

Dimensionality Dependence of the Conductivity Dispersion in Ionic Materials

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The dielectric response of many materials exhibits universal behavior in the form of a power law frequency dependence of the ac conductivity. This response is seen in all types of structures both crystalline and amorphous and for all types of polarizing species including dipoles and ions. Here I demonstrate that for ionic materials the power law exponent decreases with decreasing dimensionality of the ion conduction pathways. Although percolation concepts such as random walks on a self-similar fractal lattice provide a qualitative explanation, experimental findings instead indicate that the dispersion is the result of localized ion motion occurring on an atomic length scale.

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In 1977, Jonscher [1] published a compilation of dielectric studies to demonstrate how a wide variety of materials (single crystal, polycrystalline, glassy) involving all types of polarizing entities (dipoles, hopping electrons, ions) quite commonly exhibit a power law dispersion of the ac conductivity of the form $\sigma(f) \approx f^n$, or equivalently of the susceptibility $\chi(f) \approx f^{n-1}$, at frequencies above the characteristic relaxation rate. In addition to the rather narrow range ($0.5 < n < 1$) reported by Jonscher for the exponent, it is also remarkable that, when plotted together, most of the $\sigma(f)$ data, encompassing some ten decades in frequency, generally fell within a range bounded below by $\sigma(f) \approx 10^{-12}f$ and above by $\sigma(f) = 10^{-10}f$ (in Ω^{-1}/m). The source of this “universal dynamic response” remains something of a mystery, although many conceptual pictures [2–7] have developed.

In the case of ionic materials, long range diffusion of ions results in a frequency independent (d.c.) contribution to the conductivity in addition to the power law response, and the overall frequency dependence is well approximated by $\sigma_1(f) = \sigma_0[1 + (f/f_0)^n]$. With decreasing temperature, both the dc conduction (σ_0) as well as the power law contribution decrease with the result that $\sigma(f)$ at different temperatures can be scaled so as to collapse to a single curve [8]. While the exponent n remains temperature independent over a range of high temperatures, it appears to increase at lower temperatures to a value of approximately unity well before zero degrees kelvin is reached [9,10]. Since Jonscher’s study, many have recognized that this temperature dependence is in reality the result of a superposition of two polarizing processes [10,11]: the first due to ionic motion [$\sigma_1(f)$] which is sensitive to temperature changes, and the second [$\sigma_{II}(f) \approx Af$] that exhibits a nearly linear frequency dependence and only a weak temperature dependence. Evidence [10] suggests that this latter process is distinct from the motion of ions giving rise to $\sigma_1(f)$, and while its origins are yet unclear, some believe that it may be the result of low energy distortions occurring in the lat-

tice [3,10]. In addition to its weak temperature dependence, $\sigma_{II}(f)$ displays its own “universal” behavior [9] in that values of A are often about $10^{-12} \text{ sec}/\Omega \text{ m}$ (to within a decade) [12]. Thus, as Jonscher observed, $\sigma(f)$ data are typically bounded below by $\sigma(f) = 10^{-12}f$.

In Jonscher’s original study, the distinction was not made between these two separate polarizing processes, leading to the conclusion that n varies between 0.5 and unity. However, when $\sigma(f)$ is treated as two separate processes [$\sigma_1(f)$ and $\sigma_{II}(f)$] one finds that the universality is enhanced. This can be seen in Table I, where values are compiled of the power law exponent of several ion conducting materials obtained from analysis of data available in the literature [13]. In these instances care has been exercised to insure that the data being analyzed were at least a decade above $10^{-12}f$ so that the influence of $\sigma_{II}(f)$ could be neglected. What is clear from the Table is a pronounced tendency for many of these materials to exhibit $n \approx 2/3$ to within about 0.1, a range that is considerably narrower than that quoted by Jonscher.

On closer examination of Table I though, a variation of the exponent with differing classes of materials is discernible. For example, the oxide glasses at the top of the table show $n = 0.67 \pm 0.05$, while halide-containing (Cl, Br) glasses and mixed ion glasses (those which contain equal amounts of two cation species) exhibit a lower exponent (0.58 ± 0.05). Further down the Table are crystalline materials in which conduction occurs chiefly along two-dimensional planes (alkali β -alumina) and along one-dimensional channels (hollandite). These, too, have exponents substantially lower than 0.67.

