# **Dielectrics Newsletter**

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#### The AC And DC Conductivity (Dielectric Constant) Of Composites

This paper will show how to analyze the AC and DC conductivity, or complex dielectric constant, of binary (a conducting and an insulating phase)-composites (media, compacts), where the better conducting component has a volume fraction  $\phi$ . Most binary and some tertiary media (with some ingenuity the analysis can be applied to tertiary media), are found in practice to at least approximate one of the two basic micro(nano)structures [1]. The first are matrix dominated media, where the matrix phase surrounds the granular (particle) phase at all volume fractions. These are usually best described using the Maxwell Wagner Effective Media Equation (also known as the Maxwell-Garnet equation). The Maxwell-Wagner model is formally equivalent to the Hashin-Shtrikman [2] lower bound (insulator host) and upper bound (conductor host) [3,4]. For matrix dominated media, the Bricklayer Model [5] is also useful. Matrix dominated media are not dealt with in detail this in paper. The second micro (nano)-structure is where the conducting particles, in a two phase material, can make electrical contact with each other, when their volume fraction  $\phi$  reaches a certain critical  $\phi_c$ , where a continuous conducting path or spanning cluster forms [1]. The complex electrical conductivity of these systems is best [6, 7] described by the Two Exponent Phenomenological Percolation Equation (TEPPE)(also known as the General Effective Medium (GEM) equation) [8-18]. The three standard percolation equations are reviewed in [19–21], but it is shown in [6] and [7] that, while the single TEPPE reduces to the three standard equations in the appropriate limits, it is far superior in the second order terms (i.e. the imaginary dielectric constant  $\epsilon_{mi}$  in the conducting media above  $\varphi_c$  and the dielectric loss  $\epsilon_{ii}$  (or  $\sigma_{mr})$  below). The theory given here applies to nano, micro and macro media.

The AC conductivity of the media (composite) ( $\sigma_m$ ) is the sum of the real and imaginary conductivities, which is given by  $\sigma_m = \sigma_{mr} + i\sigma_{mi}$ . The conductivity of the more conducting component is given by  $\sigma_c =$  $\sigma_{cr} + i\sigma_{ci}$  or simply  $\sigma_c = \sigma_{cr}$  if ideal conductivity ( $\sigma_{cr} \gg \sigma_{ci}$ ) is assumed. For the insulating component, the conductivity is  $\sigma_i = \sigma_{ir} + i\sigma_{ii}$  where  $\sigma_{ii} = \omega \epsilon_0 \epsilon_{ir}$ .  $\sigma_i$  is often approximated as  $\sigma_i = i\omega\epsilon_0\epsilon_{ir}$  (i.e  $\sigma_{ir} \ll i\sigma_{ii}$ ). In practice,  $\sigma_{ir}$  incorporates both a, usually very small, DC conductivity and the dielectric polarization loss term ( $\omega \epsilon_0 \epsilon_{ii}$ ). The expressions for  $\sigma_c$  and  $\sigma_i$  can be frequency and/or temperature dependent. The complex conductivity and dielectric constant are related by  $\sigma = \omega \epsilon_0 \epsilon$ . As the critical volume fraction  $\phi_c$  is of great importance, its origins are briefly described here. A more detailed account can be found in [1, 3, 22]. If conducting spheres, of just sufficient size to touch their nearest neighbors, are placed at random on the sites of 3d Bravais lattices it is found that  $\phi_c$ is  $0.16 \pm 0.02$  [3,23]. If equally sized conducting and insulating spheres are placed at random in a container,  $\phi_c$ is also found to be about 0.16. This value of  $\phi_c$  is often taken to characterize 3d random media but other values of  $\phi_c$  are permitted [3, 22]. For  $\phi_c <$ 0.16 three models can be considered (for  $\phi_c > 0.16$  see [24]). The first is the grain consolidation model [3, 22] where randomly nucleated insulating spheres have grown (been sintered) so as to confine the conducting material to inter granular channels. At a  $\phi$  value of 0.03 ( $\phi_c$ ) the channels become isolated. The second model comprises of granular structures [14] where a fine conducting powder coats a coarse insulating one. Calculations for  $\phi_c$ , based on there being a percolation path on the surface of the insulating spheres, have been made

by Kusy [25]. For instance, when the ratio of the radii of the components is 30,  $\phi_c \approx 0.03$ . For particles with irregular geometries, especially extended ones (rods, discs) one must use the excluded volume model of Balberg *et al.* [26]. For rods with a length to width ratio of 10,  $\phi_c \approx 0.1$ , while for a ratio of 1000,  $\phi_c \approx 0.001$ .

