Set Inversion Via Interval Analysis applied to dielectric spectroscopy

Maëllenn AUFRAY, Adrien BROCHIER and Wulff POSSART

June 19th-20th 2008
Montpellier
SWIM 2008
Basic Principles of DES

The dielectric is considered as a medium with relaxations for both dipoles $\varepsilon^*(\omega)$ and charge carriers $\sigma^*(\omega)$:

What is really considered in DES

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

$$
\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega)
$$

$$
\tilde{\varepsilon}'(\omega) = \varepsilon'(\omega) \text{ and } \tilde{\varepsilon}''(\omega) = \varepsilon''(\omega) + \frac{\sigma_{DC}}{\omega \varepsilon_0}
$$

- The Dielectric spectroscopy measures the dielectric properties of a medium as a function of frequency.
- It is based on the interaction of an external field with the electric dipole moment of the sample.
The Debye model

Let \( \varepsilon_\infty \) be the permittivity at the high frequency limit, \( \varepsilon_s \) be the static permittivity at low frequency, and \( \tau \) be the relaxation time, then a single Debye relaxation is described by the formula:

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i \omega \tau_0}
\]

For a data set with \( m \) relaxations, let \( p_j = (\Delta \varepsilon_j, \tau_j) \) and \( p = (\varepsilon_\infty, p_1, \ldots, p_m) \). Then, the model is:

\[
f(p, \omega) = \varepsilon_\infty + \sum_{j=1}^{m} \frac{\Delta \varepsilon_j}{1 + i \tau_j \omega}
\]

Remark

The function doesn’t change if the \( p_j \) are permuted. For example, if \( m = 2 \) and \( p^* = (\varepsilon^*, p_1^*, p_2^*) \) is a given solution of the fitting problem, then the vector of parameters \( (\varepsilon^*, p_2^*, p_1^*) \) is an equivalent solution.
Curves expected and obtained!

Ideally, a single Debye relaxation is:

Real curve: epoxy monomer material relaxation + conductivity + electrodes polarization!

at -90 degrees

at 60 degrees
That is why other models were imagined.

- The Debye model
  \[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_0} \]

- The Cole-Cole model
  \[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_0)\alpha}, \quad 0 < \alpha \leq 1 \]

- The Davidson-Cole model
  \[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau_0)\beta}, \quad 0 < \beta \leq 1 \]

- The Havriliak-Negami model
  \[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{(1 + (i\omega\tau_0)\alpha)\beta}, \quad 0 < \alpha\beta \leq 1 \]

⇒ Only the Debye model has a physical meaning: the other one are phenomenological.

Adrien BROCHIER (ASPG)  SIVIA applied to DES  SWIM 2008 5 / 15
Aim of the study: to model dielectric curves in order to have a better comprehension of dielectric relaxations.

### Least Square Approximation

- Choice of initial values
- Relevance of the result (local minimum, convergence, physical meaning, ...)
- Complexity of the model (non-linearity, dimension and symmetries of the parameters space, ...)
- No possibility to take in account limitations (bound on the parameters)
Interval analysis

Requirements

- Simultaneous fit of real and imaginary part
- Use of Debye model (the only one model with a physical meaning)
- Guaranteed results and automatic guess of the number of relaxation

Reformulation of the problem in the setting of interval analysis

- Bounded error context → CSP
- Each measured value $y_i$ leads to an interval $[y_i] = [y_i - e_i, y_i + e_i]$ according to the measurement accuracy
- The set of feasible parameters is

$$\mathcal{F} = \left\{ p \in \mathbb{R}^k \mid \forall 1 \leq i \leq n, \ f(x_i, p) \in [y_i] \right\}$$
Set Inversion Via Interval Analysis

- SIVIA: branch and bound algorithm → return a list of boxes (i.e. $k$-dimensional intervals) which approximate the set of feasible parameters
- Used together with a contractor, a procedure which decreases the size of the tested boxes.
- Very promising results, but:
  - Difficulty determining an interval for each parameter from returned list of boxes
  - Computing time and memory usage in practice

Remark

As any permutation of the parameters leaves the model invariant:

- $\mathcal{F}$ is a non-connected set
- All the connected component of $\mathcal{F}$ are “the same up to symmetry”

So it would be sufficient to approximate only one of the connected component of $\mathcal{F}$. 
First modification

- Search of the bounding box of the set of feasible parameters
- Use of the convex union instead of the usual one
- The memory usage becomes almost constant
- A lot of boxes have no more to be tested: decrease of the computing time

But... The bounding box of a non-connected set is not relevant.
Breaking the symmetries

- We need to select one single connected component of the feasible parameters set.
- For numerical parameters, we could impose some order on the parameters, for example that $\tau_i < \tau_{i+1}$.
- For interval parameters $[\tau_i] = [\tau_i^-, \tau_i^+]$, we assume that
  \[ \tau_i^- < \tau_{i+1}^- \quad \tau_i^+ < \tau_{i+1}^+ \]
- It’s a weaker condition, but it works if the relaxations aren’t too close to one another.
- This also decreases the computing time by cutting off the search space.
Guess of the number of relaxations

- Nice property of SIVIA: It finds something... only if there is something to find!

- In particular, if the supposed number of relaxation is too small, it return (very quickly) an empty set

- Therefore, by successives tries, the algorithm computes the smallest number of relaxations which leads to a nonempty set

- On the other hand, if the supposed number of relaxation is too big, there are too many degree of freedom: this mean that the number of relaxation determined by the algorithm should be considered as optimal
Some results

\[ \varepsilon^*(\omega) = \varepsilon_\infty + \sum_j \frac{\Delta \varepsilon_j}{1 + i\omega\tau_j} - i \frac{\sigma_{DC}}{\omega\varepsilon_0} \]
Some results

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j}{1 + i\omega\tau_j} - i\frac{\sigma_{DC}}{\omega\varepsilon_0}
\]

The polarisation of the electrodes is represented by a very big Debye relaxation
Interval analysis methods lead to an algorithm which:

- gives a strong criterion for evaluating the optimal number of relaxations
- works well even if some relaxations are close to one another, are hidden by some noise or are partially outside of the experimental range
- leads to intervals which are directly related to the experimental errors, which is much more satisfactory than single values from a physical point of view.

**consequence**

This algorithm validates the Debye model

$\Rightarrow$ The Debye model is able to match real life experimental data
Thanks for your attention

Contact

- E-mail: maelenn.aufray@ensiacet.fr