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Critical Behavior of the Complex Dielectric Constant near the Percolation Threshold of a Heterogeneous Material

David J. Bergman and Yoseph Imry
Department of Physics and Astronomy, Tel-Aviv University, Ramat-Aviv, Israel
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The behavior of the effective bulk conductivity σ_e and of the effective bulk dielectric constant ϵ_e of a heterogeneous mixture of a conducting phase and an insulating dielectric phase is analyzed in the vicinity of the percolation threshold. Exact considerations of a general nature lead to the conclusion that ϵ_e diverges as the conductivity threshold is approached from either side. The introduction of a homogeneity or scaling hypothesis leads to relations between the critical behavior of σ_e and ϵ_e.

The behavior of classical random heterogeneous systems near the percolation threshold has been the subject of numerous investigations.[1] Experimental observations of this phenomenon have been restricted almost entirely to measurements of the electrical conductivity of such a system where one pure component is conducting while the others are nonconducting. On the theoretical side, much numerical work has been done on the behavior of discrete random resistor networks, and on various discrete-lattice models of percolation using various analytical and numerical techniques (i.e., series expansions). The results include expressions for the singular behavior near threshold of quantities such as the conductivity and the probability for finding an infinite cluster of the conducting material, both of them as functions of the fraction of conducting material present, p.

The question of what occurs when the nonconducting component is replaced by a very small but nonzero conductance, or by a reactive component (e.g., a capacitance), has received some attention within the framework of a scaling theory of the percolation transition,[2-4] as well as by the use of effective-medium theory.[5] The results of the scaling theories are at present of somewhat limited validity since they depend on a homogeneity or scaling assumption which, although very plausible, is as yet unproven.

In this Letter we show that many properties of such a system and of similar ones near the percolation threshold can be obtained without having to make any scaling assumptions. All that is needed are some general analyticity properties of the bulk effective complex dielectric constant of a random heterogeneous mixture, κ_e, as a function of the (complex) dielectric constants of the pure components.[6] In this way we will show that near the percolation threshold in a mixture of a pure conductor and a pure dielectric we get a singular behavior not only of the effective conductivity σ_e, but of the effective dielectric constant ϵ_e as well: The dc conductivity is nonzero only above the threshold, increasing as a power of $p-p_c$, where p_c is the critical fraction of conducting material at the threshold. Below p_c there is a frequency-dependent ac conductivity which increases as the threshold is approached. The dc dielectric constant diverges as p_c is approached from either side. At p_c, both ϵ_e and σ_e exhibit a peculiar kind of frequency dependence, varying as a power of ω. The frequency dependences of σ_e and ϵ_e appear despite the fact that in the pure phases ϵ and σ are frequency independent. Some of these singularities have been derived before but only on the basis of a scaling assumption.[2,3]

In order to derive these properties, we must solve the problem of calculating κ_e for a composite material, where the local dielectric constant $\kappa(\vec{r})$ varies from phase to phase but has a fixed value in a given phase. The local electric field inside the composite $\vec{E}(\vec{r})$ is general complex and satisfies the following equations:

$$\nabla\cdot(\kappa\vec{E})=0, \tag{1}$$

$$V^{-1}\int\vec{E}\,dV=\vec{E}_0, \tag{2}$$

where the integral is over the entire volume of the system and $\vec{E}_0$ is the externally applied field. The bulk effective complex dielectric constant κ_e is defined by

$$\kappa_e\equiv\epsilon_e+4\pi\sigma_e/i\omega\equiv V^{-1}\int\kappa|E/E_0|^2dV. \tag{3}$$

We now restrict our discussion to the case of a two-phase medium with (complex) dielectric constants κ_1 and κ_2. Because κ_e is a linear homogeneous function of κ_1 and κ_2, it is convenient to discuss its behavior in terms of the following function:

$$f(u)\equiv1-\kappa_e/\kappa_2=1-\int(1-u\theta_1)|\nabla\psi|^2dV, \tag{4}$$
$$u\equiv1-\kappa_1\kappa_2.$$

Here $\theta_1(\vec{r})$ is equal to 1 when $\vec{r}$ is inside phase-1 material, and equal to 0 otherwise, while $\nabla\psi=\vec{E}/E_0$. In Ref. 6 a similar function was defined [see Eq. (7) of Ref. 6], except that the simple square $(\nabla\psi)^2$ appeared in the integral instead of the absolute value squared $|\nabla\psi|^2$ which appears in (4). Nevertheless, the two definitions are equivalent, since they coincide for real values of u and they lead to a function which is analytic everywhere else.

