Scaling behavior and surface-plasmon resonances in a model three-dimensional metal-insulator composite

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We calculate the ac dielectric function of a model Drude metal-insulator composite, using a threedimensional ($d=3$) transfer-matrix algorithm. The real part of the effective conductivity, $\hat{\sigma}(\omega)$, reveals (i) a Drude peak that appears only above the percolation threshold $p_c$; and (ii) a broad spectrum of surface-plasmon resonances whose lower edge approaches zero frequency at $p_c$. Sufficiently near $p_c$, the dielectric function is consistent with an expected scaling form previously verified in $d=2$. The surface-plasmon spectrum resembles effective-medium predictions except for a weak but persistent peak near $0.4\omega_c/\omega_p$.

I. INTRODUCTION

The electrical and optical properties of composite materials differ greatly from those of ordinary bulk materials. These differences are particularly marked near the percolation threshold $p_c$ in composites of metal and insulator, defined as the volume fraction where the metallic component first forms an infinite connected path. For example, the static effective conductivity $\sigma_e$ is believed to obey

$$\sigma_e \propto \sigma_n (p - p_c)^{s^t} \quad (1)$$

where $\sigma_n$ and $p_c$ are the static conductivity and volume fraction of the normal metal. Below $p_c$, the effective static dielectric constant $\varepsilon_e$ is thought to diverge as

$$\varepsilon_e \propto \varepsilon_n (p_c - p)^{-\gamma} \quad (2)$$

(An analogous expression governs $\sigma_e$ in a normal metal/perfect conductor composite.) $s$ and $t$ depend on dimensionality and possibly also on the composite microstructure. For lattice models, $t \approx 1.3$ in two dimensions ($d=2$) (Refs. 7 and 8) and $t \approx 2.0$ in $d=3$, while $s \approx 1.3$ in $d=2$ (Ref. 7) and $s \approx 0.76$ in $d=3$.3

The similarity between the percolation and conventional phase transitions suggests that scaling theory can be extended to percolation problems. Such a treatment has been extensively developed.1,3,5,9–11

II. FINITE-SIZE SCALING OF DIELECTRIC FUNCTION

We derive the relevant finite-size scaling form, by analogy with conventional dynamic scaling.5 In this picture, a wave-vector- and frequency-dependent susceptibility $\chi(k,\omega)$ near the critical point has the form

$$\chi(k,\omega) = \xi^{\gamma \tau} Y(\omega^\tau, k \xi) \quad (3)$$

where $\gamma$ describes the divergence of the static susceptibility, $\xi$ is the correlation length, which diverges near the critical point according to the law $\xi \propto |\tau|^{-\gamma}$, $\tau = (T - T_c)/T_c$, and $Y$ is a universal function which may have different forms above and below $T_c$.

We now translate (3) into the language of percolation theory. First, the analog of the quantity $\tau$ is $\Delta \equiv (p - p_c)/p_c$. Secondly, for a finite system of linear dimension $L$, the wave vector $k$ is replaced by $L^{-1}$. Finally, in a metal-insulator composite at sufficiently low frequencies, the complex dielectric functions of the metallic and insulating components can be expressed (in Gaussian units) as $\varepsilon_e = \varepsilon_m + 4\pi i \sigma_m/\omega$, $\varepsilon_i = \varepsilon_i(0)$ where $\sigma_m$ is the static conductivity of the metal, $\varepsilon_m$ and $\varepsilon_i$ are the (real) static dielectric constants of the metal and insulator, and $\omega$ is the frequency. Hence, at sufficiently low frequencies $\omega$ is related to $\varepsilon_i/\varepsilon_m$ by

$$\varepsilon_i/\varepsilon_m$$
\[
\epsilon_i/\epsilon_m = C \omega \\
C = \epsilon_{i0}/4\pi i\sigma_m.
\]
Substituting (4) into (3), and identifying \(\chi\) with the normalized effective complex dielectric function of the composite \(\epsilon_e(L,\omega)/\epsilon_i\), we obtain
\[
\epsilon_e(L,\omega)/\epsilon_i = G_\pm Z_\pm[(\epsilon_i/\epsilon_m)^{\gamma}Z_\pm/L],
\]
where \(G_\pm\) are scaling functions which apply above and below \(p_c\). The subscript denotes the percolation correlation length \(\xi_p\).

The exponents \(\gamma\) and \(\nu\) are easily connected to the conventional percolation indices. Since
\[
\xi_p(p) = \xi_0(p_p - p_c)/\xi_p, \tag{7}
\]
Eq. (6) is consistent with Eqs. (1) and (2) only if
\[
\gamma = s, \tag{8}
\]
\[
z = (t + s)/\nu. \tag{9}
\]
With these identifications, Eq. (6) is equivalent to the forms assumed in Refs. 11 and 12.

