

Scaling and universality of ac conductivity and dielectric response in disordered materials under pressure

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Scaling of physical quantities describing the ac response is a common feature of disordered matter, while in some cases, empirical functions have been proposed. The exact forms of analytic functions that scale complex conductivity and permittivity are derived in this work by exploring the effect of pressure at various temperatures on the ac conductivity of polypyrrole. The scaling behavior is visualized within the frame of percolation and self-similarity. © 2010 American Institute of Physics. [doi:10.1063/1.3466904]

Scaling and universality of ac conductivity and dielectric response of numerous different solids with disorder as their only common feature, are substantial concepts which indicate a common underlying physical characteristics of electric charge flow in disordered matter to materials which are in other respects miscellaneous. Important phenomena in nature are related with scaling behavior of quantities (e.g., see Refs. 1 and 2). It is commonly accepted that percolation is what causes and regulates the occurrence of ac universality and hence scaling.³⁻⁵

In this paper we pose the question about the effect of pressure on a percolating system, namely, whether a change in scale influences a percolation governed material, i.e., changes in size and mass of the percolating cluster or of the isolated “islands,” of the links between them, of the correlation length ξ and consequently of the ac response of the system. Is it possible, ac conduction and dielectric response to reveal a hidden characteristic which allows scaling to occur varying the pressure? It is worth noticing that although we study conducting polypyrrole as a representative member of disordered solids for the experiment, the emerged results appertain and reproduce the scaling behavior of several amorphous materials.

One of the most important properties of ac conductivity is that frequency dependent conductivity $\sigma(\omega)$ at different temperatures T can be scaled into one master curve, the shape of which is almost the same for all disordered solids. This master curve can be represented by

$$\tilde{\sigma} \equiv \frac{\sigma(\omega)}{\sigma(0)} = F \left[C \frac{\omega}{\sigma(0)} \right], \quad (1)$$

where $\sigma(0)$ is the dc conductivity and C is the scaling constant that depends on the temperature and the charge carrier concentration. From this, one can derive (Barton–Nakajima–Namikawa) (BNN) relation⁶⁻⁸

$$\sigma(0) = p \Delta \varepsilon \varepsilon_0 \omega_m, \quad (2)$$

which associates the dc conductivity σ_0 with the dielectric loss peak frequency ω_m . The intensity of the relaxation is $\Delta \varepsilon = \varepsilon(0) - \varepsilon_\infty$, with ε_0 is the permittivity of free space and ε_∞ is the high frequency permittivity, while p is a numerical

constant of order of unity. Later Summerfield⁹ assuming substantially that $\Delta \varepsilon$ follows a Curie law proposed

$$\frac{\sigma(\omega)}{\sigma(0)} = F \left[\frac{A \omega}{T \sigma(0)} \right], \quad (3)$$

as the scaling law with, A , a parameter depending on charge carrier concentration. A more general scaling was proposed by Sidebottom¹⁰

$$\frac{\sigma(\omega)}{\sigma(0)} = F \left[\frac{\omega \varepsilon_0 \Delta \varepsilon}{\sigma(0)} \right], \quad (4)$$

the validity of which was proved later by Schroder and Dyre.¹¹

A widely applied empirical function^{4,12,13} which approximates well the scaling behavior of ac conductivity is^{14,15}

$$\sigma(\omega) = \sigma(0) \left[1 + \left(\frac{f}{f_0} \right)^n \right], \quad (5)$$

where f_0 is a characteristic frequency. When Almond and West¹⁶ suggested the above formula in order to describe a crystal with defects and an activated number of charge carriers, they used during the procedure for deriving Eq. (5) as a trial¹⁷ equation the

$$\lim_{T \rightarrow \infty} \left[\frac{\sigma(0)}{A} \right] = \omega_e^n, \quad (6)$$

where A is given by the frequency dependent part of the real part of conductivity $\sigma_{ac} = A \omega^n$ and ω_e is an effective attempt frequency.

As it will become obvious later on, Eq. (3) is not just a suitable equation which serves as an intermediate mathematical manipulation necessary to lead us to a good fitting equation in order to scale ac conductivity but also an experimental fact without temperature restrictions which involves physical causality and has further consequences.

Another physical quantity closely related to conductivity is (relative) permittivity ε . Scaling of ac permittivity was suggested and verified for ion-conducting glasses¹⁸

$$\frac{\varepsilon' - \varepsilon'_\infty}{\Delta \varepsilon} = G_1 \left(\frac{\varepsilon_0 \Delta \varepsilon}{\sigma_0} f \right), \quad (7)$$

and conducting polymers¹⁹

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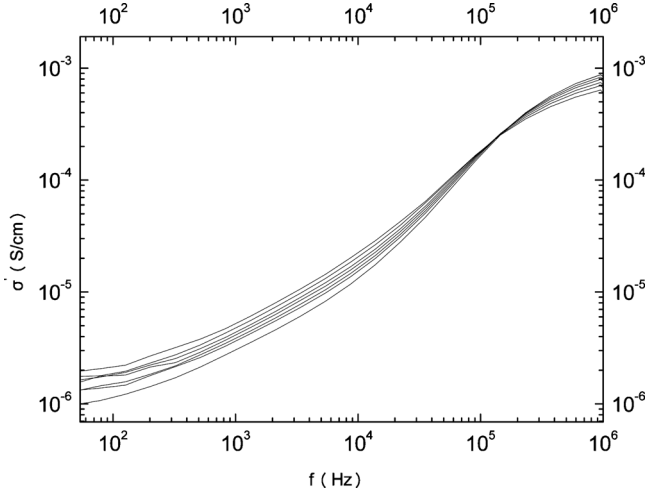


FIG. 1. The real part of ac conductivity vs frequency for different pressures at 303 K. From bottom to top: ambient pressure, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 GPa.

$$\frac{\varepsilon' - \varepsilon_\infty'}{\Delta\varepsilon} = G_1 \left(\frac{\omega}{\omega_0} \right), \quad (8)$$

$$\frac{\varepsilon_d''}{\Delta\varepsilon} = G_2 \left(\frac{\omega}{\omega_0} \right), \quad (9)$$

where ω_0 is a characteristic frequency proportional to a hopping critical rate and ε_d'' the imaginary part of permittivity after deducing the conductivity contribution.

Experimental. Details about the sample preparation of semiconducting polypyrrole were reported in a previous publication.²⁰ Ac conductivity measurements were performed from 10^{-2} Hz to 10 MHz by employing a Solartron SI 1260 frequency response analyzer. Isobaric conditions to 0.35 GPa were achieved in a fluid transmitting pressure vessel, which was immersed in a heat bath maintaining isothermal conditions. Controlled and standard measurements were performed to exclude the possibility of any parasitic resonance type signals arising from cabling. Here, we performed isobaric measurements up to 0.35 GPa for three temperatures, 303, 318, and 328 K.

Results. In Fig. 1 plots of the real part of the conductivity as a function of frequency, at different pressures are depicted. We will focus on a particularly interesting characteristic that spring from the measurements regardless of the variation in temperature. (We have detected the same characteristic in plots of ion conducting compounds too).²¹ The ac conductivity has the same value, i.e., is pressure independent, at a particular frequency $\omega_c(T)$ near the dielectric loss peak frequency ω_m , thus we have

$$\left. \frac{\partial(A\omega^n)}{\partial P} \right|_{\omega=\omega_c} = 0, \quad (10)$$

whose solution is

$$\log A = -n \log \omega_c + \log c, \quad (11)$$

and setting this to

$$\sigma_{ac} = A\omega^n, \quad (12)$$

we get

$$\sigma_{ac} = \left(\frac{\omega}{\omega_c} \right)^n c. \quad (13)$$

As ω approaches ω_0 , σ_{ac} converges to $\lambda\sigma_0$ hence we get

$$\log A = -n \log \omega_0 + \log \lambda\sigma_0 \quad \text{or} \quad \frac{\lambda\sigma_0}{A} = \omega_0^n, \quad (14)$$

where, from now on, we label ω_0 is the crossover frequency separating the low-frequency dc region from the high-frequency dispersive one. The constant λ can be calculated either from relative experiments or from best-fit curves at different temperatures and it is expected to take values around 2.

