



## Numerical differentiation methods for the logarithmic derivative technique used in dielectric spectroscopy<sup>#</sup>

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### Abstract

*In dielectric relaxation spectroscopy the conduction contribution often hampers the evaluation of dielectric spectra, especially in the low-frequency regime. In order to overcome this the logarithmic derivative technique could be used, where the calculation of the logarithmic derivative of the real part of the complex permittivity function is needed. Since broadband dielectric measurement provides discrete permittivity function, numerical differentiation has to be used. Applicability of the Savitzky-Golay convolution method in the derivative analysis is examined, and a detailed investigation of the influential parameters (frequency, spectrum resolution, peak shape) is presented on synthetic dielectric data.*

**Keywords:** dielectric spectroscopy, logarithmic derivative, Savitzky-Golay method

### I. Introduction

Dielectric relaxation spectroscopy (DRS) has become a popular and powerful technique for studying the dielectric properties of almost any kind of material. Modern measurement systems allow the acquisition of relaxation spectra over a wide range in frequency and temperature with a high accuracy. Hence we are able to obtain information about molecular relaxation dynamics and conduction processes, leading to a deeper understanding of the materials' nature.

In order to extract most of the information carried by the measurement data, mathematical methods may be applied. In broadband dielectric spectroscopy the so-called harmonic analysis is used. This means that the value of the permittivity function is only known at given measurement frequencies. Since the spectra are discrete datasets, only numerical approximations can be used. Therefore, the result of the evaluation depends strongly on the precision of these methods.

In this paper we will present numerical derivative calculations on synthetic dielectric data. All the influ-

ential parameters are considered, and the capabilities and limitations of the approach are discussed.

### II. Theoretical Background

In DRS the frequency-dependent complex dielectric function is used to determine the electrical/dielectric properties of materials [1]:

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

where  $\varepsilon'(\omega)$  is the real and  $\varepsilon''(\omega)$  is the imaginary part of the complex dielectric function.

If the measured sample contains mobile charge carriers, i.e. it exhibits conduction, a considerable increase shows up in the low frequency part of the imaginary permittivity spectrum (loss spectrum). In moderately to highly conducting materials this "conductivity tail" hampers the proper analysis of slow dipolar relaxations. Furthermore, if the charge carriers are mobile ions, an undesirable effect, the so-called electrode polarization takes place (EP) [2]. This is due to the partial blocking of the charge exchange at the sample/electrode interfaces which results in the formation of two double layers. These double layers give rise to large capacitances in series to the conducting bulk of the sample. This manifests itself in a high apparent dielectric constant typically in the low frequency range. There are several meth-

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ods which help reduce the covering effect of the conduction and the electrode polarization. One of them is the numerical Kramers–Kronig transform, which is an elegant way to remove Ohmic conduction from measured loss spectra. It transforms the real part of the complex dielectric function into the imaginary part, which is now solely based on relaxation phenomena. It can be calculated by numerical techniques described in literature [3,4].

An alternative to the numerical Kramers–Kronig transform is based on the logarithmic derivative:

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

which approximately equals the Ohmic-conduction-free dielectric loss for rather broad peaks [5]. For non-distributed Debye relaxations, i.e. for single-relaxation time processes, the derivative results in peaks that are sharper [6].

For the double-stretched Havriliak-Negami function we have for the imaginary part  $\varepsilon''$ :

$$\varepsilon'' = -\Im \left\{ \frac{\Delta \varepsilon}{(1 + (i\omega\tau)^\alpha)^\beta} \right\} = \Delta \varepsilon \sin(\beta\Phi) \left[ 1 + 2(\omega\tau)^\alpha \cos\left(\frac{\pi\alpha}{2}\right) + (\omega\tau)^{2\alpha} \right]^{-\frac{\beta}{2}}$$

where

$$\left[ \Phi = \arctan \frac{\sin\left(\frac{\pi\alpha}{2}\right)}{(\omega\tau)^{-\alpha} + \cos\left(\frac{\pi\alpha}{2}\right)} \right]$$

$\Delta \varepsilon = \varepsilon_s - \varepsilon_\infty$  is the relaxation strength,  $\varepsilon_s$  and  $\varepsilon_\infty$  is the permittivity as the frequency  $\omega \rightarrow 0$ , and  $\omega \rightarrow \infty$ .

