Tunneling and Nonuniversality in Continuum Percolation Systems

C. Grimaldi[1,2] and I. Balberg[3]

[1]LPM, Ecole Polytechnique Fédérale de Lausanne, Station 17, CH-1015 Lausanne, Switzerland
[2]DPMC, Université de Genève, 24 Quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland
[3]The Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel

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The values obtained experimentally for the conductivity critical exponent in numerous percolation systems, in which the interparticle conduction is by tunneling, were found to be in the range of t_0 and about $t_0 + 10$, where t_0 is the universal conductivity exponent. These latter values are, however, considerably smaller than those predicted by the available ''one-dimensional''-like theory of tunneling percolation. In this Letter, we show that this long-standing discrepancy can be resolved by considering the more realistic ''three-dimensional'' model and the limited proximity to the percolation threshold in all the many available experimental studies.

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While the existence of nonuniversality in physical properties of percolation systems has been established some 18 years ago [1,2], the discrepancy between the numerous experimental results and the corresponding available theories is still an unresolved issue [3,4]. In particular, the values of the critical exponent of the electrical conductivity t, reported in hundreds of works [4–9] on various composite materials in the past 20 years, are not quantitatively accounted for by those theories. The major difficulty in the comparison of the theoretical predictions with the experimental results appears to be the lack of the experimental geometrical-structural information that is expected to yield the diverging (but normalizable) distributions of the local conductances. The latter is the well known [1–3] prerequisite for the nonuniversal behavior [10]. The essence of the nonuniversal behavior is that the global resultant resistance of a percolation system that is given by

$$R_t \propto (p - p_c)^{-t} \tag{1}$$

is determined by

$$R_t \propto \langle R \rangle (p - p_c)^{-t_0}, \tag{2}$$

where $\langle R \rangle$ is the average value of the ''bond'' (inter-nearest-neighbor conducting particles) resistance in the system, p is the bond occupation probability, p_c is the threshold of the system's electrical connectivity, t is the conductivity exponent, and t_0 is the ''universal'' critical exponent that is determined solely by this connectivity. Since in a random system there is no correlation between the geometrical position of a bond and its resistance, any random subsystem of p_c bonds for a given p will provide a connected-conducting network. In particular, if the latter network is chosen by the descending values of the bond conductance g, the value of $\langle R \rangle$ will be an average that is determined by g_c, the smallest value of g in that subnetwork [10]. In the case where the distribution of the g values $h(g)$ diverges as $g \to 0$, the value of g_c will diminish as p approaches p_c, yielding a diverging behavior of $\langle R \rangle$. This behavior has been demonstrated by Kogut and Straley (KS) [10] for the distribution:

$$(1 - \alpha) g^{-\alpha}, \tag{3}$$

yielding that $\langle R \rangle = [(1 - \alpha)/\alpha](g_c^{-\alpha} - 1)$. Hence, for the nondiverging case ($\alpha < 0$), $\langle R \rangle$ is finite while, for ($0 < \alpha < 1$) the diverging (but normalizable) case, one finds that [10]: $\langle R \rangle \propto (p - p_c)^{-t_n}$, where, for the distribution given in Eq. (3), $t_n = \alpha/(1 - \alpha)$. Hence, the nonuniversal contribution to the conductivity exponent ($t_n = t - t_0$) is determined only by $\langle R \rangle$, and, thus, we are able to limit our discussion here to the evaluation of this quantity.

Turning to the problem at hand, i.e., the large quantitative discrepancy between the theoretical predictions and the experimental observations, we note that, in both systems for which theories were advanced, the porous media [1] and the tunneling-percolation problem [2] (see below), the conductors distribution was mapped onto the KS [10] distribution [Eq. (3)] yielding specific predictions as to the values of t_n. However, the experimental results were found to be, in general, larger than expected in the first class of systems [3] and smaller or much smaller [2,4–9] than expected in the second class of systems [2,4,11]. One of us has explained [3] the first observation by applying phenomenologically a modified $h(g)$ distribution that still retains the KS dependence [Eq. (3)]. That approach yielded new limits to the theoretical predictions that seem to accommodate all relevant experimental data [3].

In this Letter, we seek a general understanding of the nonuniversal behavior of the second class of systems; i.e., in systems in which the conducting particles are embedded in an insulating matrix and the transport between the particles is by tunneling [2,4,5,11]. While some qualitative explanations [4,9,11,12] were proposed for the above-mentioned discrepancy in those systems, they were unable to account systematically for it [9,13]. Moreover, only qualitative specific explanations have been given [14,15] to the fact that in some conducting composites the critical

behavior of the transport has been found [6,14,16,17] to be composed of a few ''nonuniversal'' regimes. We note in passing here that the dominant network that contributes to R_t is that of the nearest neighbors' network that yields in practice a bona fide percolation system [4,18]. This is, of course, because of the exponential decay of the tunneling probability with the interparticle distance r. Correspondingly, the possible divergence of the average bond resistance $\langle R \rangle$ is determined by the largest r's of the nearest neighbors. The corresponding distribution of the nearest neighbors distance in the continuum $P(r)$ that was considered previously [2,11] in order to evaluate the origin of the nonuniversality of the tunneling-percolation model within the framework of the KS model, was the ''one-dimensional'' (1D) Hertz distribution [19,20]:

$$\frac{1}{a-b}\exp\left(-\frac{r-b}{a-b}\right). \tag{4}$$

Here r is the distance between the centers of two nearest-neighbor spherical conducting particle, b is their diameter, and a is the average nearest-neighbor interparticle (three-dimensional) distance that can be estimated from Refs. [2–4]: $\frac{4\pi}{3}(a/2)^3 N = 1$, where N is the density of the conducting particles. Combining this 1D distribution with the simple (normalized, $0 \leq g \leq 1$) tunneling dependence of the interparticle conductance on r [2,4,11], $g(r) = \exp[-(r-b)/d]$, where d is the typical tunneling decay parameter, one obtains an $h(g)$ distribution of the form given in Eq. (3) but with [2,4,11]:

$$\alpha = 1 - \frac{d}{a-b}. \tag{5}$$

While this 1D-like theory, leading to the simple analytic prediction of Eq. (5), appeared to capture the essence of the problem and yielded the very simple and convenient physical parameter $d/(a-b)$ for the description of the physical system, it yields t values that were much larger than the very many values of t found experimentally. For example, the $(a-b)/d$ values in many composites [5–9] are expected [4,6,11], according to the 1D-like phenomenological model, to be of the order of 50 ($d \approx 1$ nm, $a - b \approx 50$ nm), but the highest observed [5,7] values of t in corresponding composites was about 10. Another related phenomenon, noticed by us, following the compilation of many experimental data [4,5], is the general trend of the decrease of t with the increase of the critical volume fraction of the conducting phase v_c as well as the scatter of the observed t values within the t_0 and (about) $t_0 + 10$ interval for *a priori* similar systems [6,8,11]. On the theoretical end, while the above-mentioned simplified model was, for the sake of simplicity [2], a 1D-like model, no trials were made to test the consequences of this 1D-like simplification, both conceptually and mathematically, and the findings of one of us [21] concerning the dependence of $h(g)$ on the dimensionality has not been translated to a prediction of t.

In the present Letter, we show that the consideration of the effect of dimensionality beyond the 1D simplification yields even a qualitatively different behavior. In particular, the corresponding new predictions of the higher-dimension model enables one to account for the above-mentioned collection of experimentally observed phenomena. In fact, we have realized already [2] upon the introduction of the 1D-like model that the probability of finding a nearest neighbor should decrease slower than the decrease of g with increasing r in order to enable a diverging distribution of $h(g)$. This is since if this is not the case (i.e., $a < d$ or $\alpha < 0$) a nondiverging $h(g)$ and thus a universal behavior of R_t will be obtained. In the 3D case, the leading term in the $P(r)$ distribution [19,20] is of the form of $\exp[-(r^3 - b^3)/(a-b)^3]$ (see below), and, correspondingly, for any values of $(a-b)$ and d, for large enough r, $P(r)$ decreases faster than $g(r)$ yielding a nondiverging $h(g)$ as $g \to 0$, and, thus, the asymptotic $p \to p_c$ critical behavior is expected to be universal. On the other hand, this situation cannot be mapped onto a simple KS-like result for t_n, and another framework is needed in order to evaluate the t values that are to be compared with the experimental observations. However, since α encloses the physical information of the tunneling-percolation system, we keep using it for the system characterization in all dimensions.

The approach we have chosen is the effective medium approximation (EMA) [22]. This choice is justified following its validity in general [23] and for the determination of $\langle R \rangle$ in composite systems [24] in particular, as well as our above realization that the contribution t_n comes only from the average $\langle R \rangle$. Hence, the fact that the universal conductivity EMA exponent t_0 is 1 and that p_c is $1/3$ in the cubic lattice, rather than the values expected from percolation theory (~ 2 and ~ 0.25, respectively), simply means that the t_0 value acts as a reference for the t_n value that we are examining (see below). This yields that, considering the $t_0 \approx 2$ value for the universal 3D percolation system [1–4], the ''correct'' value of t will be larger than the t value derived from our EMA calculations just by a unity.

Turning to the EMA calculation, we consider a bond percolation model for a cubic lattice with a bond conductance distribution function of the form: $\rho(g) = ph(g) + (1-p)\delta(g)$, where the nonzero conductance values are distributed according to $h(g)$. Assuming that the nearest-neighbor interparticle distances r are distributed according to a given distribution function $P(r)$, $h(g)$ reduces to $h(g) = \int_0^\infty dr P(r)\delta[g - g(r)]$, yielding [10] the EMA average bond conductance G as the solution of the following integral equation:

$$\int_0^\infty dr \frac{P(r)}{g(r) + 2G} = \frac{p - p_c}{2Gp}. \tag{6}$$

For a 3D homogeneous dispersion of impenetrable spheres of diameter b, $P(r)$ is well approximated by [20]:

$$P(r) = \frac{24v(\gamma_1 x^2 + \gamma_2 x + \gamma_3)}{b} \exp[-8v\gamma_1(x^3 - 1) - 12v\gamma_2(x^2 - 1) - 24v\gamma_3(x - 1)]\theta(x - 1), \quad (7)$$

where $x = r/b$, $0 < v < 1$ is a dimensionless parameter (coinciding with the volume fraction of the conducting inclusions), θ is the unit step function, and

$$\gamma_1 = \frac{1 + v}{(1 - v)^3}, \qquad \gamma_2 = -\frac{v}{2}\frac{3 + v}{(1 - v)^3}, \qquad \gamma_3 = \frac{1}{2}\frac{v^2}{(1 - v)^3}. \quad (8)$$

The parameter v controls the value of the mean nearest-neighbor interparticle distance a [that we used in solving Eq. (6)] through the relation $a = \int_0^\infty drrP(r)$. From Eqs. (6) and (7), it is clear that the effective medium conductance G is governed by the parameter a/b that characterizes $P(r)$ and by the tunneling parameter d. A numerical solution of the integral equation given in Eq. (6) is plotted in Fig. 1 for the case of "dot" particles ($b = 0$, left panel) and for hard-core spheres with the typical [4] $d/b = 0.15$ value (right panel). The different plots of G are shown for different values of the characteristic parameter α [see Eq. (5)]. In order to better appreciate the behavior of G as $p \to p_c$, the "local" transport exponent defined as

$$t(p) = \frac{d\ln(G)}{d\ln(p - p_c)} \quad (9)$$

is plotted in Fig. 2 for the data exhibited in Fig. 1. It is clear that for small values of α the local exponent is only weakly dependent on p and it is very close to $t = 1$, i.e., to the universal value of the EMA. For larger α values, $t(p)$ acquires a stronger $p - p_c$ dependence which would correspond to an apparent nonuniversality when p is not too close to p_c. However, as $p \to p_c$, the local exponent asymptotically reduces to the universal value of $t_0 = 1$.

We have seen that our predicted t values depend on the proximity $p - p_c$ to the percolation threshold p_c, and, thus, as we turn to the discussion of the experimental observations, we have to compare the parameters that are commonly used to quantify this proximity in the continuum with the above, lattice, $p - p_c$ parameter. We note, in particular, that in the latter case p_c is of the order of unity (0.247 in bond percolation, or 1/3 in EMA, on the cubic lattice). On the other hand, in the continuum one commonly [5,6] considers the fractional volume (weight) content of the conducting phase v (w) and its critical value v_c (w_c). However, the latter critical values can be vanishingly small [3,5,14,25], and, thus, while the absolute values of $v - v_c$ (or $w - w_c$) may be very small compared to unity, they do not correspond to a close proximity to v_c or w_c. Hence, in general, the proximity in both cases is better described [26] in the present context by $(p - p_c)/p_c$ and $(v - v_c)/v_c$ or $(w - w_c)/w_c$. Since we noted that $(p - p_c)/p_c \sim (p - p_c)$, the comparison of the t values obtained in the theory and the experiment has to be made for the same values of $p - p_c$ and $(v - v_c)/v_c$ or $(w - w_c)/w_c$. Moreover, to appreciate the experimental "resolution" limits of $(v - v_c)$ or $(w - w_c)$ that are achievable thus far in composites, in general, and in systems in which the percolation-tunneling model applies, in particular, let us consider the cosputtered granular metals [4,18,27]. For these systems, one can typically achieve a fiftyfold division of the sample with values of v that vary from (ideally) 0 to 1. Hence, for the typical [27] $v_c \sim 0.5$, the smallest $v - v_c$ interval that can be examined, away from v_c, is $0.02v_c$, yielding that the closest proximity of $p - p_c$ ($p_c \sim 0.25$, see above) is not smaller than about 0.01. As far as we know this is about the closest proximity achieved thus far in the study of experimental systems, and, thus, all the available experimental data correspond to the lattice percolation range of, at most, $1 \gtrsim p - p_c \gtrsim 0.01$.

Examining our above EMA results (Fig. 2) in light of the above considerations, we see that, over the above widest

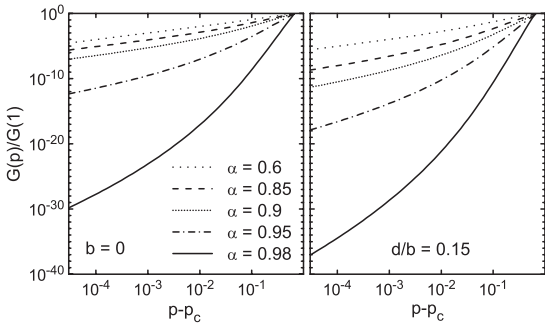

FIG. 1. Left panel: Our calculated EMA conductance G as a function of $p - p_c$ for dot particles ($b = 0$) with a nearest-neighbor distribution that is given by Eq. (7). The different cases refer to different values of the parameter $\alpha = 1 - d/(a - b)$. Right panel: The same as for the left panel but for hard-core spheres with diameter $b > 0$. The cases shown have the same α values as those in the left panel.

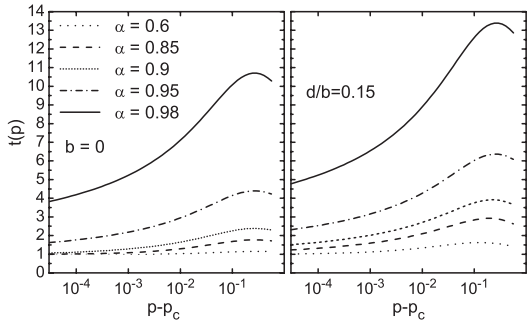

FIG. 2. The local transport exponent $t(p)$, Eq. (9), as derived from the calculated data shown in Fig. 1.

experimentally achievable $p - p_c$ range, the value of t may be taken as a constant with a deviation of not more than $\pm 20\%$. Hence, it is not surprising that the common fit done in the literature for experimental results is taken as representing a single t value over the accessible (less than 2 orders of magnitude) $p - p_c$ range, while in fact a variable t is present over that range. Indeed, as we noted above, indications for the variation of the measured transport exponents over the above $p - p_c$ range can be found in the literature [6,14,16,17]. Also, the fact that the ''measured'' t values are scattered and vary between very similar composites [6,8,14], but within the limits of t_0 and t of the order of $t_0 + 10$, as suggested here, indicates that these observations follow a combination of the small variation in internal system parameters (a, b, d) and the limited $p - p_c$ intervals that are considered. On the other hand, if higher experimental resolutions will be achieved (in the preparation of series of samples), a more detailed verification of our present EMA predictions, concerning the $p - p_c$ dependence of t, is expected to be realized.

As we saw in Fig. 2, the peak in the t values shifts to smaller $p - p_c$ values with the increase of $(a - b)/d$; i.e., higher t values will be observed the larger the value of $(a - b)/d$ (or α), for the accessible $p - p_c$ range. For this range, this is qualitatively similar to the behavior to be expected from the 1D-like model, but it is by far more moderate in this range. However, the most important finding is that the t values predicted here are of the order of those observed experimentally for the a, b, and d parameters that characterize the studied composites. In fact, our present findings that yield relatively low [compared to the 1D-like prediction $t_0 + (a - b)/d - 1$] t values confirm our above conjecture that it is the (diverging 1D and the nondiverging 3D) $h(g)$ distributions that are responsible for the different behavior of the 1D-like and the higher-dimension percolation-tunneling systems. The other general trend of the many experimental results is that the smaller the v_c (or w_c) values (diminishing [21] even below 0.01), the larger the t value. This is well explained now by the above-mentioned fact that the $v - v_c$ values in these composites are much smaller than the (proper) lattice-$p - p_c$ values, and, thus, their farther proximity to the threshold in these composites yields, as seen in Fig. 2, larger t values.

In conclusion, we have shown that the values expected to be measured for the conductivity exponent t, in tunneling-percolation systems in the continuum, are between 2 and the order of 10 for typical ratios of the tunneling decay constant and the size of the conducting particles. The dependence of t on the proximity to the percolation threshold accounts for the many reported experimental values and for their scatter between the above values, as well as for the increase of the t values with the diminishing percolation threshold when it is characterized, as is usually the case, by the fractional volume or fractional weight of the conducting phase in the system.

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