Higher-order effects in the dielectric constant of percolative metal-insulator systems above the critical point

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The dielectric constant of a conductor-insulator mixture shows a pronounced maximum above the critical volume concentration. Further experimental evidence is presented as well as a theoretical consideration based on a phenomenological equation. Explicit expressions are given for the position of the maximum in terms of scaling parameters and the (complex) conductances of the conductor and insulator. In order to fit some of the data, a volume-fraction-dependent expression for the conductivity of the more highly conductive component is introduced.

The ac and dc conductivities of resistor and resistor-capacitor (RC) networks and continuum conductor-insulator composites have been extensively studied for many years. In systems where there is a very sharp change (metal-insulator transition or MIT) in the dc conductivity at a critical volume fraction or percolation threshold denoted by ϕ_c, the most successful models, for both the dc and ac properties, have proved to be approaches using percolation theory. Review articles, containing the theory and some experimental results, on the complex ac conductivity and other properties of binary metal-insulator systems include Refs. 1–3.

In Refs. 4–6 the following equation was introduced:

$$\frac{(1-\phi)(\sigma_I^{1/s}-\sigma_M^{1/s})}{(\sigma_I^{1/s}+A\sigma_M^{1/s})}+\frac{\phi(\sigma_C^{1/t}-\sigma_M^{1/t})}{(\sigma_C^{1/t}+A\sigma_M^{1/t})}=0, \qquad (1)$$

which gives a phenomenological relationship between σ_C, σ_I, and σ_M. They are, respectively, the conductivities of the conducting and insulating component and the mixture of the two components. Note that all three quantities σ_C, σ_I, and σ_M can be real or complex numbers in Eq. (1). The conducting volume fraction ϕ ranges between 0 and 1 with $\phi=0$ characterizing the pure insulator substance ($\sigma_M\equiv\sigma_I$) and $\phi=1$ the pure conductor substance ($\sigma_M\equiv\sigma_C$). The critical volume fraction or percolation threshold is denoted by ϕ_c, where a transition from an essentially insulating to an essentially conducting medium takes place, and $A=(1-\phi_c)/\phi_c$. For $s=t=1$ the equation is equivalent to the Bruggeman symmetric media equation.[7] Equation (1) yields two limits, for $|\sigma_C|\to\infty,\sigma_M=\sigma_I\phi_c^s/(\phi_c-\phi)^s$ if $\phi<\phi_c$ and for $|\sigma_I|\to 0,\sigma_M=\sigma_C(\phi-\phi_c)^t/(1-\phi_c)^t$ if $\phi>\phi_c$, which characterize the exponents s and t. Note that these expressions are the normalized percolation equations. At $\phi=\phi_c$,

$$\sigma_{MC}=\sigma_C/A^{(st)/(s+t)}(\sigma_I/\sigma_C)^{t/(s+t)} \qquad (2)$$

up to higher-order terms in σ_I/σ_C.

When using the above expressions to analyze ac systems the complex conductivities ($\sigma_x=\sigma_{xr}-i\omega\epsilon_o\epsilon_{rx}$, where ω is the angular frequency, ϵ_o the permittivity of free space, and ϵ_{rx} the real relative dielectric constant of the component) must be inserted in Eq. (1). Below ϕ_c the leading term yields the imaginary conductivity $\mathrm{Im}\sigma_M^-$, which is the real dielectric constant $\mathrm{Re}\epsilon_M^-$, while the next-order term gives the real conductivity $\mathrm{Re}\sigma_M^-$. In turn, above ϕ_c the real conductivity $\mathrm{Re}\sigma_M^+$ is the leading term, and the real dielectric constant $\mathrm{Re}\epsilon_M^+$ appears in the next-order term $\mathrm{Im}\sigma_M^+$, upon which the present paper focuses. In many instances the approximation $\sigma_C=\sigma_{cr}$ and $\sigma_I=-i\omega\epsilon_o\epsilon_r$ is made.[1–3]

In a recent series of papers[4–6] it has been shown that the first-order analytic expressions for $\mathrm{Im}\sigma_M^-$ and $\mathrm{Re}\sigma_M^+$, obtained from Eq. (1), agree with the power laws $|\phi_c-\phi|^{-s}$ or $|\phi-\phi_c|^{-t}$ as given in Refs. 1–3; here $x_-=\sigma_I/\sigma_C[\phi_c/(\phi_c-\phi)]^{s+t}$ (for $\phi<\phi_c$) and $x_+=\sigma_I/\sigma_C[(\phi-\phi_c)/(1-\phi_c)]^{s+t}$ (for $\phi>\phi_c$) are less than 1. Agreement with the power laws given in Refs. 1–3 was also found, when x_- and x_+ are greater than 1, which is called the crossover region. In this region, the first- and second-order terms for σ_M vary as $\sigma_I^{s/(s+t)}\sigma_C^{s/(s+t)}$ on both sides of ϕ_c. Note that with $\sigma_I=i\omega\epsilon_r\epsilon_i$ the system is dispersive with $\sigma_M\sim\omega^{t/(s+t)}$. Wu and McLachlan[4] showed that their ac experimental data agreed with the scaling functions, obtained from Eq. (1), for all x_- and x_+ in the frequency range 10 Hz to 100 MHz. The ac scaling functions generated from Eq. (1) in Ref. 4 were obtained using the parameters obtained from dc measurements.[5] These results show that Eq. (1) is a valid expression for both first order terms for all x_- and x_+. Subsequently McLachlan *et al.*[8] have found this to also be the case for measurements ranging from 10^{-2} Hz to 1 GHz made on the cellular systems (fine conducting powders coating larger insulating particles) described in Ref. 9.

McLachlan *et al.*[6,8] showed that the second-order dielectric loss terms $\mathrm{Re}\sigma_M^-$ are dominated by the dielectric loss in the insulator. However, careful measurement and analysis have shown that the contribution due to the dispersed conductor $\mathrm{Re}\sigma_M^-$ does not vary as ω^2 as given in Refs. 1–3 and that it is closer to the $\omega^{(1+t)/t}$ dependence, obtained from Eq. (1). The second-order term $\mathrm{Im}\sigma_M^+$ or $\mathrm{Re}\epsilon_M^+$, which is the subject of this paper, can, due to instrumental limitations, only be measured close to ϕ_c when $\mathrm{Re}\sigma_M^+$ is not too much large than $\mathrm{Im}\sigma_M^+$. References 1–3 give the volume fraction variation of $\mathrm{Re}\epsilon_M^+$ as $(\phi-\phi_c)^{-s}$, which is not in agreement with any observed data, but is in agreement with Eq. (1) only when $i\omega\epsilon_r\epsilon_i/\sigma_C$ tends to zero for the first- and second-order terms. We begin with a further theoretical investigation of the behavior of the dielectric constant ϵ just above ϕ_c using

Eq. (1). Since σ_M is in general the result of finding numerically the root of a transcendental equation, this can only be achieved by expanding σ_M around ϕ_c. With the ansatz $\sigma_M(\phi)^{1/t}=\sigma_{MC}^{1/t}+\delta$ we obtain from Eq. (1)

$$\delta=\frac{\sigma_{MC}^{1/t}\sigma_I^{1/s}(A-1)+\Delta\phi\sigma_C^{1/t}\sigma_{MC}^{1/s}}{A(t/s+1)\sigma_{MC}^{1/s}-t/s\,\Delta\phi\sigma_C^{1/t}\sigma_{MC}^{1/s-1/t}-(A-1)\sigma_I^{1/s}}, \tag{3}$$

with $\Delta\phi=(\phi-\phi_c)/\phi_c$. Note that δ does not vanish when $\Delta\phi=0$, as we have to take into account additional terms of lower order that do not vanish for $\phi=\phi_c$. These terms are omitted in Eq. (2) but they are of the same order as terms linear in $\phi-\phi_c$ and must be incorporated for reasons of consistency. Inserting the right-hand side of Eq. (2) for σ_{MC} it is now straightforward, albeit tedious, to obtain the position of the maximum of the imaginary part. The calculation yields for the maximum

$$\phi_{\max}=\phi_c+\frac{s+t}{2t}\,\frac{(1-\phi_c)(1-2\phi_c)}{\phi_c}A^{-2s/(s+t)}\left(\frac{|\sigma_I|}{\sigma_C}\right)^{2/(s+t)}+O\left(\left(\frac{\sigma_I}{\sigma_C}\right)^{3/(s+t)}\right). \tag{4}$$

We emphasize that the deviation of $\phi_{\max}$ from ϕ_c is obtained only when the expansion in powers of $(\sigma_I/\sigma_C)^{1/(s+t)}$ is taken beyond the first power; in fact, the result given can be obtained only if the expressions are expanded up to the third power. We have checked the reliability of this analytic expression by comparing with numerical solutions over a wide range of frequencies and are satisfied with its performance.

Equation (4) allows important conclusions to be drawn for the position of the maximum. Note that $\phi_{\max}$ does not depend on individual values of σ_I or σ_C; in other words the maximum position depends only on the ratio σ_I/σ_C (or equivalently on $\omega\epsilon_0\epsilon_r/\sigma_C$). Note the following in particular.

(1) The deviation of $\phi_{\max}$ from ϕ_c starts with the second-order term in $(\sigma_I/\sigma_C)^{1/(s+t)}$; recall that this first-order term determines the width of the crossover region.[1–3]

(2) The larger the ratio σ_I/σ_C, the further the maximum is pushed away from the transition point ϕ_c. In turn, the position of the maximum tends towards ϕ_c for $\sigma_I/\sigma_C\to 0$, as it should.

(3) For finite values of the ratio σ_I/σ_C the distance $\phi_{\max}-\phi_c$ increases the more rapidly the more pronounced the inequality $s+t>2$.

(4) To lowest order, the frequency dependence of the distance $\phi_{\max}-\phi_c$ is proportional to $\omega^{2/(s+t)}$.

The derivative of $\mathrm{Im}\sigma_M$ at ϕ_c is easier to obtain, but the result is slightly more involved. We here report the essential result

$$\left.\frac{d\,\mathrm{Im}\,\sigma_M}{d\phi}\right|_{\phi_c}\propto \mathrm{Im}\left[\left(\frac{\sigma_I^{t/s}}{\sigma_C^{s/t}}\right)^{1/(s+t)}\sigma_I^{1/s}\sigma_C^{1/t}\right].$$

We stress that the derivatives of $\mathrm{Re}\sigma_M$ and $\mathrm{Im}\sigma_M$ at ϕ_c are always continuous and tend to zero for $(\sigma_I/\sigma_C)\to 0$.

For our first analysis of experimental data (Fig. 1) we examine a relatively simple percolation system with a t value close to the universal value of 2.[2,3] A system that satisfies this requirement is a water-oil emulsion, using a surfactant to ensure uniform drop size. Data for such systems have been published in Refs. 10–12 and we present in Fig. 1 data from Fig. 1 of Ref. 10 and from Fig. 4 of Ref. 11, which have been fitted using Eq. (1) with the same value of σ_C above and below ϕ_c. The values used, i.e., $\sigma_C=1.9(1.5)(\Omega\ \mathrm{m})^{-1}, \sigma_I=-i\,2\times 10^{-11}\omega$, $\phi_c=0.2(0.06)$ for the left (right) display and $\nu=10^5$ Hz, are based on the dielectric and conductivity curves given in the quoted papers. The fitting curves use $s=1.15(1.35)$ and $t=1.85(2.1)$. Note that the values of t are close to the universal value. Better fits should be obtained with a more precise knowledge of the system parameters. Note that these data have been previously analyzed using Eq. (1) with a single exponent $(s=t)$ in Ref. 13.

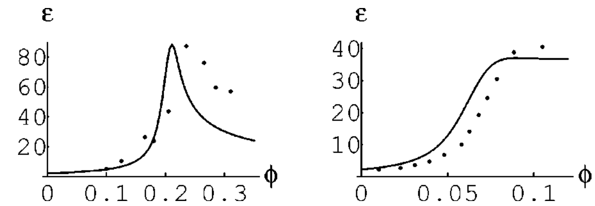

FIG. 1. Fits of experimental data at 100 KHz of a water-oil emulsion using a hydrophil agent for uniform droplet size.

Unfortunately, as shown in Ref. 6, Eq. (1) only qualitatively fits the data for systems with a high nonuniversal value of t. We propose an expression for σ_C for such systems that will allow us to fit the data. In continuum systems all models[14–16] for a nonuniversal t are based on the premise that a distribution of conductances in the conducting component has a power law singularity. As the models given in Refs. 15 and 16 do not allow for t values as high as those actually observed, Balberg[14] has recently proposed a model that allows still higher t values. Therefore, in order to better fit the dielectric data we propose an effective dependence of σ_C on ϕ that is based in spirit on the model due to Balberg for nonuniversal values of t. The model accounts for values of t higher than those allowed by the random void (RV) and inverse random void model (IRV).[15,16] In this model Balberg assumes that the resistance distribution function $h(\epsilon)$, where ϵ is the proximity parameter, has the form ϵ^{-w} as $\epsilon\to 0$, and does not tend towards a constant as in the RV and IRV models. Using the approach of Refs. 16 and 17 and keeping the underlying node links and blobs model,[18] Balberg derives an expression for a nonuniversal t that is equal to the one obtained from the RV model when $w=0$ but can give a larger t for $w>0$. For $w>0$ the model also shows that the average resistance in the network can diverge when $\phi\to\phi_c$. The increase in t beyond its universal value t_{un} as found by Balberg can be added into $t=t_{\mathrm{un}}+t_{\mathrm{nun}}+r$, where r is the extra contribution due to the *characteristic* resistance of the network diverging at $\phi\to\phi_c$. This increase in *characteristic* resistance is incorporated into Eq. (1) and hence into its limits, by substituting σ_C with

$$\sigma_C^{\mathrm{eff}}=\sigma_{00}+\sigma_{c0}\left(\frac{\phi-\phi_c}{1-\phi_c}\right)^r,\qquad \phi>\phi_c \tag{5}$$

with $r>0$. The solution of Eq. (1) should yield a continuous σ_M across ϕ_c, which means that the conductivity σ_C should

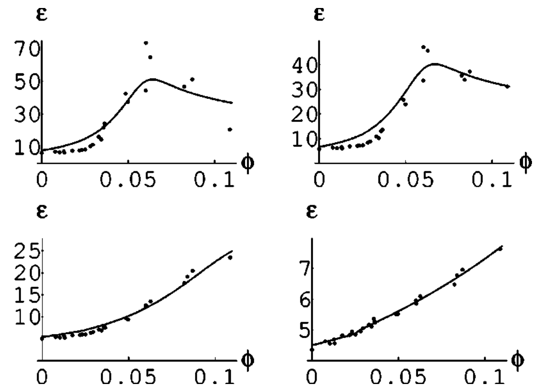

FIG. 2. Fits of experimental data at 1 Hz, 10 Hz, 1 kHz, and 1 MHz (top left to bottom right) for conducting Fe_3O_4 grains in a wax-coated talcum-powder matrix. The parameters used are given in the text.

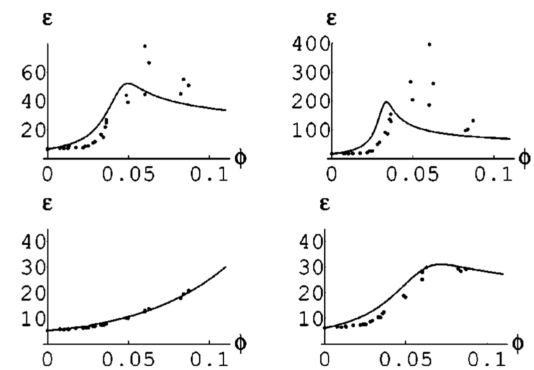

FIG. 3. Fits of experimental data at 1 Hz for $T=25°$ C (top left) and $T=120°$ C (top right). The bottom row displays corresponding results for 1 KHz. The system is the same as in Fig. 2. The parameter values are given in the text.

nowhere vanish. As a consequence, σ_C must reach a nonzero value denoted by σ_{00} at ϕ_c, which is expected to be considerably lower than σ_{c0}. To avoid too many parameters the simplest assumption was made for $\phi<\phi_c$, that is, $\sigma_C \equiv \sigma_{00}$ We note that, while the exponent r is justified by Balberg's model, the new parameter σ_{00} is necessitated to avoid an unphysical singularity at ϕ_c. This choice should be reasonably valid just below ϕ_c. We stress that the effect of the modification by Eq. (5) is virtually indiscernible with regard to first-order effects for the solution σ_M of Eq. (1) or the corresponding percolation power laws in the region where the power laws are obeyed $(x_+, x_- < 1)$. Computer simulations show that using Eq. (5) or a constant σ_C in Eq. (1) causes a difference in $\sigma_M(\phi-\phi_c)(\phi>\phi_c)$ or $\epsilon_M(\phi_c-\phi)$ $(\phi_c>\phi)$, which is too minute to be resolved from available experimental data. The same holds for dispersion plots against ω of σ_M above ϕ_c and ϵ_M below ϕ_c as given in Ref. 4. For this reason it has never been necessary previously to consider the modification given by Eq. (5). However, in our context the higher-order effects are discernible in the dielectric constant just beyond ϕ_c and can be fitted much more satisfactorily than in Ref. 6 using Eqs. (1) and (5).

In Fig. 2 we display data and corresponding fits for conducting Fe_3O_4 grains in a wax-coated talcum-powder matrix.[8,9] The fits are better than those presented in Ref. 6. We have chosen (somewhat arbitrarily) $\sigma_{00}=\sigma_C/10$ with the values $\sigma_C=\sigma_{c0}=2.63\times10^{-1}\ (\Omega\ \mathrm{m})^{-1}$ obtained from extrapolating dc experimental results to $\phi=1$, and $\sigma_I=-i\omega\epsilon_0\epsilon_r$, where ϵ_r is measured separately at each frequency. Good fits are obtained for $(t-r,r,s)=(4.7,0.5,0.97),(4.3,0.7,0.98),(4.4,0.6,1.0)$, and (5.6,0.4,1.6) when moving from the top left to the bottom right display in Fig. 2. The value $\phi_c=0.025$, obtained from dc measurements, is used in Figs. 2 and 3. Note that $t=t_{\mathrm{un}}+t_{\mathrm{nun}}+r$ is somewhat larger than the separately measured nonuniversal dc value of 4.2. Also note that in all cases it turned out that $r<1$. This implies a steep increase of σ_C^{eff} just above ϕ_c. The fits are not necessarily optimal as the multiparameter landscape of the least-square expression $|\sigma_M^{\mathrm{expt}}-\sigma_M^{\mathrm{num}}|^2$ in the parameters t,s, and r (for fixed σ_{00}) has many local minima. However, the quality of the fits at the different local minima does not vary greatly for acceptable fits.

While this second-order behavior of ϵ is in principle a complicated function of the various parameters the position of the maximum at $\phi_{\max}$ is essentially dependent only on the quotient σ_I/σ_C. This implies that a decrease of frequency (which is a decrease of σ_I) has an effect similar to a corresponding increase of σ_C, which can be obtained by an increase of temperature. This is convincingly demonstrated in Fig. 3 where fits are obtained for the same system as in Fig. 2 at different temperatures, i.e., at different values of σ_C and ϵ_r. The experimental data and the theoretical curves show that an increase in σ_C is equivalent to a decrease in ω (or σ_I). The experimental data appear somewhat erratic as they usually do for the low frequency chosen (1 Hz). The data in the first column of Fig. 3 are slightly different from those in the first column of Fig. 2, as the former are taken in a temperature-controlled oven. Much better fits are obtained for higher frequencies as illustrated in the bottom row of Fig. 3 (1 kHz) as the dielectric data are more reliable at higher frequencies. Similar to Fig. 2, experimental values are used for $\epsilon_r(\omega,T)$ with $\sigma_{c0}=\sigma_C=3.22\times10^{-1}\ (\Omega\ \mathrm{m})^{-1}$ at 25° C and $\sigma_{c0}=\sigma_C=1.42\ (\Omega\ \mathrm{m})^{-1}$ at 120° C. The fits were obtained with the parameters $(t-r,r,s)=(4.65,0.5,1.0),(3.4,0.6,1.0),(4.4,0.6,1.0),(3.5,0.9,1.0)$, again choosing the fixed value $\sigma_{00}=\sigma_C/10$.

To summarize, the pronounced hump observed experimentally for the dielectric constant of percolative metal insulator systems just above the critical concentration can be modeled using the higher-order terms of Eq. (1) near ϕ_c. In the cases where t is well above the universal value, Eq. (5), the effects of which are seen only in the second-order terms, must be used to quantitatively model the dielectric data. Note also that all previous experiments on the dielectric constant ''below'' ϕ_c, where ϕ_c has not been independently measured by dc conductivity measurements, have probably incorrectly identified values of ϕ_c. Based on the results of the present paper we believe that the theoretical and experimental results in Refs. 4–6 show that for nonvanishing σ_I/σ_C Eq. (1) is an appropriate equation for real continuum systems rather than the power laws given in Refs. 1–3. Note also that Eq. (1) provides an analytic expression that generates the scaling functions F_- and F_+, which are valid for all ϕ and ω (up to 1 GHz).

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