

PACS number(s): 77.22.Gm; 02.60.Ed

EVOLUTION STRATEGY FOR FITTING OF COEFFICIENTS IN HAVRILIAK–NEGAMI EQUATION IN DIELECTRIC RELAXATION PHENOMENON

Ł. Laskowski, M. Laskowska, G. Lach, J. Świątek

*Physics Department of Jan Długosz University
ul. Armii Krajowej 13/15, 42-200 Częstochowa*

The main goal of this thesis is presenting of computer program for fitting of coefficients in Havriliak–Negami equation, in the way of describe of observed relaxation phenomenon the most accuracy.

In the first part of thesis, the problem of fitting theoretical function for experimental data is described. Next the computer program for finding coefficient in Havriliak–Negami equation is presented. Lastly the test of considered program and comparison with commercial programs was carried out.

Key words: dielectric relaxation, fitting, Havriliak–Negami equation, computer program.

Dielectric spectroscopy [1], [2], [3], [4] is an experimental tool witch enable to find many significant information about dielectric properties of matters. In dielectric relaxation region dielectric constant in frequency domain describes the interaction of electromagnetic waves with matter and reflects by that the underlying molecular mechanisms. In order to find parameters of observed phenomenon (relaxation time, conductivity, dielectric increment etc.) is necessary to fit theoretical function. The data can be described by a generalized relaxation function. Nowadays the phenomenological Havriliak–Negami equation is uses the most frequently. This function is presented below, on equation 1.

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau)^{\alpha}\right]^{\beta}} + \frac{\sigma_{dc}}{i\varepsilon_0\omega^n}. \quad (1)$$

This approach was used to model the experimental results and allows the determination of the relaxation time τ , the associated distribution parameters α and β representing, respectively, the symmetrical and asymmetrical broadening of the dielectric functions. The first term in equation 1 depends on the steady state conductivity σ_{dc} while ε_0 is the vacuum permittivity and the dielectric strength $\Delta\varepsilon$ represents the difference between the low (relaxed) frequency dielectric permittivity and the high (unrelaxed) frequency one (ε_0).

In order to fit H-N function to observed phenomenon, finding six parameters (ε_{∞} , $\Delta\varepsilon$, τ , σ_{dc} , α i β) is necessary in the case only one relaxation. With additional phenomenon the number of parameters increase by a four. This problem might be reduce to optimization issue: for what value of parameters ε_{∞} , $\Delta\varepsilon$, τ , σ_{dc} , α and β the sum of square of difference between couple of points: empirical and point for Havriliak–Negami

curve, for the same frequency is minimal. The problem lies in finding theoretical chart (parameters in Havriliak–Negami equation), which good fits to empirical charts. Crucial is, that rarely all empirical points lies in theoretical curve.

Using classical optimization method isn't good idea yet, for the sake of amount of searching parameters. Sometimes it is possible existence a few relaxation phenomenon in narrow range of frequency. In this case the general dielectric behavior can be described by a few Havriliak–Negami equation, and complexity of problem increase.

For this optimize problem evolution strategy [5], [6] is appropriate. The virtues of this kind of algorithm is that much information about problem isn't require. The first derivative of objective function isn't necessary.

The mentioned above type of algorithm can be used to construct program for fitting experimental data by Havriliak–Negami function.

The program SFit 2.0 realize evolution strategy for fitting parameters in Havriliak–Negami equation described relaxation phenomenon in the most accuracy way. The program was create witch using free software for no commercial using. The program language was C++ with Qt [7], [8] and OpenGL [9] library.

The interface of program is presented on figure 1.

