Dielectric spectroscopy of complex systems in Time and Frequency Domains: Problems and solutions

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Dielectric response on mesoscale

Dielectric spectroscopy is sensitive to relaxation processes in an extremely wide range of characteristic times \((10^5 - 10^{-12} \text{ s})\)

**Broadband Dielectric Spectroscopy**

**Time Domain Dielectric Spectroscopy; Time Domain Reflectometry**

- **Porous materials and colloids**
- **Macromolecules**
- **Clusters**
- **Glass forming liquids**
- **Single droplets and pores**
- **Water**
- **ice**

\(f (\text{Hz})\)
**Measurement Setup**

**Broad-Band Dielectric Spectrometer BDS 80 (NOVOCONTROL)** in the frequency range 10 µHz – 1.8 GHz with automatic temperature control by QUATRO Cryosystem (temperature range -150 °C - +400 °C)

\[
Z^*(\omega) = Z'(\omega) + iZ''(\omega) = \frac{U_s(\omega)}{I_s(\omega)}
\]

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = -i / 2\pi fZ(f)C_0
\]
Time domain dielectric spectroscopy

100KHz – 18 GHz


\[ V(t) = V_0(t) + R(t) \]

\[ I(t) = \frac{1}{Z_0} [V_0(t) - R(t)] , \]

\[ Q(t) = C_0 \left[ \varepsilon_\infty V(t) + \int_0^t \dot{\Phi}(t - t') V(t') dt' \right] \]

\[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{1}{Z_0 C_0 L} \frac{L[Q(t)]}{L[V(t)]]} \]

\[ \varepsilon_s - \Phi(t) \approx \Gamma(t) = \frac{<M(0)\bar{M}(t)>}{<M(0)\bar{M}(0)>} \]

Dipole Correlation Function

Spectrum

Lumped capacitance approximation in time domain:
\[ r = \lim_{t \to \infty} \frac{V(t)}{I(t)} = Z_0 \lim_{t \to \infty} \frac{V_0(t) + R(t)}{V_0(t) - R(t)} \]

\[ I_R(t) = \frac{V(t)}{r} = \frac{V_0(t) + R(t)}{Z_0} \lim_{t \to \infty} \frac{V_0(t) - R(t)}{V_0(t) + R(t)} \]

\[ I_D(t) = \frac{1}{Z_0} \left\{ \left[ V_0(t) - R(t) \right] - \left[ V_0(t) + R(t) \right] \lim_{t \to \infty} \frac{V_0(t) - R(t)}{V_0(t) + R(t)} \right\} \]

\[ \sigma = \frac{\varepsilon_0}{Z_0 C_0} \lim_{t \to \infty} \frac{V_0(t) - R(t)}{V_0(t) + R(t)} \]

\[ Q(t) = \int_0^t I_D(t') dt' \]
TDS Problems

Mismatch of signals in time

\[ I(t) \propto V_{\text{open}}(t + \delta) - V_{\text{sample}}(t) \]

Solution:
Time Shift in signal using the criteria

\[ \left. \frac{dI}{dt} \right|_{t=\text{max}} = 0; \quad \left. \frac{d^2V}{dt^2} \right|_{t=\text{max}} = 0 \]
Mismatch of signals in time

\[ I(t) \propto V_{\text{open}}(t + \delta) - V_{\text{sample}}(t) \quad \Rightarrow \quad i(\omega) = \exp(i\omega\delta)v_{\text{open}}(\omega) - v_{\text{sample}}(\omega) \]
Solution:
Time Shift in signal using the criteria

\[ \frac{dI}{dt} \bigg|_{t_{\text{max}}} = 0; \quad \frac{d^2V}{dt^2} \bigg|_{t_{\text{max}}} = 0 \]
TDS Problems

Vertical Shift in signal

\[ V_{\text{short}}(t) \rightarrow V_{\text{short}}(t) + \Delta \]

