Critical behavior of the piezoresistive response in RuO$_2$-glass composites.

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Abstract. We re-analyse earlier measurements of resistance $R$ and piezoresistance $K$ in RuO$_2$-based thick-film resistors. The percolating nature of transport in these systems is well accounted by values of the transport exponent $t$ larger than its universal value $t \approx 2.0$. Furthermore, we show that the RuO$_2$ volume fraction dependence of the piezoresistance data fit well with a logarithmically divergence at the percolation threshold. We argue that the universality breakdown and divergent piezoresistive response could be understood in the framework of a tunneling-percolating model proposed a few years ago to apply in carbon-black–polymer composites. We propose a new tunneling-percolating theory based on the segregated microstructure common to many thick-film resistors, and show that this model can in principle describe the observed universality breakdown and the divergent piezoresistance.

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1. Introduction

The term thick-film resistors (TFRs) commonly indicates glass-conductor composites based on RuO$_2$ (or also Bi$_2$Ru$_2$O$_7$, Pb$_2$Ru$_2$O$_6$, and IrO$_2$) grains mixed and fired with glass powders of usually lead borosilicate type. The most successful commercial applications of TFRs exploit their quite large change in bulk resistivity when subjected to applied deformation. Given their low temperature sensitivity and high stability, TFRs are therefore often used in sensor applications like pressure or force sensors [1, 2].

Besides their applications, TFRs are also a quite unique type of metal-insulator composite due to their complex microstructure [3, 4, 5], nonuniversal behavior of transport [3, 4], coexistence of quantum tunneling with percolating behavior [4], marked microscopic elastic heterogeneities [8]. These peculiarities, which to our best knowledge are only partially shared by other compounds, contribute to make the TFRs an interesting playground for basic research on metal-insulator composites.

Concerning their microstructure, TFRs are often in a segregated structure regime in which large regions of glass of about 1$\mu$m in size constraint the much smaller conducting

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grains (from 10 µm to about 300 µm) to be segregated in between the interstices of neighbouring glass grains. In addition, as a result of the firing process, there is strong evidence of diffusion of nanosized particles of metal inside the glass, leading therefore to a modified glassy region around the original metallic grains [9].

The role played by these ultrasmall conducting particles in transport has not yet been elucidated. The observation that the original larger metallic grains are separated by thin glass films of only 1-2 nanometer thickness has suggested direct tunneling as the main mechanism of transport [10]. However, recent electric force microscopy measurements have revealed that the diffused metallic ultrasmall particles can contribute in a substantial way to the electrical connectivity of the conducting regions, suggesting therefore a possible active role in transport of such a modified glass [11, 12].

In spite of their differences, the above scenarios both indicate or are at least consistent with tunneling transport (between adjacent original metallic grains or assisted by the small particles diffused in the glass). Furthermore, the tunneling hypothesis is sustained also by the high values of the piezoresistive response, i.e. the sensitivity of electrical resistance upon applied strain, and the variable-range-hopping like temperature dependence of transport at low temperatures [13].

The above picture, together with the percolating behavior observed as a function of the metallic volume concentration, suggests that TFRs can be regarded as a sort of segregated tunneling-percolation systems: i.e. a non-homogeneous mixture of metal-insulating phases in which tunneling coexists with percolation. A typical homogeneous counterpart is encountered in some carbon-black–polymer composites where the tunneling-percolating behavior takes place within a homogeneous and random arrangement of conducting and insulating phases [14].

Among the different unusual aspects of TFRs, the often observed nonuniversality of transport is certainly one of the most interesting ones, both from the point of view of material science and basic statistical physics. According to the classical theory of transport in percolating systems, the resistance $R$ of a metal-insulator composite with metallic volume concentration $x$ follows a power-law behavior of the form [15, 16]:

$$ R \simeq R_0 (x - x_c)^{-t}, $$

(1)

where $R_0$ is a prefactor, $x_c$ is the percolation critical concentration and $t$ is the transport critical exponent. Random resistors network theories predict that $R_0$ and $x_c$ depend on the microscopic details of the composite, such as the arrangement of the conducting phase within the sample and the elemental resistances connecting two neighbouring sites [15, 16]. Conversely, the value of the transport exponent $t$ is quasi-universal: for percolation on a lattice of resistances with non-pathological distributions, $t$ depends only upon lattice dimensionality $D$ [16]. According to the most recent and accurate calculations, $t \simeq 2.0$ for $D = 3$ [14, 18].

