \eta < 0 \), the absorption peaks are blue shifted with decreasing \( \eta \), while, for \( \eta > 2 \), the absorption peaks redshifted with increasing \( \eta \).

II. A SUM RULE IN THREE-COMPONENT COMPOSITE NETWORK

In the binary square network, there are \( n \) impurity bonds with the admittance \( e_1 \) embedded in the otherwise homogeneous infinite networks with the admittance \( e_0 \) in each bond. When dielectric resonance \( s = 1/[1 - (e_1/e_0)] \) happens, \( e_1/e_0 \) has a branch cut with the number \( n \) in the negative real axis.\(^{2,5} \) In GFF, Green’s matrix \( \tilde{M} \) in the clusters subspace maps the geometry of the clusters. The element of \( \tilde{M} \) has the form \( \tilde{M}_{xy} = \sum_{z \in C(y)} (G_{xy} - G_{xz}) \), where \( z \in C(y) \) means that the jointing points \( x \) and \( y \) belong to the clusters subspace and are the nearest neighbors, and \( G_{xy} \) is Green’s function of Laplace operator on the infinite square network, i.e., \( -\Delta G_{xy} = \delta_{xy} \) with \( G_{xx} = 0 \). The nontrivial eigenvalues of \( \tilde{M} \) form the dielectric resonance spectrum. The dielectric resonances lie in the range \( 0 \leq \omega \leq 1 \).\(^{1} \) For a cluster with \( n \) bonds, it is known that the summation of the nontrivial resonances obeys a sum rule: \( \sum_{i=1}^{n} s_i = n/2 \). The correction of this relation is checked for various binary systems.\(^{2,5} \) In our numerical calculations, this sum rule is always used to check the correction of Green’s matrix and the rationality of the resonances.

Now consider a three-component composite. \( n_1 \) impurity bonds}
bonds with admittance $\epsilon_1$ and $n_2$ impurity bonds with admittance $\epsilon_2$ exist simultaneously in an otherwise inhomogeneous network with admittance $\epsilon_0$. They are defined as color 1 cluster and color 2 cluster, forming the clusters subspace. By introducing a difference admittance ratio $H = (\epsilon_2 - \epsilon_0)/(\epsilon_1 - \epsilon_0)$, the element of Green’s matrix $\tilde{M}$ becomes

$$\tilde{M}_{x,y} = \sum_{z \in C_i(y)} (G_{x,y} - G_{x,z}) + \eta \sum_{z \in C_i(y)} (G_{x,z} - G_{x,y}),$$

where $C_i$ means color $i$ cluster. The Green’s matrix $\tilde{M}$ is greatly modified with varying $H$. The eigenvalues of $\tilde{M}$ (or the dielectric resonances) are extended to $-\infty \leq \eta \leq \infty$, when $H$ is negative, there exists at least one negative eigenvalue. In the full region of $H$, i.e., $-\infty \leq H \leq \infty$, we find a relation between the summation of dielectric resonances $S$ and the difference admittance ratio $\eta$.

$$S = \sum_{i=1}^{n} s_i = \frac{n_2}{2} \eta + \frac{n_1}{2}$$

with $n_1$ bonds for color 1 cluster, $n_2$ bonds for color 2 cluster, and the total bond $n = n_1 + n_2$. The summation of dielectric resonances is in proportion to the difference admittance ratio $\eta$ with the slope $n_2/2$ and the intercept $n_1/2$. At $\eta = 0$ or $\eta = 1$, the three-component composite comes back to the binary one. From the sum rule, we deduce that the dielectric resonances have the same order as $\eta$. So when $\eta \rightarrow \pm \infty$, there are $n_2$ branches of resonance approaching $\pm \infty$. Similar to the binary case, this sum rule is also not strictly proved in mathematics, but always found correct in the numerical calculations.

III. EIGENMODE TRANSFER OF LOCAL FIELD

It is known that for a resonant binary composite, due to the existence of impurity clusters, dielectric resonance occurs in the external field or sources. These resonances are determined by the geometry of the impurity clusters, so they are also called the geometric resonances. When resonance happens, the inhomogeneous field is localized within or around the clusters. However, for a three-component composite with color 1 cluster having $n_1$ bonds and color 2 cluster $n_2$ bonds, there are $n(n_1 + n_2)$ dielectric resonances for a given difference admittance ratio $H$. For the $i$th eigenmode, subject to the point source $(0,0)$, the residues of local field can be written as

$$\text{Residue}(F_{x,0}) = \frac{1}{\epsilon_0} \sum_{y \in C} L_{i,y} \tilde{G}_{y,0} \sum_{z \in C} M_{x,z} \tilde{R}_{i,z},$$