False Conductivity

\[
\sigma = \lim_{t \to \infty} \frac{I(t)}{V(t)} \propto \frac{V_{\text{open}}(t) - V_{\text{sample}}(t)}{V_{\text{sample}}(t) - V_{\text{short}}(t) - \Delta}
\]

\[
\approx \sigma_0 \left( 1 + \frac{\Delta}{V_{\text{sample}}(t) - V_{\text{short}}(t)} \right)
\]
TDS Problems

Vertical Shift in signal

\[ V_{\text{short}}(t) \rightarrow V_{\text{short}}(t) + \Delta \]

False Conductivity

\[
\sigma = \lim_{t \to \infty} \frac{I(t)}{V(t)} \propto \frac{V_{\text{open}}(t) - V_{\text{sample}}(t)}{V_{\text{sample}}(t) - V_{\text{short}}(t) - \Delta}
\]

Incorrect Amplitudes

\[
\approx \sigma_0 \left(1 + \frac{\Delta}{V_{\text{sample}}(t) - V_{\text{short}}(t)}\right)
\]
\[ Q(t) = \int_{0}^{t} I_D(t') dt' \]
TDS Problems

Fourier Transforms – 2 main problems:

Truncation errors

Using derivatives - \( i \omega F(f(t)) = F(\dot{f}(t)) \) Or Samolooun Algorithm

Descrete data

Attenuation factor based on cubic spline with end point correction

\[
\frac{1}{T} \leq f \leq \frac{1}{2\Delta} \Rightarrow \left[ h(t) \right](f) = H_n \approx \Delta \sum_{k=0}^{N-1} h_k e^{-2\pi kn/N} + O(\Delta^2)
\]

The frequencies of the FFT are, in essence, integral cycles on the interval. Therefore at high frequencies the summation can be smaller than the second order errors (previously ignored). A correction must be added.

\[
h(t) \approx \sum_{k=0}^{M} h_k \psi \left( \frac{t-t_k}{\Delta} \right) + \sum_{k=\text{endpts}} h_k \phi \left( \frac{t-t_k}{\Delta} \right)
\]

\[
W(2\pi n / N) = \int_{-\infty}^{\infty} ds e^{i2\pi n/N} \psi(s)
\]

\[
\alpha_k(2\pi n / N) = \int_{-\infty}^{\infty} ds e^{i2\pi n/N} \phi_k(s - k)
\]

\[
F \left[ h(t) \right] = H_n \approx \Delta e^{i2\pi fa} \left( W \left( 2\pi \frac{n}{N} \right) \sum_{k=0}^{M} h_k e^{ik2\pi n/N} + \sum_{k=\text{endpts}} h_k \alpha_k \left( 2\pi \frac{n}{N} \right) \right)
\]
For $\varepsilon \approx 1000$?

**Figure 12-24.**
Typical Permittivity Measurement Accuracy ($\varepsilon_r$ v.s. Frequency, @thickness = 3 mm)
Figure 11-8. Impedance Read-out
Sample Holders in BDS and TDS Measurements

**Solids**
- Low Frequency (<10⁷ Hz)
- Small angle spattering
- Contacts
- Slide electrodes, open ended coaxial or mesh electrodes
- High Frequency (>10⁸ Hz)

**Liquids**
- Electrode polarization
- Polish electrodes

**P, V conditions**
- \( R \leq \frac{0.24\lambda}{2\pi\sqrt{\varepsilon}} \)
- \( \lambda > \pi\sqrt{\varepsilon(b + a)} \)
The 3 electrode sample cell

How to account for leakage from a samples cell during an extended measurement?

How to maintain a constant pressure during a wide temperature regime?

How to establish a fixed geometry for a liquid?

How to overcome expansion problems for liquids?