The logarithmic derivative of this function is:

$$\frac{\partial \varepsilon'_{HN}}{\partial \ln \omega} = -\frac{\alpha\beta\Delta\varepsilon(\omega\tau)^\alpha \cos\left[\frac{\alpha\pi}{2} - (1+\beta)\Phi\right]}{\left[1 + 2(\omega\tau)^\alpha \cos\left(\frac{\pi\alpha}{2}\right) + (\omega\tau)^{2\alpha}\right]^{\frac{1+\beta}{2}}}$$

where  $0 < \alpha, \beta \leq 1$  are the shape parameters. There are three special cases. If  $\alpha, \beta = 1$  the relaxation peak is the sharpest possible and it is called a Debye peak caused by a Debye-type relaxation.  $\alpha$  and  $\beta$  make peaks broader in a symmetrical ( $\beta = 1$ ) or in an asymmetrically ( $\alpha = 1$ ) way. The first case is called a Cole-Cole, the latter a Cole-Davidson peak. The frequency where the function reaches its maximum equals with the characteristic frequency for Debye and Cole-Cole peak, but not for Cole-Davidson peak, where the difference between them depends on the  $\beta$  shape parameter.

Fig. 1 shows the peak sharpening effect, which makes possible to resolve nearby peaks better. Because the derivatives are sensitive to noise, a proper numerical technique should be chosen for the differentiation of the data. Wübbenhorst and van Turnhout suggested to use either one based on a low pass quadratic least squares filter or a quadratic logarithmic-equidistant five point spline. These two techniques are special cases of the so-called Savitzky-Golay method (SG) for differentiation [7,8], which is a convolution of a uniformly-spaced  $(2m + 1)$  point (with a positive integer  $m$ ) data array with a set of  $b_k$  coefficients derived from the least-squares-fit formulas of  $n$ -degree polynomial:

$$\varepsilon''_{der}(\omega) = \sum_{k=-m}^m b_k \varepsilon'(r^k \omega)$$

For differentiating the entire spectrum one has to slide this  $(2m + 1)$  point „window” through the measured data points (except for  $m$  points at each end of the data array

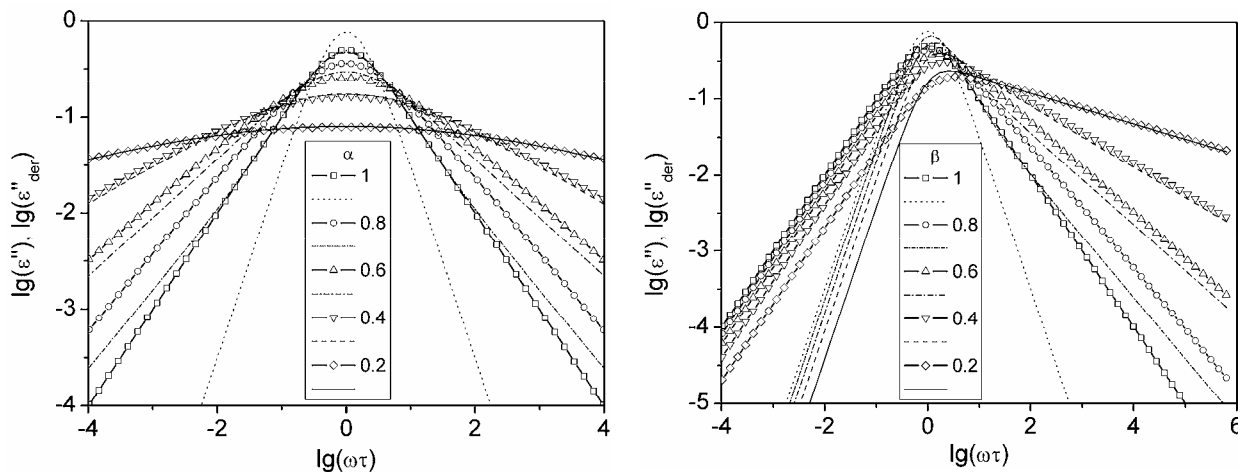


Figure 1. Comparison of dielectric loss  $\varepsilon''(\omega)$  (lines with symbols) and  $\varepsilon''_{der}(\omega)$  (dashed lines) for symmetric (left) and for asymmetric (right) HN functions for  $\alpha, \beta = 0.2, 0.4, 0.6, 0.8, 1$