Note that no experimental details will be given here, for these the reader should consult the original papers. As previously stated a recent series of papers [8–12, 14–16] has shown that the TEPPE which is:

$$\begin{array}{rcl} (1-\phi) \frac{\sigma_{i}^{1/s} - \sigma_{m}^{1/s}}{\sigma_{i}^{1/s} + A \sigma_{m}^{1/s}} & (1) \\ + \phi \frac{\sigma_{c}^{1/t} - \sigma_{m}^{1/t}}{\sigma_{c}^{1/t} + A \sigma_{m}^{1/t}} & = & 0, \end{array}$$

with  $A = (1 - \phi_c)/\phi_c$  and the exponents *s* and *t*, best describes experimental results for percolation systems, especially the second order terms [11, 12].

Equation (1) yields the two limits for  $|\sigma_c| \to \infty$  :

$$\begin{split} \sigma_{\rm m} &= \sigma_{\rm i} \left( \frac{\varphi_{\rm c}}{\varphi_{\rm c} - \varphi} \right)^s \, {\rm or} \\ \epsilon_{\rm mr} &= \epsilon_{\rm ir} \left( \frac{\varphi_{\rm c}}{\varphi_{\rm c} - \varphi} \right)^s, \\ \varphi &< \varphi_{\rm c}, \end{split} \tag{2}$$

and  $|\sigma_i| \to 0$  :

$$\begin{split} \sigma_{\rm m} &= \sigma_{\rm c} \left( \frac{\varphi - \varphi_{\rm c}}{1 - \varphi_{\rm c}} \right)^t \, {\rm or} \\ \epsilon_{\rm mr} &= \epsilon_{\rm ir} \left( \frac{\varphi - \varphi_{\rm c}}{1 - \varphi_{\rm c}} \right)^t, \\ \varphi &> \varphi_{\rm c}. \end{split} \tag{3}$$

These equations are the normalized standard percolation results [19, 20] and characterize the exponents *s* and *t*. In the crossover region, where  $\phi \cong \phi_c$  and

$$\begin{split} \phi_{c} &- (\sigma_{i}/\sigma_{c})^{1/t+s} < \phi < \\ \phi_{c} &+ (\sigma_{i}/\sigma_{c})^{1/t+s} \end{split} \tag{4}$$

or

$$\begin{split} \phi_{c} &- (\omega \epsilon_{0} \epsilon_{ir} / \sigma_{cr})^{1/t+s} < \phi < \\ \phi_{c} &+ (\omega \epsilon_{0} \epsilon_{ir} / \sigma_{cr})^{1/t+s} \end{split} \tag{5}$$

holds, Eq. (1) gives

$$\sigma_{\rm m} \approx \sigma_{\rm i}^{t/(s+t)} \sigma_{\rm c}^{s/(s+t)}$$
 (6)

or

$$\sigma_{\rm m} \approx (\omega \epsilon_0 \epsilon_{\rm ir})^{t/(s+t)} \sigma_{\rm cr}^{s/(s+t)}, \ (7)$$

which is in agreement with the theory given in [19] and [20].

Eq. (6) shows that, in the crossover region, the conductivity  $\sigma_{mr}$  should be proportional to  $\omega^{t/(s+t)}$  and the dielectric constant  $\varepsilon_{mr}$  (recall that  $\varepsilon_{xy} = \sigma_{xy}/\omega\varepsilon_0$ ), is proportional to  $\omega^{s/(s+t)}$ . Note that Eqs. (2) and (3) are not valid in the crossover region.

Arguably the best DC conductivity results, for a percolation system, are those measured on compressed Graphite-hBN discs, which are given in Fig. 1, from which  $\phi_c$ , s, t,  $\sigma_c$ and  $\sigma_i$  can easily be determined using Eq. (1) [8].

Figure 2 shows the AC conductivity plotted as a function of frequency for a loosely packed Graphite-hBN mixture [9]. Note how one can clearly distinguish between samples above and below  $\phi_c$ .