How to ensure that there will be no air pockets between electrode and sample?

\[ C_0 = \frac{2\pi\epsilon_0}{\ln\left(\frac{b}{a}\right)} \]
$$C_0 = \frac{2\pi \varepsilon_0}{\ln\left(\frac{b}{a}\right)}$$
DS of Glycerol
TDDS Sample Cell

Upper electrode

Sample

Sample Cell

Inner electrode

Coaxial line

Upper electrode

Inner electrode

Gold plated Sample

Coaxial line
Typical Results

Time domain
Dielectric response function: $\Phi(t)$

Frequency domain
Spectrum of dielectric permittivity: $\varepsilon'(\omega)$
Dielectric Response in Biological Systems

Dielectric spectroscopy is sensitive to relaxation processes in an extremely wide range of characteristic times ($10^{-5}$ - $10^{-11}$ s)

**Broadband Dielectric Spectroscopy**

**Time Domain Dielectric Spectroscopy**

Temperature

- ice
- Cells
- Proteins
- DNA, RNA
- Tissues
- Water
- Lipids

Dispersion

- $\alpha$-Dispersion
- $\beta$-Dispersion
- $\delta$-Dispersion
- $\gamma$-Dispersion
dc conductivity

- In the cathode
  - \( \text{Na}^+ + \) electron \( \rightarrow \) Na
  - \( \rightarrow \) \( 2\text{Na} + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{OH}^- + \text{H}_2 \)

- In the anode
  - Cl\(^-\) - electron \( \rightarrow \) Cl
  - \( \rightarrow \) \( 2\text{Cl} \rightarrow \text{Cl}_2 \)
  - Metal + Cl \( \rightarrow \) MCl (e.g., CuCl\(_2\))

Problems are:
  - increase of pH,
  - birth of gases and corrosion of the electrode.
  - These are significant if current is not small.
What is the electrode polarization?

Electrode polarization effect

Measured characteristic

True characteristic of material

Electrical double layer

Frequency
Electrode Polarization

- List of possibilities of the corrections
  - Substitution method
  - Single exponent method (F3)
  - Fractal method (F2)
  - Blocking electrode
  - Electromagnetic induction method
  - Combination of plate-capacitance and fractal method
  - Change of the distance ($d$) of plate-capacitance
  - Others?

Electric double layer
Data treatment from time domain to frequency domain

E.g., human erythrocyte suspension

Signals in time domain

Dielectric spectrum in frequency domain

Fourier transform
Electrode polarization
Single exponent method

for low conductive sample

\[ I(s) = V_0(s) \frac{(s \tau_0 + 1)sC_p}{(s \tau_0 + 1)(s \tau_p + 1) + s \tau_R} \]

\[ V_p(s) = V_0(s) \frac{s(\tau_R + \tau_0) + 1}{(s \tau_0 + 1)(s \tau_p + 1) + s \tau_R} \]

\[ \tau_p = Z_0C_p, \quad \tau_R = RC_p, \quad \tau_p = RC, \quad s = j\omega \]

Electrode polarization correction function

\[ V_{ec}(t) = \frac{\tau_p}{\tau_R + \tau_p} \left(1 - e^{-t/\tau_2}\right), \]

where \( \tau_2 = \frac{1 - V_p(t_{max})}{V_p(t_{max})} \)
Example B: Human lymphocyte suspension

**Graph 1:**
- **Y-axis:** $\log(V_{air} - V_p)$
- **X-axis:** $t$ / nsec

**Graph 2:**
- **Y-axis:** $\varepsilon''$
- **X-axis:** $\log f$ / Hz

**Diagram:**
- Membrane
- Cytoplasm
- Nuclear envelope
- Nucleoplasm

**Conductivity of Membrane (New v.f.)**
- B-cells
  - Cancer
  - Normal
  - Transformed
- T-cells
  - Normal

**Table:**
- Conductivity values for different cell lines:
  - B-norm.
  - Magala
  - Farage
  - Raji
  - Bjab
  - Daudi
  - Peer
  - HDMar
  - T-nor.
This behavior allows us to suggest the frequency (or time) self-similarity of the electrode polarization phenomenon, i.e., the fractal nature of this effect.
Fractal approach can be applied to high conductive sample

Electrodes should be polished carefully because the electrode polarization depends on the fractal nature of the electrodes surfaces.