The exponents reported in Table I are plotted in Fig. 1 as a function of the dimensionality of the conduction pathways. Oxide, thiosilicate, and thioborate glasses form homogeneous, disordered networks, and in the absence of evidence to the contrary are regarded as possessing three-dimensional pathways. The halides and mixed ion glasses are distinguished from the oxide glasses as there is evidence from neutron scattering [14,15] that

TABLE I. Results of a literature survey of various ionic materials listing the power law exponent (n), mass density (ρ), and correlation length (ξ). Densities shown in parentheses are approximated. The last column indicates the temperature range examined and frequency ranges that differ appreciably from 10 Hz–1 MHz.

Ref.	System	n	ρ (g/cm ³)	ξ (Å)	Comment
Glass					
[13a]	Na ₂ O-3SiO ₂	0.67 ± 0.05	2.49	1.2 ± ?	294 K
[13b]	K ₂ O-3SiO ₂	0.65 ± 0.05	2.49	1.4 ± ?	323 K
[13c]	Li ₂ O-Al ₂ O ₃ -2SiO ₂	0.68 ± 0.05	2.44	1.6 ± ?	297 K
[13d]	Na ₂ O-B ₂ O ₃ -SiO ₂	0.65 ± 0.05	2.50	0.95 ± 0.1	300–340 K
[13e]	Li ₂ O-3B ₂ O ₃	0.65 ± 0.05			370–430 K
[13f,26]	0.03Li ₂ O-0.97GeO ₂	0.64 ± 0.05	3.8	2.7 ± 0.1	400–460 K, low conc.
[13g,26]	0.1Na ₂ O-0.9GeO ₂	0.69 ± 0.05	4.0	3.0 ± 0.1	500–560 K, low conc.
[13h]	0.41Li ₂ O-0.59P ₂ O ₃	0.66 ± 0.05	2.35	0.86 ± 0.1	320–370 K
[10]	NaPO ₃	0.67 ± 0.03	2.53	0.93 ± 0.1	310–430 K
[13i]	0.5FeO-0.5P ₂ O ₅	0.68 ± 0.05	2.92	5.5 ± 0.5	300–450 K, e ⁻ hopping
[13j]	0.56Li ₂ S-0.44SiS ₂	0.70 ± 0.1	(2.5)	0.95 ± 0.1	140–180 K
[13k]	0.005Na ₂ S-0.995B ₂ S ₃	0.68 ± 0.05			400–450 K, low conc.
[13l]	0.008K ₂ S-0.992B ₂ S ₃	0.69 ± 0.05	1.8	5.9 ± 0.2	300–450 K, low conc.
Mixed ion					
[13m]	0.5Na ₂ O-0.5K ₂ O-3SiO ₂	0.54 ± 0.05	2.49	1.6 ± ?	406 K
[26]	0.05Li ₂ O-0.05Na ₂ O-0.9GeO ₂	0.58 ± 0.03	4.0	2.9 ± 0.1	580–680 K
[10]	0.25Li ₂ O-0.25Na ₂ O-0.5P ₂ O ₅	0.61 ± 0.05	2.46	0.95 ± 0.1	430–500 K
[13n,25]	0.4Ca(NO ₃) ₂ -KNO ₃	0.61 ± 0.05	2.23	1.1 ± 0.5	300–350 K, melt
Halide					
[13o]	10CdF ₂ -11CdO-3CdCl ₂ -6LiF-4KF-30AlF ₃ -30PbF ₂ -4YF ₃ -2LaF	0.56 ± 0.05	(2.5)	3.0 ± 0.5	430–500 K, melt
[13p]	0.3Na ₂ F-0.7Na ₂ O-3B ₂ O ₃	0.63 ± 0.05	(2.5)	0.38 ± 0.1	380–430 K
[13q]	0.7Li ₂ O-0.6LiCl-B ₂ O ₃	0.63 ± ?	(2.5)	0.90 ± 0.1	250–280 K
[17]	xLi ₂ O-yLi ₂ Cl ₂ -(1-x-y)B ₂ O ₃	0.57 ± 0.05			550 K, 5 MHz–10 GHz
[13r]	0.56Li ₂ O-0.45LiBr-B ₂ O ₃	0.60 ± ?	(2.5)	1.1 ± 0.2	323 K, 0.1 kHz–0.1 GHz
[13s]	xAgI-(1-x)AgPO ₃	0.58 ± 0.05	(2.5)	1.6 ± ?	200–300 K
Crystal					
Two dimensional					
[13t]	Na-β Alumina	0.60 ± 0.05	3.9	5 ± 2	120–300 K
[13u]	Ag-β Alumina	0.61 ± 0.05	3.9	7 ± 2	121 K
[13v]	β-AgI	0.51 ± 0.05	6.0	0.4 ± ?	292 K
Mixed ion					
[13u]	(Na/Ag)-β Alumina	0.46 ± 0.05	3.9	2 ± 1	210–240 K
One dimensional					
[13w]	K _x (Mg, Ti) ₈ O ₁₆ (Priderite)	0.33 ± 0.1			300 K, 0.1 kHz–1 GHz
[13x]	K _{1.54} Mg _{0.77} Ti _{7.23} O ₁₆ (Hollandite)	0.40 ± 0.1			200 K, 10 kHz–1 MHz
[13y]	Ba _{1.33} Fe _{1.33} Ti _{7.34} O ₁₆ (Hollandite)	0.22 ± 0.1			270 K, 0.1 kHz–0.1 MHz

