Analysis and modelling of dielectric relaxation data using DCALC

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Short course, Lodz, 8 October 2008

Part I – dielectric theory, representation of data…
Schedule

1st session (8 October 2008):
1) A brief introduction into DRS including dielectric relaxation theory, presentation of dielectric relaxation data in f- and T-domain, empirical relaxation functions and their temperature dependence (~ 45 min).
2) Presentation of the internal structure of DCALC, import/export of data, 2D and 3D graphical presentation capabilities and quick data analysis, example: PVAc.

2nd session (9 October 2008):
3) General fit-functions in the frequency domain, Fit-functions and options in DCALC, demonstration case PVAc or P2VP
4) "Hands-on" session (Please bring your own laptop with you and have DCALC installed and tested in advance)

3rd session (date t.b.a.):
5) Advanced numerical algorithm of DCALC: 1D and 2D derivatives, KK-transform, conductivity analysis
6) Fits using $\varepsilon''_{\text{der}}$ and fitting in temperature domain; 2D-fits and temperature depending HN-parameters
Outline

- Electrostatic relations
- Polarization – microscopic approach
- From macroscopic to macroscopic quantities
- The complex permittivity, the $f$-domain experiment
- Relaxation time (spectra)
- Empiric dielectric functions
- Temperature dependence of the dielectric properties
- Experimental implementation if DRS
- Representation of dielectric relaxation data
Dielectric response

Electrostatic relations on a parallel-plate capacitor:

Electrical field $E$ between plates in vacuum:

$$E = V/d$$

Charges $+Q$ and $-Q$ on surface:

$$Q = \varepsilon_0 EA$$

Vacuum capacitance $C_0$:

$$C_0 = \frac{Q}{V}$$

Dielectric constant of the material $\varepsilon$:

$$\varepsilon = \frac{C}{C_0} = \frac{Q + PA}{Q} \quad \text{or} \quad \varepsilon = \frac{\varepsilon_0 E + P}{\varepsilon_0 E}$$

$$\varepsilon_0 = 8.85 \times 10^{-12} \text{ As/Vm}$$

$$[C] = F \text{ (Farad)} = \frac{As}{V}$$

$P$ : polarisation
Dielectric response (2)

Total electrical polarisation in a dielectric:

\[ P = (\varepsilon - 1)\varepsilon_0 E + P_s \]

\( P \) is the total electrical polarisation in a dielectric.

- **induced polarisation**: For all dielectric materials with \( \varepsilon > 1 \), there is an induced polarisation due to the external electric field \( E \).
- **spontaneous polarisation**: For materials that exhibit pyroelectricity, piezoelectricity, or ferroelectricity, there is a spontaneous polarisation \( P_s \).

**Dielectric properties**

- passive
- active

Further:
\[ \chi_{el} = \text{electrical susceptibility} \]
\[ \chi_{el} = \varepsilon - 1 \]

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Polarisation – microscopic approach

\[ P = N_0 \alpha E_L \]

**molecular polarisability** \( \alpha \)

- **orientation**
  - \( \alpha_o \)
- **atomic**
  - \( \alpha_a \)
- **electronic**
  - \( \alpha_e \)

**Electronic and atomic polarisability:**

- fast displacements of electrons and atoms at optical frequencies
- (almost) T-independent
- property of all *nonpolar* materials
  \[ \Rightarrow \text{ refractive index } n > 1 \]

\( N_0 \): concentration of dipoles
\( E_L \): local electric field

\[ P = N_0 (\alpha_e + \alpha_a + \alpha_o) E_L \]
Polarisation – microscopic approach (2)

**DRS – characteristic time scales**

- Dipole orientational
- Atomic
- Electronic

Molar polarisation, \( \chi_m \)

Frequency (Hz)

Relaxation phenomena

IR, VIS/UV

Orientational polarisability
Orientational polarisation

No field, $E=0$:
Direction of mobile *molecular dipoles* arbitrary and driven by thermal energy $kT \rightarrow$ no average orientation

$E>0$:
Change of angular distribution due to directing electrical field, energy is $mE_L$

Effective (induced) dipole moment $m$:

$$
\bar{m} \approx \frac{\mu^2 E_L}{3kT}
$$

$m$ : molecular dipole moment
Orientational polarisation

Langevin function

\[ L(x) = \frac{\bar{m}}{\mu} = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} \quad \text{with} \quad x = \frac{\mu E_L}{kT} \]

