Tunneling and Non-Universality in Continuum Percolation Systems

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The existence of non-universality in physical properties of percolation systems has been established some eighteen years ago [1, 2] the discrepancy between the numerous experimental results and the corresponding available theories is still an unresolved issue [3]. In particular, the values of the critical exponent of the electrical conductivity, $t$, reported in hundreds of works [1, 2, 3, 4, 5, 6, 7, 8, 9] on various composite materials in the last twenty 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, 2, 3] pre-requisite for the non-universal behavior [10]. The essence of the non-universal behavior is that the global resultant resistance of a percolation system that is given by

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

is determined by

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

where $\langle R \rangle$ is the average value of the “bond” (inter-nearest-neighbour 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 sub-network [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 [10] (KS) for the distribution:

$$\langle R \rangle = [(1 - \alpha)/\alpha](g_c^{-\alpha} - 1)$$

yielding that $\langle R \rangle$ is finite while, for $(0 < \alpha < 1)$ the diverging (but normalizable) case, one finds that $\langle R \rangle \propto (p - p_c)^{-t_0}$ where, for the distribution given in Eq. (3), $t_n = \alpha/(1 - \alpha)$. Hence the non-universal contribution to the conductivity exponent $(t_n = t - t_0)$ is determined only by $(R)$ 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 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 than expected in the second class of systems [4, 5, 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 non-universal 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, 3, 4, 5, 11]. While some qualitative explanations [4, 5, 6, 7, 8, 9, 10] were proposed for the above mentioned discrepancy in those systems, they were unable to account systematically for it [4, 12]. Moreover, only qualitative specific explanations have been given [10, 15] to the fact that in some con-
ducting composites the critical behavior of the transport has been found \[4,11,15,16\] to be composed of a few “non-universal” 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 the nearest neighbors’ network that yields in practice a description of the physical system, it yields 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 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 \(i.e.\ a < d, \ or \ a < 0\) a non-diverging \(h(g)\) and thus a universal behaviour 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 non-diverging \(h(g)\) as \(g \to 0,\) and thus, the asymptotic \(p \to p_c\) critical behaviour 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 \(a\) 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 \((R)\) in composite systems \([24]\) in particular, as well as our above realization that the contribution \(t_n\) comes only from the average \((R).\) 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 \((\sim 2 \ and \ \sim 0.25\) respectively), simply means that the \(t_0\) value acts as a reference for the \(t_n\) value that we are examining \((\text{see below}).\) This yields that, considering the \(t_0 \approx 2\) value for the universal 3D percolation system \([1,2,3,4]\), 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 non-zero conductance values are distributed according to \(h(g).\) Assuming that the nearest-neighbour inter-particle 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:

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

(6)

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

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

(7)

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

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

(8)

The parameter \( v \) controls the value of the mean nearest-neighbor interparticle distance \( a \) (that we used in solving Eq. 4 through the relation: \( a = \int_0^\infty dr r P(r) \). 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. 4 is plotted in Fig. 1 for the case of “dot” particles \( (b = 0, \text{left panel}) \) and for hard-core spheres with the typical \( d/b = 0.15 \) value (right panel). The different plots of \( G \) are shown for different values of the characteristic parameter \( \alpha \) (see Eq. 4). In order to better appreciate the behaviour of \( G \) as \( p \to p_c \), the “local” transport exponent defined as

\[ t(p) = \frac{d \ln(G)}{d \ln(p - p_c)} \]  

(9)

is plotted in Fig. 2 for the data exhibited in Fig. 1. It is clear that for small values of \( \alpha \) 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 \( \alpha \) values, \( t(p) \) acquires a stronger \( p - p_c \) dependence which would correspond to an apparent non-universality 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 [2, 13] 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, 4, 11, 23] 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 [20] 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 co-sputtered granular metals [1, 13, 23]. For these systems one can typically achieve a 50 fold division of the sample with values of \( v \) that vary from (ideally) 0 to 1. Hence, for the typical \( v_c \) \( \sim 0.5 \), the smallest \( v - v_c \) interval that can be examined, away from \( v_c \), is 0.02\( v_c \), 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...
Portant finding is that the range this is qualitatively similar to the behavior in fact a variable transport exponents over the above order of those observed experimentally for the "measured" data. Also, the fact 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 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 a), 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 non-diverging 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 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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