We suppose now that phase 2 is a pure conductor and that phase 1 is a pure dielectric. In that case

$$\kappa_1=\epsilon_1,\quad\kappa_2=4\pi\sigma_2/i\omega,\quad u=1-i\omega\epsilon_1/4\pi\sigma_2. \tag{5}$$

If $|\kappa_1|\ll|\kappa_2|$, then u is close to 1, and we can expand $f(u)$ around $f(1)$. In this way find

$$\kappa_e=\kappa_2[1-f(u)]\cong\epsilon_1\left.\frac{df}{du}\right|_{u=1}+\frac{4\pi\sigma_2}{i\omega}[1-f(1)]. \tag{6}$$

The singular behavior near the percolation threshold of phase 2, which occurs when the volume fraction of the conducting phase p_2 satisfies $p_2=p_c$, is due to the fact that $f(u)$ has a branch cut along the real axis whose lower edge $u_c(p_2)$ satisfies[6]

$$\begin{aligned}&u_c(p_2)>1\text{ for }p_2\neq p_c,\\&u_c(p_2)\to1\text{ for }p_2\to p_c.\end{aligned} \tag{7}$$

Because $f(u)$ also satisfies

$$\begin{aligned}&f(1)<1\text{ for }p_2>p_c,\\&f(1)=1\text{ for }p_2<p_c,\\&f'(1)\to\infty\text{ for }p_2\to p_c,\end{aligned} \tag{8}$$

we can write the following approximate form for $f(u)$, valid when p_2-p_c is positive and small, and when u is sufficiently close to $u_c(p_2)$:

$$f(u)=1-A(p_2-p_c)^\alpha-B[1-u+C(p_2-p_c)^\gamma]^\beta, \tag{9}$$

where

$$A,B,C,\alpha,\gamma>0,\quad0<\beta<1. \tag{10}$$

Using this form to evaluate the terms in Eq. (6), we get

$$\kappa_e\cong\frac{\epsilon_1\beta B}{[C(p_2-p_c)^\gamma]^{1-\beta}}+\frac{4\pi\sigma_2}{i\omega}\{A(p_2-p_c)^\alpha+B[C(p_2-p_c)^\gamma]^\beta\}, \tag{11}$$

which is a valid approximation as long as $(u-1)f''(1)\ll f'(1)$, i.e.,

$$(1-\beta)/C(p_2-p_c)^\gamma\ll4\pi\sigma_2/\epsilon_1\omega. \tag{12}$$

Thus, while the effective conductivity σ_e tends to zero as $p_2\to p_c$, the effective dielectric constant ϵ_e increases as $(p_2-p_c)^{-\gamma(1-\beta)}$ except for a small region around p_c whose size is proportional to $\omega^{1/\gamma}$.

For $p_2<p_c$, i.e., below the percolation threshold of phase 2, it is convenient to consider a different function,[6]

$$\hat{\varphi}(u)\equiv1-\kappa_1/\kappa_e\cong1-A'(p_c-p_2)^{\alpha'}-B^{-1}[1-u+C'(p_c-p_2)^{\gamma'}]^{1-\beta}, \tag{13}$$

where

$$A', C', \alpha', \gamma' > 0. \tag{14}$$

The same B and β from Eq. (9) appear again here because for $p_2 = p_c$ the two expressions (9) and (13) must satisfy the following relation:

$$(1-f)(1-\hat{\varphi}) = 1 - u. \tag{15}$$

By analogy with (6), (11), and (12) we now get

$$\frac{1}{\kappa_e} = \frac{1}{\kappa_1}[1-\hat{\varphi}(u)] \cong \frac{1-\hat{\varphi}(1)}{\epsilon_1} + \frac{i\omega}{4\pi\sigma_2}\frac{d\hat{\varphi}}{du}\Big|_{u=1}$$

$$= \frac{1}{\epsilon_1}\{A'(p_c-p_2)^{\alpha'} + B^{-1}[C'(p_c-p_2)^{\gamma'}]^{1-\beta}\} + \frac{i\omega}{4\pi\sigma_2}\frac{(1-\beta)B^{-1}}{[C'(p_c-p_2)^{\gamma'}]^{\beta}}, \tag{16}$$

which is valid when

$$\beta/C'(p_c-p_2)^{\gamma'} \ll 4\pi\sigma_2/\epsilon_1\omega. \tag{17}$$

In this case, it is also true that

$$\mathrm{Im}\kappa_e^{-1} \ll \mathrm{Re}\kappa_e^{-1}, \tag{18}$$

so that ϵ_e and σ_e are given by

$$\epsilon_e \cong \epsilon_1\{A'(p_c-p_2)^{\alpha'} + B^{-1}[C'(p_c-p_2)^{\gamma'}]^{1-\beta}\}^{-1}, \tag{19}$$

$$\sigma_e \cong \left(\frac{\omega}{4\pi}\right)^2 \frac{\epsilon_1^2}{\sigma_2}\frac{(1-\beta)B^{-1}}{[C'(p_c-p_2)^{\gamma'}]^{\beta}}\{A'(p_c-p_2)^{\alpha'} + B^{-1}[C'(p_c-p_2)^{\gamma'}]^{1-\beta}\}^{-2}. \tag{20}$$

For any $p_2 < p_c$, we can always choose ω to be small enough so as to satisfy (17), as well as make σ_e arbitrarily small. At the same time, ϵ_e can be made to attain large values (i.e., far in excess of ϵ_1) by making the denominator of (19) small enough to begin with. Experiments to observe such an increase in ϵ_e just below the percolation threshold would provide an obvious test for this theory.