In Frequency domain:

\[
C_{v_i}(s) \equiv C_{v_i} \cdot s^{-\nu_i} = R_{i} \left( R_{i} C_{i} \right)^{-\nu_i} s^{-\nu_i}
\]

\[i=1,2; \ 0<\nu<1\]
In Time domain:

\[ V(t) \propto \frac{C_{v_1}}{\nu_1 \Gamma(\nu_1)} t^{\nu_1} + \frac{C_{v_2}}{\nu_2 \Gamma(\nu_2)} t^{\nu_2} + R[1 - \exp(-t/\tau_c)] \]

\( \nu \) dominates if \( \tau_c \ll 1 \)

\[ V(t) = B t^\nu + R t/\tau_c \quad \text{for} \quad t/\tau_c \ll 1 \]

\[ V(t) = B t^\nu + c \quad \text{for} \quad t/\tau_c \gg 1 \]

\( \nu \) dominates if \( \tau_c \gg 1 \)

\[ V(t) = B \nu_1 t^{\nu_1} + B \nu_2 t^{\nu_2} + R t/\tau_c \quad \text{for} \quad t/\tau_c \ll 1 \]

\[ V(t) = B \nu_1 t^{\nu_1} + B \nu_2 t^{\nu_2} + R \quad \text{for} \quad t/\tau_c \gg 1 \]

\( \nu \) dominates if \( \tau_c \gg 1 \)

\( v_1 \neq v_2; \quad C_{v1} \neq C_{v2} \)

\( v_1 = v_2; \quad C_{v1} = C_{v2} \)

Both electrodes of the sample holder have the same (or equivalent) electrode polarization.

There is no dispersion of the conductive solution (sample) in the time window defined by \( \tau_c (= t_{min} = 1/\omega_{max}) \)

\( \tau_c \ll 1 \)

\( \tau_c \gg 1 \)
Electromagnetic inductive method
- additional remark for near future -

The HP Sensor

Primary coil

Secondary coil

Solution

There is no electrode polarization!

Problem is amount of sample (400 ml).

Data Treatment

**What function?**

Frequency Domain

\[
\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \hat{L}\left[-\frac{d}{dt} \phi(t)\right]
\]

Havriliak-Negami (HN)

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{\left[1 + (i\omega\tau_m)^\alpha\right]^\beta}
\]

**Fitting?**

Time Domain

**dc conductivity correction?**

**Fitting?**

Power \times stretched exponential

\[
\phi(t) = A\left(\frac{t}{\tau_1}\right)^{-\mu} \exp\left\{-\left(\frac{t}{\tau_m}\right)^\nu\right\}
\]

for \( t / \tau_1, >> 1 \)

- **Graph 1:** Graph showing \( \varepsilon' \) vs \( \varepsilon'' \)
- **Graph 2:** Graph showing \( \log|\gamma(t/\tau)| \) vs \( t / \tau_1 \) for different temperatures.
Simultaneous fit of both real and imaginary components of the complex dielectric permittivity data;

Problems in selecting the proper fitting function, such as:

- The limited frequency and temperature ranges of the experiment;
- Distortion influences of the sample holder;
- Overlapping of several physical processes with different amplitudes in the same frequency and temperature ranges.

Continuous parameter estimation;

dc conductivity problems.
New Fitting Software—”MatFit”
**Key features of the program**

- Simultaneous fit of both real and imaginary components of the complex dielectric permittivity data;

- Linear and nonlinear fitting methods, from least squares and logarithmic to fitting procedures based on entropy norm;

- Global fit procedure on all selected temperature ranges for continuous parameter estimation;

- Hilbert Transform for computing dc conductivity.
Complex systems involve the appearance of a new "mesoscopic" length scale, intermediate between molecular and macroscopic.

- Complex liquids (microemulsions, emulsions, etc.)
- Porous materials (porous glasses, porous silicon, etc.)
- Ferroelectrics
- Glass forming liquids and polymers including composites
- Biological systems (protein solutions, membranes and cell suspensions)
What is the percolation phenomenon?