Practical (low-field) conditions:

\[
\begin{align*}
E &= 1V/50\mu m \\
T &= 300K \\
\mu &= 2D
\end{align*}
\]

\[ \frac{\mu E}{kT} \approx 3.2 \times 10^{-5}! \]

→ linear approximation holds
From microscopic to macroscopic quantities

\[ P = N_0 (\alpha_e + \alpha_a + \alpha_o) E_L \]

local field \( \neq \) external field

Clausius-Mosotti relation:

\[ \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M_W}{\rho} = \frac{N_A \alpha}{3 \varepsilon_0} \]

- \( M_W \): molecular weight
- \( \rho \): density
- \( N_A \): Avogadro’s number

local field considerations
see e.g. Blythe, Electrical Properties of Polymers
From microscopic to macroscopic quantities (2)

Dielectric experiment → capacity $C$

$$C = \frac{A \varepsilon \varepsilon_0}{d}$$

$$\varepsilon = \frac{C}{C_0}$$

Alternating voltage:

$$V(t) = V_0 e^{i \omega t}$$

Current response of capacitor $C = \varepsilon C_0$

$$I(t) = \varepsilon C_0 \frac{dV(t)}{dt} = i \omega \varepsilon C_0 V(t)$$

90° phase shift
From microscopic to macroscopic quantities (3)

Non-ideal capacitor: polarisation build-up requires finite time

- complex dielectric constant
  
  $\varepsilon^* = \varepsilon' - i\varepsilon''$

this leads to 2 components of the current:

\[
I_C = i\omega C_0 \varepsilon' V \\
I_R = \omega C_0 \varepsilon'' V
\]

imaginary (capacitive) component, real (resistive) component, 
I and V are out of phase, energy dissipation term

- additional phase lag $\delta$ beteen V and I
  
  $\tan \delta = \varepsilon'' / \varepsilon'$
Single-Time Relaxation Process

Relaxation of $P_0$ into thermal equilibrium

Characteristic time to attain thermal equilibrium:

relaxation time $\tau$

$P(t) = P_0 \exp\left(-\frac{t}{\tau}\right)$
Single-Time Relaxation Process

Statistical nature of single-exponential relaxation

$E = 0$

$\langle m \rangle_t = 0$

$E \gg 0$

$\langle m \rangle_t > 0$

thermal energy: rotational diffusion of individual dipoles

\[ \rightarrow \text{time } \tau \text{ involves many small-step rotations} \]
Dielectric relaxations

Alternating electrical field at angular frequency $\omega$:
complex dielectric “constant”

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

All molecules have the same $\tau$ $\Rightarrow$ Debye relaxation

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2}$$
$$\varepsilon''(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau$$

equivalent circuit: $\tau = RC$

$$C_0 (\varepsilon_s - \varepsilon_\infty)$$

$\varepsilon_\infty \cdot C_0$
Relaxation time spectra

deviation of peak shape from Debye type
→ no single relaxation time behaviour

formal approach:

distribution in relaxation time $L(\tau)$

$\varepsilon^*(\omega) = \varepsilon_\infty + \Delta \varepsilon \int \frac{L(\tau)}{1 + i\omega \tau} d\ln \tau$

with $\int L(\tau) d\ln \tau = 1$
Relaxation time spectra

molecular reasons:

• real distribution in molecular potentials causes distribution in relaxation time

  e.g.: secondary peaks

• cooperativity – many-body interactions between relaxing units

  e.g.: $\alpha$-relaxation (segmental process)
Relaxation time spectra – model functions

Debye equation:
\[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + i\omega\tau} \]

Cole/Davidson:
\[ \varepsilon_{CD}^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{(1 + i\omega\tau_{CD})^\beta} \]
\[ \rightarrow \text{asymmetric broadening} \]

Cole-Cole:
\[ \varepsilon_{CC}^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i\omega\tau_{CC})^\beta} \]
\[ \rightarrow \text{symmetric broadening} \]
Relaxation time spectra

Havliliak-Negami:

\[ \varepsilon_{HN}^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{\left(1 + (i\omega \tau_{HN})^\beta\right)^\gamma} \]