The physical reason for the divergence of ϵ_e as p_c is approached from below is the existence of many almost pure conducting channels which stretch across the entire length of the system and are blocked off only by very thin barriers. Every channel of this type contributes an abnormally large capacitance, and all of these are connected in parallel. This picture also suggests that there may be strong nonlinearities in the dielectric response when ϵ_e is large due to the large electric fields in the thin barriers. Likewise, quantum-mechanical tunneling through the barriers may become important near p_c.

Another point worth noting is that for a superconductor–normal-metal mixture, $\sigma_e \to \infty$ as the percolation threshold is approached from below. If the microscopic geometry is then the same as or similar to that of the normal-metal–dielectric mixture discussed above, the critical behavior of σ_e just below the superconductivity threshold will be identical to the critical behavior of ϵ_e just below the normal-conductivity threshold.

At $p_2 = p_c$, we cannot expand $f(u)$ around $u = 1$, because that is then a branch point of the function. Returning to Eq. (9) we see, however, that in this case we get

$$\kappa_e = B\kappa_1^{\beta}\kappa_2^{1-\beta} = B\epsilon_1^{\beta}(4\pi\sigma_2/i\omega)^{1-\beta}, \tag{21}$$

so that σ_e and ϵ_e satisfy

$$\sigma_e \sim \omega^{\beta}, \quad \epsilon_e \sim \omega^{\beta-1}. \tag{22}$$

In order to make further progress, we now assume, after Straley[2] and Efros and Shklovskii,[3] that $m \equiv \kappa_e/\kappa_2$ has the following homogeneity or scaling properties as a function of $h \equiv \kappa_1/\kappa_2$ and of $t \equiv p_2 - p_c$ when both of these variables are small:

$$m(t,h) = \begin{cases} |t|^{\gamma\beta}F_+(h/|t|^{\gamma}) & \text{for } t>0, \\ |t|^{\gamma\beta}F_-(h/|t|^{\gamma}) & \text{for } t<0. \end{cases} \tag{23}$$

A similar hypothesis has also been made by Harris and Fisch.[4] At present, the reasons for making such a hypothesis are that if is obeyed by effective-medium theory and by the Bethe-lattice model, and that one expects such a behavior by the analyogy with ordinary critical behavior at a second-order phase transition. In particular, the sharp conductivity threshold at $t=0$ is only observed for $h=0$. Furthermore, our Eqs. (9) and (13), while they do not automatically satisfy this hypothesis, are nevertheless very suggestive in that the branch-cut part by itself obeys scaling on either side of p_c. In order to show that the full expressions also obey Eq. (23), we would have to demonstrate that $\alpha>\gamma\beta$, $\alpha'>\gamma'(1-\beta)$, and $\gamma=\gamma'$. We note that our scaling assumption is of a maximal type since we assume that $\gamma=\gamma'$. A less drastic assumption would obviously lead to weaker results than those that we will now proceed to present.

Noting the fact that $F_-(0)$ must vanish (because $\kappa_1=0$ entails $\kappa_e=0$ below the threshold), we can expand $F_\pm(x)$ for small x as follows:

$$F_+(x)=A_+ + B_+x+\dots \qquad F_-(x)= \qquad B_-x-C_-x^2+\dots, \tag{24}$$

where all the coefficients which appear are positive. In this way we get the following results for κ_e:

$$\kappa_e=\epsilon_1 B_+(p_2-p_c)^{\gamma(\beta-1)}+(4\pi\sigma_2/i\omega)A_+(p_2-p_c)^{\gamma\beta}, \quad \text{for } p_2>p_c$$
$$\kappa_e=\epsilon_1 B_-(p_c-p_2)^{\gamma(\beta-1)}-(i\omega\epsilon_1^2/4\pi\sigma_2)C_-(p_c-p_2)^{\gamma(\beta-2)}, \quad \text{for } p_2<p_c. \tag{25}$$

For $p_2=p_c$ we get the same results as before.

The values of the critical indices in Eqs. (23) and (25) can be obtained from results of numerical simulations of random resistor networks that have been published before.[2,7,8] In this way we find

$$\gamma\beta=1.6\pm0.1, \quad \gamma(1-\beta)=0.6\pm0.1,$$
$$\gamma(2-\beta)=2.8\pm0.3, \quad \beta=0.73\pm0.05. \tag{26}$$

We note that the problem of experimentally determining the correct scaling functions F_+ and F_- in (23) requires that measurements of κ_e be made for various values of h at small t. Different values of h can be obtained by using mixtures of various pairs of good and bad conductors (the mixtures must all have similar microscopic geometries). Other ways for getting various values of h are by using the normal-metal–superconductor mixture, or a metal-dielectric mixture. In the latter case, complex values of h are obtained, and both the magnitude and the phase of h can conveniently be made to vary by changing the frequency.[3,5,9] Because other physical properties are also described by the same function $f(u)$ or $m(t,h)$,[6] they too can exhibit critical behavior near the percolation threshold; e.g., a mixture of a good and a bad conductor of heat will exhibit critical behavior in the effective heat conductivity near the percolation threshold of the good conductor.

Finally, we would like to mention the intriguing possibility of designing composite materials close to a percolation threshold with a large effective dielectric constant and exotic optical properties.

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