where $\tilde{R}$ and $\tilde{L}$ are the $i$th right and left eigenvectors of Green’s matrix $\tilde{M}$, $\tilde{G}_{y,0}$ is Green’s function of the site $y$ within the clusters subspace subject to the point source $(0,0)$, and $M_{x,z} = \sum_{z \in C_i(x)} (G_{x,z} - G_{x,y}) + \eta \sum_{z \in C_i(x)} (G_{x,z} - G_{x,y})$. This section is to investigate the local field evolution of these $n$ resonances with varying the difference admittance ratio $\eta$. For simplicity, consider various two-bond clusters with $n_1 = n_2 = 1$, as shown in Fig. 1. Figure 1(a) is a linear two-bond cluster, which we will discuss in detail, while Fig. 1(b) a parallel one and Fig. 1(c) a corner one. In the following calculations, the point source is always at $(0,0)$. Figure 2 displays two branches of dielectric resonances with varying $\eta$, say $s_1$ and $s_2$, corresponding to the linear two-bond cluster shown as Fig. 1(a). The numerical calculations indicate that at $\eta = 0$ or $\eta = 1$, namely, a binary composite, there exists an eigenmode transfer of local field in the different resonance branches.

Figure 3 displays the eigenmode transfer of local field at $\eta = 0$. The transfer occurs in branch $s_2$ of Fig. 2 [the configuration of cluster is shown as in Fig. 1(a)]. We observe that the eigenmode from one localization form shown as Fig. 3(a) at $\eta = -0.1$ transfers to another one shown as Fig. 3(b) at $\eta = 0.1$, while at $\eta = 0$, in branch $s_1$, it is a trivial eigenmode and no local-field distribution is provided. We calculate the values of the admittance $\epsilon_1$ and $\epsilon_2$ in branch $s_2$ at $\eta = \pm 0.1$. As shown in Table I(a), the admittance $\epsilon_1$ is jumped from a positive value 22.460 to a negative one $-20.786$. So at $\eta = 0.0$, the admittance jump causes the eigenmode transfer. In this process, in branch $s_1$, we only find a little change in the intensity of local field, without an eigenmode transfer. We also note that near $\eta = 0.0$ the intensity of local field in branch $s_1$ is greater larger than that in branch $s_2$. So the eigenmode in branch $s_1$ will influence the optical properties well near $\eta = 0.0$.

In contrast, at $\eta = 1$, in branch $s_1$ of Fig. 2, the eigenmode of local field from one localization as shown in Fig. 4(a) at $\eta = 0.8$, via a symmetric eigenmode$^5$ in Fig. 4(b) at $\eta = 1.0$, transfers to another shown in Fig. 4(c) at $\eta = 1.2$. The

FIG. 1. Various two-bond color clusters. (a) linear, (b) parallel, and (c) corner.

FIG. 2. Two resonance branches $s_1$ and $s_2$ for a linear two-bond color cluster as shown in Fig. 1(a).
corresponding values of $e_1$ and $e_2$ in branch $s_1$ at $\eta = 0.8, 1.0, 1.2$ are shown in Table I. It is found that $e_1 < e_2$ at $\eta = 0.8$, $e_1 = e_2$ at $\eta = 1.0$, and $e_1 > e_2$ at $\eta = 1.2$. Instead of the admittance jump, at $\eta = 1.0$, the competition between the admittance $e_1$ and $e_2$ leads to the eigenmode transfer of local field. Similarly, there are only weak changes in the intensity of local field at branch $s_2$ varying $\eta$ from 0.8, via 1.0, to 1.2. We also find that in this process the intensity of local field in branch $s_2$ is greater than that in branch $s_1$. So the eigenmode in branch $s_2$ will influence the optical properties well near $\eta = 1.0$.

We have checked other three-component composites, such as a parallel two-bond cluster shown as Fig. 1(b), a corner two-bond cluster shown as Fig. 1(c), and several percolating composites. The eigenmode transfer of local field is found too. So, in a three-component composite, at $\eta = 0$ or $\eta = 1$, i.e., a binary case, the eigenmode transfer of local field is a general phenomenon.

### IV. OPTICAL RESPONSES

We have found the avoiding crossing of dielectric resonances\textsuperscript{16} and eigenmode transfer of local field with varying the difference admittance ratio $\eta$ in a three-component composite.

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**TABLE I.** The values of the admittance $e_1$ and $e_2$: (a) in resonance branch $s_2$ and near $\eta = 0.0$ and (b) In resonance branch $s_1$ and near $\eta = 1.0$.

