

Anomalous Power Law Dispersions in ac Conductivity and Permittivity Shown to be Characteristics of Microstructural Electrical Networks

D. P. Almond and C. R. Bowen

*Materials Research Centre, Department of Engineering and Applied Science, University of Bath,
Claverton Down, Bath, BA2 7AY, United Kingdom*

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The frequency dependent ac conductivity and permittivity of porous lead zirconate titanate ceramic with the pore volume filled with water are shown to match the simulated electrical response of a large network of randomly positioned resistors and capacitors. Anomalous power law dispersions in conductivity and permittivity are shown to be an electrical response characteristic of the microstructural network formed by the porous lead zirconate titanate pore structure. The anomalous power law dispersions of a wide range of materials are also suggested to be microstructural network characteristics.

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The anomalous fractional power law dependence on the frequency of the ac conductivity and permittivity, found in a very wide range of materials, remains a topic of intense experimental and theoretical interest. The experimental evidence and reasons advanced to explain the phenomena have been the subject of a number of recent reviews [1–3]. The theoretical interpretations can be divided broadly into three categories: relaxation time distribution analysis, many-body effects on relaxation processes, and electrical network analysis. A particularly important characteristic of the phenomena is its near “universality” [1–5]. Identical anomalous power law dispersions are widely observed in all classes of material: single crystals, polymers, glasses, technical ceramics, conducting polymer composites, and even concrete. In addition, the phenomena are common to both ion and electron conducting materials. In our opinion, it is essential to account for this ubiquity. For this reason we have been investigating the effects of microstructural heterogeneity on the measured bulk electrical characteristics of materials. A complex microstructure, which forms an equally complex network of conduction paths, is a feature common to many classes of material. In a recent series of publications [6–8], we have demonstrated that large networks of randomly positioned resistors and capacitors exhibit electrical characteristics that are identical with the universal anomalous characteristics under discussion here. The suggested implication is that, at a microstructural level, many materials behave as a network of conducting and capacitive regions and that it is the electrical response of this complex network that is obtained from bulk electrical measurements. The important corollary is that, at a microscopic level within the material, conduction processes are perfectly conventional. There is no need to introduce any “new physics,” in the form of novel many-body relaxation processes, to explain the widely observed fractional power law dispersions as these are characteristics of the microstructural network across

which the measurements have been made. It has been suggested [8] that the power law dispersions are “emergent” phenomena characteristic of any system that is effectively a complex random network of resistors and capacitors. The purpose of this Letter is to present an experimental examination of this network approach by comparing the measured electrical properties of a carefully selected and characterized real material system with those predicted for a random RC network.

The electrical response [7] of a typical network of randomly positioned resistors and capacitors is shown in Fig. 1. The network was a square 512 component lattice in which 60% of the components were 1 k Ω resistors and the remaining 40% were 1 nF capacitors. Essentially, identical responses have been obtained for much larger (up to 32 768 component) networks [8]. The low frequency plateau in network conductivity, Fig. 1(a), corresponds to the one or more randomly configured percolation paths of resistors across the network, and this is found to have great variability for different random networks [8]. At

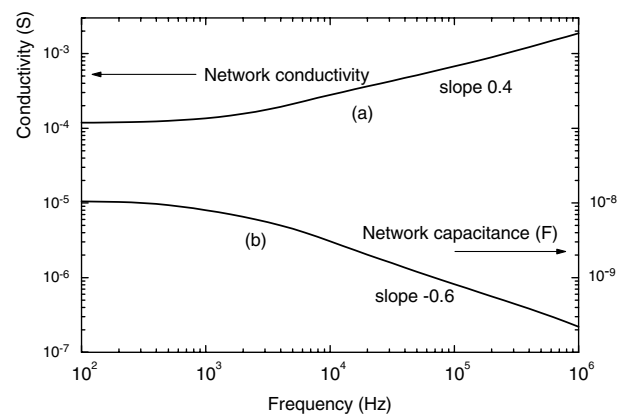


FIG. 1. Simulations of (a) conductivity and (b) capacitance of a 2D square network containing 512 randomly positioned components, 60% 1 k Ω resistors and 40% 1 nF capacitors.

higher frequencies, the ac conductivity rises and the network capacitance, Fig. 1(b), falls as fractional powers of frequency. These effects occur at frequencies where the admittance magnitudes of the capacitors, ωC , become comparable to those of the resistors, R^{-1} (ω is angular frequency $2\pi f$). At these frequencies, ac currents flow across the network via a complex set of paths with all components contributing to the network conductivity. This contrasts sharply with the low frequency region where the capacitor admittances are very small, making them effective insulators and leaving the percolation paths of the resistors alone to determine network response.

