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Correlation and clustering in the optical properties of composites: A numerical study

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We have numerically investigated the effects of correlation and clustering on the far-infrared (FIR) absorption and surface-plasmon modes of a model two-dimensional metal-insulator composite. We model the composite as a diluted resistor-inductor-capacitor (*RLC*) network. Two-site and nearest-neighbor-site correlations among the conducting bonds are found to enhance the FIR absorption per metallic bond by a factor of 5 relative to a network of the same concentration with a purely random distribution of metallic bonds. Ring-shaped clusters (which model insulating particles with a metallic coating), and percolation clusters are found to produce a FIR absorption enhanced by more than 2 orders of magnitude per metallic bond. The surface-plasmon absorption peak in a percolation cluster is found to be strongly broadened relative to the predictions of the Maxwell Garnett approximation. In the two-site correlation model, the surface-plasmon absorption peak is weakly split, whereas in the nearest-neighbor site-correlation model, it is weakly red shifted. Ring-shaped clusters are found to produce double and triple peaks in the surface-plasmon frequency range. Possible explanations for these novel features are briefly discussed.

I. INTRODUCTION

The optical properties of granular materials have attracted much attention in recent years. Many experimental studies[1-5] of the far-infrared (FIR) absorption by small metallic particles embedded in an insulating matrix have shown unusual results. Earlier studies show that the magnitude of the FIR absorption is a few orders of magnitude larger than the predictions of classical electromagnetic theory, even though the classical theory gives correctly the frequency, size, and concentration dependence of the absorption. This discrepancy remains even when magnetic dipole absorption is taken into account.[6] Many theoretical explanations for this discrepancy[7-23] have been proposed. Among these are a broad distribution of particle sizes, absorption due to resistive coating on particles, quantum size effects, clustering of small metal particles into clumps, and the formation of percolation clusters and fractal clusters of various geometries.

In this article, we study numerically the effects of correlation and clustering on the optical properties of two-dimensional metal-insulator (M/I) composites. The composite is modeled as a resistor-inductor-capacitor (*RLC*) network, such as has been used previously[24] to describe random metal-insulator composites. The ac response of this network is calculated using a very fast numerical algorithm proposed by Lobb and Frank,[25] based on the Y-Δ transformation familiar to electrical engineers. Various models with short-range order are then studied numerically and are shown to give widely varying responses both in the far-infrared and in the optical frequency ranges.

We turn now to the body of the paper. The model and the numerical algorithm are described in Sec. II, and numerical results are given in Sec. III. A brief discussion follows in Sec. IV.

II. MODEL

We study a thin-film composite of Drude metal and insulator, modeled as a two-dimensional random lattice of resistors, inductors, and capacitors. Several studies of this nature have already been carried out,[24,26-30] but for purely random lattices. Each bond in the network is either an insulating bond or a metallic bond. The former is represented by a capacitor with admittance

$$\sigma_I = i\omega C' . \tag{1}$$

A metallic bond is represented by a series of resistor and inductor in parallel with a capacitor, and has admittance