Percolation: The transition associated with the formation of a continuous path spanning an arbitrarily large ("infinite") range.

The percolation cluster is a self-similar fractal.
Dielectric response in microemulsions

Three dimensional plots of frequency and temperature dependence of the dielectric permittivity $\varepsilon'$ for the AOT/water/decane microemulsion

$\psi(t) \approx \frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle}{\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle}$

Three-dimensional plots of the time and temperature dependence of the macroscopic Dipole Correlation Function for the AOT-water-decane microemulsion

* AOT-water-decane microemulsion (17.5:21.3:61.2 vol%), $W = 26.3$, $R_{wp} = 35.6$ Angstrom

Dielectric response of the porous glass materials

Sample A

additional treatment in 0.5N KOH
rinsing in deionized water
drying at 200°C

Sample B

Sample C

Sample C after heating

Sample D
\[ \Psi(t) = A \left( \frac{t}{\tau_1} \right)^{-\mu} \exp \left[ - \left( \frac{t}{\tau_m} \right)^{\nu} \right] \]

**Morphology parameters:**
- \( s_m \): cut-off cluster size
- \( \gamma \): polydispersity index
- \( \eta \): cut-off rate index

**Dynamic parameters:**
- \( \alpha \): scaling parameter
- \( \tau_1 \): minimal time

**Dynamic exponent:**
\[ \Psi(t) \sim \exp \left[ - \left( \frac{t}{\tau_m} \right)^{\nu} \right] \]

**Fractal dimension:**
\[ D_f = 3\nu, \] where \( D_f \) is a fractal dimension

\[ D_s = \frac{D_d}{1 - D_d \frac{\lg \Theta}{\lg s_m}} \]

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(Chem. Phys. (2002) V. 284, 139-168)
Dielectric relaxation in percolation

**Percolation:** Transfer of electric excitation through the developed system of open pores

\[ \varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \Lambda \left( -\frac{d}{dt} \Psi(t) \right) \]

\[ \Psi(t) \sim \exp \left[ -\left( \frac{t}{\tau_m} \right)^{\nu} \right] \]

\[ D_f = 3\nu, \]

where \( D_f \) is a fractal dimension.
The Fractal Dimension of Percolation Pass

Sample | A | B | C | D
--- | --- | --- | --- | ---
Fractal dimension $D_f$ | 0.99 | 1.89 | 1.31 | 2.5
Porous medium in terms of regular and random fractals

\[ \phi = \frac{V_p}{V} \]

\[ \Phi = \int_{\mu}^{1} \phi(\xi, D)w(\xi)d\xi \]

\[ \mu = \frac{\lambda}{\Lambda} \]

\[ w(\xi) = A\xi^{\alpha}\exp\left(-a\xi^{\beta}\right) \]

\[ \phi = \left(\frac{\lambda}{\Lambda}\right)^{d-D} \]

\[ \Lambda, \lambda : \text{upper and lower limits of self-similarity} \]

\[ D : \text{regular fractal dimension of the system} \]

\[ w : \text{size distribution function} \]

\[ \alpha, \beta, A : \text{empirical parameters} \]
Porosity Determination

\[ \phi \approx \frac{1 + \alpha}{1 + \alpha + d - D} \cdot \frac{1 - \mu^{1 + \alpha + d}}{1 - \mu^{1 + \alpha}}, \quad \text{when } \alpha \ll 1, \mu \ll 1 \]

\[ \phi \approx \frac{1}{4 - D} \]


<table>
<thead>
<tr>
<th>Sample</th>
<th>Fractal dimension ( D_f )</th>
<th>Porosity ( \phi ) (%) (obtained from relative mass decrement measurements)</th>
<th>Porosity ( \phi ) (%) (obtained from dielectric measurements)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.99</td>
<td>38</td>
<td>33</td>
</tr>
<tr>
<td>B</td>
<td>1.89</td>
<td>48</td>
<td>47</td>
</tr>
<tr>
<td>C</td>
<td>1.31</td>
<td>38</td>
<td>37</td>
</tr>
<tr>
<td>D</td>
<td>2.5</td>
<td>50</td>
<td>68</td>
</tr>
</tbody>
</table>
PS HR-TEM micrographs and dielectric response