2 shape parameters:
- \( \beta \): symmetric broadening
- \( \gamma \): asymmetry

- empirical function
- nevertheless, widely used to model dielectric spectra
Relaxation time spectra (HN-function)
Relaxation time spectra (model-free)

distribution in relaxation time $L(\tau)$

$$\varepsilon^* (\omega) = \varepsilon_\infty + \Delta \varepsilon \int \frac{L(\tau)}{1 + i\omega\tau} d\ln \tau$$

Computation of $L(\tau)$ by numerical techniques possible, e.g. Tikhonov regularization
Temperature dependence of the relaxation time

Molecular processes usually thermally activated processes → Arrhenius law

dielectric relaxations: gain in \textit{orientational polarisability} with temperature

mechanical relaxations: gain in “softness” with temperature
Thermally activated processes

Temperature dependence of relaxation time: Arrhenius law

\[ \tau(T) = \tau_\infty \exp\left(-\frac{E_a}{kT}\right) \]

\( \tau \) - process

\( \beta \) - process

T-dependence \( \tau(T) \) of \( \alpha \) and \( \beta \) process in a poly(ether ester) [Mertens et al. 1999, pol. 1a]
Thermally activated processes

Physical meaning of the **Arrhenius law**
→ thermal activation of a motion over energy barrier

**Barrier model**: T-independent height of energy barrier $E_a$ (activation energy)

**typical Arrhenius processes in polymers**:
- local (secondary) relaxations in glassy state
- dynamics in liquid crystalline polymers
## Dipoles in polymers

### Some dipole moments of simple molecules

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dipole moment $\times 10^{-30}$ Cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>6.1</td>
</tr>
<tr>
<td>HF</td>
<td>6.4</td>
</tr>
<tr>
<td>HCl</td>
<td>3.6</td>
</tr>
<tr>
<td>HBr</td>
<td>2.6</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>4.9</td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>5.3</td>
</tr>
<tr>
<td>C$_2$H$_5$OH</td>
<td>5.7</td>
</tr>
<tr>
<td>(C$_2$H$_5$)$_2$O</td>
<td>3.8</td>
</tr>
<tr>
<td>C$_6$H$_5$Cl</td>
<td>5.7</td>
</tr>
<tr>
<td>C$_6$H$_5$NO$_2$</td>
<td>14.0</td>
</tr>
</tbody>
</table>

### Dipole moments in polymers

- PVC
  - $\text{H} - \text{C} - \text{Cl}$
  - Dipole moment $\mu$

- PVDF
  - $\text{C} - \text{F}$
  - Dipole moment $\mu$

Remember: dielectric response

$$\propto \mu^2$$

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Dipoles in polymers

Location of dipole moments in the polymer chain:

Type A: dipole moment along chain axis

Type B: dipole moment perpendicular to chain axis

Type C: dipole moment in side group
Experimental techniques for DRS

measurement of (complex) capacitance or resistance by e.g.
• bridge techniques
• frequency response analyser

phase sensitive measurement of voltage and current

sample configurations:

comb electrode: parallel plate config.:
Experimental techniques for DRS

RLC meter HP4284A (Agilent)
20 Hz – 1MHz
Medium resolution in loss

Dielectric spectrometer (Novocontrol)
Alpha-Analyser (high resolution)
0.001 Hz – 10 MHz
Experimental techniques for DRS

Time-domain setup

Prof. Yuri Feldman, Jerusalem

- Up to 10 GHz
- Time domain data need transformation to frequency space

Figure 1. Circuit diagram of a TDS set-up.
Specific application: DRS on ultrathin film "capacitors"

1. thermal evaporation of **lower metal electrode** on glass substrates.
2. **spin-coating** of very dilute (filtered) polymer solutions
3. **drying + annealing** in vacuum
4. **2nd evaporation** → patterned top electrode

Clean room for thin film preparation
Dielectric instrumentation:

- Subject of separate lectures

Last part of this part:

- Various representation of complex dielectric spectra
Representation of relaxation spectra

1) Spectra of the real ($\varepsilon'$) and imaginary part ($\varepsilon''$) of the permittivity