Deviations from universality have been repeatedly reported for various composites [14, 19] and, notably, for RuO$_2$-based TFRs which can display values of $t$ of about $t \simeq 3-4$ [6, 20] or even up to $t \simeq 7.0$ [3]. It is the subject of this paper to investigate
further on the universality breakdown of TFRs and its microscopic origin by re-analysing earlier data on transport and piezoresistance. We show that reported metallic concentration dependences of the piezoresistive response for different RuO$_2$-based TFRs imply tunneling-distance dependence of the exponent $t$. We argue that a possible origin of such universality breakdown stems from tunneling-percolating processes with strong fluctuations in tunneling distances, as previously proposed by Balberg for $D = 3$ homogeneous random arrangements of conducting and insulating phases [21]. Finally, we propose a model of TFRs where segregated structures and fluctuating tunneling distances are treated on the same level.

2. Transport and piezoresistance of RuO$_2$-glass composites

Among the several published experimental results concerning the transport properties of TFRs, many of them report the contemporary measurement of resistance and piezoresistance on commercial samples for which, however, the actual compositions are not known with sufficient accuracy. Since we are interested on the evolution of transport as the conducting concentration is varies in a controlled way, the literature based on commercial TFRs is of little use. However, we have been able to single out two published sets of data of RuO$_2$-based TFRs [20, 22] which, to the best of our knowledge, are the only reports providing both the sheet resistance $R_{\square}$ and the piezoresistance as a function of the RuO$_2$ volume concentration $x$. According to Refs. [20, 22], both sets of measurements have been done for RuO$_2$ powders with different specific surface areas (SA) mixed with borosilicate [20] or high lead silicate [22] glasses, and the final resistors were obtained after standard firing cycles.

In figure (1) we report the sheet resistance $R_{\square}$ data as a function of RuO$_2$ volume

![Figure 1. Sheet resistance $R_{\square}$ as a function of RuO$_2$ volume fraction $x$ for different grain sizes of the metallic powders. Open symbols: Ref. [20]; full symbols: Ref. [22].](image-url)
fraction for different RuO$_2$ grain sizes $\Phi$ as extracted from the SA values [23]. The open symbols refer to the data reported in Ref.[20], while the full symbols to Ref.[22]. All sets of data show a strong increase of $R_\square$ as $x$ decreases, reflecting the vicinity to a percolation threshold where $R_\square$ diverges. The percolating nature of transport in these composites is demonstrated in the log-log plot of figure (2) where all data collapse in a single straight line in accord with the power-law behavior of equation (1). The values of $R_0$, the critical concentration $x_c$ and of the exponent $t$ have been obtained by least-square fits to (1), and are reported in table 1.

There are a few points worth to be discussed. First, as it is clear from the data of Ref.[20] in table 1, the critical concentration $x_c$ decreases as the surface areas SA (or mean grain size $\Phi$) of the RuO$_2$ powders increases (decreases). This trend is also observed in the data of Ref.[22] and it can be understood by realizing that finer RuO$_2$ powders occupy more likely the interstitial regions between neighbouring glass grains. As shown by Refs.[3, 4, 5], this enhanced segregation effect is reflected in a reduction of $x_c$. Note that, however, the SA vs $x_c$ data of Ref.[20] do not merge with those of Ref.[22]. Maybe the different nature of the glass used in these two types of TFRs is at the origin of this discrepancy.

A second important point is that the values of the transport exponent $t$ are well above the universal value $t \simeq 2.0$ of three dimensional lattices. This result confirms other similar findings [3, 6] and clearly indicates breakdown of transport universality in RuO$_2$-based TFRs. It is worth to remind that transport nonuniversality implies that the exponent $t$ acquires a dependence on microscopic details such as local intergrain resistances and microstructure. In this respect, we note that the samples of Refs.[24, 22] display an increase of $t$ with the critical volume fraction $x_c$ as shown in the inset of figure.
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Table 1. Specific surface areas (SA) and corresponding RuO$_2$ grain sizes $\Phi$ for the samples used in Refs. [20, 22]. $R_0$, $x_c$, and $t$ are the values of the parameters of equation (1) extracted by least square fits of the data reported in Refs. [20, 22]. $K_0$ and $B$ values are the corresponding fits of the piezoresistance data to equation (4). The bracketed values are only indicative since they have been obtained by fitting a set of only two points.