It should be noted that the conductivities, below  $\phi_c$  in Fig. 2, contain contributions due to the isolated conducting clusters and the dielectric loss of the insulating component. In most other systems such conductivity results are dominated by the contributions of the insulating component.

A system where the conducting clusters clearly dominate is given in [11]. Figure 3 [11] shows that the dielectric constants as a function of frequency are not even qualitatively in accord with the predictions of the standard equations, (Eqs. (2) & (3) and [19–21]).

Note that the top most curve is for a sample above  $\phi_c$ . Further, a close examination of Fig. 3 shows that if the results are re-plotted as  $log(\epsilon_{ir})$  as a function of  $\log |\phi - \phi_c|$ , the values obtained for s will be frequency dependent, a fact first pointed out in [14]. Second order dielectric results of this nature can be qualitatively fitted using Eq. (1) [11], but a more complex model is needed to fit these results more accurately [12]. AC conductivity results can be fitted using Eq. (1) as demonstrated in [17,18]. However it is more usual to scale all the results onto a single master curve first. This is done by dividing each AC conductivity curve (plotted as a function of

 $10^{0}$   $10^{10}$   $10^{10}$   $10^{12}$   $10^{16}$  0 0.2 0.4 0.60.8

Volume Fraction  $\phi$ 





ω/2Π(Hz)







The scaling functions  $F_{-}(\omega/\omega_c)$  and  $F_{+}(\omega/\omega_c)$  are given by,

$$\sigma_{\rm m} = \sigma_{\rm c} \left(\frac{\phi_{\rm c} - \phi}{\phi_{\rm c}}\right)^t F_{-} \left(\frac{\omega}{\omega_{\rm c}}\right), \quad (8)$$

for  $\varphi < \varphi_c$  and

$$\sigma_{\rm m} = \sigma_{\rm c} \left( \frac{\phi - \phi_{\rm c}}{1 - \phi_{\rm c}} \right)^t F_+ \left( \frac{\omega}{\omega_{\rm c}} \right) \tag{9}$$

for  $\phi > /\phi_c$ . Here,  $\sigma_m$  may originate either from theoretical calculations, using Eq. (1), or experimental results.

This is shown in Fig. 4 and shows that Eq. (1) can be used to fit AC conductivity results from experiment. In this case the DC values of the parameters  $\phi_c$ , *s*, *t*,  $\sigma_c$  and  $\sigma_i$ , were used in deriving F<sub>-</sub>( $\omega/\omega_c$ ) and F<sub>+</sub>( $\omega/\omega_c$ ), but in most cases different values of *s* and *t* have to be used to obtain a satisfactory fit.

Note that Eq. (1), with complex conductivities, is not easy to solve. However, a Mathematica package which does this is available from godfrey\_sauti@yahoo. com. A further publication in an upcoming newsletter will deal with scaling and universality in more depth and explain why the  $\omega_c$  values obtained from experiment and theory do not agree, as well as, show how  $\omega_c$  can be calculated directly from impedance curves where these are available [15, 16].

Unfortunately the values of s and t do not tell one much about the microstructure of the media but does indicate some thing about the inter-particle (inter-cluster) resistances. The universal value of exponent t ( $t_{un}$ ), which is usually observed in computer simulations and for "ideal" systems, is 2.0. It was shown theoretically and by computer simulations [27] that if the low conductance bonds in the percolation network, or the inter-granular conductances of the conducting component in a continuum system, have a very wide distribution, then t can be larger than  $t_{un}$ . This distribution can be due to a large range of effective geometrical resistivity factors in a continuous homogeneous conduct-



Fig. 4: A plot of the log of the scaled conductivities against the log of the scaled frequency for a 55%G - 45%BN powder. The origin of the  $F_+$  and  $F_-$  plots onto which the experimental curves are scaled along the  $(\omega/\omega_{c+})$  or  $(\omega/\omega_{c-})$  axis is discussed in the text and in greater detail in [9].

ing phase, of a medium such as a Swiss Cheese (which contains Random Voids) [28, 29]. In this model a range of very thin and highly resistive threads of conductor (cheese), between the large overlapping voids (air), give rise to a wide distribution in the conductances between the more extended or bulky regions of conductor. This model give values for t in the range 2.0-2.5, but an extension of it allows far higher values [30]. A model which considers the conducting paths in terms of Links, (large conducting) Blobs and Nodes (multiple link sites) gives an upper limit of 2.35. Note that all of the above models assume a homogeneous (non-granular) conducting phase. A model for granular conducting systems [31,32], based on the dominant resistances in the current carrying Links and Blobs (now consisting of a granular conductor), being due to a large range of inter particle tunneling contacts has been proposed. In virtually all media with a granular conducting phase  $t > t_{un}$  is observed due to a range of inter particle tunneling distances [33]. A combination of the Swiss Cheese and tunneling model which would further enhance t has also been proposed [34].