At the higher frequencies, the full network of resistors and capacitors, randomly connected in series and parallel, produces the power law dispersions in electrical response. It has been suggested [9,10] that a logarithmic mixing rule [11] should account for the characteristics of such complex arrangements of components. Specifically, if a fraction α of the components are capacitors, then the network complex conductivity σ^* and complex capacitance C^* are given by

$$\sigma^* = (i\omega C)^\alpha (R^{-1})^{1-\alpha} \quad (1)$$

$$C^* = \sigma^*/i\omega. \quad (2)$$

The circuit simulation results, Fig. 1, are found to be in close agreement with these expressions at higher frequencies. The power laws exponent for the conductivity equals 0.4, for the fraction of the network filled with capacitors, and the magnitude of the conductivity is in good agreement with Eq. (1). Similarly, the power law decrease in network capacitance has an exponent of -0.6 , matching the resistor fraction. Although these results were obtained in the simulation of a 2D network, arguments [6,10,11] for the applicability of the logarithmic mixing rule are not confined to 2D and would suggest that similar results would be found in 3D networks.

Many of the materials in which the anomalous power law dispersions have been observed are effectively electrical two-phase systems, comprising a conducting phase within an insulating/dielectric host. A good example is Na β alumina in which the conducting sodium ions are found in conducting channels sandwiched between insulating alumina blocks. Another is a conducting polymer in which electrically conducting graphite flakes are distributed throughout an insulating polymer matrix. If such systems are to be modeled as large networks of conductive and capacitive islands, the measurable bulk conductivity and relative permittivity predicted by the logarithmic mixing rule are [6,7,10,11]

$$\sigma_{\text{meas}} = (\omega \varepsilon \varepsilon_0)^\alpha (\sigma)^\alpha \cos(\alpha\pi/2) \quad (3)$$

$$\varepsilon_{\text{meas}} = (\omega \varepsilon_0)^{\alpha-1} \varepsilon^\alpha \sigma^{1-\alpha} \sin(\alpha\pi/2), \quad (4)$$

where σ and ε are the conductivity and relative permittivity

of the conducting and dielectric/insulating phases, ε_0 is the permittivity of free space, and α is the fractional volume of the material occupied by the dielectric phase.

An experimental test of the validity of the random RC network explanation of the power laws necessitates, first, a material with a microstructure that is a network of interconnected conductive and dielectric phases; second, these phases must be well characterised and frequency independent; and third, the power law dispersions must occur in the frequency range within which they are commonly observed, i.e., at frequencies below ~ 10 MHz. This third requirement is a particularly significant factor in the selection of the conductive phase. It was noted above that the network power law dispersions occur where the magnitudes of the admittances of the two phases are similar. In materials this amounts to requiring $\sigma \sim \varepsilon \varepsilon_0 \omega$, if the two phases occupy regions of roughly similar shape and volume. Since relative permittivities of dielectrics fall in the comparatively small range ~ 2 to ~ 3000 , the conducting phase conductivity must be $\lesssim 10^{-1}$ S/m, excluding metallic materials.

The two materials selected to form a test system were the ferroelectric ceramic lead zirconate titanate (PZT) as the dielectric phase and water as the conductive phase. PZT powder was sintered to form a low density porous pellet which was infused with tap water. The measured relative permittivity of the PZT pellet, prior to the introduction of the water, is shown in Fig. 2(a). The pellet had a diameter of 10.5 mm, a thickness of 3 mm, and a density 78% of the theoretical density of PZT. Silver paste electrodes were applied to the two circular faces, and measurements were made using a Solatron 1260 impedance analyzer with a Solatron 1296 dielectric interface. The measured relative permittivity is featureless across the frequency range shown, but has a magnitude that is lower than that, 1500, for fully dense bulk material. The