| SA [m$^2$/g] | $\Phi$ [nm] | $R_0$ [\$\Omega$] | $x_c$ | $t$ | $K_0$ | $B$ |
|--------------|--------------|---------------------|-------|-----|-------|-----|
| 67$^a$       | 13           | 0.145               | 0.0413| 2.71 ± 0.07 | -13 ± 4 | 3.8 ± 0.7 |
| 13$^a$       | 66           | 0.06                | 0.0592| 2.80 ± 0.01 | -11 ± 3 | 3.8 ± 0.6 |
| 5$^a$        | 172          | 0.0392              | 0.1035| 3.6 ± 0.1   | -5 ± 2  | 3.4 ± 0.5 |
| 60$^b$       | 14           | 0.515               | 0.0151| 2.42 ± 0.03 | (-4.12) | (1.73) |
| 9$^b$        | 96           | 0.597               | 0.0581| 3.4246      | -12 ± 1 | 7.3 ± 0.4 |

$^a$ Ref. [20]  
$^b$ Ref. [22]

We have noticed a qualitatively similar behavior also in the transport measurements of Ref. [24], where $t$ increases from $t = 2.49$ to $t = 5.38$ as $x_c$ is varied from $x_c = 0.0237$ to $x_c = 0.0401$. Whether the increase of $t$ with $x_c$ is a general feature of RuO$_2$-glass compounds is still an open question and further studies are needed to settle this point. However it should be stressed that other ruthenate TFRs (Bi$_2$Ru$_2$O$_7$ and Pb$_2$Ru$_2$O$_6$) display a quite different behaviour, i.e., $t$ remains constant and very close to its universal value (Bi$_2$Ru$_2$O$_7$) or slightly decreases as $x_c$ increases (Pb$_2$Ru$_2$O$_6$) [25].

The authors of Refs. [20, 22] have also measured the RuO$_2$ concentration dependence of the longitudinal piezoresistance coefficient $K_L$ defined as:

$$K_L = \frac{d \ln(R)}{d\varepsilon}.$$  \hspace{1cm} (2)

The above quantity is also often called the (longitudinal) gauge factor and it is obtained by recording the change of the sheet resistance caused by a strain $\varepsilon$ applied along the direction of the external voltage drop. When $\varepsilon$ is orthogonal to the voltage drop, the resistance change gives rise to the transverse gauge factor $K_T$. Both $K_L$ and $K_T$ depend on the geometry of the sample, but they can be expressed in terms of the intrinsic longitudinal and transverse piezoresistive coefficients, $\Gamma_\parallel$ and $\Gamma_\perp$, defined as the logarithmic change of the resistivity under uniaxial strains applied parallel and orthogonal to the voltage drop, respectively [26]. The values of $K_L$ as a function of $x$ are reported in figure (3) for the same samples of figures (1) and (2). Clearly, $K_L$ seems to diverge as $x$ approaches to the same critical volume fraction values for which $R_\Box$, figure (1), goes to infinity. The origin of such a divergence has been previously discussed by the authors of Ref. [20]. Here, we disprove their arguments and propose an alternative interpretation based on the universality breakdown displayed by the data of figure (2) and table [1].

Our arguments go as follows. First, since for all the $x$ values considered the samples are well within the critical region $|x - x_c| \ll 1$, then there is not marked difference
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Figure 3. Values of the longitudinal piezoresistance $K_L$ as a function of RuO$_2$ volume fraction $x$ for different specific areas of the metallic powders. Open symbols: Ref. [20]; full symbols: Ref. [22].

between longitudinal and transverse piezoresistive responses, and the samples can be considered, in a first approximation, as electrically isotropic even if an uniaxial strain has been imposed to evaluate $K_L$. This is due to the tortuosity the current path has in flowing through the sample when $x$ is close to $x_c$. More specifically, the piezoresistive anisotropy factor defined as $\chi = (\Gamma_\parallel - \Gamma_\perp)/\Gamma_\parallel$ goes to zero as $(x - x_c)^\lambda$ with $\lambda \simeq 0.5$ for three dimensional systems [26], so that for $|x - x_c| \ll 1$ and apart from geometric factors, the $x$-dependence of uniaxial strain is basically indistinguishable from that obtained by applying equal strain along all directions. Hence, in the critical region, it is a good approximation to evaluate $K_L$ directly by differentiation of equation (1) with respect to $\varepsilon$, just as done in Ref. [20]:

$$K_L \simeq \frac{d \ln(R_0)}{d \varepsilon} - \frac{d}{d \varepsilon} \left[ t \ln(x - x_c) \right].$$  \hspace{1cm} (3)