<table>
<thead>
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<th>$\eta$</th>
<th>$S_1$</th>
<th>$e_1$</th>
<th>$e_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.1</td>
<td>-0.0466</td>
<td>22.460</td>
<td>-1.146</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0459</td>
<td>-20.786</td>
<td>-1.179</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$S_1$</th>
<th>$e_1$</th>
<th>$e_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.5820</td>
<td>-0.718</td>
<td>-0.375</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6366</td>
<td>-0.571</td>
<td>-0.571</td>
</tr>
<tr>
<td>1.2</td>
<td>0.7078</td>
<td>-0.413</td>
<td>-0.695</td>
</tr>
</tbody>
</table>
composite. Then what about its optical responses? Consider a three-component network with a point source (0,0), the effective linear and nonlinear optical responses are given by\[ e_a \frac{\partial F_a}{\partial \alpha} \]
where the summation is over all bonds and \( \frac{\partial F_a}{\partial \alpha} \) is the potential difference across the bond \( a \). For the impurity bond, \( e_a = e_1 \) or \( e_2 \), and \( \chi_a = \chi_1 = \chi_2 = 1.0 \). While, for the rest, \( e_a = e_0 \) and \( \chi_a = 0.0 \). From Eqs. (3) and (4), it is found that near resonance the local field around the impurity clusters will influence the optical properties well.

Drude free electronic model is employed to calculate the optical properties of three-component composites. The admittance \( e_1 \) of the impurity metallic bonds is
\[ e_1 = 1 - \frac{\omega_p^2}{\omega(\omega + i \gamma)^2}, \]
where \( \omega_p \) is the plasma frequency and \( \gamma \) a damping constant. For metal, the plasma frequency \( \omega_p \approx 10^{16} \) being in the ultraviolet region. We choose \( \gamma = 0.01 \omega_p \), which is the typical value of a metal. Let \( e_0 = 1.77 \), which is the dielectric constant of water for model calculations. The value of \( e_2 \) is given by the relation \( e_2 = e_0 + \eta(e_1 - e_0) \). In this case, the range of optical responses is \( \omega / \omega_p \in (0,1) \). For simplicity, in the following figures, only the effective linear responses are considered. The corresponding effective nonlinear responses have similar features as that exhibited in the linear responses for the further calculations.

Figure 5 displays the imaginary part of effective linear optical responses for a linear two-bond cluster. (a) \( \eta = 2.0,3.0,4.0,6.0 \), (b) \( \eta = 0.0,0.5,1.0,1.5,2.0 \), and (c) \( \eta = 0.0,-1.0,-2.0,-5.0 \).

FIG. 5. (Color online) The imaginary parts of effective linear optical responses for a linear two-bond cluster. (a) \( \eta = 2.0,3.0,4.0,6.0 \), (b) \( \eta = 0.0,0.5,1.0,1.5,2.0 \), and (c) \( \eta = 0.0,-1.0,-2.0,-5.0 \).

Moreover, we investigate the optical responses of the par-
allel and corner two-bond clusters [shown in Figs. 1(b) and 1(c)] and various disordered composites. Numerical calculations indicated that for $\eta<0$, the absorption peaks are blue shifted with decreasing $\eta$, while for $\eta>2$, the absorption peaks are redshifted with increasing $\eta$. While for $\eta \in (0,2]$, the spectra are very sensitive to the values of $\eta$. As an example, Fig. 6 displays the effective linear optical responses in the three-component percolating composites. Here the sample size is $20 \times 20$. The impurity bonds with the admittance $\varepsilon_1$ and $\varepsilon_2$ have the same contribution, i.e. $p_1=p_2=0.25$. For $\eta>2$, as shown in Fig. 6(a), the absorption peaks have a blue shift with increasing $\eta$, while for $\eta<0$, as shown in Fig. 6(c), the absorption peaks have a redshift with decreasing $\eta$. However, the intensities of absorption peaks do not exhibit obvious changes. The same as that found in the linear two-bond cluster, for $\eta \in (0,2)$, as shown in Fig. 6(b), the absorption spectra become complicated and are sensitive to $\eta$ due to the competition among the eigenmodes belonging to the different resonance branches. Finally, we point out that for $\eta \in (0,2]$, not only the avoiding crossing of dielectric resonances but also the sensitivity to the optical responses occur due to the competition of various eigenmodes.

V. SUMMARY

In this paper, we have investigated the eigenmode transfer of local field and the effective optical responses in the three-component composites with a change of the difference admittance ratio $\eta$. Our numerical calculations indicate that at $\eta=0$ and $\eta=1$ the eigenmodes transfer from one form to another for various two-bond clusters, as well as for the disordered composites. We think it is a general phenomena in three-component composites. For $\eta<0$, the absorption peaks are blue shifted with decreasing $\eta$, while for $\eta>2$, the absorption peaks are redshifted with increasing $\eta$ and for $\eta \in (0,2]$, the optical responses of the three-component composites are very sensitive to $\eta$ due to the competition among the eigenmodes. Finally, we report a sum rule in three-component square network between the summation of dielectric resonances and $\eta$: $\sum_{i=1}^{n} s_i = (n/2) \eta + n_i/2$ with the total bond $n = n_1 + n_2$.

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