

Dielectric and optical properties close to the percolation threshold

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We have analyzed the dielectric and conductivity properties of a metal-insulator composite, using the Bruggemann approximation. We have concluded that it is possible to predict the existence of an optical threshold at a concentration p^* slightly higher than the percolation threshold p_c . At that concentration, which is defined by the vanishing of the real part of the dielectric constant and which depends on the dimensionality and on the relaxation time τ , the composite optical conductivity (or the optical absorption) is constant up to near-infrared frequencies. This result can be related to the percolation scaling laws of a mixture of resistors, self-inductors, and capacitors. We discuss recent experimental data, which indicate that the transition to a metallic regime occurs at p^* .

An understanding of the disorder-induced dispersion of the metallic or ionic conductivity in disordered materials such as thin films, Cermets, smokes, porous materials, polymers, etc., is one of the most challenging problems in the field of inhomogeneous materials.¹⁻⁴ Recently several papers⁵⁻⁹ have been devoted to the behavior of optical properties close to the percolation threshold p_c . It has been observed that in the vicinity of p_c the near-infrared transmittance and reflectance as well the optical absorption become almost frequency independent.

The purpose of this paper is first, to show that the Bruggemann approximation (BA), which has been used widely to explain the dielectric and optical properties of composite materials,¹⁰⁻¹³ is able to account for this frequency independence at a concentration p^* which can be very close to p_c for good conductors and second, to show, using a circuit representation, that this frequency independence occurs when the effective medium quality factor is 1 (i.e., the circuit is in unit power resonance). This is, as we will see, a direct consequence of the scaling laws of a mixture of two conductors in the infrared region. In the conclusion we will reexamine some related experimental data in the light of the present work.

In the BA the effective medium dielectric constant $\epsilon^*(\omega) = \epsilon_1^*(\omega) + \epsilon_2^*(\omega)$ is the solution of the self-consistent relation

$$p \frac{\epsilon^{(m)}(\omega) - \epsilon^*(\omega)}{\epsilon^*(\omega) + g(\epsilon^{(m)}(\omega) - \epsilon^*(\omega))} + (1-p) \frac{\epsilon^{(d)} - \epsilon^*(\omega)}{\epsilon^*(\omega) + g(\epsilon^{(d)} - \epsilon^*(\omega))} = 0. \quad (1)$$

p is the concentration of metal m , d is the insulator, and g is the depolarization factor which depends on the shape of the inclusions. In the case of spherical inclusions one has $g = \frac{1}{3}$ ($\frac{1}{2}$) for 3 (2)D systems. If the metal conductivity is described by the Drude formula, one has, for the metal dielectric constant,

$$\epsilon^{(m)}(\omega) = \left[\epsilon^{(m)}(\infty) - \frac{\tau \sigma_m(0)}{\epsilon_0(\omega^2 \tau^2 + 1)} \right] + i \frac{\sigma_m(0)}{\epsilon_0 \omega(\omega^2 \tau^2 + 1)} = \epsilon_1^{(m)} + \epsilon_2^{(m)}, \quad (2)$$

where $\sigma_m(0) = \tau \omega_p^2 = \tau n e^2 / \epsilon_0 m$ is the dc metallic conductivity of m . In the limit $\omega \rightarrow 0$, it is easy to show^{12,13} that the BA (1) yields, for $p > g$,

$$\sigma^*(0) = \left[\frac{p-g}{1-g} \right] \sigma_m(0) \quad (3)$$

and

$$\epsilon_1^*(0) = \left[\frac{p-g}{1-g} \right] \epsilon_1^{(m)}(0) + \frac{p(1-p)}{(1-g)^2} \left[\frac{1-g}{p-g} \right] \epsilon^{(d)}. \quad (4)$$

The percolation threshold is $p_c = g$. $\epsilon_1^*(0)$ diverges for $p = g = p_c$. These results have a form similar to those of the classical percolation theory if we use the mean field values $t = s = 1$ for the conductivity and superconductivity exponents. Since $\epsilon_1^*(0)$ is strongly negative there is a characteristic concentration p^* for which $\epsilon_1^*(0)$ is zero. This is the optical threshold. For $p < p^*$, the behavior is dominated by the dielectric divergence. For $p > p^*$ it is dominated by the metallic behavior $\epsilon_1^*(0) < 0$. We are going to show that it is at that concentration p^* that the optical properties are frequency independent.