The first term is the usual contribution to the piezoresistance and it generally measures the strain sensitivity of the mean junction resistance between two neighboring conducting particles. Since, by construction, this term is independent of the RuO$_2$ concentration, all the $x$ dependence of $K_L$ reported in figure (3) must come from the last term of equation (3). The authors of Ref. [20] have assumed that $t$ and $x_c$ are not strain sensitive, and argued instead that $x$, being a volume concentration, depends on $\varepsilon$. In this way, from equation (3), they obtained a $(x - x_c)^{-1}$ divergence of $K_L$ for $x \to x_c$ which fitted in a satisfactory way their data [open symbols in figure (3)]. There is however a misconception in this reasoning. In fact, in percolation theory, $x$ is actually a measure of the concentration $p$ of (tunneling) intergrain junctions with finite resistances present in the sample. Current can flow from one end to another of the composite as long as a macroscopic cluster of junctions spans the entire sample. Hence the application
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Figure 4. Universal semi-log plot of \((K_1 - K_0)/B\). The straight line is equation (4).

of a strain, which is typically only of order \(\varepsilon \sim 10^{-4}\), can eventually change the value of the junction resistances (affecting therefore \(R_0\)) but cannot modify the concentration \(p\) of junctions \([28]\).

The dependence of \(x\) upon strain claimed in Ref. \([20]\) is therefore erroneous and the \(x\) dependence of \(K_L\) must have a different origin. Since also \(x_c\) is \(\varepsilon\)-independent, the only quantity left which could have a strain dependence is the exponent \(t\). This hypothesis is perfectly in agreement with the universality breakdown demonstrated by the \(t\) data of table \([\text{I}]\). Hence, by allowing a nonzero derivative of \(t\) with respect to \(\varepsilon\) we obtain from equation (3):

\[
K_L \simeq K_0 + B \ln \left( \frac{1}{x - x_c} \right), \tag{4}
\]

where we have defined

\[
K_0 = \frac{d \ln(R_0)}{d \varepsilon}, \quad B = \frac{dt}{d \varepsilon}. \tag{5}
\]

In figure (4) we report the results of fitting the data of figure (3) to equation (4), represented by the straight line. The agreement is fairly good and indicates that the \(K_L\) data are indeed consistent with a logarithmic divergence at \(x \to x_c\). The fitted values of the parameters \(K_0\) and \(B\) are reported in the last two columns of table \([\text{I}]\) where the main feature is that \(B\) is always positive while \(K_0\) is always negative. This latter result is quite interesting. In fact, naively, one expects that if \(R_0\) is a measure of the mean interparticle tunnel junction resistance, then it is a good approximation to set \(R_0 \propto \exp(2a/\xi)\), where \(a\) is the mean tunneling distance and \(\xi \propto 1/\Box V\) is the tunneling factor (or localization length) and \(V\) is the tunneling barrier potential. Under a tensile strain \(\varepsilon\), the mean tunneling distance is enhanced by \(a\varepsilon\), while \(\xi\) remains constant. In this situation therefore \(K_0 \sim 2a/\xi\) is always positive, contrary to the \(K_0\) values of
We shall see in the next section that this apparent contradiction is solved by allowing for sufficiently strong fluctuations in the tunneling distances. In this case in fact the notion of mean tunneling distance $a$ can be meaningless and $K_0$ can assume also negative values.

3. Balberg’s model

In the previous section, the logarithmic divergence of $K_L$ has been obtained by allowing a strain-dependence of the resistance exponent $t$. From a microscopic point of view, this property is equivalent to require that $t$ is a functional of the intergrain tunneling distances $r_{\text{tun}}$ between two neighbouring RuO$_2$ particles. In fact, an applied strain $\varepsilon$ would modify the intergrain distance $r_{\text{tun}}$ to $r_{\text{tun}}(1+\varepsilon)$ leading therefore to a variation of $t$. Actually, a microscopic theory of this kind exists and has been proposed by Balberg a few years ago as a possible mechanism of nonuniversality in carbon-black–polymer composites [21]. Briefly, the theory of Balberg goes as follows. Consider a random resistor network where the interparticle (bond) conductance distribution is given by:

$$\rho(g) = p h(g) + (1 - p) \delta(g),$$  \hspace{1cm} (6)