Generally:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

2 spectra that carry (almost) equivalent information

Kramers-Kronig integral transforms:

$$\varepsilon'(\omega_0) = \varepsilon_\infty + \frac{2}{\pi} \int_0^\infty \varepsilon''(\omega) \frac{\omega}{\omega^2 - \omega_0^2} d\omega,$$

$$\varepsilon''(\omega_0) = \frac{\sigma_{dc}}{\varepsilon_\infty \omega_0} + \frac{2}{\pi} \int_0^\infty \varepsilon'(\omega) \frac{\omega_0}{\omega^2 - \omega_0^2} d\omega$$
Representation of relaxation spectra

2) KK-transform – numerically computed by DCALC

\[ \varepsilon''(\omega_0) = \frac{\sigma_{dc}}{\varepsilon_\nu \omega_0} + \frac{2}{\pi} \int_0^\infty \varepsilon'(\omega) \frac{\omega_0}{\omega^2 - \omega_0^2} d\omega = \varepsilon''_{KK} \]

Note:
\( \varepsilon''_{KK} \) lacks conduction term

- Good reproduction of \( \varepsilon'' \) in the peak region
- Additional features at low frequencies revealed

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Representation of relaxation spectra

2) KK-transform – effect of frequency spacing!

• DCALC algorithm optimized for geometric f-series (f, 2f, 4f…)

less is more!
Representation of relaxation spectra

3) An approximation of the KK-transform – $\varepsilon''_{\text{deriv}}$

$$\varepsilon''_{\text{der}} = -\frac{\pi}{2} \frac{\partial \varepsilon'(\omega)}{\partial \ln \omega} \approx \varepsilon''_{\text{rel}}$$

- Good reproduction of $\varepsilon''$ in the peak region for broad processes
- For narrow (Debye) processes $\rightarrow$ extra-sharp peak in $\varepsilon''_{\text{der}}$
- Additional features at low frequencies revealed

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Representation of relaxation spectra

3) $\varepsilon''_{\text{deriv}}$ – effect of peak shape
4) Loss tangent – a mixed quantity

\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'} \]

- “normalized” dielectric loss
  \( \rightarrow \) eliminates dimensional problems
- peak in \( \tan \delta \) shifted compared to \( \varepsilon'' \)
5) The Cole-Cole plot

$\varepsilon'' \text{ vs } \varepsilon'$

- Allows easy consistency check between $\varepsilon''$ and $\varepsilon'$ data (KK relation fulfilled)
- Frequency not explicit displayed
- Easy graphical inspection of peak symmetry and broadening
- Commonly used in impedance spectroscopy (Nyquist-plot)
Representation of relaxation spectra

5) The Cole-Cole plot \(\rightarrow\) Nyquist Diagram

Nyquist Diagram

General Nyquist diagram

Nyquist diagram for impedance
Representation of relaxation spectra

5) Dielectric modulus

\[ M^*(\omega) = 1/\varepsilon^*(\omega) = 1/(\varepsilon' - i\varepsilon'') \]

\[ M^*(\omega) = M'(\omega) + iM''(\omega) \]

\[ = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + i\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \]

Note that \( \tan \delta \) is the same as for \( \varepsilon^* \)

\[ \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = \tan \delta \]
Representation of relaxation spectra

5) Dielectric modulus

Imaginary part shows “conduction” peak in the conduction region,
Maximum yields Ohmic relaxation time:

\[ \tau_\sigma = \varepsilon_\infty \varepsilon_v / \sigma \]

- Relaxation peaks appear shifted in \( M'' \)-representation

\[ (\omega \tau)_{M''}^{\max} = \varepsilon_s / \varepsilon_\infty \]

- This shift is twice of the shift in \( \tan \delta \) because of

\[ (\omega \tau)_{\tan \delta, \max} = (\varepsilon_s / \varepsilon_\infty)^{1/2} \]
Representation of relaxation spectra

5) Dielectric modulus in CC-representation

Conduction peak

α-peak
Representation of relaxation spectra

6) Conductivity representation

\[ \sigma = \varepsilon'' \varepsilon_0 \omega \]

Increasing T

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6) Conductivity representation – filtered data

Special function of DCALC:
Exclusive display of (nearly) frequency independent $\sigma$-values
Representation of relaxation spectra

More options, e.g.

- Admittance \( Y^*(\omega) = Y' - jY'' \)
- Impedance \( Z^*(\omega) = Z' - jZ'' \)
- Capacitance \( C^*(\omega) = C' - jC'' \)
- etc.

Further reading: