Effects of clustering in binary composites: Random fractals

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The effects of random-fractal clustering on the electromagnetic properties of two-dimensional binary composites at low frequencies are studied within a random-admittance-network model consisting of metallic and insulating bonds. The diffusion-limited cluster-cluster aggregation model is used for fractal-cluster formation. The effective admittance of the random network is calculated using the Y-Δ transformation algorithm. The real part of the effective admittance per metallic bond, which is proportional to the absorption coefficient of a dilute composite, is calculated at different states of the aggregation process. As particles join together to form clusters and clusters join together to form larger ones, the absorption coefficient gradually increases and reaches its highest value when all the particles aggregate into a single cluster. Results are compared to those obtained within a differential effective-medium approximation.

I. INTRODUCTION

The enhancement of far-infrared absorption in composites consisting of a dilute concentration of small metallic particles embedded in an insulating host has been a subject of intensive experimental and theoretical interest.[1,2] Such an enhancement over classical predictions was first observed by Tanner, Sievers, and Buhrman.[3] Since then, much experimental and theoretical effort[4–22] has been aimed at sorting out the origin of such enhancement. Among the theoretical suggestions are magnetic dipole absorption, oxide coatings on the small particles, clustering of small particles, quantum size effects, and localization effect. Certainly each of the suggested reasons may contribute to the enhancement. The dominant mechanism, however, may vary from sample to sample as it should strongly depend on the sample preparation process and the microgeometry within the sample.

A variety of experimental evidence suggests that clumping is a major factor in far-infrared enhancement.[6,15] Curtin and Ashcroft[16] have developed a cluster-percolation model to account for these experiments. In order to make the consideration of clustering effects more explicit, Hui and Stroud[2,18] studied a model for treating electromagnetic absorption due to *fractal clusters* using a differential effective-medium approximation. In particular, these authors showed that such fractal clusters lead to enhancements in both the electric and magnetic dipole absorption with enhancement factors depending on the cluster size and fractal dimension.

Numerical simulations have been a useful way to study problems in composites.[23–27] Zeng, Hui, and Stroud[28] studied the effects of clustering numerically by assuming that the particles in a mixture join together in some ordered way. Recently, Hoffman and Stroud[29] studied some deterministic fractals numerically and found that the enhancement factors are in reasonable agreement with that predicted in Ref. 18. In the present work, we extend the previous studies to the case of *random-fractal* clustering. A model describing realistic fractal formation is the diffusion-limited cluster-cluster aggregation.[30] By modeling the particles in the aggregate as metallic particles, the effective response of such an aggregate embedded in an insulating host can be studied within a random-resistor network model. The effective response of the random network is studied using the "Y-Δ transformations" method described by Lobb and Frank.[31] We demonstrate that as the aggregation proceeds, the absorption of the system gradually increases and reaches its maximum value when all the particles join together to form a single cluster.

The plan of the paper is as follows. Section II describes the model of cluster formation that we use in this work. Section III gives results of our numerical simulation on the real part of the effective admittance, which is related to the absorption coefficient in a composite. Results are summarized in Sec. IV.

II. MODEL

The random-fractal model that we use in this work is the diffusion-limited cluster-cluster aggregation model (DLCA).[30,32,33] The model is related to the fractal geometry seen in clusters found in small gold-particle colloids.[34] It gives a convenient way to obtain more realistic fractals. The lattice version of the model starts with a certain fraction of randomly occupied sites in a lattice. The particles carry out random walks on lattice sites. When two particles occupy neighboring sites, they form a cluster. A cluster of particles moves together during random walks. Clusters of smaller sizes join together to form large clusters as they become neighbors. The process is schematically shown in Fig. 1. As the aggregation

process proceeds, the number of clusters decreases and eventually only one big cluster consisting of all the particles remains. It was found that the resultant cluster is a fractal when the concentration of particles is low.[30] Its shape is similar to those clusters found in gold-particle aggregates in colloids. In three dimensions (3D), the fractal dimension d_f was found to be 1.75, and in 2D, $d_f = 1.45$.