where $p$ is the fraction of bonds with finite conductance $g$ with distribution $h(g)$. The resistor network is constructed in order to mimic a system constituted by a random arrangement of spherical particles of given diameter $\Phi$ and it is assumed that electrons can tunnel from one particle to its nearest neighbouring particle with a tunneling junction conductance of the form:

$$g = g_0 e^{-2r_{\text{tun}}/\xi},$$  \hspace{1cm} (7)

where $g_0$ is a constant, $\xi$ is the localization length assumed to be smaller than the average interparticle distance $a$, and $r_{\text{tun}} = r - \Phi$ is the distance between the surfaces of two neighbouring spheres whose centers are separated by $r$. Since the particle centers are distributed more or less randomly, the distance $r$ depends on the particular couple of particles considered. Hence to obtain the distribution function $h(g)$ of the tunneling conductances one needs the distribution function $P(r)$ of inter-particles distances. Balberg proposed that the relevant distribution function is of the form:

$$P(r) = \frac{e^{-r/a}}{a},$$  \hspace{1cm} (8)

where $a$ is the mean inter-sphere distance and $a \gg \Phi$. By using

$$h(g) = \int_{\Phi}^{\infty} dr P(r) \delta\left(g - g_0 e^{-2r_{\text{tun}}/\xi}\right),$$  \hspace{1cm} (9)

then the distribution function of tunneling conductances reduces to

$$h(g) = \frac{1 - \alpha}{g_0} \left(\frac{g}{g_0}\right)^{-\alpha},$$  \hspace{1cm} (10)

where

$$\alpha = 1 - \frac{\xi}{2a},$$  \hspace{1cm} (11)
is supposed to vary between $\alpha = 0$ and $\alpha = 1$. As it is well known, distributions of the form of equation (10) lead to nonuniversal behavior of the transport exponent $t$ [29]. In fact, according to renormalization group results and highly disordered resistor networks analysis, the overall resistance close to the percolation threshold is given by equation (1) with [30, 31]:

$$t = \begin{cases} 
  t_0 & \text{if } (d-2)\nu + 1/(1-\alpha) < t_0 \\
  (d-2)\nu + 1/(1-\alpha) & \text{if } (d-2)\nu + 1/(1-\alpha) > t_0
\end{cases}$$

(12)

where $t_0$ is the universal value of the exponent ($t_0 \simeq 2.0$ in three dimensions), $d$ is the dimension of the system, and $\nu$ is the correlation-length exponent ($\nu \simeq 0.88$ in three dimensions). We have therefore arrived at the result that, as soon as $\alpha$ is sufficiently large, the transport exponent depends upon the tunneling distance $a$ and so can be affected by an applied external strain $\varepsilon$. Hence, from equations (1), (3), and (12) it is easily found that the piezoresistance $K_L$ follows equation (4) with

$$B = \frac{dt}{d\varepsilon} = \frac{1}{1-\alpha}.$$  

(13)

Since $\alpha < 1$, the parameter $B$ is always positive, in agreement therefore with the sign of the $B$ values reported in table [1].

The distribution function of equation (10) can also explain the negative values of $K_0$ shown in the last column of table [1] and that, as we have pointed out in the last section, are not expected when ordinary interparticle conductance distributions are considered. In fact, let us consider an effective medium approximation (EMA) to the bond conductance distribution of equations (6) and (10):

$$\int dg \rho(g) \bar{G} - g \bar{G} = 0,$$

(14)

where $G$ is the effective macroscopic conductance [14]. For $|p-p_c| \ll 1$ (where $p_c = 1/3$ in EMA) the integral in equation (14) can be evaluated by setting $x = g/\bar{G}$ with $\bar{G} \ll 1$ [29]. The resulting resistance $\bar{R} = 1/\bar{G}$ is then:

$$\bar{R} \simeq g_0^{-1} \left[ \frac{3\sin(\pi\alpha)}{2^{1-\alpha}\pi(1-\alpha)} \right]^{-1/(1-\alpha)} (p-p_c)^{-1/(1-\alpha)}.$$ 

(15)

from which the EMA piezoresistance $\bar{K}$ reduces to $\bar{K} = \bar{K}_0 + 1/(1-\alpha) \ln(p-p_c)^{-1}$ where:

$$\bar{K}_0 = -\frac{1}{1-\alpha} \ln \left[ \frac{3\sin(\pi\alpha)}{\pi(1-\alpha)} \right] - \left[ \frac{1}{1-\alpha} + \frac{\pi}{\tan(\pi\alpha)} \right].$$

(16)

As shown in figure (3), where the above expression is plotted as a function of $\alpha$, $\bar{K}_0$ is always negative in agreement therefore with the sign of the $K_0$ values extracted by the fits to the experimental data of Refs. [20, 22] (table [1]). The possibility of having $K_0 < 0$ stems from the fact that the distribution function (8) has variance equal to the mean intergrain distance $a$. Hence the resistance prefactor $R_0$ is no longer a measure of the mean intergrain tunnel junction resistance so that the arguments of the last section do not apply.
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Figure 5. $K_0$ in the effective medium approximation [equation (16)] as a function of the tunneling parameter $\alpha = 1 - \xi/2a$.