This paper has shown how the AC

and DC conductivity (dielectric constant) results can be analyzed in terms of the Two Exponent Phenomenological Percolation (TEPPE) equation. As the actual complex conductivities appear in the expressions it is theoretically possible to determine the dispersive conductivities for both components and, for percolation systems, the critical volume fraction as well as the exponents s and t. In practice, even when a large amount of data is available on both sides of the critical volume fraction, this is a formidable task. Therefore, it is usually advisable to know, or measure or model, the complex conductivity of at least one of the components first. Note that in a real medium the conductivity, especially that of a granular conductor, may be modified by surface reactions or dominated by inter particle contacts.

#### References

- David S. McLachlan, Godfrey Sauti, Journal of Nanomaterials 2007 (2007).
- [2] Z. Hashin, S. Shtrikman, J. Appl. Phys. 33 (1962) 3125.
- [3] David S. McLachlan, Michael Blaszkiewicz, Robert E. Newnham, J. Am. Ceram. Soc. 73 (1990) 2187.
- [4] M.A. Campo, L.Y. Woo, T.O. Ma-

son, E.J. Garboczi, J. Electroceram. 9 (2002) 49.

- [5] Jin-Ha Hwang, D.S. McLachlan, T.O. Mason, J. Electroceram 3 (1999) 7.
- [6] D. S. McLachlan, C. Chiteme, W. D. Heiss, Junjie Wu, Physica B 338 (2003) 256.
- [7] D. S. McLachlan, C. Chiteme, W. D. Heiss, Junjie Wu, Physica B 338 (2003) 261.
- [8] Junjie Wu, D. S. McLachlan, Phys. Rev. B 56 (1997) 1236.
- [9] Junjie Wu, D. S. McLachlan, Phys. Rev. B 58 (1998) 14880.
- [10] D. S. McLachlan, Michael B. Heaney, Phys. Rev. B 60 (1999) 12746.
- [11] D. S. McLachlan, W. D. Heiss, C. Chiteme, Junjie Wu, Phys. Rev. B 58 (1998) 13558.
- [12] W. D. Heiss, D. S. McLachlan, C. Chiteme, Phys. Rev. B 62 (2000) 4196.
- [13] Christian Brosseau, J. Appl. Phys. 91 (2002) 3197.
- [14] C. Chiteme, D. S. McLachlan, Phys. Rev. B 67 (2003).
- [15] Cosmas Chiteme, David S. McLachlan, Godfrey Sauti, Phys. Rev. B 75 (2007) 094202.
- [16] David S. McLachlan, Godfrey Sauti, Cosmas Chiteme, Phys. Rev. B 76 (2007).
- [17] Ian J. Youngs, Ph.D. thesis, Electronic and Electrical Engineering, University College, London, 2001.
- [18] Ian J. Youngs, J. Phys. D: Appl. Phys. 35 (2002) 3127.
- [19] J. P. Clerc, G. Giraud, J. M. Laugier, J. M. Luck, Adv. Phys. 39 (1990) 191.
- [20] D. J. Bergman, D. Stroud, Solid State Phys. 46 (1992) 148.
- [21] Ce-Wen Nan, Progress in Materials Science 37 (1993) 1.
- [22] David S. McLachlan, J. Electroceram 5 (2000) 93.
- [23] Richard. Zallen, The Physics of Amorphous Solids, Wiley-Interscience, New York, 1983.
- [24] D. S. McLachlan, R. Rosenbaum, A. Albers, G. Eytan, N. Grammatica, G. Hurvits, J. Pickup, E. Zaken, J. Phys.: Condens. Matter 5 (1993) 4829.
- [25] R. P. Kusy, J. Appl. Phys. 48 (1977) 5301.
- [26] I. Balberg, C. H. Anderson, S. Alexander, N. Wagner, Phys. Rev. B 30 (1984) 3933.
- [27] P. M. Kogut, J. P. Straley, J. Phys. C 12 (1979) 2151.
- [28] B. I. Halperin, Shechao Feng, P. N. Sen, Phys. Rev. Lett. 54 (1985) 2391.
- [29] Shechao Feng, B. I. Halperin, P. N. Sen, Phys. Rev. B 35 (1987) 197.
- [30] I. Balberg, Phys. Rev. B 57 (1998) 13351.
- [31] H. E. Stanley, J. Phys. A: Math. Gen. 10 (1977) L211.
- [32] A. Coniglio, J. Phys. A: Math. Gen. 15 (1982) 3829.
- [33] I. Balberg, Philos. Mag. B 56 (1987) 991.
- [34] C. Chiteme, D. S. McLachlan,