Applying this condition, Eq. (13) takes the form of

$$\sigma_{ac} = \lambda\sigma_0 * (\omega/\omega_0)^n, \quad (15)$$

subsequently the conductivity for the entire frequency domain (i.e., including both the low frequency region and the high frequency one since for $f < f_0$, $1 + \lambda(f/f_0)^n \rightarrow 1$)

$$\sigma' = \sigma_{dc} + \sigma_{ac} = \sigma_0 \left[1 + \lambda \left(\frac{f}{f_0} \right)^n \right]. \quad (16)$$

Using BNN equation [Eq. (2)], Eqs. (15) and (16) can be rewritten as

$$\sigma_{ac}/\sigma_0 = (\omega\Delta\varepsilon/\sigma_0)^n \lambda (p\varepsilon_0\omega_m/\omega_0)^n, \quad (17)$$

and

$$\sigma'/\sigma_0 = 1 + (\omega\Delta\varepsilon/\sigma_0)^n \lambda (p\varepsilon_0\omega_m/\omega_0)^n, \quad (18)$$

respectively.

It is apparent that ω_m has the same temperature dependence as ω_0 , which is in accordance with the experimental results. Thus ω_0 is close (or identical) to the characteristic frequency proportional to the critical hopping rate.¹⁹

A potential difference between Eqs. (15) and (16) with Eqs. (17) and (18), respectively, is that the latter couple of relations require that BNN relation applies to the material under consideration. Nevertheless this is not always the case,^{21,22} deviations from BNN have been observed in some amorphous materials. This fact explains why experimental data fail to collapse into a single curve when plotting according to Eq. (4) [or to Eq. (17)] and are better represented by Eq. (5) [or to Eq. (16)].

Furthermore, if we insert Eq. (15) into

$$\varepsilon_d'' = \frac{\sigma_{ac} - \sigma_0}{\varepsilon_0\omega}, \quad (19)$$

and divide by $\Delta\varepsilon$ we obtain an expression for the imaginary part of permittivity in the dispersion high-frequency region

$$\frac{\varepsilon_d''}{\Delta\varepsilon} = \frac{p\omega_m}{\omega_0} \left[\lambda \left(\frac{\omega}{\omega_0} \right)^n - 1 \right] \left(\frac{\omega}{\omega_0} \right)^{-1}. \quad (20)$$

The shape of Eq. (20) is compatible with the experimentally observed scaling¹⁹ for ac permittivity (Fig. 2).

Moreover, applying Kramers–Kronig transformation we get

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{A}{\varepsilon_0} \tan(n\pi/2) \omega^{n-1}. \quad (21)$$

The above relation on the one hand and combined with the general relation $\varepsilon' - \varepsilon_\infty = \sigma''/\varepsilon_0\omega$ on the other, yields the real

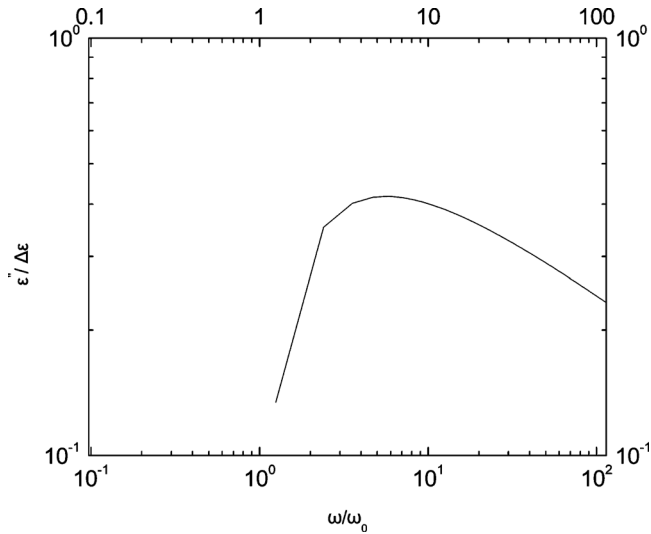


FIG. 2. $\epsilon''/\Delta\epsilon$ is plotted as a function of ω/ω_0 according to Eq. (20). The curve is qualitatively compatible with the experimentally observed scaling (Ref. 19) for ac permittivity.

part of permittivity and the imaginary part of conductivity, scale according to

$$\frac{\epsilon' - \epsilon_\infty}{\Delta\epsilon} = \lambda p \frac{\omega_m}{\omega_0} \left(\frac{\omega}{\omega_0} \right)^{n-1} \tan(n\pi/2), \quad (22)$$

and

$$\frac{\sigma_{ac}''}{\sigma_0} = \left(\frac{\omega\Delta\epsilon}{\sigma_0} \right)^n \lambda \left(\frac{p\epsilon_0\omega_m}{\omega_0} \right)^n \tan(n\pi/2), \quad (23)$$

respectively.