these materials possess enhanced intermediate range order. In the halides, it is believed that introduction of the halide anion results in dendritic pathways of higher free volume [14] that are responsible for the “fast ion conduction” properties often reported for these materials. A similar dendritic feature emerges in the mixed ion situation. Current models for mixed ion dynamics [16] emphasize that the two dissimilar ions (A, B) reside in dissimilar sites (α, β) and that motion of an ion (e.g. A) into an ill-configured site (β) is energetically unfavored relative to motion into an appropriately configured site (α). Thus, a dominant contribution to the conduction in

mixed ion systems occurs along clusters (dendritic) of favorably configured sites. In both instances (addition of halide to an oxide glass [17] and mixing of cations [10]), studies have demonstrated a systematic decrease in the power law exponent.

Since cluster formation in an otherwise three-dimensional (3D) network would likely result in a morphology that is intermediate between 3D and 2D (i.e., fractal), I have chosen to position the exponents for the halides and the mixed ion glasses at a dimension of 2.5 in Fig. 1. For similar reasons, the exponent for the mixed ion β -alumina is placed at a dimension of 1.5. These

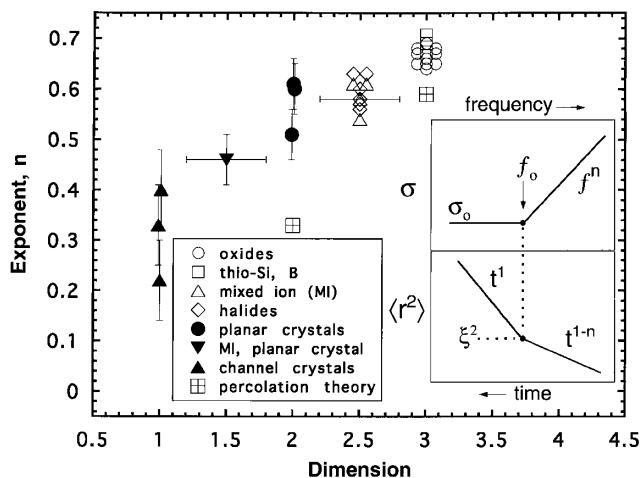


FIG. 1. The power-law exponents reported in Table I plotted against the effective dimension of ion conduction pathways. Some data have been shifted slightly along the abscissa for clarity. The inset shows how features of $\sigma(f)$ are related to the two diffusion regimes discussed in the text.

positions are consistent with the fractal dimension of some model fractals [18] (e.g., the Sierpinski sponge and gasket), but, are intended only to approximate the distinctions for the halide and mixed ion systems discussed above.