 I. Balberg, Phys. Rev. B 67 (2003).
 [35] N. F. Mott, E. A. Davies, Electronic Processes in Noncrystalline Solids, Clarendon, Oxford, 1979.

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#### Bernhard Roling and Sevi Murugavel Nonlinear Ionic Conductivity of Solid Electrolytes

For electrochemical energy storage and conversion applications, such as batteries and fuel cells, the use of solid electrolytes offers several advantages over conventional liquid electrolytes based on aqueous or organic solvents. In particular, solid electrolytes exhibit often a higher chemical and electrochemical stability, resulting in reduced safety problems in batteries. Furthermore, miniaturised electrochemical cells, such as microbatteries [1]. can be manufactured based on multilayer stacks of thin electrode and electrolyte films. The application of thin electrolyte films offers the additional advantage that the electrical resistance of the film decreases with decreasing thickness. For calculating the electrical resistance, one has to take into account, however, that in a thin film even a small voltage drop may cause a high electric field resulting in a field-dependent (nonlinear) ionic conductivity. For instance, a dc voltage drop of 5 V in an electrolyte film with a thickness between 100 nm and 1  $\mu$ m leads to a dc electric field between 500 kV/cm and 50 kV/cm. In this field range, the resulting dc current density j depends on the dc field *E* in a nonlinear fashion:

$$j(E) = \sigma_1 E + \sigma_3 E^3 + \sigma_5 E^5 + \dots$$
(1)

In this power series,  $\sigma_1$  denotes the low-field conductivity, while  $\sigma_3$ ,  $\sigma_5$ 

etc. are higher-order conductivity coefficients.

The simplest theoretical approach to interpret this nonlinear electrical behaviour is to consider a simple regular hopping model with distance a between adjacent sites. For this model it turns out that [2]

$$j(E) \propto \sinh(qaE/(2k_BT))$$
. (2)

This expression implies that in the framework of this model, it is possible to extract the elementary hopping distance a from field-dependent electrical data.

Therefore, one may use the two lowest coefficients  $\sigma_1$  and  $\sigma_3$  of the power series of j(E) to define an apparent jump distance  $a_{app}$  via

$$(a_{app})^2 \equiv 24 \cdot \frac{\sigma_3}{\sigma_1} \cdot \frac{(k_B T)^2}{q^2}.$$
 (3)

This definition is based on a powerseries expansion of Eq. (2) and is chosen such that in the regular hopping model, the hopping length a is given by

$$a = a_{app}.\tag{4}$$

Real solid electrolytes are often complex disordered materials (e.g. structurally disordered crystals, glasses, polymers, nanocomposites) with ions moving in a disordered potential landscape quite different to the regular hopping model. In this case, it is a theoretical challenge to elucidate the physical meaning of the apparent hopping distance  $a_{app}$  and to find out in what way it is related to pecularities in the potential landscape of the ions in the respective material.

In experiments,  $\sigma_1$  and  $\sigma_3$  can be obtained by applying different dc fields E to a thin sample and by fitting the detected current densities i(E) to Eq. (1). Using this method, no information is available, however, about Joule heating effects. Joule heating may lead to an increase of the sample temperature, resulting in an increase of the ionic conductivity. Therefore, it is advantageous to use ac electric fields rather than dc fields. A nonlinear ionic conductivity leads to higher harmonic contributions to the current density spectrum, while this is not the case for Joule heating [3]. According to Eq. (1), the application of a sinusoidal electric field E(t) = $E_0 \cdot \sin(\omega t)$  leads to the following expression for the current density being

