Tunneling and Nonuniversal Conductivity in Composite Materials

I. Balberg
The Racah Institute of Physics, The Hebrew University, 91 904 Jerusalem, Israel
(Received 29 January 1987)

A simple model based on interparticle tunneling conduction and a percolative network is shown to imply a diverging distribution of high resistors in the system. This distribution is expected to yield a nonuniversal behavior of the electrical conductivity. An experimental study of carbon-black–polymer composites seems to confirm this expectation, as well as explaining why a nonuniversal behavior has not been observed in previous experimental studies on such composites.

PACS numbers: 64.60.Fr, 72.60.+g, 81.20.Jz

While it was eight years ago[1] that a nonuniversal behavior of the electrical conductivity was predicted to be found in percolating networks, it was only recently[2] that it was shown that such a behavior can be found in a particular, quite realistic, system. In the model of the system, known as the random-void model, the voids between the particles carry the current. Comparison with experimental studies of conductivity and permeability seem to justify the application of this model to rocks[2,3] and some composite materials.[4] Other three-dimensional continuum models, such as the one where permeable particles in the percolating system carry the current (the "touching particles" model), have been argued to yield a universal behavior of the conductivity.[2] Hence, only one model has been proposed[2] and confirmed[4] with regards to a nonuniversal behavior of the *conductivity.*[5] In this Letter, I would like to suggest a new system, the carbon-black–polyvinylchloride (PVC) composites,[6] for which a nonuniversal behavior is predicted and observed.

By examining the literature concerning the electrical conductivity in composites, one finds two well-studied systems: that of granular metals[7] and that of carbon-black particles embedded in an insulating plastic.[8-11] For the granular materials, it appears that the percolation transition is due to the coalescence of metallic particles[7] and thus the touching-particles model is applicable. Indeed, a universal behavior with a conductivity exponent of $t=1.9$ was found[7] in these composites. For carbon-black–PVC composites,[11] it has been shown that fluctuation-induced tunneling accounts for the temperature, electric field, and ac stress dependencies of the electrical conductivity.[6] On the other hand, the sharp rise of the conductivity at a critical conducting-particle concentration,[8-11] the universal behavior of the conductivity,[10] and the concentration dependence of the geometrical noise[12] all suggest the applicability of percolation theory to these composites. Since the tunneling-conductivity behavior is observed[6] above the percolation threshold, it must be concluded that these composites are made of percolating networks in which the local-resistance values are determined by a tunneling mechanism. While the reasoning to be presented below suggests a nonuniversal behavior, the only carbon-black polymer on which a detailed conductivity study[10] was carried out (Ketjen black in PVC) indicated a universal ($t=2.0$) behavior. A hint that a nonuniversal behavior may still be found in such composites was provided, however, in the recent work of Chen and Chou,[13] who found (in a composite of a somewhat different nature) a value of $t=2.3$, rather than the universal value[14,15] of $t_{\mathrm{un}}=2.0$. Unfortunately, their data are not good enough and one cannot conclude that the difference between these two values is beyond the experimental and/or statistical uncertainties. Nonetheless, this finding has motivated us to extend our previous experimental studies[10] on the conductivity of carbon-black composites. Indeed, being directed by the model to be outlined below, we found such a behavior beyond these uncertainties.

Since the "random-void" model is definitely an improper description of the above composites (conducting particles and insulating-plastic voids) and since the touching-particles model is not expected[2] to yield a nonuniversal behavior of the conductivity, one has to come up with another model for a possible nonuniversal behavior in the carbon-black composites. However, such a model must be based on interparticle tunneling in a percolating network (see above). One notes, in passing, that the present problem is significantly different from the random-void problem,[2] since it must rely on large interparticle distances with a diminishing probability for the existence of such distances (see below).

In order to see whether tunneling can yield a nonuniversal behavior, one has to determine the conductance distribution function of the network $f(g)$. The tunneling conductance, g, between two impermeable spherical particles of radius b separated by a distance r (with the assumption that $b \ll r$; see below, however) is given by

$$g=g_0 e^{-r/d}, \tag{1}$$

where g_0 is a constant, and d is the characteristic tunneling distance (which is typically[6,16] of the order of tens of angstroms).

Now, to find $f(g)$ one must know the distribution function of the interparticle distances, $D(r)$. In the case under discussion (i.e., $b \ll r$), if one assumes a random arrangement of N particles in a unit volume, the average distance a between two adjacent particles is given by[16] $a = 2(3N/4\pi)^{1/3}$, and thus $D(r)$ is expected to be peaked around $r = a$. The most common distribution which is relevant to such a problem (for $r \gg b$) is the Hertz distribution,[16]

$$P(r) = (3r^2/a^3)\exp[-(r/a)^3]. \quad (2)$$

Qualitatively, the significant feature of $P(r)$ is the peaked (or decaying for large r) nature of the distribution. I am interested here in tunneling and thus in $h(r)$, the distribution function of the distances between the *surfaces* of two adjacent particles. In the case of $r \gg b$, $D(r) = P(r) \simeq h(r)$. From elementary probability it is known that[17]

$$f(g) = h(r)(dr/dg) \equiv H(g)(dr/dg). \quad (3)$$

For mathematical simplicity, consider a simple function which carries the essence of the problem, i.e., being peaked around some $r = a$ and having a distribution width which is also of the order of a. Such a function will be

$$h(r) \propto (r/a)\exp(-r/a). \quad (4)$$

Use of Eq. (3) with relations (1) and (4) then yields

$$f(g) \propto \ln(g_0/g) g^{(d/a)-1}. \quad (5)$$

Since the logarithmic divergence, for small g values, will be suppressed in the $d > a$ case and dominated by the

$$g^{(d/a)-1} \equiv g^{-\alpha} \quad (6)$$

divergence in the $d < a$ case, it can be seen that the essential part of the distribution is given by Eq. (6). The distribution $g^{-\alpha}$ is well known[1,2] now to yield a nonuniversal behavior.

A dependence of the kind given by Eq. (6) is to be expected in the general case of $r \gtrsim 2b$ since then $g = g_0\exp[-(r-2b)/d]$, and thus the r dependence of Eq. (1) is maintained. In applying this model, however, one has to show that in the system under consideration the conductance dependence [such as Eq. (1)] decays faster than the probability $h(r)$ [such as Eq. (4)] since otherwise, as illustrated by Eq. (6) (the negative α case), an average conductance can account for the network and a universal behavior will be obtained.[2] For example, if the distribution given by Eq. (2) (which is the most likely to occur for very large r values) is assumed, one must have some faster ("screening") decay of $g(r)$. Alternatively, one has to show that the distances between the particle surfaces have a weaker decay than $g(r)$. In the materials to be discussed below, some kind of "screening" is possible.[11] In some of these materials (e.g., Cabot black) there is evidence from small-angle x-ray studies[18] that $h(r)$ [not $P(r)$; see above] has a simple exponential form, such as the one given by Eq. (4), at least up to distances of the order of $10d$. Hence, in practice, the near-neighbor $h(r)$ function may be well approximated by Eq. (4), and thus the simplest form of tunneling conductance [Eq. (1)] is expected to yield the nonuniversal behavior [Eq. (6)].

In view of the above discussion, electrical conductivity studies were started with the Mogul-L composite which is composed of spherical carbon-black solid particles of 200-Å diameter.[6,11] The electrical measurements were carried out by the four-probe method described previously.[10] The results obtained for the dependence of the conductivity of this material on the deviation from the percolation threshold are shown in Fig. 1. Unfortunately, only a few "loadings" (carbon wt.% concentrations) are available to me for this kind of black, and thus an accurate value for t cannot be derived. However, the results clearly indicate a nonuniversal behavior ($t \approx 4$) and thus seem to support the tunneling argument above. The question which arises then is this: Why, in contrast to this composite, does the Ketjen-black composite show[10] the universal behavior[14,15] mentioned above? In the rest of this Letter, I try to establish the above-mentioned experimental conclusion and answer this question.

Since there is quite an extensive literature[6,11,19] concerning the structure of carbon-black particles and the corresponding composites,[8,11] I mention here only the properties which are relevant to the conduction process.

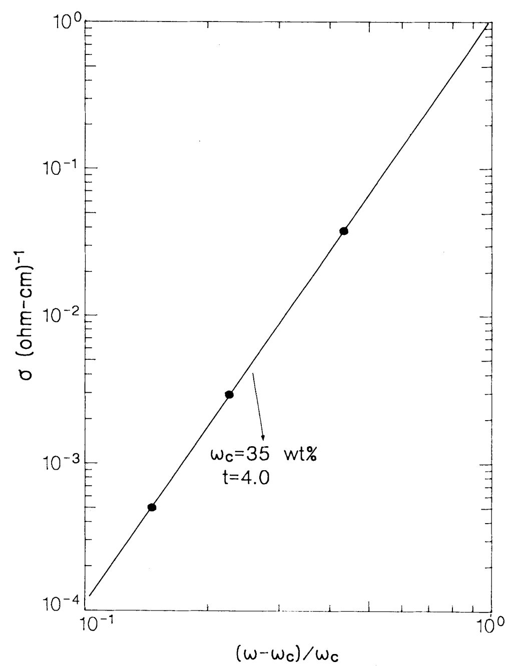

FIG. 1. Conductivity dependence on the relative deviation of the sample's wt.% from its critical value ω_c. The results were obtained on a set of isotropic samples in which the carbon black was Mogul-L black.

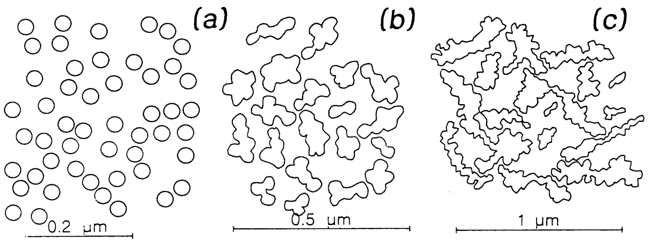

FIG. 2. (a) Schematic descriptions of composites made of "no-structure" black, (b) "intermediate-structure" black, and (c) "high-structure" black. If the scales shown are considered, these illustrations correspondingly describe composites made of Mogul-L black, Cabot black, and Ketjen black.

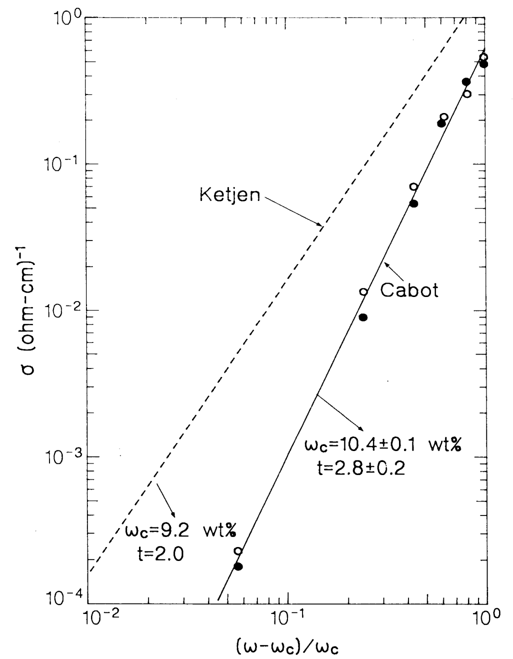

FIG. 3. Conductivity dependence on the relative deviation of the sample's wt.% from its critical value ω_c. The new results were obtained on two sets of isotropic samples in which the carbon was Cabot black. Previous results, shown by the dashed curve, were obtained on Ketjen-black composites (see Ref. 10).

Carbon blacks of large and complicated particles, known as aggregates, are usually[8,20] called "high-structure" blacks, while smaller and geometrically simpler aggregates are called "low-structure" blacks. Upon the compounding of the carbon black and the plastic, a composite is formed such that the conducting aggregates are separated by the insulating polymer. The larger the weight percent ω of the carbon black in the composite, the smaller the average distance between two aggregates. Experimental evidence[6,8,11,19] indicates that even for compounding under high pressure and for $\omega \gg \omega_c$, the aggregates do not merge and a narrow polymer (or insulating additives) layer of about 20 Å is maintained between "touching" aggregates. Figure 2 explains the reason for the coexistence of a tunneling conductance and a percolationlike network in the carbon-black composites. The strong dependence of g on the distance between the surfaces of two particles, $r-2b$, and the fact that $d \ll b$ where b is some average (e.g., gyration) radius of the carbon-black aggregate, imply that an aggregate is "connected" in practice only to "nearest neighbors" (for which r is of the order of the average quantity a). The better the tunneling cutoff approximation (the less important the orders-of-magnitude–smaller contribution of the conduction through the next-nearest neighbors) the smaller the interval $\omega - \omega_c$ above which the measured conductivity will assume the dependence expected from percolation theory. (This situation resembles, in a way, the dependencies associated with finite-size scaling, where only somewhere above the percolation threshold the expected dependence of the geometrical or physical properties is obtained.[15])

The most likely explanation for the universal behavior observed for the Ketjen-black composite (see Fig. 2) is that the particle dispersion during the preparation of the composite is such that the "arms" of the aggregates get entangled while their centers still form a random distribution.[11] Hence, the interparticle tunneling distances (between the two closest points of adjacent particles) r_t, have a distribution $h(r_t)$ which is much narrower than the $h(r-2b)$ distribution used above for the spherical particles. A narrow [with respect to $g(r)$, see above] $h(r_t)$ distribution then yields a resistor network which can be approximated by a system of equal resistors of some average value.[2] Such a system is known to exhibit a universal behavior.[21]

As was seen above, the data on the Mogul-L composites were too sparse to derive an accurate exponent. However, many compositions of Cabot-black materials could be prepared for the derivation of an accurate exponent. Fortunately, the lower degree of "structure" of the corresponding aggregates (with respect to that of the Ketjen black) provides a wide-enough exponential distribution[18] of $h(r)$ (see above) so that the nonuniversality in these composites can be confirmed, quantitatively.

The Cabot composite used for the measurements has been described before,[12] and its qualitative structural features are exhibited in Fig. 2. The results of my resistivity measurements on two sets of samples of this isotropic composite are shown in Fig. 3. Using my least-squares–fit method,[10] I found the high nonuniversal exponent $t=2.8$. It is apparent from Fig. 3, beyond any uncertainty, that the value obtained is larger than the universal exponent,[14,15] $t_{un}=2.0$. The fact that an intermediate value of t is obtained for the Cabot black, the particles of which have an intermediate "structure" between the two other blacks discussed in this paper, indicates that there is a correlation between the structure of the conducting particles and the critical behavior of the conductivity. This observation then lends further support to my model and my interpretation of the results since, according to the above discussion, the particle structure determines the competition between the neighbor closest-distance distribution function and the two-particle conductance function.

The author is grateful to S. Alexander for useful discussions and to S. Bozowski and I. J. Chen for their technical help.

[1]P. M. Kogut and P. Straley, J. Phys. C **12**, 2151 (1979).

[2]B. I. Halperin, S. Feng, and P. N. Sen, Phys. Rev. Lett. **54**, 2391 (1985); S. Feng, B. I. Halperin, and P. N. Sen, Phys. Rev. B **35**, 197 (1987). These authors have nicknamed the random-void model the "Swiss-cheese" model, and the conducting–permeable-spheres model the "inverted Swiss-cheese" model.

[3]I. Balberg, Phys. Rev. B **33**, 3618 (1986).

[4]Actually, the best experimental proof was obtained in composites where the insulating particles are much larger than the metallic particles. Hence, the metallic particles form a conducting liquidlike network. A nonuniversal behavior of these composites was reported first by G. E. Pike, in *Electrical Transport and Optical Properties of Inhomogeneous Media,* edited by J. C. Garland and D. B. Tanner (American Institute of Physics, New York, 1978), p. 366, and more recently by S. Lee, Y. Song, T. W. Noh, X. Chen, and J. R. Gaines, Phys. Rev. B **34**, 6719 (1986). This is a better proof than the results obtained on sedimentary rocks, where different porosites were achieved on "similar" samples rather than on well-defined mixtures of particles.

[5]A nonuniversal behavior seems to be confirmed and explained through the critical behavior of the $1/f$ noise [see A.-M. S. Tremblay, S. Feng, and P. Breton, Phys. Rev. B **32**, 2077 (1986), and reference therein]. We are concerned here, however, with a direct observation of the nonuniversal behavior of the electrical conductivity.

[6]E. K. Sichel, J. I. Gittleman, and P. Sheng, Phys. Rev. B **18**, 5712 (1978); E. K. Sichel, P. Sheng, J. I. Gittleman, and S. Bozowski, Phys. Rev. B **24**, 6131 (1981); P. Sheng, Phys. Rev. B **21**, 2180 (1980).

[7]B. Abeles, H. L. Pinch, and J. I. Gittleman, Phys. Rev. Lett. **35**, 247 (1975); B. Abeles, Appl. Solid State Sci. **6**, 1 (1976).

[8]J. H. Smuckler and P. M. Finnerty, Adv. Chem. Ser. **134**, 171 (1974).

[9]W. F. Verhelst, K. G. Wolthuis, A. Voet, P. Ehrburger, and J. B. Donnet, Rubber Chem. Tech. **50**, 735 (1977).

[10]I. Balberg and S. Bozowski, Solid State Commun. **44**, 551 (1982); I. Balberg, N. Binenbaum, and S. Bozowski, Solid State Commun. **47**, 989 (1983).

[11]For detailed information on these composites and their properties, see *Carbon Black–Polymer Composites,* edited by E. K. Sichel (Marcel Dekker, New York, 1982).

[12]I. Balberg and J. Blanc, Phys. Rev. B **31**, 8295 (1985).

[13]C. C. Chen and Y. C. Chou, Phys. Rev. Lett. **54**, 2529 (1985).

[14]B. Derrida, D. Stauffer, H. J. Herrmann, and J. Vennimonus, J. Phys. (Paris), Lett. **44**, 1701 (1983).

[15]D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).

[16]B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, Berlin, 1984).

[17]This argument has been previously applied to the random-void model by P. N. Sen, J. N. Roberts, and B. I. Halperin, Phys. Rev. B **32**, 3306 (1985). We are using this argument here because it is concise. One can show that the same result can be obtained by using a singly-connected–bonds argument such as the one used in Ref. 2.

[18]J. Wendorff and W. Schneider, unpublished.

[19]K. T. Chung, A. Sabo, and A. P. Pica, J. Appl. Phys. **53**, 6867 (1982).

[20]For electron micrographs of the carbon blacks discussed in this paper see, for example, Refs. 9–11.

[21]I. Balberg and N. Binenbaum, Phys. Rev. A **31**, 1222 (1985).