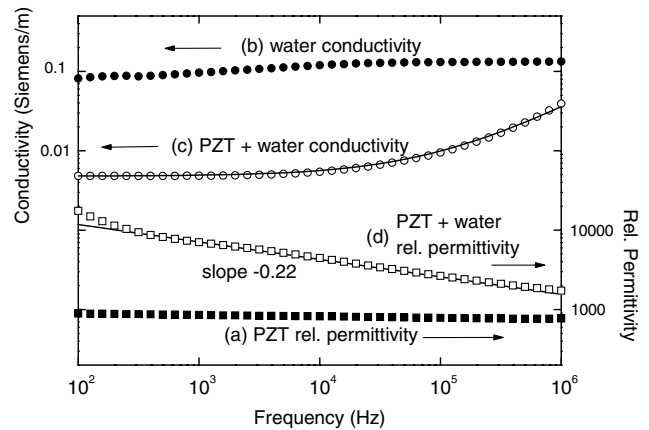


FIG. 2. Measurements of (a) relative permittivity of a porous PZT sample, (b) conductivity of water at equilibrium with immersed PZT fragments (see text), (c) the conductivity, and (d) the relative permittivity of the sample saturated with water.

frequency dependence of the conductivity of the water is shown in Fig. 2(b). PZT ceramic pieces were immersed in the water sample for several days prior to the measurements to ensure that a good indication of the conductivity of water within the pores of the ceramic was obtained. It was found that the ceramic pieces raised the water conductivity by a factor of ~ 5 , presumably by the dissolution of ionic impurity compounds on the ceramic surfaces. The fall in conductivity at low frequencies is an electrode polarization effect that is commonly observed in ac measurements of all types of ionic conductor.

The ac conductivity and relative permittivity of the porous PZT sample saturated with water are shown in Figs. 2(c) and 2(d). The ac conductivity shows a high frequency dispersion that is qualitatively similar to that observed in numerous materials. The relative permittivity is raised above the magnitude measured in the dry sample, and it exhibits a clear power law decrease with frequency. Both of these characteristics are consistent with the random RC network results shown in Fig. 1. The power law exponent for the decrease in relative permittivity with frequency is seen in Eq. (4) to be $-(1 - \alpha)$. Sample density measurements indicated α to be 0.78. Hence the slope of data in Fig. 2(d) is predicted to be -0.22 . The line drawn in Fig. 2(d) is the relative permittivity obtained from Eq. (4), setting $\alpha = 0.78$, using the bulk PZT relative permittivity, ϵ , of 1500 and a water conductivity of 0.13 S/m, indicated by the measurements shown in Fig. 2(b). The overall agreement with the data is excellent. The same properties were used in Eq. (3) to calculate the frequency dependent component of the ac conductivity. This was added to the percolation plateau value (0.0048 S/m) to generate the curve shown in Fig. 2(c). Again, the overall agreement with the data is excellent. The addition of the two components follows the practice widely employed to fit experimental data [1–3]. The simulations indicate this to be an overestimation as the percolation conductivity must decline at high frequencies as the power law term takes over the conduction process. However, they also indicate this to be a good approximation where, as here, the power law exponent is large ($\alpha = 0.78$). Measurements of a second sample with a porosity of 15% were found to be in simi-

lar excellent agreement with the predictions of Eqs. (3) and (4).