The above results for $B$ and $K_0$ have been derived by a straightforward derivative of $R$ with respect to the applied strain $\varepsilon$. However, elastic heterogeneities can have important effects. This should be particularly true for RuO$_2$-glass systems where quite stiff metallic particles are embedded in a much softer glass. The main effect of such elastic heterogeneity is that the external applied strain induces highly varying local strains which depend on the relative bulk moduli of the metallic and insulating phases and on the microstructure [8]. We can approximately describe the main effect of elastic heterogeneity by arguing that the tunneling distances are affected by a local strain $\varepsilon_{loc} \simeq A\varepsilon$, where $A$ is a function of the relative bulk moduli of the conducting and insulating phases. In this way, $B$ and $K_0$ of equation (5) reduce to:

$$K_0 = A \frac{d \ln(R_0)}{d\varepsilon_{loc}}, \quad B = A \frac{dt}{d\varepsilon_{loc}}.$$ (17)

Since the local strains are concentrated mainly within the softer (insulating) phase through which the electrons tunnel, then $A$ is expected to be larger than the unity [8]. The elastic heterogeneity has therefore the main effect of amplifying the piezoresistive response by enhancing the absolute values of $B$ and $K_0$, however leaving their signs unchanged.

4. Tunneling and percolation in segregated compounds

In the previous sections we have provided evidences that RuO$_2$-based thick-film resistors have nonuniversal behavior of transport and that their piezoresistance response fits well with a logarithmic divergence about the critical concentration $x_c$. Furthermore, we have shown that such a divergent piezoresistance arises naturally from a specific model of tunneling transport in percolative composites proposed some years ago by Balberg. Although these results are quite encouraging, we are going to see that there are several
open questions regarding Balberg’s theory in general and its applicability to TFRs in particular.

Let us start by considering the interparticle distribution function of equation (8). The reasons which prompted Balberg to use equation (8) are discussed in his original paper [21], where the interested reader can directly refer. However, if we literally consider a three dimensional random arrangement of spheres, then instead of equation (8) the inter-sphere distance distribution function for low volume densities is more correctly given by the Hertz distribution [32]:

\[
P(r) = 3\Gamma(4/3)^3 \frac{r^2}{a^3} e^{-\Gamma(4/3)^3(r/a)^3},
\]

(18)

where \( \Gamma(4/3) \approx 0.893 \). As shown in Ref. [33], the above expression is also the exact distribution function for a random set of fully impenetrable spheres at arbitrary density. For large \( r \), equation (18) falls to zero more rapidly than equation (8), leading to a quite drastic effect on \( h(g) \). In fact, from equations (7), (9) and (18) and again assuming for simplicity \( \Phi \ll a \), the resulting tunneling conductance distribution function reduces to:

\[
h(g) = \frac{3\Gamma(4/3)^3(1-\alpha)^3}{g_0} \ln^2 \left( \frac{g_0}{g} \right) \left( \frac{g}{g_0} \right)^{1-\Gamma(4/3)^3(1-\alpha)^3 \ln^2(g_0/g)}.
\]

(19)

The above expression is plotted in figure 6 for different values of \( \alpha \). Clearly, in contrast to equation (10), \( h(g) \) does not diverges for \( g \to 0 \) but instead it goes to zero at \( g = 0 \). In Ref. [33] very accurate analytical expressions for interparticle distance distribution functions of impenetrable (hard-core) spheres are reported. We checked that \( h(g = 0) = 0 \) also for this case so that such a vanishing limit is a general feature of randomly distributed spheres in three dimensional space. Since transport nonuniversality and the appearance of a tunneling distance dependence of the exponent \( t \) have as necessary condition a divergent \( h(g) \) behavior for \( g \to 0 \), then the distribution