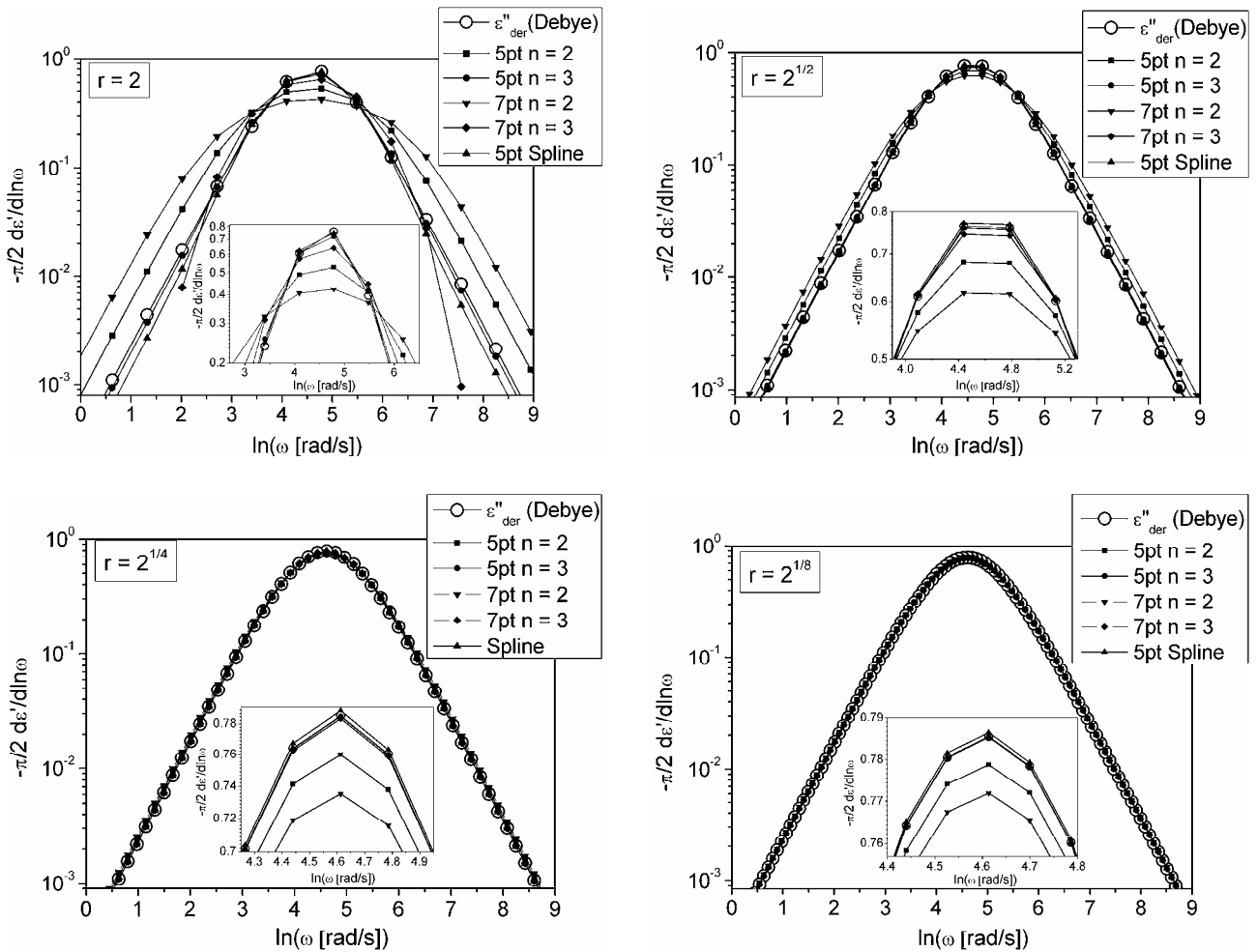


Figure 2. Numerical approximation of the logarithmic derivative of the Debye peak at four different spectrum resolutions ( $r = 2, 2^{1/2}, 2^{1/4}, 2^{1/8}$ )

that must be treated separately, using special coefficients to calculate the derivative [9]). The values of the coefficients depend on the degree of the fitted polynomial and the chosen width of the „window” and were published for a broad range of parameters in [7,9].