III. MODELS

To verify (6), and also to calculate the surface-plasmon spectrum of a metal-insulator composite in \(d=3\), we consider a \(d=3\) random network of complex impedances, slightly generalizing a model of Derrida and Vannimenus.\(^\text{12}\) The network is a simple cubic mesh on an \(L \times L \times L\) lattice, with \(L_i \gg L\). The planes \(x=0\) and \(L\) are held at potentials \(V\) and \(V\), with periodic boundary conditions in the \(y\) direction. The bonds are of two types, labeled \(m\), and \(i\), having different complex impedances, with probabilities \(p = 1 - p_c\); the occupations of different bonds are assumed uncorrelated ("bond randomness"). We calculate the complex conductance per layer (a "layer" is an \(L \times L\) square perpendicular to the \(z\) axis) by averaging over \(L\) layers. The effective impedance \(Z_m\) is calculated using the transfer-matrix algorithm.\(^\text{12}\) By using \(L_i \gg L\), we effectively average over a large number of \(L \times L \times L\) cubes, thereby greatly reducing numerical fluctuations.

We use a simple resistor-capacitor model ("Model I") to verify Eq. (6). The impedance of type-\(m\) (conducting) bonds is taken to be real and frequency independent, such that \(Z_m = R\). The type-\(i\) (insulating) bonds have pure imaginary impedance, \(Z_i = 1/(i\omega C)\). We choose units such that \(R = C = 1\). The effective network impedance is calculated at different values of the ratio
\[
Z_m/Z_i = \omega RC \equiv \Omega. \tag{10}
\]
and at different values of \(L\).

We study the surface-plasmon spectrum using impedances in which the insulating bond is a pure capacitor ("Model II").\(^\text{14}\) The metallic bond is represented by an \(RLC\) circuit consisting of an inductor \(L\) and a capacitor \(C'\) in series, the whole arrangement in parallel with a resistance \(R\) which damps the \(LC\) resonance. The whole impedance of the metallic bond is
\[
Z_m = (R + i\omega L)/(1 + i\omega RC' - \omega^2 LC') \tag{11}
\]
To allow comparison with previous two-dimensional calculations,\(^\text{14}\) we assume the same parameters:
\(C' = C = L = 1\) and \(\tau = L/R = 10\).

IV. TEST OF FINITE-SIZE SCALING IN \(d=3\)

Equation (6) can be rewritten using Eqs. (7) (9) and the transformation
\[
G_\pm(x,y) = x^{-1}H_\pm(x,y).
\]

The result is
\[
\epsilon_i/\epsilon_m = (\xi_p/L)^{-(t + s)/\nu} \tag{12}
\]
To test this form, one can calculate \(\epsilon_i/\epsilon_m\) holding the second argument \(y\) fixed, while varying \(x\), i.e., by varying both \(L\) and \(\Delta p\) in such a way that \(|\Delta p|^{-1/\nu}L\) remains constant. Since \(H_+(x,y)\) and \(H_-(x,y)\) are universal functions, plots of \(\epsilon_i/\epsilon_m\) for samples of different dimension \(L\) should collapse onto a single curve, as long as \(y\) is held constant. This collapse should hold in the "scaling regime," where \(\xi_p \gg 1, L > 1\), and \(\xi_p \gg 1\). Here \(\xi_p\) is an effective dimension-dependent length defined by \(\xi_p = (\epsilon_i/\epsilon_m)^{-(t + s)/\nu}\); and lengths are measured in units of the lattice constant.

Precisely at \(p = p_c\), and assuming that \(\xi_p\) becomes infinite at \(p_c,\)(10) Eq. (12) can be manipulated to express \(\epsilon_i\) in terms of a single scaling variable:
\[
(\epsilon_i/\epsilon_m)^{1/(1 + s)}J(L (\epsilon_i/\epsilon_m)^{1/(1 + s)}), \tag{13}
\]
where \(J(u)\) is a complex function of the complex variable \(u = (\epsilon_i/\epsilon_m)^{1/(1 + s)}\).

To verify (6) for \(p > p_c\), we consider four samples: \(\Delta p = 0.02, L = 4; \Delta p = 0.01262, L = 6; \Delta p = 0.02, L = 6;\) and \(\Delta p = 0.01262, L = 8\). Samples 1 and 2 both have \(|\Delta p|^{-1/\nu}L = 7.817\), while samples 3 and 4 have \(|\Delta p|^{-1/\nu}L = 5.211\). We use the same model to verify Eq. (13), varying \(L\) and \(\omega\) so as to hold the ratio \(L (\epsilon_i/\epsilon_m)^{1/(1 + s)}\) fixed at \(p = p_c = 0.2492\). Finally, rather than computing the effective dielectric functions \(\epsilon_i\) of the networks, we calculate the effective admittance \(g_m\) which obey scaling relations analogous to Eqs. (12) and (13), with the replacements \(\epsilon_i \rightarrow g_i\); and \(\epsilon_m \rightarrow g_m,\)(10)

Figure 1 shows the real and imaginary parts of \(|\Delta p|^{-1/\nu}(g_m/\epsilon_m)\) as functions of \(\omega \Delta p\) for this model. At low frequencies, the eight plots collapse reasonably onto four curves (two each for the real and imaginary parts) which depend only on the ratio \(|\Delta p|^{-1/\nu}L\). At larger frequencies, we start to leave the scaling regime in which \(|g_i/g_m| \ll 1\), and this collapse begins to fail. At sufficiently large \(\omega\), the values of \(|\Delta p|^{-1/\nu}(g_m/\epsilon_m)\) are nearly independent of \(L\), depending only on \(\Delta p\) and \(\omega\). This effect, which is unrelated to the scaling hypothesis, can be easily understood. At large \(\omega\), \(|g_i| \gg |g_m|\). Hence, the network admittance is determined mainly by the dielectric bond, i.e., by \(\omega\) and \(\Delta p\), the parameters which control the impedance and concentration of these dielectric
bonds, and does not depend on $g_m$.