In conclusion, we derived experimentally a condition which led us to scale ac conduction and dielectric response according to the observed scaling relations (verifying scaling functions reported in the literature). At the same time we proposed scaling functions for the other related physical quantities. Attempting to interpret the effect of pressure to a percolating medium, we employ the concept of self-similarity.²³ This is very likely to be so since percolation is a critical phenomenon and criticality is always associated with self-similarity (e.g., see Refs. 24–26). The disordered solid is likely to maintain its self-similarity under the effect

of pressure which acts as a renormalization process. Hence, a system very close to the percolation threshold (in proportion to ω_0) with its individual parts interacting coherently, will remain the “same” on a smaller scale (increased pressure) since the corresponding correlation length will become accordingly smaller [within a specific range of frequencies, near $\omega_c(T)$].

¹P. A. Varotsos, *The Physics of the Seismic Electric Signals* (Terrapub, Tokyo, 2005).

²J. Dyre, *Rev. Mod. Phys.* **78**, 953 (2006).

³J. C. Dyre and T. B. Schröder, *Rev. Mod. Phys.* **72**, 873 (2000).

⁴D. L. Sidebottom, *Rev. Mod. Phys.* **81**, 999 (2009).

⁵J. C. Dyre, P. Maass, B. Rolling, and D. L. Sidebottom, *Rep. Prog. Phys.* **72**, 046501 (2009).

⁶J. L. Barton, *Verres et Refract.* **20**, 328 (1966).

⁷T. Nakajima, *Proceedings of the Annual Report Conference on Electric Insulation and Dielectric Phenomena* (National Academy of Sciences, Washington, DC, 1972), p. 168.

⁸H. Namikawa, *J. Non-Cryst. Solids* **18**, 173 (1975).

⁹S. Summerfield, *Philos. Mag. B* **52**, 9 (1985).

¹⁰D. L. Sidebottom, *Phys. Rev. Lett.* **82**, 3653 (1999).

¹¹T. B. Schröder and J. C. Dyre, *Phys. Rev. Lett.* **84**, 310 (2000).

¹²A. K. Jonscher, *Nature (London)* **267**, 673 (1977).

¹³A. K., Jonscher, *Universal Relaxation Law* (Chelsea Dielectrics, London, 1996).

¹⁴P. Dutta, S. Biswas, and S. K. De, *J. Phys.: Condens. Matter* **13**, 9187 (2001).

¹⁵J. Planès, A. Wolter, Y. Cheguettine, A. Pron, F. Genoud, and M. Nechtschein, *Phys. Rev. B* **58**, 7774 (1998).

¹⁶D. P. Almond and A. R. West, *Solid State Ionics* **9–10**, 277 (1983).

¹⁷D. P. Almond, A. R. West, and R. J. Grant, *Solid State Commun.* **44**, 1277 (1982).

¹⁸D. L. Sidebottom and J. Zhang, *Phys. Rev. B* **62**, 5503 (2000).

¹⁹S. Capaccioli, M. Lucchesi, P. A. Rolla, and G. Ruggeri, *J. Phys.: Condens. Matter* **10**, 5595 (1998).

²⁰A. N. Papathanassiou, J. Grammatikakis, I. Sakellis, S. Sakkopoulos, E. Vitoratos, and E. Dalas, *Appl. Phys. Lett.* **87**, 154107 (2005).

²¹G. D. Mukherjee, S. N. Achary, A. K. Tyagi, and S. N. Vaidya, *J. Phys. Chem. Solids* **64**, 611 (2003).

²²A. N. Papathanassiou, J. Grammatikakis, I. Sakellis, S. Sakkopoulos, E. Vitoratos, and E. Dalas, *J. Appl. Phys.* **96**, 3883 (2004).

²³D. Stauffer and A. Aharony, *Introduction to Percolation Theory*, 2nd ed. (Taylor and Francis, London, 1992).

²⁴P. A. Varotsos, N. V. Sarlis, E. S. Skordas, H. K. Tanaka, and M. S. Lazaridou, *Phys. Rev. E* **74**, 021123 (2006).

²⁵P. A. Varotsos, N. V. Sarlis, and E. S. Skordas, *Chaos* **19**, 023114 (2009).

²⁶N. V. Sarlis, E. S. Skordas, and P. A. Varotsos, *Phys. Rev. E* **80**, 022102 (2009).