We examined the effect of the polynomial degree and the width of the dataset, used in one calculation step, on the quality of the approximation of the derivative at four different spectrum resolutions for three basic dielectric peaks. A normalized Debye, a Cole-Cole and a Cole-Davidson peak were chosen for that with the following parameters:  $\Delta\epsilon = 1, \tau = 0.01, (\beta = 1, \alpha = 0.22), (\alpha = 1, \beta = 0.2)$ . The SG coefficients of the used approximations are listed in Table 1.

At  $n = 2$  and  $(2m + 1) = 5$  the two different set of coefficients are the quadratic five-point SG and the quadratic spline, respectively [10].  $r$  is the logarithmic spacing between the measurement points chosen as  $r = 2, 2^{1/2}, 2^{1/4}, 2^{1/8}$ . Thus, spacing is halved in every step (doubled the resolution) on a logarithmic scale.

### III. Results and discussion

The results of the numerical differentiation with the five techniques for the Debye peak are presented in

Fig. 2. One can easily compare the exact derived peak with the numerically calculated ones visually. The inset graphs magnify the peaks at their maxima. As a general rule we can state that as the resolution of the analyzed spectrum increases, all tested approximations provide good results. The larger the resolution, the more precise the technique is. At the same time we have to consider that in broadband dielectric spectroscopy the number of measurement points could not be increased arbitrarily because the measurement time strongly depends on it, especially in the low frequency regime. Remember that at 0.001 Hz one total period takes  $\sim 17$  min, hence a dielectric measurement in the  $10^{-3}$ – $10^7$  Hz range takes hours or even days at very high resolution. There are cases where this can be realized (with stable sample, or quenched measurement technique [11]), but with sensitive or time-dependent systems [12] time is of primary importance. Therefore, results at lower resolutions are of great practical significance.

The most emphatic differences between the applied numerical techniques are at  $r = 2$  logarithmic spacing. It can be seen, that as the degree of the polynomial decreases or the width of the dataset increases, the numerically derived peak is broadened its maximum is lowered.

**Table 1.**  $b_k$  coefficients used for the calculation of the logarithmic derivative

$(2m + 1)$	$n = 2$		$n = 3$
5	$\frac{(-2,-1,0,1,2)}{10 \ln r}$	$\frac{(1,-6,0,6,-1)}{8 \ln r}$	$\frac{(1,-8,0,8,-1)}{12 \ln r}$
7	$\frac{(-3,-2,-1,0,1,2,3)}{28 \ln r}$		$\frac{(22,-67,-58,0,58,67,-22)}{252 \ln r}$

The explanation of the first observation is that a higher degree polynomial can describe rapid changes better. Since the Debye peak is the sharpest peak that theoretically exists in dielectric spectroscopy, such a function fits better onto the data. However, higher degree polynomials are not considered in the following in order to avoid overfitting which would describe random error instead of the underlying process in a real, noisy measurement.

The latter statement is also easy to understand by recalling the calculation procedure applied in the convolution method. A set of data points is multiplied with a set of coefficients in order to get the smoothed derivative at the middle of the data set and then this “window” is slid forwards. Practically, this is a weighted moving average which suppresses here not only the transients (in the case of noisy data), but the whole peak. As the fitted dataset broadens, the suppression is more and more notable.