The agreement shown in Fig. 1 is quite sensitive to the assumed values of the exponents. For example, the best scaling collapse, for the assumed values of $s$, $v$, and $p_r$, occurs for $t=1.8$, rather than the accepted value of $t=2.0$, or another trial value of $t=1.6$. We show the scaling collapse for $\text{Re}(g_e/g_m)$ in the inset to Fig. 1, using $t=1.8$. Evidently, the improvement is only slight relative to $t=2.0$. The choice $t=2.2$ on the other hand, yields a worse scaling collapse than $t=2.0$. Since the exponent values used in Fig. 1 are thought to be numerically established to within less than 10%, we do not attribute great significance to the slight discrepancy between the best value of $t$ for producing a scaling collapse, and the accepted value of $t$. Rather, we take the fit shown in Fig. 1 as suggestive, but not conclusive, evidence in favor of both our scaling hypothesis and the standard values of the percolation exponents.

The scaling function $J(x)$ is plotted over a range of $x$ in Fig. 2, assuming $L=10$. For $x$ larger than about 5 and $L=10$, the requirement $\xi_0 > 1$ is not satisfied so we cannot plot the asymptotic $J(x)$ in this regime. From the plot, Re$J(x)$ falls off with small $x$, while both Re$J(x)$ and Im$J(x)$ show some inconclusive hints of saturating at large $x$. The inset to Fig. 2 shows Re$J(x)$ and Im$J(x)$ as functions of $L$ for $x=5$. Both increase slightly with $L$ at small $x$. Re$J(x)$ saturates at large $L$ ($L>12$), while the scaling form should become asymptotically exact, while Im$J(x)$ has not yet saturated by $L=15$. The saturation of Re$J(x)$ may be considered a further verification of the scaling relation (13).

V. SURFACE-PLASMON SPECTRUM

Next, we discuss the results of our surface-plasmon calculation, using Model II [Eq. (11)]. Most of our calculations involve samples of dimension $10 \times 10 \times 5000$, with a few as large as $10 \times 10 \times 10000$. The 1000-layer samples gave obvious statistical fluctuations and were not used.

Figure 3 shows $\text{Re}_{\omega}(\omega)$ for a number of metal concentrations. The resulting spectra are qualitatively similar to previous $d=2$ results. For $p < p_c$, significant absorption sets in only at a nonzero frequency threshold [signaled by an edge in $\text{Re}_{\omega}(\omega)$]. Below this frequency there is a gap with little optical absorption (except for a small tail due mostly to the finite $L/R$ relaxation time). The gap approaches zero near $p = p_c$ and is then expected to open up again at larger $p$, as found previously in $d=2$. This reopening of the gap is somewhat masked by the finite relaxation time. Similar behavior is also predicted by the EMA (shown as the full curves) and by earlier scaling theories. The shape of $\text{Re}_{\omega}(\omega)$ agrees well with the EMA over a broad range of frequencies. The most important discrepancies are the difference in $p_c$ ($=1/3$ in the EMA, 0.25 in exact calculations) and the weaker shoulder which occurs near $\omega = 0.4 \omega_p$ in the numerical results but not in the EMA. Presumably this shoulder, whose frequency is independent of concentration, arises...
VI. DISCUSSION

We have carried numerical calculations which are consistent with a postulated finite-size, finite-frequency scaling relation for the complex dielectric function of a metal-insulator composite in $d=3$, assuming currently accepted values of the percolation exponents. Our approach is to use a transfer-matrix algorithm for a $d=3$ sample with bond percolation. The efficiency of our program permits calculations which average over a large number of cubic samples to reduce statistical fluctuations. The scaling collapse cannot yet be considered conclusive, because of the relatively small transverse sample dimensions, and the fact that only two data sets are available for the scaling plots.

We have also numerically calculated the surface-plasmon spectrum of a metal-insulator composite in $d=3$. Our results are consistent with mean-field theory except for a weak shoulder near $\omega = 0.4 \omega_p$. Although the use of networks to simulate real materials certainly idealizes the geometry, it is encouraging that one nevertheless obtains physically reasonable results. This encourages the study of more complex properties of composite media. For example, a recent generalization of the transfer-matrix algorithm\textsuperscript{16} permits calculation of the electric field distribution in that network. Such a generalization allows one to compute the nonlinear properties of that network and to search for enhancement in various nonlinear susceptibilities at finite frequencies. We will present the results of such a study elsewhere.

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