**Figure 6.** Tunneling conductance distribution function of equation (19) resulting from a random arrangement of conducting spheres in three dimensional space.
function of conductances resulting from a random arrangement of (impenetrable or not) spheres is not able to account for nonuniversality and the consequent logarithmic divergence of the piezoresistive response. Such a conclusion is quite at odds with Balberg’s theory and its extension for the piezoresistive problem discussed in the previous section. However there are a couple of points worth to be stressed. First, as shown in figure 6, $h(g)$ has a maximum which shifts at lower values of $g$ and sharpens as $\alpha$ is made larger. Already for $\alpha = 0.6$, the peak of $h(g)$ occurs at $g/g_0 \simeq 0.03 \ll 1$. In this situation, the critical region where the resistance follows equation (1) with universal exponent $t = t_0 \simeq 2.0$ is expected to be considerably narrowed. Hence if $p$ is not very close to $p_c$ the resistance could appear to have the form of equation (1) with an apparent nonuniversal value of $t$.

A second important point concerns the use of interparticle distance distribution functions derived from random arrangements of spheres. In real composites, interactions between conducting and insulating phases and microstructural inhomogeneities can easily make the idealized model of randomly distributed spheres of little use. A remarkable example is provided actually by thick-film resistors where the segregation effect due to the different sizes of glass and RuO$_2$ particles is completely missed by, for example, equation (18). However the segregation effect has interesting consequences on the tunneling distance distributions. Let us consider the microstructure model of TFRs proposed originally by Pike [3] (see also Refs.[4, 5]). In this model, the conducting particles (approximated by spheres of diameter $\Phi$) are arranged in such a way to occupy narrow channels along the edges of large cubes of side $L \gg \Phi$ which represent the glass particles. These channels form a cubic lattice spanning the whole sample and each channels can be occupied or free of conducting spheres. We can imagine the channels to be quasi-one dimensional so that each occupied channel is actually given by a series of adjacent metallic particles separated by the sintered glass. Each channel can contain up to about $L/\Phi$ number of spheres and, for typical TFRs, $L/\Phi$ is roughly between 50 and 500 depending on the relative sizes of the glass and conducting particles. The interesting point here is that equation (8) is the exact interparticle distance distribution function for a one-dimensional random arrangement of penetrable spheres. Hence, $h(g)$ given by equation (10) is the relevant conductance distribution function for the junction conductances inside an occupied channel. The question is now whether the total channel conductance $G$ has a power law diverging distribution as well. If a channel is occupied by $L/\Phi > N \gg 1$ spheres, then the total channel conductance is that given by $N$ junctions in series each with conductance $g_i \ (i = 1, \ldots, N)$:

$$G^{-1} = \sum_{i=1}^{N} \frac{1}{g_i} \simeq g_{\text{min}}^{-1} + \frac{1 - \alpha}{\alpha} (N - 1) g_{\text{min}}^{-\alpha},$$

(20)

where the distribution function (10) has been used and $g_{\text{min}}$ is the minimum interparticle conductance for a row of $N$ particles. In writing equation (20), we have set $g_0 = 1$ and have implicitly assumed that $N$ is large enough to replace the summation with an integral. The quantity $g_{\text{min}}$ (and so $G$) varies from channel to channel and to find its
distribution function $f(g_{\text{min}})$ consider the probability that, in a given channel, $g_{\text{min}}$ is larger than a given arbitrary value $\delta$:

$$\text{Prob}(g_{\text{min}} \geq \delta) = \int_{\delta}^{1} dg_{\text{min}} f(g_{\text{min}}).$$  \hspace{1cm} (21)

The above probability must equal the probability that none of the $N$ junctions within a channel has conductance smaller than $\delta$:

$$\text{Prob}(g_{\text{min}} \geq \delta) = \left[ 1 - \int_{0}^{\delta} dg \ h(g) \right]^N = (1 - \delta^{1-\alpha})^N. $$  \hspace{1cm} (22)

$f(g_{\text{min}})$ is then readily found by equating the right hand sides of equations (21) and (22) and by taking the derivative with respect to $\delta$:

$$f(g_{\text{min}}) = (1 - \alpha)N(1 - g_{\text{min}}^{1-\alpha})^{N-1}g_{\text{min}}^{-\alpha}. $$  \hspace{1cm} (23)

The final distribution function $F(G)$ of channel conductances $G$ is then obtained by combining equation (20) with equation (23). An asymptotic estimate of $F(G)$ for small $G$ can be derived from equation (20) by realizing that for $g_{\text{min}} \ll (1/N)^{1-\alpha}$ the total channel conductance is dominated by the smallest junction conductance: $G \simeq g_{\text{min}}$. Hence in this limit and from equation (23):

$$F(G) \propto G^{-\alpha}, \text{ for } G \ll (1/N)^{1-\alpha}. $$  \hspace{1cm} (24)

The validity of the above limit is demonstrated in figure 7 where we have plotted computer generated values of $F(G)$ for $\alpha = 0.5$ and for different number $N$ of junctions. Clearly, in accord with equation (24), the numerical distribution function diverges as $G^{-\alpha}$ independently of $N$.