The following order of decreasing accuracy of the applied methods can be deduced from Fig. 2 at  $r = 2$ : five-point cubic SG (5pt  $n = 3$ ), five-point quadratic spline (Spline), seven-point cubic SG (7pt  $n = 3$ ), five-point quadratic SG (5pt  $n = 2$ ), and seven-point quadratic SG (7pt  $n = 2$ ). It is also obvious that this order is just an impression from the figure and does not take the effect of the frequency into account. Furthermore, at higher resolutions the differences between the function and the numerical results decrease with each applied method, hence with increasing resolution the use of lower degree polynomials or wider datasets provides also a good result. In those measurements where huge amounts of data can be collected and these data suffer from considerable noise, the use of larger arrays should be considered.

Visual comparison allows important qualitative conclusions to be drawn but it lacks the possibility of exact numerical characterization of the applied methods. In our case the absolute and the relative error is defined as:

$$\Delta \mathcal{E}_{der}''(\omega) = \mathcal{E}_{der,num}''(\omega) - \mathcal{E}_{der}''(\omega)$$

and

$$\frac{\Delta \mathcal{E}_{der}''(\omega)}{\mathcal{E}_{der}''(\omega)} = \frac{\mathcal{E}_{der,num}''(\omega) - \mathcal{E}_{der}''(\omega)}{\mathcal{E}_{der}''(\omega)}$$

The lack of the absolute value function in the definition of the relative error allows this quantity to take negative values that show the direction of the deviation from the approximated function.

The quantitative results for the Debye, Cole-Cole, and Cole-Davidson peaks are given in Fig. 3. Since the quadratic Savitzky-Golay approximations are the worst ones, only the three other techniques (five-point quadratic spline, five-point cubic SG, seven-point cubic SG) are the subjects of our further investigations. Fig. 3 is technically a matrix, in its rows results for the three peaks at one specific resolution, whilst in its columns calculations for one specific peak at four different resolutions are presented.

As expected, the accuracy of the approximations strongly differs with changing peak shapes. A broader peak could be fitted by any of the tested methods with an acceptable error. The difference in the absolute and relative errors for the Debye and for the Cole-Cole peak is about four-five order of magnitude at any resolution. Furthermore, the accuracy depends on the measured frequency as well, so results near and far from the maximum are discussed separately.

Hence the original accuracy order established on the basis of Fig. 2. must be reconsidered, or more exactly, a detailed one needs to be determined in the light of the error calculations.

At  $r = 2$  spacing, near the maximum of the Debye peak the quadratic spline provides the best result, followed by the five-point, and the seven-point SG with -0.9 %, -3.8 %, -11.7 % absolute, and -1.3 %, -5.0 % and -15.4 % relative errors. At lower and higher frequencies the five-point SG claims the first place (-0.02 % absolute, -15,1 % relative error), the spline is the second (-0.04 % absolute, -40.3 % relative error), and the seven-point SG is the third best choice (-0.1 % absolute, and -127.9 % relative error).

In the case of the Cole-Cole peak at the peak maximum the five-point SG is the most accurate method ( $-1.1 \times 10^{-4}$  % absolute,  $-1.5 \times 10^{-3}$  % relative error) followed by the seven-point SG ( $-7.2 \times 10^{-4}$  %, absolute,  $-8.9 \times 10^{-3}$  % relative error) and the quadratic spline ( $6.7 \times 10^{-3}$  % absolute, and  $8.4 \times 10^{-2}$  % relative error). In Fig. 3. points for spline divided by ten are plotted in order to scale all results to the same order of magnitude. Further from the maximum the same order of accuracy can be found with approximately half of absolute errors which means slightly better relative errors (5pt  $n = 3$ :  $5.4 \times 10^{-5}$  % abs.,  $1.2 \times 10^{-3}$  % rel.; 7pt  $n = 3$ :  $3.4 \times 10^{-4}$  % abs.,  $7.2 \times 10^{-3}$  % rel.; Spline:  $-1.4 \times 10^{-3}$  % abs.,  $-3.4 \times 10^{-2}$  % relative error) in spite of the decreasing function values.

