Removing the effects of temperature and of inappropriate critical point proximity on the electrical resistivity percolation exponent

A. Aparecido-Ferreira [a,b,*], G.M. Ribeiro [a], J.F. Sampaio [a]

[a] Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, 31270-901 Minas Gerais Brazil
[b] Departamento de Física, Universidade Federal de Viçosa, Viçosa 36570-900 Minas Gerais, Brazil

ABSTRACT

Percolating systems have been widely studied, but questions remain elusive: How to define the critical range where the standard percolation equation would be properly applicable, and the universal exponent t would be found? How to remove external effects, such as temperature, which would dramatically have an influence on the t determination? The lack of clear answers may be the reason for the spread of t exponents reported in the literature. Here we suggest rational methods to rule out such spurious effects and to reliably find the t exponent. We hope our work will call the readers' attention to how to carefully carry out experiments on percolating systems.

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1. Introduction

The percolation theory describes the connectedness probabilities of conductors dispersed in another kind of material or placed at sites of a discrete lattice [1]. It is well established that some physical properties of percolating systems have a critical behavior when the volume concentration p of the dispersed material is close enough to a critical value p_c that defines the percolation threshold. For p in that *critical region*, those properties behave like the power law $(p-p_c)^u$ whose u exponent is expected to have a universal value that depends only on the dimensionality of the system. This is believed to hold also for continuum systems, even though most of the conclusions on the percolation theory come from computer simulation on discrete lattices. For a composite consisting of a mixture of an electrical insulator and a conducting material, with a concentration equal to p, the electrical resistivity ρ follows a power law and the exponent is usually called t:

$$\rho = \tilde{\rho}(p-p_c)^{-t}. \qquad (1)$$

In three dimensions it is widely accepted [1,2], that the universal value of t is $t_{un}=2.0$. However, this is not always in agreement with the experimental results.

Kogut and Straley [3] and Straley [4] have shown that there can be percolating systems with non-universal exponents. In particular, they used a resistor for which the normalized bond

conductance g, such that $0 \leq g \leq 1$, has the probability $1-p$ of being zero and p of being non-zero, but with a distribution function $h(g) = (1-\alpha)g^{-\alpha}$, for $0 < \alpha < 1$. For this system, the value of t is the maximum of the two values t_{un} and $t_1 + \alpha/(1-\alpha)$, where $t_1 \equiv 1 + (\bar{d}-2)\nu$, ν is the universal exponent of the percolation correlation length ξ, and $\bar{d}$ is the system dimension. If one considers the value $\nu=0.88$ given for 3D systems [1], then $t_1=1.88$, and whenever one finds an experimental t value larger than t_{un}, the t value should be given by $t = 1.88 + \alpha/(1-\alpha)$.

Halperin et al. [5] have modeled the "Swiss cheese" systems, consisting of insulating holes in a conducting host media, and found that, for three dimensions, the exponent is $\bar{t} = t_{un} + 1/2$. They also have found that for "inverted Swiss cheese" systems, where the holes are replaced by conducting objects and the surrounding media is an insulator, the exponent value should be the universal one. Experimental realization of these systems has been worked out with glass spheres in an indium host and silver coated spheres immersed in a Teflon matrix [6]. The first system has shown a t value equal to 3.1 ± 0.3, well above the predicted one. The inverted system, however, has shown the expected universal value. Polymer-carbon black (CB) composites could be considered, at first thought, as "inverted Swiss-cheese" systems, so their exponent should be the universal one. However, this has been proven to be untrue. There are results in close agreement with the universal value [7,8], but also values as high as 2.9 ± 0.1 in CB-polyethylene [9], 4 and 2.8 for two composites with different carbon blacks [10], and even an exponent as high as 6.4, have also been found [11].

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* Corresponding author at: Departamento de Física, Universidade Federal de Viçosa, Viçosa 36570-900, Minas Gerais, Brazil.
E-mail address: alex@ufv.br (A. Aparecido-Ferreira).

Balberg [10] has shown that if the electric conduction between the conductors in the host is by tunneling, and if the system has a special distribution function $P(r)$ for the nearest neighbor inter-particle distance, then the Kogut–Straley conductance distribution can be present. More recently, Grimaldi and Balberg [12], by using a more realistic $P(r)$ function, came to the conclusion that the tunneling mechanism leads to t values higher than the universal one, but they tend to it if p is close enough to p_c. So the spread of t values in the literature most likely comes from two effects: some diversity on the proximity to the percolation threshold, and the temperature influence on the t exponent.

Several experimental realizations of the t values have used a wide range of $p - p_c$. However, Eq. (1) is an approximation that is only valid for systems with concentration in the critical region, and there is not a clear criterion to define such concentration range. Also, it is known [13] that a set of samples with the same concentration p will exhibit sample-to-sample fluctuations that increase when $p - p_c$ decreases. So the closer to the critical point, the higher the experimental error.

The other challenging issue is the effect of temperature on the electrical properties of percolating systems. The original percolation theory is based on the contact between neighbor conducting particles and, in a first approach, the t exponent should not depend on the temperature that would just change the microscopic resistances of the conducting units (bonds or sites). This would influence $\tilde{\rho}$ in Eq. (1), but not p_c and t. But if the system has some conductance distribution function leading to a non-universal behavior, such distribution may change with the temperature and this would lead to a temperature dependence of the percolating parameters. For instance, if the microscopic conducting mechanism involves temperature assisted tunneling, like hopping conduction, then the temperature can change both the conductance units and the electrical connectivity. Moreover, the two connectivity channels between conducting particles (contact or hopping) have been shown to lead to different exponent and threshold percolation, depending on the ratio of size of the conductors and the tunneling length [14]. If the tunneling length changes with the temperature, it will also change that ratio.