The dimension dependence of n shown in Fig. 1 has not been previously reported, and provides new insight into ion dynamics as well as an important test for proposed models of the power law dispersion. Several models are currently touted including those based upon distributions of energy barriers [19], those which attribute the dispersion to an inter-ionic interaction [4] or correlated motion [5], and those which achieve power law dispersion through the introduction of percolated pathways and random walks on a fractal lattice [7]. Of these, only the latter percolation models provide an explicit dimension dependence of the exponent.

It is well established that particles performing random walks on a regular lattice exhibit Fickian diffusion, such that the mean squared displacement $\langle r^2 \rangle$ varies as $6Dt$, where D is the diffusivity. However, computer simulations of random walks on a self-similar fractal exhibit non-Fickian diffusion [18,20]. The fractal lattice limits the possible moves the particle can make in a given step, reducing the overall displacement in comparison with Fickian diffusion. For excursions shorter than the correlation length ξ (over which the self-similarity persists), the mean squared displacement, $\langle r^2 \rangle$, varies as a power law $\langle r^2 \rangle \approx t^{1-n}$. At length scales in excess of ξ , self-similarity is absent and the diffusion returns to Fickian with $\langle r^2 \rangle \approx t$. If the particles possess a charge, q , then the conductivity can be related to the evolution of $\langle r^2 \rangle$ by [19,21]

$$\sigma(f) \approx -\frac{Nq^2 4\pi^2 f^2}{6kT} \int_0^\infty \langle r^2 \rangle e^{-i2\pi ft} dt, \quad (1)$$

for which one finds two regimes of ac conductivity: a power law regime where $\sigma(f) \approx f^n$ accompanied at lower frequency by a frequency-independent regime where $\sigma(f) \approx \sigma_0$. This relationship between $\langle r^2 \rangle$ and the ac conductivity is shown schematically in the inset to Fig. 1.

The exponent n can be obtained by numerical simulations of such walks occurring in different dimensions, and results for both 2D and 3D computer simulations [18,22] are included in Fig. 1. While the percolation exponents fall below that of the experimental data in Fig. 1, more recent simulations [23] that incorporate Coulomb interactions between the charges find increased exponents with increasing interaction strength. Experimental investigations of the power law dispersion with decreasing cation concentration, however, indicate that the exponent remains unchanged, despite an order-of-magnitude increase in the average cation separation distance [24–26], and hence contradict the notion that inter-cation interactions play any significant role in the power law dispersion.

Furthermore, estimates of the correlation length hint that the above percolation picture may be inaccurate. From the inset to Fig. 1, the transition of $\langle r^2 \rangle$ from non-Fickian to Fickian (occurring when $\langle r^2 \rangle \approx \xi^2$) corresponds to the frequency (f_0) where $\sigma(f)$ crosses over from power law to dc. In the percolation picture, the Fickian diffusion at $f < f_0$ can be thought of as an unrestricted random walk with “steps” of size ξ occurring at a rate f_0 . In this regime, Eq. (1) reduces to the familiar Nernst-Einstein relation,

$$\sigma_0 = \frac{\gamma N q^2 \xi^2}{6kT} H_R f_0, \quad (2)$$

where γ is the fraction of charge carriers that are mobile and the Haven ratio H_R expresses the presence of possible cross correlation in the diffusion ($H_R < 1$) [27]. In Eq. (2), N is the total density of charge carriers.

From literature data the correlation length is computed using Eq. (2) under the strong electrolyte ($\gamma = 1$) assumption and neglecting cross correlations ($H_R = 1$). Results are included in Table I. For glasses containing moderately high densities of charge carriers ($N \approx 2 \times 10^{22} \text{ cm}^{-3}$) one finds $\xi \approx 1.5 \pm 0.5 \text{ \AA}$. Glasses containing considerably lower alkali concentrations exhibit somewhat larger ξ , often increasing [25] as $N^{-1/3}$. While the value $\xi = 1.5 \text{ \AA}$ may be increased by letting both γ and H_R differ from unity, even in an extreme case where $H_R \approx 0.3$ and $\gamma \approx 0.3$ the correlation length remains less than 5 \AA . This length is clearly at odds with the conceptual picture of extensive regions of self-similar structure. Instead it suggests that the power law dispersion is the result of a highly localized motion that evolves over $\langle r^2 \rangle$ comparable to atomic scales.