in phase with the electric field, j':

$$\begin{aligned} j' &= \sigma_1' \cdot E_0 \cdot \sin(\omega t) \\ &+ \sigma_3' \cdot (E_0)^3 \cdot \sin^3(\omega t) \\ &+ \sigma_5' \cdot (E_0)^5 \cdot \sin^5(\omega t) + \dots \\ &= \sigma_1'(\omega) \cdot E_0 \cdot \sin(\omega t) \quad (5) \\ &+ \frac{3}{4} \sigma_3'(\omega) \cdot (E_0)^3 \cdot \sin(\omega t) \\ &- \frac{1}{4} \sigma_3'(3\omega) \cdot (E_0)^3 \cdot \sin(3\omega t) \\ &+ \frac{10}{16} \sigma_5'(\omega) \cdot (E_0)^5 \cdot \sin(\omega t) \\ &- \frac{5}{16} \sigma_5'(3\omega) \cdot (E_0)^5 \cdot \sin(3\omega t) \\ &+ \frac{1}{16} \sigma_5'(5\omega) \cdot (E_0)^5 \cdot \sin(5\omega t) \\ &+ \dots \end{aligned}$$

Thus, the higher harmonic currents can be used to determine values for the higher order–conductivity coefficients  $\sigma_3$ ,  $\sigma_5$  etc., while Joule heating effects can be definitely excluded as the reason for the field dependence of the current [3]

In Fig. 1 we show a schematic illustration of an experimental setup for nonlinear ac conductivity measurements on thin ion-conducting glass samples. The sample thickness is typically in the range from 60-100  $\mu$ m, and we use ac voltages with amplitudes up to 500 V for achieving ac electric fields that are sufficiently high for detecting higherharmonic currents. The thin glass samples are attached to a highly resistive quartz glass tube (conductivity  $< \hat{10}^{-16}$  S/cm) by means of a high-voltage resistant Araldite glue (Vantico). The quartz tube with the attached sample is placed inside a quartz glass container. Both the quartz glass tube and the quartz glass container are filled with a liquid electrolyte containing the same type of mobile cation as the glass sample. Platinum wires connected to the high-voltage measurement system are dipped into the liquid electrolyte. Since the electrical resistance of the liquid electrolyte is several orders of magnitude lower than the resistance of the glass samples, there is virtually no voltage drop in the liquid electrolyte, but the voltage applied to the platinum wires drops completely in the glass samples. Therefore, the liquid electrolyte solutions act as non-blocking electrodes.

The high-voltage measurement system is based on the Novocontrol Alpha-AK high resolution dielectric analyser, which is equipped with a broadband high-voltage amplifier, a broadband dielectric converter and a high-voltage sample head. A schematic illustration of the setup is shown in Fig. 2. The high-voltage system provides a frequency range from 3  $\mu$ Hz to 10 kHz, a maximum voltage of 500 V, and a current resolution of 5 fA. The digital waveforms of sample voltage and current are numerically Fourier transformed by a digital processor in the Alpha-AK analyser. Thereby, the amplitudes and phases of the base wave and of higher harmonics in the current spectrum are determined with respect to the sinusoidal voltage. Higher harmonics are detectable, if their amplitude is at least  $10^{-3}$  of the base wave amplitude. The sample temperature is controled by the Novocontrol Quatro Cryosystem.

In Fig. 3 we show results for the base current density j'(v) (closed symbols) and for the higher harmonic current density j'(3v) (open sym-

bols), measured after applying a sinusoidal electric field with amplitude  $E_0 = 58.8 \text{ kV/cm}$  to a Na<sup>+</sup> ion conducting glass with chemical composition 0.2  $Na_2O \cdot 0.8$  SiO<sub>2</sub>. Both j'(v) and j'(3v) are normalised by the field amplitude  $E_0$  and are plotted versus frequency v at two different temperatures, T = 293 K and 313 K. The  $j'(v)/E_0$  curves reflect the frequency dependence of the lowfield conductivity  $\sigma'_1(v)$ . The lowfield conductivity exhibits the typical features known for solid electrolytes, i.e. dc conductivity plateau at low frequencies and dispersive conductivity at higher frequencies. The  $j'(3\nu)/E_0$  curves exhibit a lowfrequency plateau as well. According to Eq. (5), we can write the following expression for j(3v):

$$\frac{-4 \cdot j'(3\nu)}{E_0} = \sigma'_3(3\nu) \cdot (E_0)^2 + \frac{5}{4} \sigma'_5(3\nu) \cdot (E_0)^4 + \dots \qquad (6)$$