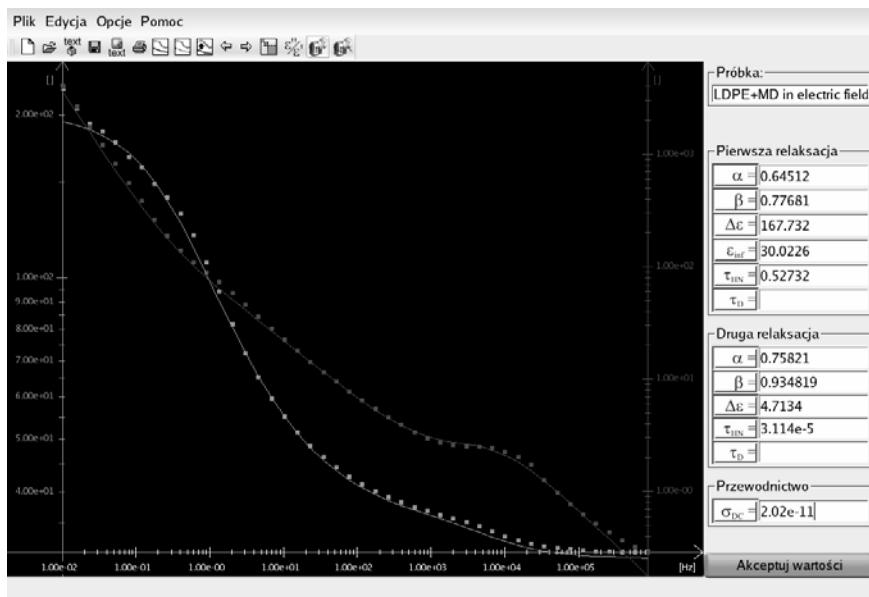


Fig. 1. The interface of program S Fit 2.0

The interface allows easy communication between user and program. The loading of measurement data from spectrometer is done by loading text file with experimental data. This resolution allow universal use of program without specify of input device. The program is finding the number of measurement points itself, but it is require appropriate format of input data. First line is treat as a comment, and is display in edit line as a information about sample. Next two lines are ignored. Starting with fourth line the program is loading experimental data to the vector. It is require separate columns by a tabulator. First column is treat as a frequency of external electric field. Second column is

read as a real part of permittivity, third as a imaginary part of dielectric permittivity. Next columns are ignored. Loaded data are used for build empirical chart, which is presented in chart editor window. User has possibility of choosing displayed value (permittivity – real, imaginary and complex, susceptibility – real, imaginary and complex, impedance – real, imaginary and complex, conductivity etc.), scale (logarithmic or linear), as well “cutting” displayed value (often extreme values are burdened high error). All displayed value on chart suit theoretical value, calculated from Havriliak–Negami equation, on the ground of its actual parameters. This constants are displayed in edit lines, on the right side of interface. User has possibility of change of their value. After acceptance parameters, chart is repaint, so user can control correctness of plot. One may hide theoretical plot–program is able to only edit chart. It is possibility change of amount Havriliak–Negami equations (one, two or three), described of observed phenomenon. The algorithm of fitting points is started by a user from defined point (initial values are load from edit lines and feed as value of genes of one chromosome). The number of iteration of evolution algorithm is fixed and may be changed by another produce of function. The final result of fitting can be corrected by a change of value in edit poles and acceptance. After any change iteration of algorithm begin anew, with random values of dispersion vector. The advantage of interference in value of parameters is that user can direct algorithm in attraction area of global minimum.

After obtaining satisfy result, user has possibility of save data as text file.

The program was tested both real experimental data and test data. The comparison with commercial program for fitting experimental points (WinFit) was carried out.

First test function was single Havriliak–Negami equation, with parameters:

$$\begin{aligned}\alpha &= 1,0, \\ \beta &= 1,0, \\ \varepsilon_{\infty} &= 31,0, \\ \Delta\varepsilon &= 100, \\ \tau_{HN} &= 1,0 \text{ s}, \\ \sigma_{dc} &= 1,0 \cdot 10^{-13} \text{ S/cm}.\end{aligned}$$

The program was able to fit appropriate theoretical function by average three starting of algorithm. On the AMD Athlon 1800 computer it took about 20s. The result is presenter on figure 2.

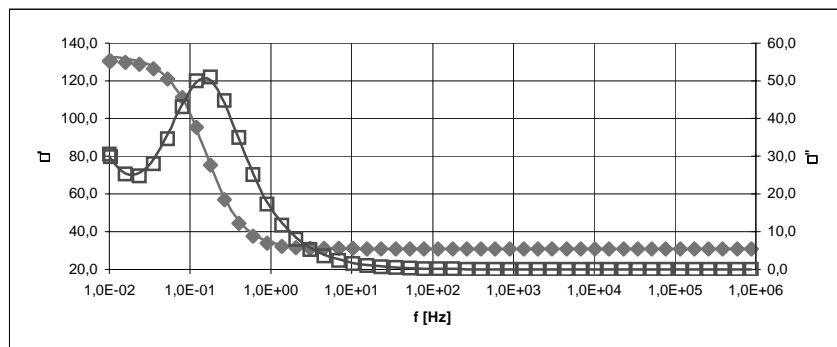


Fig. 2. The empirical chart with fitted theoretical chart for test data. The empirical data are marked as a points, theoretical function is marked as a lines

The following parameters are obtained:

$$\begin{aligned}\alpha &= 0,88583, \\ \beta &= 0,983329, \\ \varepsilon_{\infty} &= 30,8713, \\ \Delta\varepsilon &= 100,108, \\ \tau_{\text{HN}} &= 1,081831 \text{ s}, \\ \sigma_{\text{dc}} &= 1,27897 \cdot 10^{-13} \text{ S/cm}.\end{aligned}$$

It is seen, that error isn't significant and obtained plot good approximate empirical points. When starting algorithm from nearest optimum point, reaching satisfactory effect takes less time – single-time starting evolution strategy. In comparison with commercial program, SFit go more favorable. When bad selecting of start parameters commercial program get bogged down and finding appropriate resolution isn't possible, while SFit is finding satisfy parameters, with only longer time.

The program was tested on real experimental data too. The attempt at fitting theoretical plot to dielectric spectrum of low density polyethylene grafted by dodecyl maleate was made. In considered range of frequency, two relaxation phenomenon was observed, so two Havriliak–Negami equation are required for this problem. The program managed this task in average time of eight starting strategy. The result is presented on figure 3.

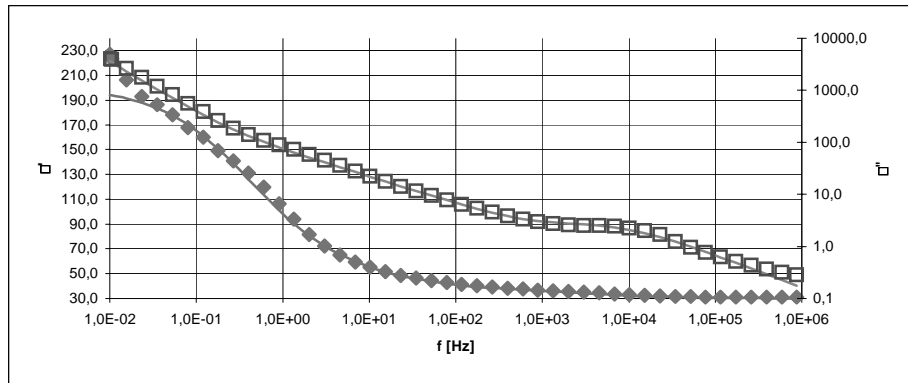


Fig. 3. The empirical chart with fitted theoretical chart for low density polyethylene grafted by dodecyl maleate. The empirical data are marked as a points, theoretical function is marked as a lines

As it can be seen theoretical plot good approximate the empirical points. The values of parameters in Havriliak–Negami equations are following:

$$\begin{aligned}\alpha^1 &= 0,641583, \\ \beta^1 &= 0,776869, \\ \varepsilon_{\infty} &= 30,8713, \\ \Delta\varepsilon^1 &= 167,732, \\ \tau_{\text{HN}}^1 &= 0,527231 \text{ s}, \\ \sigma_{\text{dc}}^1 &= 2,02846 \cdot 10^{-11} \text{ S/cm}, \\ \alpha^2 &= 0,758657, \\ \beta^2 &= 0,934819, \\ \Delta\varepsilon^2 &= 4,7134, \\ \tau_{\text{HN}}^2 &= 3,1141 \cdot 10^{-5} \text{ s}.\end{aligned}$$

The real data for this test was used and for the sake of this it is difficult estimate real relaxation parameters. Instead of this comparison with results of fitting this parameters by WinFit program. The results from WinFit are following:

$$\begin{aligned}\alpha^1 &= 0,976, \\ \beta^1 &= 0,4693, \\ \varepsilon_\infty^1 &= 30,78, \\ \Delta\varepsilon^1 &= 129,0, \\ \tau_{HN}^1 &= 0,42371 \text{ s}, \\ \sigma_{dc}^1 &= 2,339 \cdot 10^{-11} \text{ S/cm}.\end{aligned}$$

$$\begin{aligned}\alpha^2 &= 1,0, \\ \beta^2 &= 0,55470, \\ \Delta\varepsilon^2 &= 4,7134, \\ \tau_{HN}^2 &= 4,226 \cdot 10^{-5} \text{ s},\end{aligned}$$

As it can be seen, obtained results are similar and theoretical plot good approximate experimental data. So one may say that program SFit is fit for solving real problems.

There are cases yet, considered evolution algorithm don't cope with. Sometimes algorithm show tendency of getting stuck in relative extremum. Then another starting strategy don't get results. The resolution is starting evolution strategy from another start point. The stacking of algorithm in relative extremum is shown on figure 4.

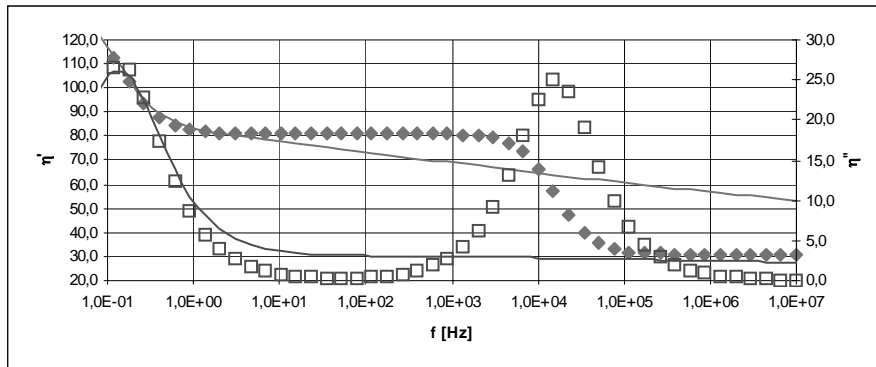


Fig. 4. Stacking of evolution strategy in relative extremum

It is clearly seen, that problem stacking algorithm in local minimums should be eliminated. It can be reach by decomposing algorithm for two modules. First responsible for fitting some parameters in based on real part of permittivity, second should find rest of parameters in the based on imaginary part of permittivity. For the sake of specification of real and imaginary parts of dielectric spectrum it can get good results.

In spite of discussed disadvantage program SFit can be very useful for fitting dielectric spectrums.

1. *Jonscher A. K.* Dielectric relaxation in solids. Chelsea Dielectric Press, London. 1978.
2. *Jonscher A. K.* Universal relaxation law. Chelsea Dielectric Press, London. 1996.
3. *Kremer F., Schönhals A.* Broadband dielectric spectroscopy. Springer, Berlin. 2003.
4. *McCrum N. G., Read B. E., Williams G.* Anelastic and dielectric effects in polymeric solids. Dover Publications, New York. 1991.
5. *Arabas J.* Wykłady z algorytmów ewolucyjnych. WNT, Warszawa. 2001.
6. *Mulawka J. J.* Systemy ekspertowe. WNT, Warszawa. 1996.
7. *Solin D.* Programowanie przy użyciu biblioteki Qt. Infoland, Warszawa. 2001.
8. www.trolltech.com.
9. *Andrzejewski P., Kurzak J.* Wprowadzenie do OpenGL. Programowanie zastosowań graficznych. Kwantum, Warszawa. 2000.
10. *Wübberhorst M., Turnhout van J.* Analysis of complex spectra. One-dimensional derivative techniques and three-dimensional modeling. Journal of Non-Crystalline Solids. 2002. Vol.305. P. 40–49.

**ЕВОЛЮЦІЙНА СТРАТЕГІЯ ДЛЯ АПРОКСИМУВАННЯ КОЕФІЦІЄНТІВ
РІВНЯННЯ ГАВРИЛЯКА-НЕГАМІ ПІД ЧАС ДОСЛІДЖЕННЯ ЯВИЩА
ДІЕЛЕКТРИЧНОЇ РЕЛАКСАЦІЇ**

Ł. Ласковскі, М. Ласковска, Г. Лак, Д. Свіонтек

*Інститут фізики, університет імені Яна Длугоша
вул. Армії Крайовей 13/15, 42-200 Ченстохова, Республіка Польща*

Розроблено комп'ютерну програму для апроксимації коефіцієнтів рівняння Гавриляка–Негамі з метою точного опису явища діелектричної релаксації.

У першій частині статті досліджено проблему апроксимації теоретично отриманої функції за експериментальними даними. Далі запропоновано програму для обчислення коефіцієнтів рівняння Гавриляка–Негамі. Окрім того, в статті описано тестування вищезгаданої програми та порівняння з комерційними аналогами.

Ключові слова: діелектрична релаксація, апроксимація, рівняння Гавриляка–Негамі, комп'ютерна програма.

Стаття надійшла до редколегії 29.05.2006

Прийнята до друку 26.02.2007