This type of localized motion is exemplified in the “jump relaxation model” proposed by Funke [5]. In this model, a given “central” cation (prior to hopping) resides in a potential energy minimum formed by the equilibrated distribution of neighboring cations. Upon hopping to an

adjacent site, the cation finds itself temporarily out of equilibrium with respect to the distribution of neighboring cations. Two things can happen. Either the neighboring charges redistribute so as to establish a new equilibrium condition about the new site, or the cation returns to its original site. At short times the latter process is favored and the cation performs a sequence of forward-backward hops which are unsuccessful at producing any net charge displacement. At longer times, redistribution of the neighboring charges allows the cation to complete a hop to the adjacent site that is successful in contributing to net conduction. Funke [5] reports that an analytic solution for the one-dimensional case indicates the correlated, forward-backward motion gives rise to power law dispersion in the a.c. conductivity with an exponent $n = 1 - \alpha$. The "mismatch parameter," α , expresses the shift ($\Delta x = \alpha x_0$) in the position of the potential minimum near the neighboring ions when the central ion hops ($\Delta x = x_0$) by one lattice spacing. Extensions of the model to higher dimensions are unavailable, but could lead to variation of n due to the increased number of neighboring ions which contribute to the mismatch parameter.

In conclusion, the ac conductivity of ionic materials exhibits a power law dispersion in frequency in which the exponent appears to depend only upon the dimension of the conduction space. Indications are that this dispersion is the result of localized ($\xi \approx 1.5 \text{ \AA}$) ion displacements, consistent with correlated motions of the cation in the vicinity of an anion site.