Thus, in a plot of  $-4 \cdot j'(3\nu)/E_0$  versus  $(E_0)^2$ , the data should lie on a straight line with a slope of  $\sigma'_3(3\nu)$ , if the second term on the right-hand side of Eq. (6) is negligible. In Fig. 4 such a plot is shown for a temperature of T = 293 K and a frequency of v = 0.0348 Hz. This frequency is in the plateau regime of j'(v) and  $j'(3\nu)$ . A closer look at Fig. 4 reveals that the data do not exactly lie on a straight line, but on a curve with a slightly negative curvature. Therefore, we fitted the data by a secondorder polynomial. From the linear term in this polynomial, we obtain directly  $\sigma'_3$ . The negative curvature of the data implies that  $\sigma'_5$  is negative.



However, the error in the curvature is so large that we can determine exclusively the sign of  $\sigma_{5,dc}$ , but not an accurate value.

Now, we can use the 'dc values' of  $\sigma_1$  and  $\sigma_3$  to calculate apparent jump distances  $a_{app}$  via Eq. (3). In Fig. 5,  $a_{app}$  is plotted versus temperature *T* for three different Na<sup>+</sup> ion conducting silicate glasses. The obtained values are in the range from about 40 Å to about 55 Å, i.e. the apparent jump distances are much larger than typical distances between nearest-neighbor sites (about 2.5-3 Å in molecular dynamics simulations [5]). For all three glasses,  $a_{app}$  decreases with increasing temperature.

In order to obtain a better understanding of the physical meaning of the absolute values of  $a_{app}$  and of its temperature dependence, theoretical analyses were carried out on one-dimensional single-particle disordered hopping models [4]. While the large apparent jump distances are reproduced in these hopping models, there are also clear discrepancies between the models and the experimental data [4]. The discussion of these discrepancies is, however, beyond the scope of this article and will be published in detail in a future paper [6]. Results for j(E) in two- and threedimensional models are not yet available. This will be the subject of future work.

#### References

- P. Vinatier, Y. Hamon, in *Charge Transport in Disordered Solids*, ed. S. Baranovski, Wiley 2006.
- [2] N. F. Mott, E. A. Davis, *Electronic processes in Non-Crystalline Materials*, Clarendon, London, 1979.
- [3] S. Murugavel, B. Roling, J. Non-Cryst. Solids 351 (2005) 2819.
- [4] A. Heuer, S. Murugavel, B. Roling, *Phys. Rev. B* 72 (2005) 174304.
- [5] A. Heuer, M. Kunow, M. Vogel,R. D. Banhatti, *Phys. Chem. Chem. Phys.* 4 (2002) 3185.
- [6] B. Roling, S. Murugavel, A. Heuer, L. Luehning, R. Friedrich, S. Roethel, to be published.

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Fig. 4: Plot of  $-4 \cdot j'(3\nu)/E_0$  versus  $(E_0)^2$  for the 0.2 Na<sub>2</sub>O  $\cdot$  0.8 SiO<sub>2</sub> glass at of T = 293 K and  $\nu = 0.0348$  Hz. The solid line denotes a fit by a second-order polynomial.



Fig. 5: Apparent jump distance  $a_{app}$  versus temperature T for three different Na<sup>+</sup> ion conducting glasses. The solid lines are drawn to guide the eye.

#### Meeting the Challenges of the 21st Century - Novel Applications of Broadband Dielectric Spectroscopy Advanced Research Workshop Suzdal, Russia, July 22 to 26, 2007

Broadband Dielectric Spectroscopy (BDS) is besides Nuclear Magnetic Resonance (NMR) and Infrared (IR) Spectroscopy the dominating experimental technique to study molecular dynamics and charge transport in soft and solid condensed matter. It is obvious that it has immediate impact on many modern technological challenges like, to name a few, liquid crystalline displays, ionic conductors in fuel cells and polymer (light weight) batteries, molecular dynamics in nanometric confinement, glassy dynamics and biological systems.