$$\sigma_M = \frac{1+i\omega RC-\omega^2 LC}{R+i\omega L} . \tag{2}$$

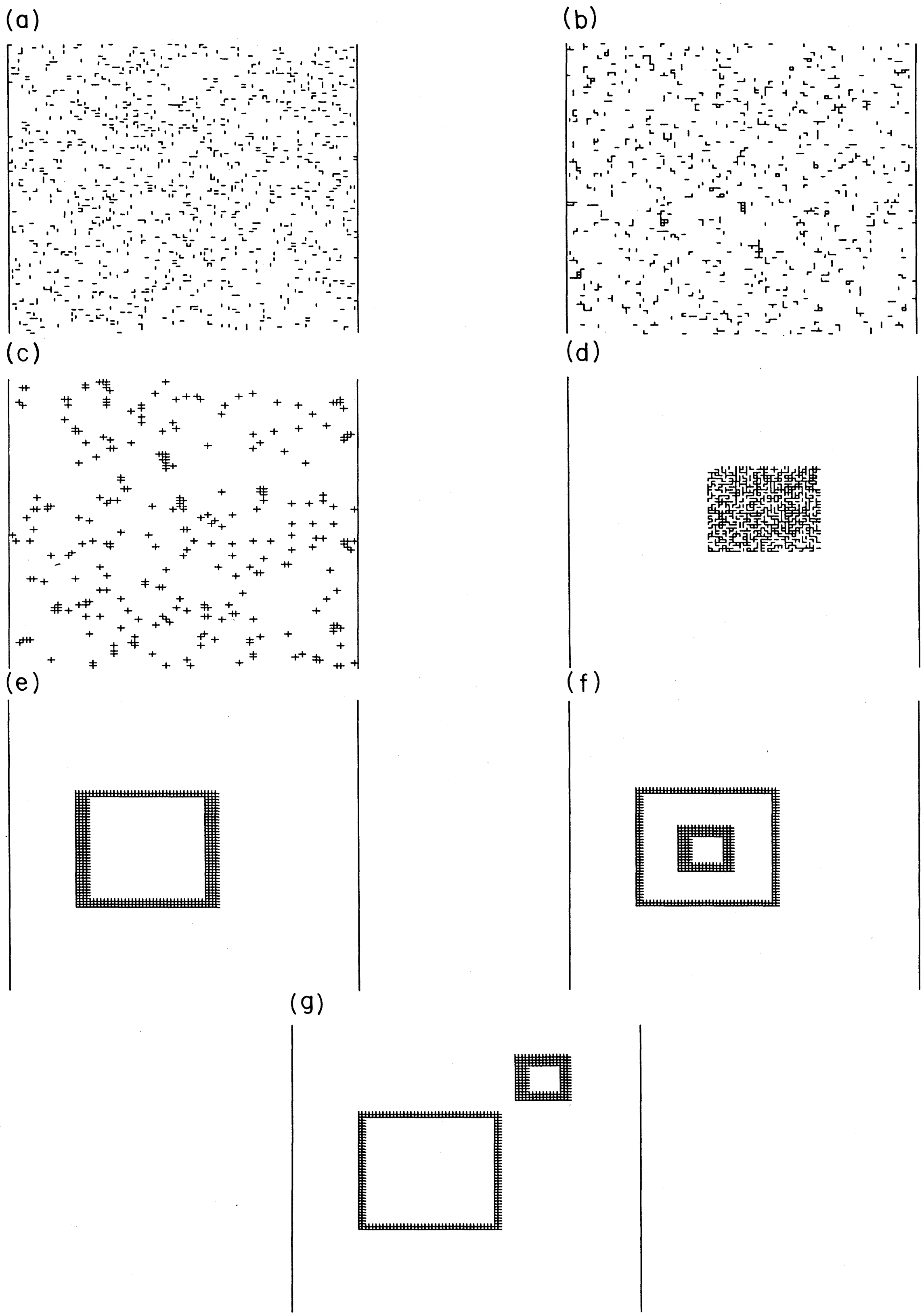

FIG. 1. Typical distribution of metallic bonds for the various models discussed in the text: (a) randomly distributed bonds, (b) two-site correlation model, (c) NNS correlation model, (d) percolation cluster, (e) single ring-shaped cluster, (f) sandwich of two ring-shaped clusters, and (g) double ring-shaped cluster. In all cases, the nominal fraction of metallic bonds is 0.05. The two vertical lines represent the superconducting bars to which the external voltage is applied.