- Disordered network of crystallites and pores
- Fractal structure
- Preserve the crystalline nature
**Porosity Determination**

\[ \Psi \left( \frac{t}{\tau} \right) \sim e^{-\left(\frac{t}{\tau}\right)^{\nu}} \]

Dielectric response at the percolation

\( D_f \) is the fractal dimension of the pore channel lengths

\[ D_f = 3 \nu \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stretching parameter</th>
<th>Fractal dimension</th>
<th>Porosity ( \phi ) (%) (obtained from dielectric measurements)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 ( \mu )</td>
<td>0.88±0.02</td>
<td>2.64±0.06</td>
<td>74±1</td>
</tr>
<tr>
<td>30 ( \mu )</td>
<td>0.87±0.02</td>
<td>2.61±0.06</td>
<td>72±1</td>
</tr>
</tbody>
</table>

**Hopping conductivity in a percolating model**

\[ \phi = \frac{1}{4 - D_f} \frac{1 - \mu^{4-D_f}}{1 - \mu} \approx \frac{1}{4 - D_f} \]
Hilbert transform - we applied the Kramers-Kronig relations to the real part of the dielectric function, and subtracted this term from the imaginary part of the measured dielectric data.
KTN Crystals

$K_{1}Ta_{0.65}Nb_{0.35}O_{3} : Cu$

Perovskite Structure $ABO_{3}$

Cu doped at 2% by weight – 1:1000 unit cell volumes

Questions

- What does Cu do to the dielectric relaxation?
- Does Cu interact with Nb?
- What effects do the differing ionic radii of Cu and K cause?

$\varepsilon_s = \frac{C}{(T - T_0)}$

High temperature $\rightarrow$ Low temperature

cubic $\rightarrow$ tetragonal $\rightarrow$ orthorhombic $\rightarrow$ rombohedralic
Crystal 120 KTN – Dielectric Losses through the Ferroelectric phase transition

Dielectric Losses through the Ferroelectric transition

Ferroelectric PT

2nd PT

3rd PT

DC Conductivity

Arrhenius Process

$$\tau = \tau_0 \exp \left( -\frac{\Delta E}{k_B T} \right)$$

Activated Process

$$\tau = \tau_0 \exp \left( \frac{D}{T - T_k} \right)$$

has been linked to dynamic relaxation of the off-centre Nb ions in their octahedral site.
Maximum Peak Frequency

Paraelectric Phase

\[ T_x = 354 \, ^\circ K \]
\[ T_k = 228 \, ^\circ K \]
\[ \Delta \mu = 0.02 \, eV \]
\[ z^* \approx 3 \]
\[ \Delta E = 0.37 \, eV \]

Ferroelectric Phase

\[ E_a = 0.12 \, eV \]
\[ E_d = 0.32 \, eV \]
\[ C = \frac{1}{\eta} = 5.5 \times 10^5 \]

Where \( \eta \) is the maximum defect concentration
Free Volume Model

- Ferroelectric Phase – Structural Shift constrains Cu relaxation
- Cu ions perturbate the Lattice structure
- Some of these “Defects” provide the space needed for the Oxygen Octahedra to “tilt”.
- Alternatively the Defects allow the migration of Oxygen Vacancies

<table>
<thead>
<tr>
<th>Ion</th>
<th>Distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>1.37</td>
</tr>
<tr>
<td>O⁻²</td>
<td>1.40</td>
</tr>
<tr>
<td>Cu⁺²</td>
<td>0.73</td>
</tr>
<tr>
<td>Cu⁺¹</td>
<td>0.77</td>
</tr>
</tbody>
</table>