The set of channels which form the cubic lattice in our model have therefore conductances $G$ with diverging distribution at small $G$. In this situation therefore,
by following the arguments of the previous section, transport universality breaks down and logarithmically divergent piezoresistive response sets in as long as $\alpha$ is sufficiently large. This interesting result can be made even more stringent by considering the more realistic situation in which the spheres inside the channels are impenetrable. Following Ref. [33], the exact interparticle distance distribution function for this case is:

$$P(r) = \frac{1}{a - \Phi} e^{-(r - \Phi)/(a - \Phi)}, \quad (25)$$

where $r > \Phi$ and, again, $\Phi$ and $a$ ($a > \Phi$) are the diameter of the spheres and the mean interparticle distance, respectively. By using equations (7) and (9) and by following the above analysis, it is straightforward to find that the distribution function $h(g)$ within a channel and the channel conductance distribution $F(G)$ are again given by equations (10) and (24), respectively, where however $\alpha$ of equation (11) is now replaced by:

$$\tilde{\alpha} = 1 - \frac{\xi/2}{a - \Phi}. \quad (26)$$

This result has not required the hypothesis that $r \gg \Phi$, as in the original formulation of Balberg, and has therefore a more general validity. A more complete analysis of our model including Monte Carlo calculations and a generalization to spheres with distributed diameters will be presented elsewhere.

Before concluding this section, it is worth to mention that in modelling the microstructure of TFRs along the lines of Pike [3] we have implicitly considered the metallic particles as more or less the original grains used in fabricating the TFRs. We have therefore not addressed the role of the small metallic clusters of nanometer size which have been shown to occupy the space between two neighbouring RuO$_2$ grains as result of metal-glass interactions [9, 11, 12]. It could be argued that these particles effectively reduce the tunneling potential barrier separating the metallic larger grains, enhancing therefore $\xi$. Further investigations and possible modifications of our model are therefore necessary for a more complete description of transport in TFRs.

5. Conclusions

In summary, we have confirmed that the sheet resistance of RuO$_2$-based thick-film resistors [20, 22] follows equation (1) with transport exponent $t$ larger than the universal value $t \simeq 2.0$ characteristic of three dimensional systems [17, 18]. Furthermore, we have shown that the piezoresistance data taken on the same samples [20, 22] are consistent with a logarithmic divergence close to the percolation threshold. We have argued that such divergence stems from a tunneling-distance dependence of the transport exponent $t$ and an analysis of Balberg’s theory [14, 21] of tunneling-induced universality breakdown seems to qualitatively reproduce some of the experimental findings of Refs. [20, 22]. Furthermore, we have adapted Balberg’s theory, which was originally proposed for homogeneously random arrangements of conducting particles in an insulating host, to the highly segregated structure of TFRs. We have shown that this model naturally gives rise to a diverging conductance distribution function leading to universality breakdown.
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of transport and logarithmically divergent piezoresistive response at the percolation thresold.

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[28] We think it is important to stress this point further. The use of the volume concentration variable \( x \) in equation (1) is very practical, but in principle other kinds of variables could equally be used like for example the RuO$_2$ mass fraction \( y = M_{\text{RuO}_2}/(M_{\text{RuO}_2} + M_{\text{glass}}) \), where \( M_{\text{RuO}_2} \) and \( M_{\text{glass}} \) are the weights of RuO$_2$ and glass forming the composite, respectively. In terms of \( y \), equation (1) becomes \( R = \tilde{R}_0(y - y_c)^{-t} \) where \( y_c \) is a critical mass fraction and \( \tilde{R}_0 \) is a new prefactor independent of \( y \). This alternative form of \( R \) is not very practical, but has the...
advantage of clearly show that the factor $y - y_c$ is, by definition, independent of volume so that 
$d(y - y_c)/d\varepsilon = 0$ and no $(y - y_c)^{-1}$ divergence of $K_L$ can be obtained.

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