Here R, L, and C are the resistance, inductance, and capacitance of the conducting element, and C' is the capacitance of the insulating element. For simplicity, we set $C = C'$, and introduce the plasma frequency $\omega_p = (LC)^{-1/2}$ and the relaxation time $\tau = L/R$. The ratio σ_M/σ_I then takes the form

$$\sigma_M/\sigma_I = 1 - \frac{\omega_p^2}{\omega(\omega - i/\tau)} , \tag{3}$$

which is identical to the ratio of dielectric functions of a Drude metal and insulator with dielectric function $\epsilon_I = 1$. For convenience, we hereafter use units such that $\omega_p = 1$.

To determine the ac response of an RLC network, we use the propagation algorithm developed by Frank and Lobb,[25] based on the Y-Δ transformation, to calculate the effective admittance σ_e of the entire network. This method has been used previously to study the surface plasmon modes in random metal-insulator composites below and above the metal percolation threshold p_c,[24] and to investigate ac transport properties in a model for continuum percolation.[30] A detailed description of this model can be found in Refs. 24 and 30.

The new feature of the present calculation is the inclusion of clustering. The characteristic feature of clustering is the existence of nonrandom short-range order among the metallic bonds. We have carried out two types of calculations. The first involves the effects of a very local short-range order, which gives rise primarily to small clusters consisting of only a few metallic bonds. The second kind leads to large clusters of metallic bonds, including ringlike clusters and percolation clusters.[15]

To treat short-range correlations, we introduce two models, to be labeled the two-site model and the nearest-neighbor-site (NNS) model, which modify the random method of bond assignment. In a purely bond-random RLC network, one would assign a random number between zero and one (say n_i) to each bond in the network. If n_i is smaller than some metallic bond fraction, say p_1 $(0 < p_1 < 1)$, one would label the ith bond as metallic; otherwise, it would be insulating. In the two-site model, the character of a particular bond is determined by the values of random numbers assigned to the two sites (the "site numbers") connected by the bond. If the *sum* of the two-site numbers exceeds a certain number $2p_1$ $(0 < p_1 < 1)$, the bond between these two sites is chosen to be conducting; otherwise, the bond is insulating. In the NNS correlation model, one initially sets all the bonds in the lattice to be insulating. Each site is then assigned a random number n_i (the site number) between zero and one. One then scans sequentially through all the sites in the lattice. For each site scanned, if the site number of a center site is larger than a certain number p_2 $(0 < p_2 < 1)$ *and* the sum of nearest-neighbor-site numbers is larger than $4p_2$, then all four bonds attached to the center site are chosen to be conducting.

Figures 1(a)–1(c) show lattices with typical metallic bond distributions produced by a purely random algorithm, the two-site model, and the NNS model. The latter two do, indeed, produce correlations between neighboring metallic bonds, but the bond morphologies are quite different in the two cases.

We have also calculated the ac response of several metal-insulator composites with percolation or ring-shaped clusters [see Figs. 1(d)–1(g)]. A number of theoretical studies[8,15,21,23] suggest that such clusters will tend to enhance the FIR absorption considerably, relative to purely random configurations. Other studies[17,19–23] have predicted double absorption peaks or red-shifted surface-plasmon peaks in the optical frequency range. All these studies are based on various analytical models. In order to confirm these predictions, we have carried out numerical simulations in RLC networks on which such clusters are generated.

III. RESULTS

We carry out our simulations on 100×100 RLC networks. For all our calculations, we have used approximately the same concentration $\approx 5\%$ metallic bonds. The characteristic relaxation time τ is chosen as $\tau = 10/\omega_p$. For all those configurations generated by random numbers, we average over five to ten realizations to obtain an effective conductance. Previous experience[24] indicates that such averages are sufficient to eliminate most of the fluctuation structure produced by small samples.

