Set Inversion Via Interval Analysis applied to dielectric spectroscopy

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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 ε_∞ be the permittivity at the high frequency limit, ε_s be the static permittivity at low frequency, and τ be the relaxation time, then a single Debye relaxation is described by the formula:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \mathrm{i}\,\omega\tau_0}$$

- 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:

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

Remark

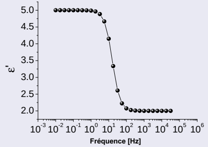
The function doesn't change if the p_j are permuted. For example, if $m = 2$ and $p^* = (\varepsilon^*, p_1^*, p_2^*)$ is a given solution of the fitting problem, then the vector of parameters $(\varepsilon^*, p_2^*, p_1^*)$ is an equivalent solution.

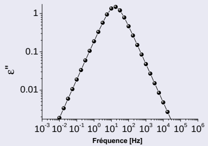
Curves expected and obtained !

Real curve : epoxy monomer

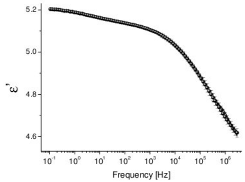
material relaxation + conductivity + electrodes polarization!

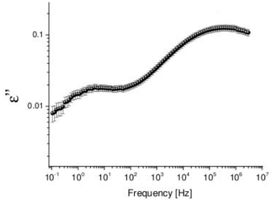
Ideally, a single Debye relaxation is:



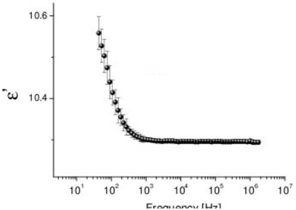


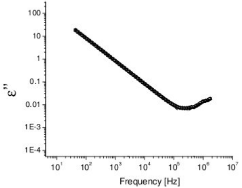
at -90 degrees





at 60 degrees





That is why other models were imagined

- The Debye model

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \mathrm{i}\,\omega\tau_0}$$

- The Cole-Cole model

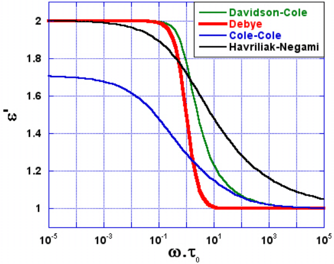
$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\mathrm{i}\,\omega\tau_0)^\alpha},\ 0 < \alpha \leq 1$$

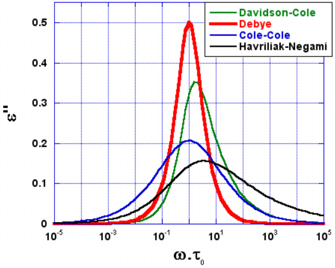
- The davidson-Cole model

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + \mathrm{i}\,\omega\tau_0)^\beta},\ 0 < \beta \leq 1$$

- The Havriliak-Negami model

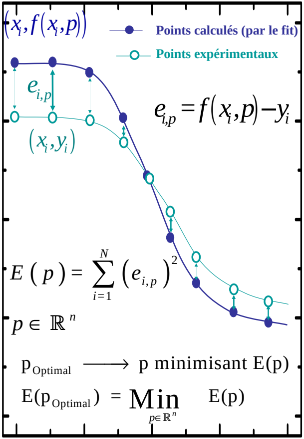
$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (\mathrm{i}\,\omega\tau_0)^\alpha)^\beta},\ 0 < \alpha.\beta \leq 1$$





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

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 $\rightarrow$ 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

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

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

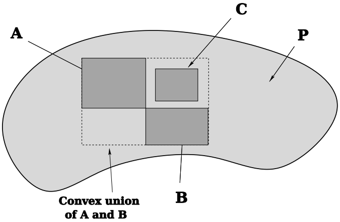
As any permutation of the parameters leaves the model invariant:

- $\mathcal{F}$ 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 $\mathcal{F}$.

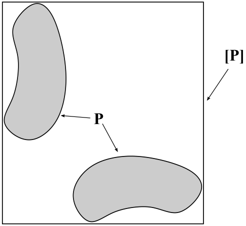
First modification

- 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

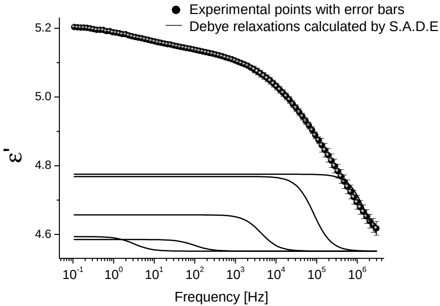
$$\tau_i^- < \tau_{i+1}^- \qquad \tau_i^+ < \tau_{i+1}^+$$

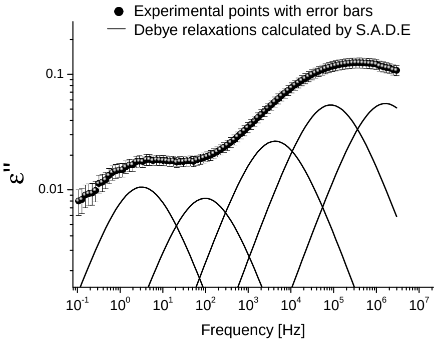
- It's a weaker condition, but it works if the relaxations aren't too close to one another
- This also decreases the computing time by cutting off the search space

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

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

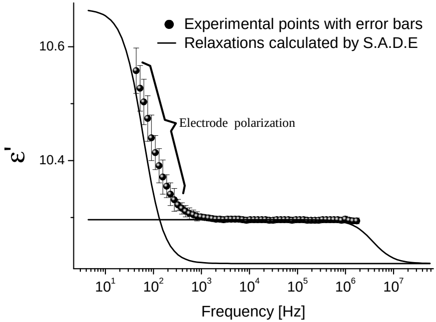


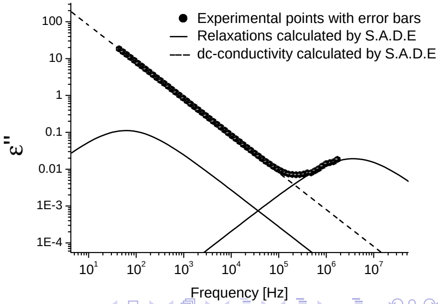


Some results

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

The polarisation of the electrodes is represented by a very big Debye relaxation





Conclusion

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

Contact

Thanks for your attention

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