In this work we have performed experiments aiming to see how to get t values from experimental data that would represent meaningful information for the study of the non-universality issue in percolating systems. We will study the influence on the t values of the proximity to p_c and of the temperature T. The resistivity of composites usually presents a strong temperature dependence [7,9,15], determined by the microscopic mechanisms of conduction. Then we can investigate whether this temperature dependence will reflect itself on the percolating parameters p_c and t. This analysis may provide some clues about the non-universality issue. Besides, the t determination will be extrapolated to $p \to p_c$.

2. Experimental procedure and results

Because there have been several studies of the percolating properties of CB composites, we chose to work with CB. But we preferred not to mix it into another solid or liquid matrix in order to avoid the effects of thermal phase transition, like the vitreous transition in polymers, and also the difference between the thermal expansion coefficient of the CB and the matrix [9,16,17]. Our samples were prepared just by filling cylindrical quartz tubes with weighed amounts of CB, the Vulcan XC72R from Cabot Inc., with medium structure (DBP 192 cm³/100 g) [18]. The tubes' bottom and the top covers are made of copper, each with two wires, one for the electrical current flow and the other for voltage measurement. A schematic figure of the experimental setup is shown in Fig. 1(a). Also, a Transmission Electron Microscope (TEM) image of a CB aggregate is shown. It is clear that each aggregate is made of CB nanoparticles of

about 40 nm and fused together to build a "chain" structure. As the samples were inserted in a flow cryostat, the cryogenic He gas filled those spaces not occupied by the carbon aggregates, and became an electrical insulator matrix that does not put stress on the carbon. As there is no matrix holding the CB clusters, they are self-supporting, and at very low sample density d they may become rearranged and the sample can change during the experiment. Such a sample's weakness will be overcome by a large number of samples measured and by a careful check of the temperature dependence of the electrical resistivity of each sample. Here d is the CB mass in the tube divided by the tube's volume and should not be confused with the density $d_0 = 1.87$ g/cm³ of the CB particles, which was determined by measuring the densities of CB-polymer samples with different CB concentrations.

Several samples were prepared with densities d covering the range of 0.059 to around 0.52 g/cm³. The relation d/d_0 gives the ratio p between the volume occupied by CB and the total volume of the cylinder, and our samples had p varying from 3.2% to 27.7%. The linear relation between p and d also allows rewriting the percolation law in Eq. (1) with d replacing p:

$$\ln(\rho) = \ln(\tilde{\rho}) - t \ln(d - d_c) \tag{2}$$

First, let us discuss temperature dependence of the resistivity. Before rigidly applying Eq. (2) to experimental data, we will look for a parameter, extracted from the resistivity measurements and with no temperature dependence. The electrical resistivity ρ of each sample was then determined, always in the ohmic regime, at temperatures from 300 K to 10 K with a rate of 2 K/min. As we have shown before [19], the temperature dependence of the electrical conduction of carbon black, measured following the same experimental procedure but at lower temperatures, is fitted by a modified 3D hopping equation:

$$\ln\left(\frac{\rho}{\rho_0}\right) = \begin{cases} (T_{ES}/T)^{1/2} & \text{if } T < T_{lim} \\ (T_M/T)^{1/4} + T_1/T & \text{if } T > T_{lim} \end{cases} \tag{3}$$

where T_{ES} and T_M are the usual characteristic temperatures of the Mott and Efros-Shiklovskii's (ES) variable range hopping (VRH) temperatures, and T_{lim} and T_1 are given by (for 3D systems):

$$k_B T_{lim} \approx 0.2\Delta^2/k_B T_{ES} \tag{4}$$

$$T_1 \approx 0.15\Delta/k_B \tag{5}$$

where Δ is the half-width Coulomb gap and k_B is the Boltzmann constant. It is clear from Eq. (3) that, when $T > T_{lim}$ and $T >> T_1$, the usual Mott's regime is recovered. For $T > T_{lim}$ and T_1/T not negligible (compared to the $(T_M/T)^{1/4}$ term), unreliable parameters ρ_0 and T_M would be found if a simple fitting of resistivity data using the Mott's equation is performed. From Ref. [19] we have learned that T_1 and T_M are around 2.5 K and 850 K, respectively, for densities around 0.07 g/cm³. For $d = 0.16$ g/cm³, their values are 1 K and 300 K; and for 0.34 g/cm³, $T_1 \approx 0.6$ K and $T_M \approx 115$ K. The ratio T_1/T is always much smaller than $(T_M/T)^{1/4}$ for all densities, indicating that we can use the simple Mott's VRH equation for temperatures higher than 10 K, the lowest temperature in our experiment. The $T^{-1/4}$ plots are well fitted by straight lines in a large range of temperatures beginning at the lowest ones, as we have shown in Fig. 1(b). But, to be sure of the safe application of the $T^{-1/4}$ equation, we must analyze the ρ_0 extracted from the fits using the Mott's equation:

$$\ln \rho = \ln \rho_0 + (T_M/T)^{1/4} \tag{6}$$

Let us use the rule of thumb for the hopping analysis that we have shown before [19,20]. Considering the resistivity data of a single sample, if the temperature range is good enough, the parameter ρ_0 extracted by the fitting of the high temperature