To illustrate this result, we use the following parameters¹⁴ to represent a gold-based Cermet: $g = \frac{1}{3}$, $\hbar \omega_p = 9.2$ eV for the plasmon frequency, $\hbar / \tau = 0.06$ eV for the inverse relaxation time, $\epsilon^{(m)}(\infty) = 6.5$, and $\epsilon^{(d)} = 2.82$. In Figs. 1-4 we present the results of the calculation of the real part of the conductivity and of the dielectric constant $\epsilon_1^*(\omega)$ for three concentrations below ($p = 0.337$), at $p = p^* = 0.3385$, and above ($p = 0.34$) the optical threshold. In this example the percolation threshold $p_c = \frac{1}{3}$.

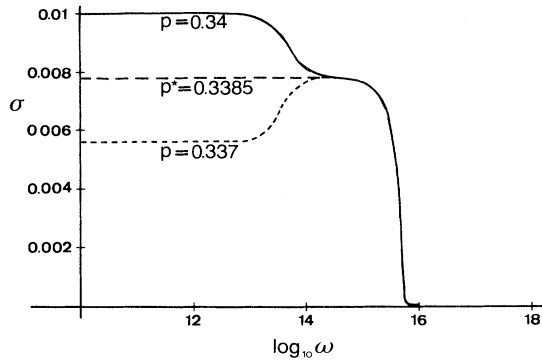


FIG. 1. Real part of the composite Bruggemann conductivity for $p=p^*=0.3385$, $p_c < p=0.337 < p^*$, and for $p=0.340 > p^*$. The metallic parameters are $\hbar\omega_p=9.2$ eV, $\hbar/\tau=0.06$ eV, and $\epsilon^{(m)}(\infty)=6.5$; the insulator parameter is $\epsilon^{(d)}=2.82$. The percolation threshold is $p_c=\frac{1}{3}$. Frequencies are expressed in radian/s.

The behavior obtained for the real part of the conductivity, the optical conductivity σ which is proportional to the optical absorption coefficient: $A(\omega)=\epsilon_2\omega/c=\sigma/\epsilon_0c$, is qualitatively similar to what has been observed by Gadanne *et al.*⁶ in granular, discontinuous gold films of different thickness around the percolation threshold. The optical conductivity close to percolation exhibits a linear behavior versus frequency; the slope of this variation is positive beyond $p^*\approx p_c$, negative below, and vanishes at the optical crossover percolation (p^*), which coincides with the vanishing of ϵ_1^* . In the chosen numerical example $p_c=\frac{1}{3}$ and $p^*=0.3385$. The difference is small. However, this value strongly depends on τ . Due to the grain size or the small film thickness, \hbar/τ in the film can be much higher than in the bulk. In Table I we give the values of p^* for different values of \hbar/τ . We also report the values obtained with the correct percolation 3D exponents t and s , i.e., by using

$$\left[\frac{p-p_c}{1-p_c} \right]^t$$

and

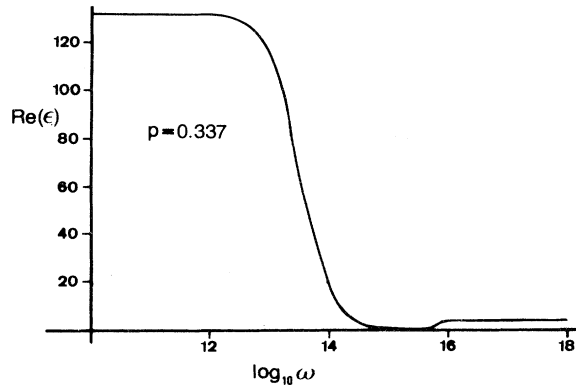


FIG. 2. Real part of the dielectric constant $p_c < p=0.337 < p^*$. The other parameters are as in Fig. 1.

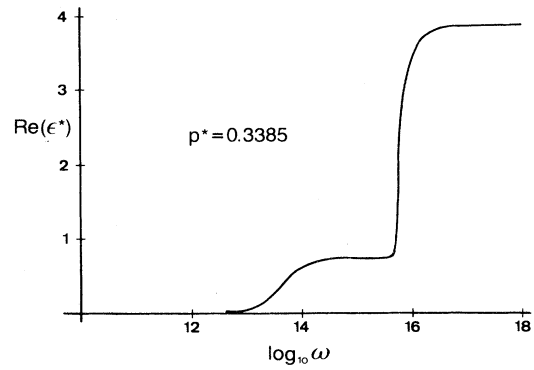


FIG. 3. Real part of the dielectric constant for $p=p^*=0.3385$. The other parameters are as in Fig. 1.

$$\left[\frac{1-p_c}{p-p_c} \right]^s$$

in (3) and (4). The procedure leading to Eqs. (3) and (4) can be extended for $\omega \neq 0$. In the numerical example chosen in this paper, $p^*(\omega)$ as a function of ω is practically constant up to the surface plasmon resonance.

To understand the physical meaning of the frequency independence at p^* , it is convenient to represent the physical system by a RLC circuit.¹⁵⁻¹⁷ In this representation the resistance $R \equiv 1/\sigma_m(0)$, the inductance $L \equiv \tau/\sigma_m(0)=m/ne^2$, and the capacitance $C_m \equiv \epsilon_0\epsilon_1^{(m)}(\infty)$. The insulator is represented by a capacitor $C_d \equiv \epsilon_0\epsilon^{(d)}$. One can define the following characteristic frequencies: the plasma frequency $\omega_p=1/\sqrt{L_m\epsilon_0}$, the relaxation frequency $\omega_{RL}=\tau^{-1}=R/L$, the Drude circuit resonance frequency $\omega_{LC_m}=1/\sqrt{L_mC_m}$, and the RC frequency $\omega_{RC_m}=1/RC_m$ to which we have to add the composite characteristic frequencies $\omega_{RC_d}=1/RC_d$ and $\omega_{LC_d}=1/\sqrt{L_mC_d}$. In these conditions using Eq. (4), the condition $\epsilon^*(0)=0$ yields

$$\left[\frac{p^*-p_c}{1-p_c} \right]^2 \left[\frac{L_m}{R_m^2} - C_m \right] = \frac{p^*(1-p^*)}{(1-p_c)^2} C_d \quad (5)$$

or defining the quality factor of the mixture

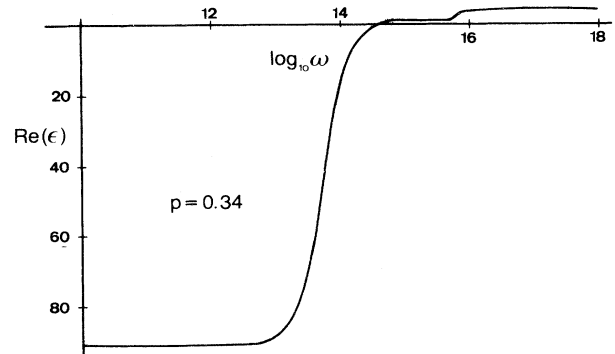


FIG. 4. Real part of the dielectric constant for $p=0.340 > p^*$. The other parameters are as in Fig. 1.

TABLE I. Values of p^* for different values of \hbar/τ .

\hbar/τ (eV)	p^*	
	($s=1, t=1$)	($s=0.75, t=1.95$)
0.06	0.3385	0.3515
0.6	0.3875	0.438
3	0.7560	0.791

$$Q_{\text{mix}}^2 = \frac{1}{R_m^2} \frac{L_m}{C_d} \quad (6)$$

and posing $A = Q_{\text{mix}}^2 - C_m/C_d$, the condition (6) reads

$$p^* = p_c + \sqrt{p^*(1-p^*)/A}. \quad (7)$$

The numerical values obtained by solving (7) coincide with those of Table I. If $R_m(\tau^{-1}) \rightarrow 0$, $p^* \rightarrow p_c$ and the optical transition occurs at p_c . If we define the effective quantities $L^* = p^*L_m/(p^* - p_c)$, $R^* = p^*R_m/(p^* - p_c)$, and $C^* = C_d^* + C_m^*$, with $C_d^* = (1-p^*)[C_d/(p^* - p_c)]$ and $C_m^* = (p^* - p_c)(C_m/p^*)$ [the $(1-p^*)d$ capacitors are coupled in parallel and the p^*m capacitors are coupled in series], the condition (6) is equivalent to $R^* = \sqrt{L^*/C^*}$. In that particular situation $Q^* = 1$ and the effective circuit is in unit power resonance if we use the standard circuit terminology. The resulting equivalent impedance is $Z^* = \sqrt{L^*/C^*}$. For finite frequencies it is easy to show that the effective circuit is resistive up to frequencies $\omega \sim \omega_{L^*C^*} = \omega_{R^*C^*} = \omega_{L^*R^*} = \tau^{-1}$. This explains the behavior of $\epsilon_1(\omega)$ and $\sigma(\omega)$ in Figs. 1–4 at $p = p^*$. Simulations on real RLC circuits^{20–23} have allowed an observation of the characteristic concentration p_c and p^* as well as the variation of $p^* - p_c$ with Q .