In the Advanced Research Workshop (ARW) sponsored by NATO with the Public Diplomacy Division, all these topics were addressed: Rotational and translational diffusion as measured by Broadband Dielectric Spectroscopy; Molecular dynamics in nanometric confinement: Dielectric spectroscopy in relation to other spectroscopic techniques; Broadband Dielectric Spectroscopy and charge transport phenomena; Dielectric spectroscopy in biological systems; Dielectric relaxation phenomena in polymers and glass forming liquids. Additionally panel discussions were arranged in which the following topics were addressed: Molecular dynamics at nanometric scales; Charge transport in ionic glassy systems; Dielectric properties of biological macromolecules and living biological matter. Furthermore two poster sessions were arranged where especially the younger scientists could present their latest results. Well-known scientists from Russia, Germany, France, USA, Israel, Belgium, Switzerland, Greece, Portugal, Japan, etc. participated in the conference. About 25 % of the participants were young scientists. The codirectors of the ARW, Profs. A. Khokhlov and F. Kremer, would like to thank also in the name of the participants

and the scientific community - NATO for the generous support.

F. Kremer, University of Leipzig

#### Announcement: Workshop "Broadband Dielectric Spectroscopy And Its Applications"

Responding to frequent demand from scientists interested in Broadband Dielectric Spectroscopy (BDS), Novocontrol Technologies announces its first workshop entitled "Broadband Dielectric Spectroscopy And Its Applications" to take place July 24-25, 2008, at the University of Leipzig, Germany under the guidance of Prof. F. Kremer.

The workshop will not only give an overview on the basics of this experimental technique, but also will elaborate on the following topics:

- fundamentals of Broadband Dielectric Spectroscopy (BDS)
- comparison to other spectroscopic techniques
- relaxational dynamics in glass forming liquids and polymers
- rotational and translational motion
- charge transport phenomena

Seminar blocks will be complemented by hands-on experience under professional guidance, participants perform and evaluate their own experiments, if possible on their own samples.

The regular participation fee for this two-day workshop will be  $\in 1500 \ (\in 700 \ \text{for academic users})$ . The number of participants is limited. Spaces are allocated on a first come first serve basis.

Prospective participients are kindly asked to register by email to **workshop@novocontrol.de**.

D. Wilmer, Novocontrol

## New Novocontrol High Voltage Extension HVB 4000

In the last couple of years, Novocontrol Technologies has constantly developed and extended its set of test interfaces for one of its key products, the broadband high-resolution gainphase analyser Alpha-A. We currently offer three "'families"' of test interfaces, focussing on (i) dielectric spectroscopy (ii) electrochemical applications and, (iii) high-field/nonlinear applications.

Responding to the increased demand for our high voltage test interfaces (HVB 300 and HVB 1000) and intending to lift the current limitation of  $500 V_p$ , Novocontrol has developed its new HVB 4000 in order to extend the maximum voltage by a factor of four.

Our new combination of Alpha-A mainframe and HVB 4000 test interface delivers up to  $\pm 2000 V_p$  AC and/or DC bias voltage to the sample, covering the frequency range from  $3\mu$ Hz to 10 kHz. The accessible measurement range covers both high and low impedances, i.e., up to  $10^{15} \Omega$ ) and down to  $100 \Omega$ , respectively. Due to the high output impedance of  $750 \text{ k}\Omega$  (selected for safety reasons), output voltages will decrease if samples with impedance below 1 M $\Omega$  are connected.

The new HVB 4000 system is fully supported by the recent version of our WinDETA software. Alternatively, it maybe fully controlled by GPIB commands issued to the Alpha-A.

D. Wilmer, Novocontrol

## A New Database of Publications on Dielectric and Impedance Spectroscopy

We frequently receive questions from our customers asking for typical publications that describe the most recent and/or most important developments in Broadband Dielectric Spectroscopy. At Novocontrol Technologies, we feel that is is not only important to solve your technical problems in this field, but also to know about the most important scientific trends.

We, therefore, kindly ask you to let us know about your scientific progress in Dielectric and Impedance Spectroscopy, especially if your experimental results have been obtained with Novocontrol measuring systems. Please send us your publications, most preferentially by email to novo@novocontrol.com in portable document format (PDF). We plan to create a database and a list of corresponding links to be presented on our web site.

D. Wilmer, Novocontrol

## OVERVIEW

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Editor: Dirk Wilmer. Abstracts and papers are always welcome. Please send your manuscript to the editor.