While we have established a case for the microstructural network explanation of electrical response employing the water-PZT system, there remains the need to investigate the broader application of this model. A useful indicator that the network model is plausible is that the frequency range over which the power law dispersions occur matches the frequency range over which the admittance of a capacitive phase becomes similar to that of a conductive phase. A difficulty in making this assessment is that, in general, the actual conductivity of the conducting phase within a solid is unknown. What is known is the low frequency plateau in conductivity, which is often considered to be the dc conductivity of the material $\sigma(0)$. Here we have presented a case in which we have been able to make an independent measurement of the conducting phase (water) conductivity. Our data show the percolation conductivity of this water through the PZT pore system to be a factor ~ 20 smaller than that of the water in the pores. We suggest that this factor is used to gain an order of magnitude estimate of actual conductivity in other systems, i.e., in the equations above set $\sigma = 20\sigma(0)$. It can be seen from Eq. (3) that $\sigma_{\text{meas}} = \cos(\alpha\pi/2)\sigma$ at the critical frequency at which the admittances of the two phases are equal. As the measured conductivity power law exponent, α , for many materials is found to lie in the range 0.6–0.8, $\cos(\alpha\pi/2) \sim 0.5$, and $\sigma_{\text{meas}} \sim 0.5\sigma \sim 10\sigma(0)$ at the critical frequency. This frequency can be readily obtained from data and then compared with the value calculated by setting $\omega\epsilon\epsilon_0 = \sigma$, i.e., $f = 20\sigma(0)/2\pi\epsilon\epsilon_0$. This introduces the host relative permittivity ϵ , a quantity that is usually available from independent measurements. Values of the measured and calculated frequencies, obtained from the published data of a wide variety of conductors, are listed in Table I and shown plotted against each other in Fig. 3. Note, this includes single crystal Na β -alumina data in which the disorder is in the Na^+ distribution. While exact matches are not expected, the overall correlation between the two frequencies is very strong. We have found no reported conductivity power law dispersion that cannot be attributed to

TABLE I. Data used to generate the comparison of critical experimental and theoretical frequencies shown in Fig. 3.

	$\sigma(0)$ (S/m)	$f[10\sigma(0)]$ (exp) Hz	ϵ	$20\sigma(0)/2\pi\epsilon\epsilon_0$ (theor) Hz
Water-PZT system (this work)	4.8×10^{-3}	1.2×10^6	1500	1.16×10^6
Na β alumina [(113 K) Ref. [12]]	2.5×10^{-5}	4×10^5	22	4×10^5
$\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass (Ref. [13])	4×10^{-8}	3×10^3	2	7.2×10^3
$\text{LiCl} \cdot \text{H}_2\text{O}$ [(−114 °C) Ref. [14]]	1×10^{-5}	6×10^5	4	9×10^5
12 mol% Y zirconia				
100 °C	2×10^{-10}	8	22	3.2
60 °C (Ref. [6])	5×10^{-12}	0.2	22	0.08
Carbon black in thermoset resin (Ref. [15])	2.5×10^{-2}	3×10^9	3.5	2.6×10^9

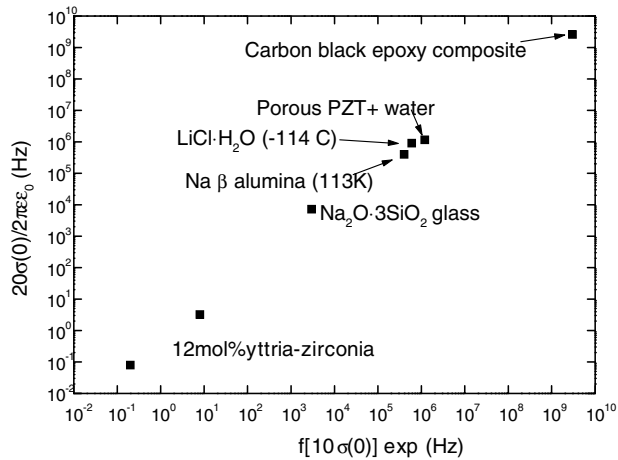


FIG. 3. Critical frequency at which conducting and insulating phases have the same admittance magnitude obtained from electrical properties compared with the frequency indicated by experimental ac conductivity versus frequency data. See TABLE I for data references.

a microstructural network when making use of the above assessment.

This work has shown that the electrical characteristics of a real material with a heterogeneous microstructure are accurately described by the logarithmic mixing rule. It is concluded that the fractional power law dispersions found are natural characteristics of the large random RC network formed by the microstructure. Their appearance in the electrical response does not indicate anything unconventional about the fundamental conduction or dielectric processes within the material. Such characteristics are, effectively, the electrical response of the “filter” formed by the microstructural network of capacitive and conductive phases. It is suggested that it is very

likely that the power law dispersions found in the electrical response of other materials can be satisfactorily explained in the same way. Microstructural heterogeneity is very common in materials, and it is possible that other unexplained anomalous characteristics may be accounted for in a similar fashion.

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