Using these results and a generalization to a mixture of self-inductors and capacitors of the scaling laws derived by Efros and Shklovskii¹⁸ and Straley¹⁹, it is moreover possible to show that at $p = p^*$, the dc conductivity is very close to the optical conductivity in the near-infrared region as observed numerically in Fig. 1 and experimentally in the vicinity of the percolation threshold.^{5–9} We note that if $(p^* - p_c)/(1 - p_c) \ll 1$ or $C_m = 0$, Eq. (5) can be written

$$\sigma^*(\omega=0, p^*) = \frac{\sqrt{p^*(1-p^*)}}{(1-p_c)} \sqrt{\sigma_d(\omega)\sigma_m(\tau^{-1} < \omega < \omega_p)} \quad (8)$$

since $\sigma_d = iC_d\omega$ and $\sigma_m(\tau^{-1} < \omega < \omega_p) \approx -i\sigma_m(0)/\omega\tau$. The right-hand side of this expression is the conductivity close to p_c of the composite in the region $\tau^{-1} < \omega < \omega_p$ given by the two conductor's^{18–20} scaling law $\sigma \sim \sigma_m(\sigma_d/\sigma_m)^{t/(s+t)}$ in the mean field approximation ($s=t=1$) or in two-dimensional systems ($s=t$). Therefore in the BA the optical threshold condition $\epsilon^*(0)=0$ is equivalent to the equality between the effective dc conductivity and the effective optical conductivity in the region $\tau^{-1} < \omega < \omega_p$ as this has been shown numerically in Fig. 1.

It is of interest to reexamine some other related experimental data in the light of the previous theoretical discussion. A decade ago, Cheshnovsky *et al.*²¹ studied the metal-nonmetal transition in metal-rare gas solid mixtures. These authors defined two metal-nonmetal transition criteria. The first is formulated on the basis of the divergence of ϵ_1 as approached from both nonmetallic and metallic regions. The second is defined as an “optical criterion” and occurs at the composition from which the real part of the dielectric constant changes sign. This criterion is equivalent to our definition of the optical threshold p^* . Cheshnovsky *et al.* have studied metal-rare gas mixtures and in particular the conductivity and optical properties of the Hg/Xe system in the metal composition range $x=0.47-100$. For $x \approx 0.69$, one observes a rapid increase of the conductivity which can be identified as a percolation threshold p_c . By contrast the concentration at which ϵ_1 changes sign is $x=0.80 \pm 0.02$. This should be related to our p^* . This is also the composition for which the onset of a negative temperature coefficient of the conductivity sets in. This transition follows a region of apparently discontinuous change of the real part of the dielectric constant from a high diverging positive value to the negative value characteristic of the metallic regime. Berthier *et al.*^{13,16} have used a position renormalization-group approach for the calculation of the effective dielectric function of Cermet films. In the particular case of Au-MgO for which $p_c=0.55$ we calculate a $p^*=0.60$ for $s=t=1$ and $p^*=0.65$ for $s=0.75$ and $t=2.2$ the values chosen by these authors to fit their conductivity and optical data. This result is in agreement with their calculation of the real part of the Cermet dielectric constant which is close to zero over a large range of frequencies for $p \approx 0.65$.

Several authors have also noticed a correlation between the change of sign of the temperature coefficient of resistance (TCR) and the occurrence of a percolation threshold. The concentration at which $\text{TCR} = 0$ is close to p_c . We conjecture that this change of sign occurs at $p = p^*$ when the system becomes metallic. This conjecture can be supported by several experimental observations. We have already mentioned the results of Cheshnovsky *et al.*²¹ For Co-Al₂O₃ the TCR changes sign¹¹ at $f_{\text{Co}} \approx 0.7$ at the maximum of the broad transition from insulator to metal. It is also in this range of concentration that the real part of the dielectric constant exhibits an abrupt decrease and that the imaginary part starts to have a metallic behavior. In the case of Al island films of NaCl substrates, it is for a concentration slightly higher than p_c that the resistivity becomes T independent.²² In these systems a detailed study of the correlation between the change of sign of the dielectric constant and of the TCR as well as the frequency independence of optical absorption, transmittivity, and reflectivity in the vicinity of p_c would be of great interest.

In conclusion, we have shown in the BA that the property of frequency independence of the optical properties of composite thin films occurs at the optical threshold p^* . The same conclusion has been obtained using the scaling law for a mixture of two conductors in the frequency range $\tau^{-1} < \omega < \omega_p$. The fact that the behavior of the

near-infrared properties of granular metals can be explained by a mean field theory is not surprising if one notes as we have shown that in $2d$ the Bruggemann theory obeys exactly the two conductor scaling laws (see Brouers *et al.*²³). It can be shown²⁴ moreover that the variation of the absorption coefficient with metallic cov-

erage or film thickness can be accounted for by the BA provided one includes the effect of the substrate.²⁵

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