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- [1] A. K. Jonscher, *Nature (London)* **267**, 673 (1977).
 [2] J. C. Dyre, *J. Non-Cryst. Solids* **135**, 219 (1991).
 [3] S. R. Elliott, *Solid State Ion.* **70/71**, 27 (1994).
 [4] K. L. Ngai, R. W. Rendell, and H. Jain, *Phys. Rev. B* **30**, 2133 (1984).
 [5] K. Funke, *Prog. Solid State Chem.* **22**, 111 (1993).
 [6] A. Hunt, *J. Phys. Condens. Matter* **3**, 7831 (1991).
 [7] A. Bunde and P. Maass, *J. Non-Cryst. Solids* **131/133**, 1022 (1991).
 [8] H. Kahnt, *Ber. Bunsen-Ges. Phys. Chem.* **95**, 1021 (1991).
 [9] W. K. Lee, J. F. Liu, and A. S. Nowick, *Phys. Rev. Lett.* **67**, 1559 (1991).
 [10] D. L. Sidebottom, P. F. Green, and R. K. Brow, *Phys. Rev. Lett.* **74**, 5068 (1995).
 [11] A. S. Nowick, B. S. Lim, and A. V. Vaysleyb, *J. Non-Cryst. Solids* **172/174**, 1243 (1994).
 [12] D. L. Sidebottom, P. F. Green, and R. K. Brow, *J. Non-Cryst. Solids* **222**, 354 (1997).
 [13] (a) V. Provenzano, L. P. Boesch, V. Volterra, C. T. Moynihan, and P. B. Macedo, *J. Am. Ceram. Soc.* **55**, 492 (1972); (b) L. P. Boesch and C. T. Moynihan, *J. Non-Cryst. Solids* **17**, 44 (1975); (c) P. B. Macedo, C. T. Moynihan, and R. Bose, *Phys. Chem. Glasses* **13**, 171 (1972); C. T. Moynihan, L. P. Boesch, and N. L. Laberge, *Phys. Chem. Glasses* **14**, 122 (1973); (d) C. H. Hsieh and H. Jain, *J. Non-Cryst. Solids* **183**, 1 (1995); (e) H. L. Downing, N. L. Peterson, and H. Jain, *J. Non-Cryst. Solids* **50**, 203 (1982); (f) O. Kanert, M. Kloke, R. Kuchler, S. Ruckstein, and H. Jain, *Ber. Bunsen-Ges. Phys. Chem.* **95**, 1061 (1991); (g) H. Jain and J. N. Mundy, *J. Non-Cryst. Solids* **91**, 315 (1987); (h) S. W. Martin and C. A. Angell, *J. Non-Cryst. Solids* **83**, 185 (1986); (i) L. Murawski and R. J. Barczynski, *J. Non-Cryst. Solids* **196**, 275 (1996); (j) F. Borsa, D. R. Torgeson, S. Martin, and H. Patel, *Phys. Rev. B* **46**, 795 (1992); (k) H. K. Patel and S. W. Martin, *Phys. Rev. B* **45**, 10292 (1992); (l) H. K. Patel, Ph.D. thesis, Iowa State University, Ames, Iowa, 1993; (m) T. J. Higgins, L. P. Boesch, V. Volterra, C. T. Moynihan, and P. B. Macedo, *J. Am. Ceram. Soc.* **56**, 334 (1973); (n) F. S. Howell, R. A. Bose, P. B. Macedo, and C. T. Moynihan, *J. Phys. Chem.* **78**, 639 (1994); (o) W. C. Hasz, C. T. Moynihan, and P. A. Tick, *J. Non-Cryst. Solids* **172-174**, 1363 (1994); (p) H. Jain and J. N. Mundy, *J. Non-Cryst. Solids* **91**, 315 (1987); (q) M. Tatsumisago, C. A. Angell, and S. W. Martin, *J. Chem. Phys.* **97**, 6968 (1992); (r) C. Cramer, K. Funke, and T. Saatkamp, *Philos. Mag. B* **71**, 701 (1995); (s) M. LeStanjuennec and S. R. Elliott, *Solid State Ion.* **73**, 199 (1994); (t) D. P. Almond, A. R. West, and R. J. Grant, *Solid State Commun.* **44**, 1277 (1982); (u) C. C. Hunter, M. D. Ingram, and A. R. West, *Solid State Ion.* **8**, 55 (1983); (v) S. Yoshikado, H. Goto, T. Murata, Y. Azuma, I. Taniguchi, Y. Ito, and B.-E. Mellander, *Solid State Ion.* **79**, 124 (1995); (w) T. Kudo and K. Fueki, in *Solid State Ionics* (VCH, Weinheim, Germany, 1990); (x) J. Bernasconi, H. U. Beyler, and S. Strassler, *Phys. Rev. Lett.* **42**, 819 (1979); (y) K. Iwauuchi and Y. Ikeda, *Phys. Status Solidi A* **130**, 449 (1992).
 [14] J. D. Wicks, L. Borgesson, G. Bushnell-Wye, W. S. Howells, and R. L. McGreevy, *Phys. Rev. Lett.* **74**, 726 (1995).
 [15] L. Borgesson, L. M. Torell, and W. S. Howells, *Philos. Mag. B* **59**, 105 (1989).
 [16] P. Maass, A. Bunde, and M. D. Ingram, *Phys. Rev. Lett.* **68**, 3064 (1992).
 [17] A. H. Verhoef and H. W. den Hartog, *Solid State Ion.* **68**, 305 (1994).
 [18] S. Havlin and D. Ben-Avraham, *Adv. Phys.* **36**, 695 (1987).
 [19] J. C. Dyre, *J. Appl. Phys.* **64**, 2456 (1988).
 [20] Y. Gefen, A. Aharony, and S. Alexander, *Phys. Rev. Lett.* **50**, 77 (1983).
 [21] H. Scher and M. Lax, *Phys. Rev. B* **7**, 4491 (1973).
 [22] A. Bunde, *Solid State Ion.* **28-30**, 34 (1988).
 [23] P. Maass, J. Petersen, A. Bunde, W. Dieterich, and H. E. Roman, *Phys. Rev. Lett.* **66**, 52 (1991).
 [24] B. Roling, A. Happe, K. Funke, and M. D. Ingram, *Phys. Rev. Lett.* **78**, 2160 (1997).
 [25] D. L. Sidebottom, P. F. Green, and R. K. Brow, *Phys. Rev. B* **56**, 170 (1997).
 [26] D. L. Sidebottom, *J. Non-Cryst. Solids* (to be published).
 [27] J. N. Mundy and G. L. Jin, *Solid State Ion.* **21**, 305 (1986).