Figure 2 shows the real part of the effective conductance per metallic bond, $\text{Re}(\sigma_e)$/bond, plotted as a function of frequency in the FIR region. As can be seen, short-range correlations (both in the two-site and the NNS correlation models) enhance FIR absorption by about a factor of 5 relative to that of a purely random network. This enhancement is even more striking in the larger clusters. For example, ring-shaped clusters, which

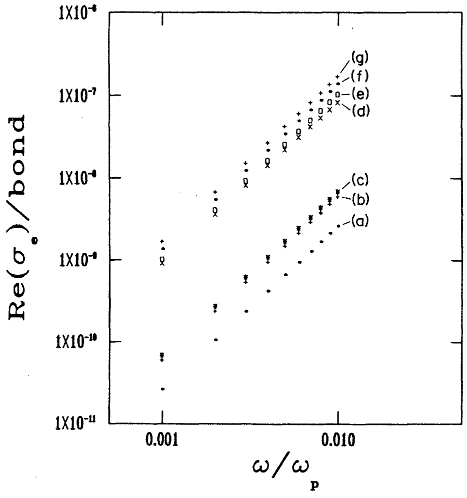

FIG. 2. Real part of the effective conductance per metallic bond, $\text{Re}(\sigma_e)$/bond, plotted as a function of frequency. The frequency range shown, $0.001\omega_p < \omega < 0.01\omega_p$, is typically within the far infrared in a free-electron metal. Calculations are carried out on 100×100 networks. For those configurations generated by random number, the plots represent averages over five realizations. The legends (a)–(g) correspond to the morphologies of Fig. 1.

represent metal-coated insulating particles, and percolation clusters each produce an enhancement of about 2 or-orders of magnitude relative to that of a random network of the same concentration. These results are consistent with some previous theoretical calculations[8,15,17] based on effective-medium and renormalization-group analyses. Note that in all the FIR calculations the absorption is found to have a nearly ω^2 frequency dependence, independent of short-range order. This dependence is consistent with experiments.[1–5]

Figures 3(a)–3(g) show Re(σ_e)/bond for frequencies near ω_p. The absorption bands in these figures are the network analogs of the surface-plasmon resonances seen in bulk metal-insulator composites; the figures show how these bands are affected by short-range order and clustering. The purely random composite [Fig. 3(a)] has a surface-plasmon band with a single peak, as predicted by the Maxwell Garnett approximation. For samples with two-site correlations [Fig. 3(b)], the surface-plasmon band is split, and for those with NNS correlations [Fig. 3(c)], it is weakly red shifted but not split. The percolation cluster [Fig. 3(d)] exhibits a surface-plasmon peak which is strongly broadened, relative to the purely random configuration [Fig. 3(a)]. Perhaps the most intriguing results are those shown in Figs. 3(e)–3(g). The single ring-shaped cluster shows a conspicuous double peak [Fig. 3(e)], while for the "sandwich" cluster a triple peak is obtained [Fig. 3(f)]. The double ring-shaped cluster shows a double-peaked structure [Fig. 3(g)], in which one of the two peaks is itself weakly split in two.

IV. DISCUSSION

Many of our numerical results can be understood, at least roughly, by simple qualitative arguments. For example, the FIR absorption is enhanced by clustering because clustering produces regions in the composite where the metal concentration is locally much greater than average. It is well known, both theoretically and experimentally,[31] that the FIR absorption coefficient $\alpha(\omega)$ of a

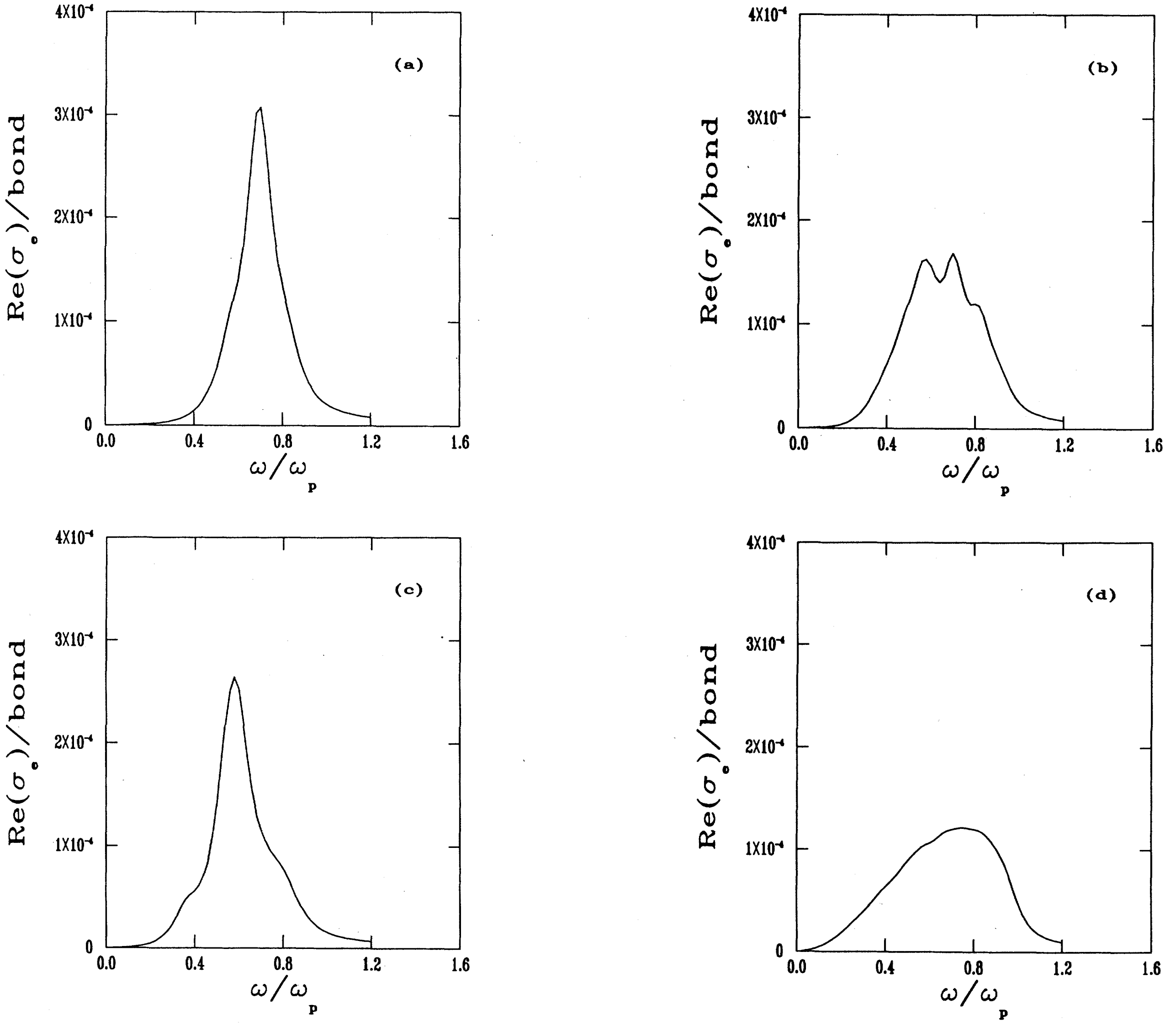

FIG. 3. Same as Fig. 2, but for a frequency range corresponding to the optical region in a typical metal. For those configurations generated by random number, the plots represent averages over ten realizations.