Our aim is to calculate the response of the system to an external applied voltage during the aggregation process so as to study the effects of clustering on absorption in dilute binary composites. We carried out numerical simulations of the DLCA on a 2D 150×150 square lattice. Figure 2 shows typical stages of the process. The number of occupied sites is 1479, which corresponds to a site concentration of 6.6%. Figure 2(a) shows the initial situation in which the sites are randomly occupied. The number of clusters for the case shown is 987. Figures 2(b) and 2(c) show two intermediate stages during aggregation.

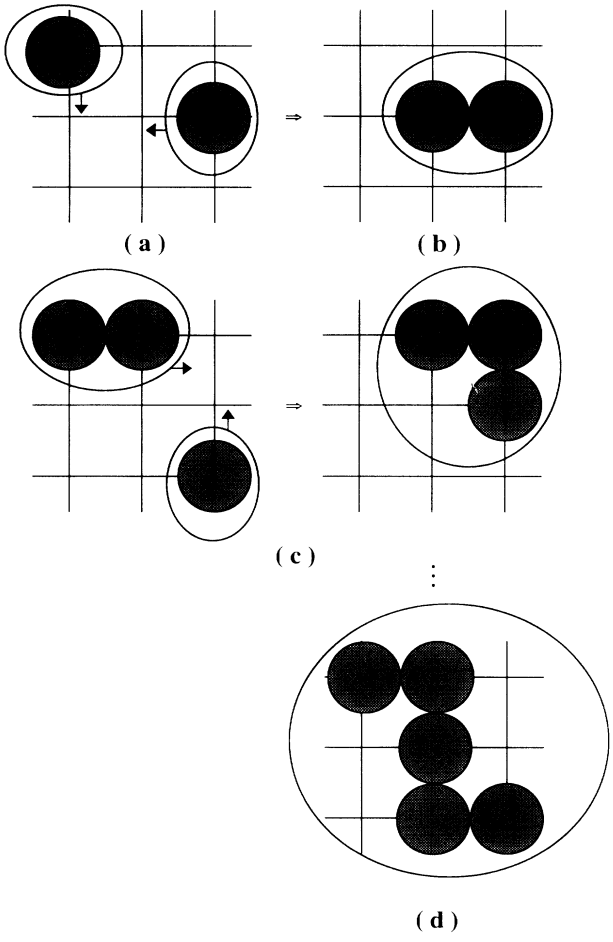

FIG. 1. A schematic sketch of the diffusion-limited cluster-cluster aggregation model. Particles are randomly placed on the sites of a lattice and they execute random walks. When particles become nearest neighbors, they form a cluster [(a) and (b)]. A cluster moves as a whole during random walks. Clusters of different sizes join together to form a larger cluster when they become nearest neighbors (c). Eventually, all the particles aggregate to form a single cluster (d).

The resultant cluster [Fig. 2(d)] gives a typical shape of the DLCA. It has a fractal dimension of 1.43 ± 0.02. Different runs give resultant clusters with different details in their shape, yet with the same characteristic feature of a loosely connected object. It is in this sense that the DLCA gives statistical fractals in contrast to those deterministic fractals obtained by iterating a certain growth rule.

To study the ac response of the aggregates, we invoke a model previously applied to study finite-frequency response in random mixtures.[28,35] A 2D random-admittance network made up of conducting and insulating bonds can be set up as follows. The aggregate obtained above is placed in a 151×151 square lattice so as to ensure that there is no connected path formed by the particles from one side of the network to another. This is the usual situation in a *dilute* composite in which the concentration of metallic particles is too low to form a path through the system. To generate the admittance network, we put a *metallic* bond between any two neighboring sites which are a part of the aggregate. All other bonds are represented by insulating bonds. The lattice is subjected to a voltage difference of $\mathrm{Re}[Ve^{i\omega t}]$ between two conducting bars on both sides of the lattice. The metallic bonds are chosen to be a capacitor C in parallel with a series of a resistor R and inductor L; the admittance is thus given by

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

The insulating bonds are chosen to be a capacitor C', thus with admittance

$$\sigma_I = i\omega C' . \tag{2}$$

This particular choice gives the ratio, after setting $C = C'$,

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

with $\omega_p = (LC)^{-1/2}$ and $\tau = L/R$. Equation (3) is of the Drude form of a dielectric function and hence has the same form as the ratio of the dielectric constants of a metallic particle-insulator composite.

The quantity of interest is the effective complex admittance of the random-admittance network. Such a calculation can be carried out most efficiently using a propagation algorithm described by Lobb and Frank.[31] The method is based on the "Y-Δ transformations" familiar to electrical engineers. A detailed description of the random-admittance model and the "Y-Δ" algorithm can be found in Refs. 27 and 31.

III. RESULTS

The physical quantity that we are interested in is the real part of the complex effective admittance $\mathrm{Re}(\sigma_{\mathrm{eff}})$. For a dilute mixture (about 3.5% of *metallic* bonds in our case) one can use the Maxwell-Garnett (MG) formula, which is valid for low concentrations, to obtain at low frequencies.

$$\mathrm{Re}(\sigma_{\mathrm{eff}}) = A_{\mathrm{MG}} p \omega^2 , \tag{4}$$

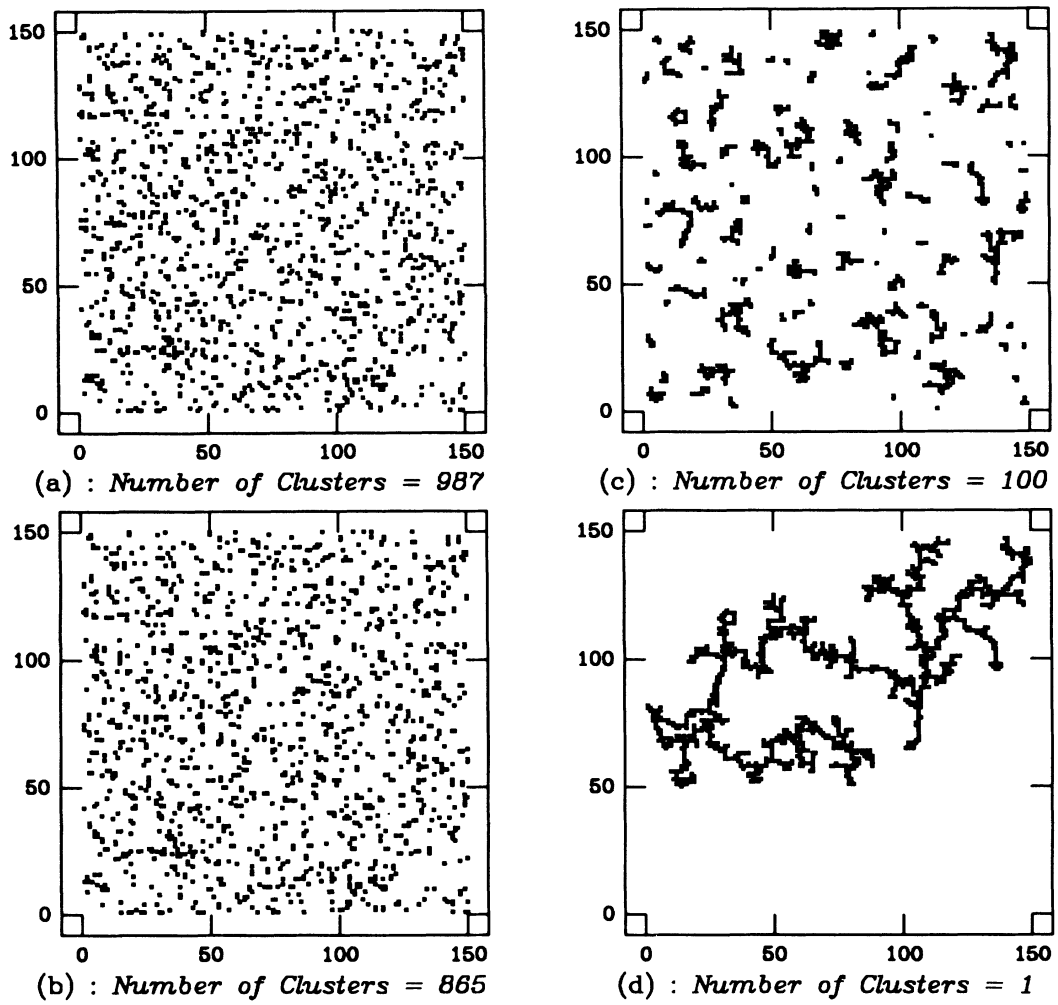

FIG. 2. Four different stages of the diffusion-limited cluster-cluster aggregation model: (a) The initial configuration consists of 1479 particles placed randomly on a 150×150 square lattice forming 987 clusters; (b) an intermediate configuration in the early stage of the aggregation process with 865 clusters; (c) an intermediate configuration at a later stage with only 100 clusters left in the system; and (d) the final configuration with one cluster containing all 1479 particles.

where p is the fraction of metallic bonds and A is a constant ($A=4RC^2$). The right-hand side of Eq. (4) has the same form as the absorption coefficient of a dilute composite[2] in which the ratio of the dielectric constants of the constituents has the form of Eq. (3). As discussed in the Introduction, it was found that the experimentally observed A_{expt} is much greater than A_{MG}. To study the effects of clustering on the absorption at low frequencies, it is thus sufficient to compare the real parts of the effective admittance per metallic bond $\text{Re}(\sigma_{\text{eff}})$/bond for the cases without and with clustering.

Figure 3 shows $\text{Re}(\sigma_{\text{eff}})$/bond as a function of frequency on a log-log plot. The set of parameters used[28,29] in our simulations is $C=C'=L=1$, $R=0.1$, so that $\omega_p\tau=10$. The four curves correspond to the four different stages during aggregation shown in Fig. 2. All the four curves have the expected ω^2 frequency dependence at low frequencies. Curve (a) corresponds to the initial random configurations and has the lowest value of $\text{Re}(\sigma_{\text{eff}})$/bond. As the particles gradually join together to form clusters [curves (b) and (c)], $\text{Re}(\sigma_{\text{eff}})$/bond increases and has its maximum value when all the particles form a single cluster. Comparing curves (d) and (a) results in an enhancement factor of about 530 at low frequencies for the case shown. Thus our numerical results indeed show that there is an enhancement in the low-frequency absorption in a dilute composite due to clustering. Similar results have recently been obtained in clusters formed by the method of diffusion-limited aggregation.[36]

Based on an effective-medium approximation (EMA), Hui and Stroud[18] suggested that the absorption will be enhanced by a factor given by $(R/a)^{3(2-d_f)}$ for fractal clusters. Here R is the "radius" of the cluster, which is basically a length describing the size of the cluster, a is the size of a particle and in our case corresponds to the lattice constant, and d_f is the fractal dimension. We repeated our numerical simulations with different initial

configurations of the particles. The resultant clusters have different geometrical details. As the aggregation proceeds, $\mathrm{Re}(\sigma_{\mathrm{eff}})$/bond gradually increases similar to the case shown in Fig. 3. Using the fractal dimension $d_f \sim 1.45$ for the clusters studied, and an averaged size of the cluster $R \sim 43a$, the effective-medium approximation gives an enhancement factor of about 500. This value compares reasonably well with the result of the case shown in Fig. 3. However, different geometry of the resultant cluster gives different enhancement factors. Typical results are shown in Fig. 4, in which the enhancement factor calculated at a fixed frequency of $\omega = 0.001\omega_p$ is plotted as a function of the average size of the cluster for four different realizations of the growth process. As the lattice is limited to 150×150, different realizations give slightly different fractal dimensions. As a guide, we included the EMA prediction in Fig. 4 using the value of $d_f = 1.45$. For nine different runs, we obtained an averaged enhancement factor of about 200 at $R \sim 43a$. Given that the absorption should be quite sensitive to the structural details of the cluster and that the fractal dimension alone does not describe completely the details of the structure, the effective-medium approximation gives a reasonable estimate of the enhancement factor.

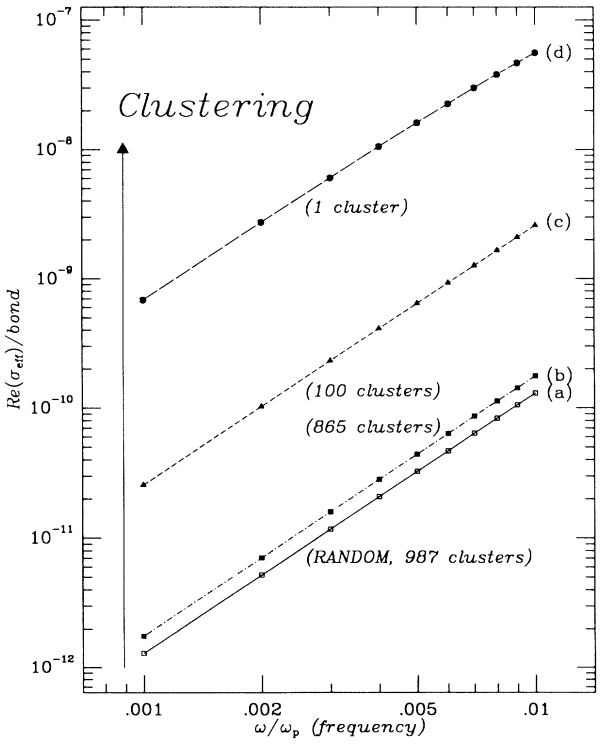

FIG. 3. The real part of effective admittance per metallic bond, $\mathrm{Re}(\sigma_{\mathrm{eff}})$/bond, as a function of frequency at low frequencies. Curves (a), (b), (c), and (d) correspond to the different stages of the aggregation process given in Fig. 2. All the curves exhibit a ω^2 frequency dependence. As particles gradually aggregate to form larger clusters, $\mathrm{Re}(\sigma_{\mathrm{eff}})$/bond increases and reaches its maximum value when there is only one cluster left in the system.

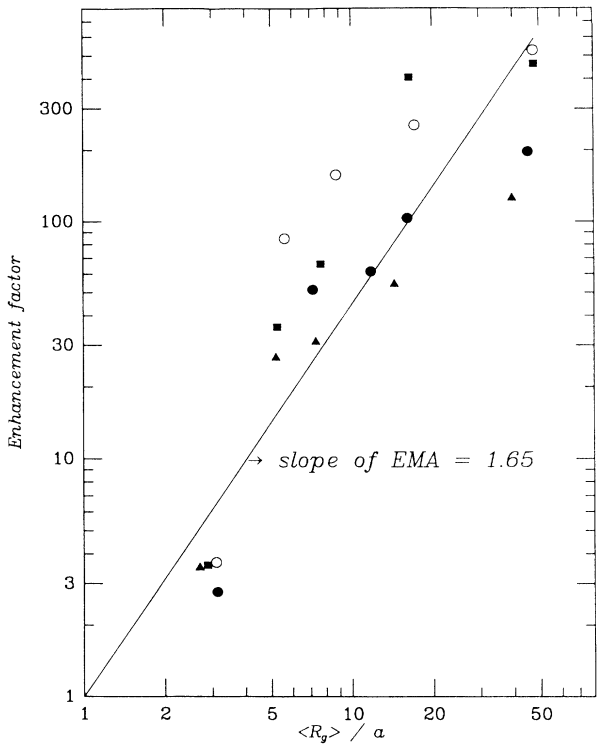

FIG. 4. The enhancement factor as a function of the average size of clusters on a log-log scale. Data are those at $\omega = 0.001\omega_p$. Different symbols correspond to four different realizations of the growth processes. As a guide, the EMA prediction is included using a value of $d_f = 1.45$.

IV. DISCUSSION

We have shown, by numerical simulations, that clustering leads to an enhancement in the absorption coefficient for a dilute composite at low frequencies. We have used the diffusion-limited cluster-cluster aggregation model as a model of fractal-cluster formation. In actual dilute composites, there are clusters of different sizes embedded in the host material and thus the configuration may be quite different from that of the DLCA, in which the final cluster is a single cluster with all the particles. However, the intermediate stages in a DLCA process may be quite similar to the situation of a dilute composite in that there are clusters of various sizes and shapes randomly embedded in the host medium. Figure 2(c) gives a typical configuration in which about 1500 particles are joined together randomly to form 100 clusters of various sizes. Our numerical results show that even in this intermediate stage, there is a substantial enhancement in the absorption.

Most studies in the subject of diffusion-limited aggregation models have been concentrated on the geometrical aspects of the growth process. Studies on the physical properties of such aggregates, however, are of great importance in order to understand the physics of the materials in which such aggregation processes readily occur. The present work thus represents an attempt to understand the low-frequency response of such systems. Our

work can readily be generalized to study other physical properties such as elastic properties of aggregates.

We conclude with a discussion on a few possible extensions of the present work. It was predicted that fractal clustering may lead to interesting effects in a superconductor–normal-metal composite.[18] In particular, the ratio of the absorption coefficient in the case in which the superconducting component is in its superconducting state to that of the case in the normal state is highly sensitive to the size and fractal dimension of the cluster. The present calculation can be readily generalized to the superconductor–normal-metal case by assuming the superconducting component has a finite-frequency conductivity of the Mattis-Bardeen form. Another possible extension is the inclusion of other suggested mechanisms, such as oxide coating of metallic particles, for the enhancement into our present framework. This can be done by modifying the form of the admittance of the metallic bond in our calculations. A more difficult extension is to study the effects of clustering in composites in which one of the components is a nonlinear material. In this case, the Y-Δ transformation does not apply in general and one may need to solve Kirchhoff's law at each node of the lattice.

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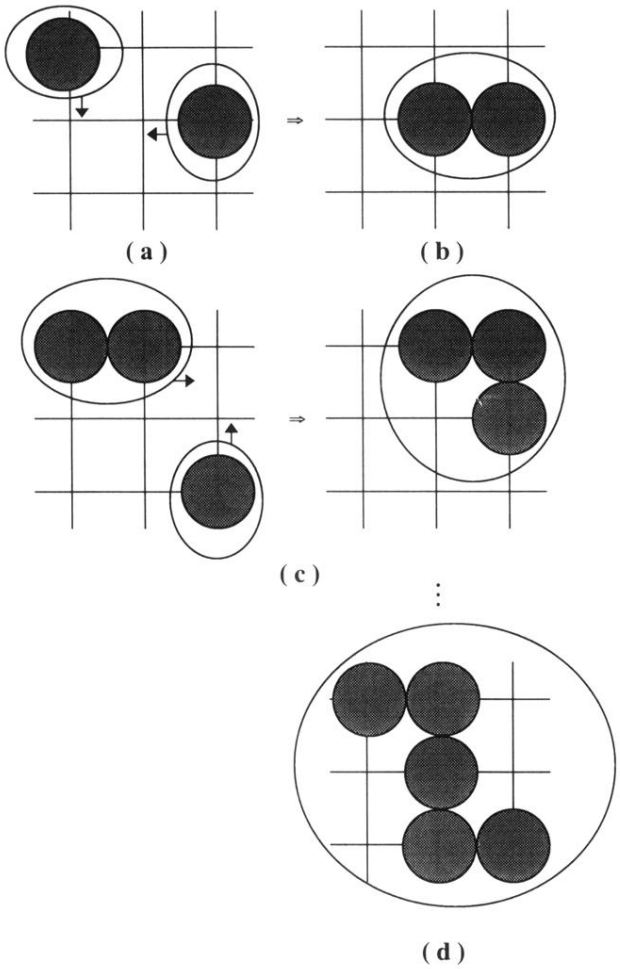

FIG. 1. A schematic sketch of the diffusion-limited cluster-cluster aggregation model. Particles are randomly placed on the sites of a lattice and they execute random walks. When particles become nearest neighbors, they form a cluster [(a) and (b)]. A cluster moves as a whole during random walks. Clusters of different sizes join together to form a larger cluster when they become nearest neighbors (c). Eventually, all the particles aggregate to form a single cluster (d).