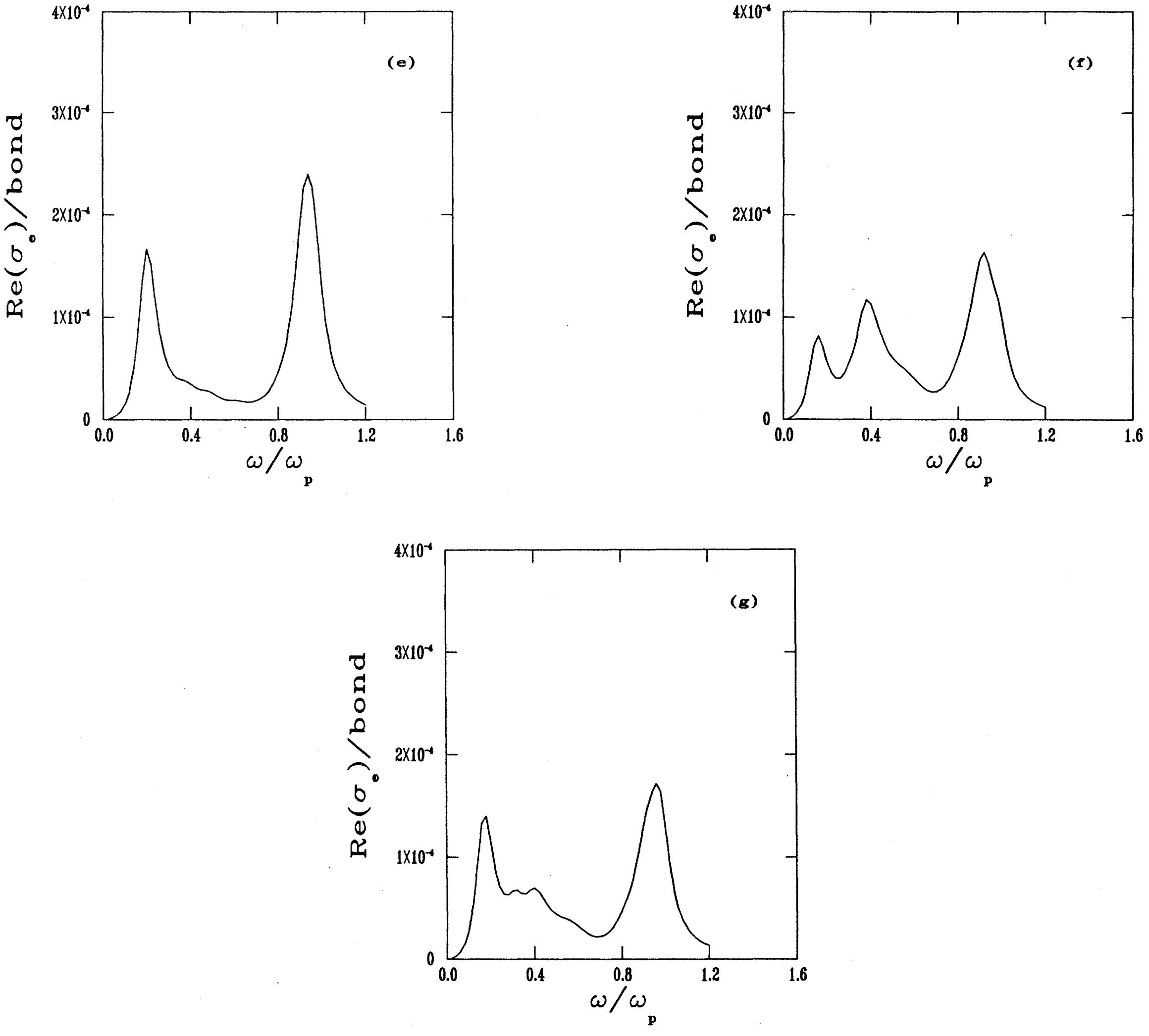

FIG. 3. (*Continued*).

metal-insulator composite varies as $\alpha(\omega) \approx A(p)\omega^2$, where the coefficient $A(p)$ tends to diverge as the metal volume fraction p approaches the percolation threshold p_c from below. As this concentration is approached, of course, larger and larger clusters are formed. When short-range order or other clustering mechanisms are introduced, such large clusters can form even at low metal concentrations. Hence, the strongly enhanced FIR absorption expected near the percolation threshold can occur at much smaller metal volume fractions.

Likewise, the structure seen in the surface-plasmon frequency range can be simply understood. The two-site correlations depicted in Fig. 1(b), for instance, lead to a number of small, chain-shaped clusters. These can be thought of as the discrete versions of ellipses. Such ellipses are characterized by two different depolarization factors and have, therefore, two distinct surface-plasmon resonances.[32,33] One thus expects the composite of Fig. 1(b) to have a split surface-plasmon peak, as observed. The two peaks correspond to the two different orientations of the chain-shaped clusters. In the NNS configuration [Fig. 1(c)], many metallic clusters are symmetric crosses. The absorption peak in this instance is weakly red shifted relative to the purely random case [Fig. 1(a)]. The red shift may perhaps be understood from a model proposed by Liebsch and González (LG).[11] LG model a cermet composite as a diluted cubic lattice of metal spheres in an insulating host. Using the coherent-potential approximation, they find that, as the average spacing between particles is reduced (at fixed metal concentration), the disorder-induced red shift of the surface-plasmon peak is increased. By analogy, the symmetric crosses of Fig. 1(c) might be viewed as spherical clumps of particles with relatively small interparticle spacing for the given concentration. Then, by analogy with the results of LG, one might expect that the surface-plasmon peak would be red shifted relative to that of the purely random distribution of Fig. 1(a).

For percolating clusters, several effective-medium calculations have been carried out.[15,17] Hui and Stroud[17] have shown that for such a cluster, the surface-plasmon absorption peak will be strongly broadened, in qualitative agreement with our numerical simulation.

At least two explanations seem plausible for the multiple absorption peaks seen in the case of the ring-shaped clusters [Figs. 1(e)–1(g)]. In the case of the simple ring-shaped clusters [Fig. 1(e)], one possible explanation is that the double absorption peak is due to the two orientations of the ring frame. The parts of the frame parallel to the external field produce the lower peak, while those perpendicular to the field generate the upper peak. We have attempted to check this analysis by moving one of the ring arms far from the remaining three, leaving a *U*-shaped metal particle and a needle; the resulting absorption spectrum is still very similar to that of Fig. 3(e). This picture suggests no simple explanation for the structures seen in Figs. 3(f) and 3(g). Another possibility is suggested by considering the standard electrostatic problem of a sphere with multiple alternating coatings, placed in a uniform external field. If the innermost sphere has the same dielectric constant as the (insulating) host medium, and if it is coated by alternate layers of Drude metal and insulator (all of equal thickness), so that there are an odd number (say, $2n+1$) of coating layers in all, then it can be shown that the composite particle exhibits exactly $2n+2$ surface-plasmon resonances. If we view the two-dimensional particles of Figs. 1(e) and 1(f) as having one and three layers, respectively, then this analysis would predict a Drude peak split into two and four subpeaks. The two peaks are indeed clearly visible. The geometry of Fig. 1(f) exhibits only three, but perhaps two of the four have coalesced into a single peak, given the rather substantial damping included in our calculation.

Note that all the results described in this paper are obtained in the so-called quasistatic approximation, in which it is assumed that $\nabla\times\vec{E}=0$, $\vec{E}$ being the electric field. In some granular metals, it is well known[6] that magnetic dipole absorption, which is absent in the quasistatic approximation, can greatly enhance far-infrared absorption. This absorption would have to be added to the clustering effects considered here, to obtain a complete theory in the far infrared. It should also be emphasized that the present calculations are two dimensional in a literal sense, and thus may not strictly apply to realistic thin granular films. In the experimental case, electric field lines may not be confined to the plane, and thus some account should probably be taken of the "three-dimensional" character of these films.

In summary, we have presented an efficient method for analyzing the effects of short-range order on the ac properties of composite media and described some initial results which show that clustering is of great importance, both in the far-infrared and in the optical frequency ranges. Although our method is applicable thus far only in two dimensions, the Y-Δ transformation can be extended to three dimensions also. Thus, the present method is a very promising tool for analyzing the ac response of a variety of granular materials.[34]

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