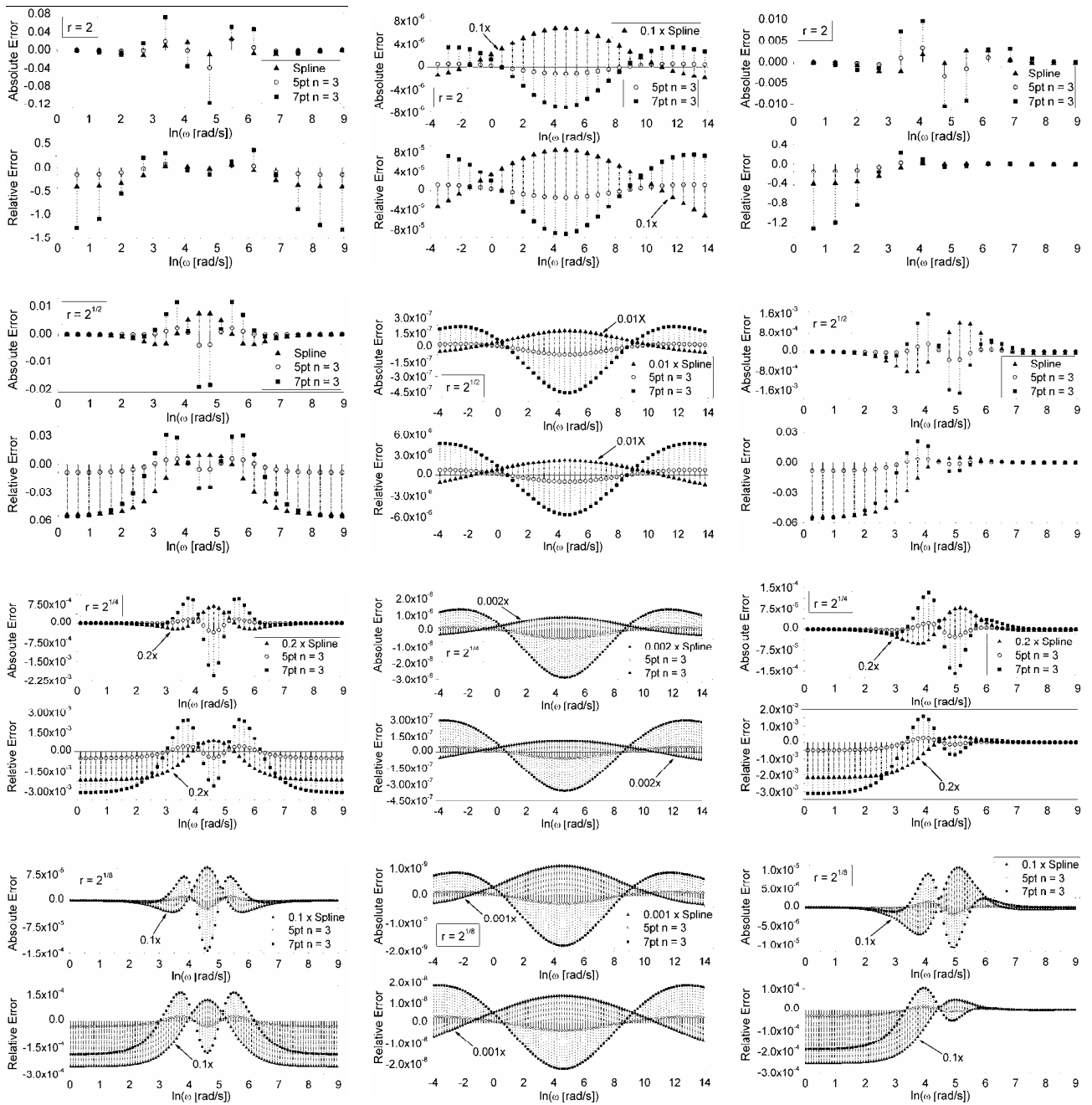


Figure 3. Comparison of the quadratic spline (Spline), the five-point cubic SG (5pt  $n = 3$ ) and the seven-point cubic SG (7pt  $n = 3$ ) numerical derivatives for the investigated three different peaks at four resolutions

As the Cole-Davidson function describes an asymmetrically broadened Debye peak where the slope of the low-frequency wing of the peak is unchanged and the slope of the high-frequency wing decreases with decreasing  $\beta$ , it could be regarded as a mixture of a Debye and a Cole-Cole peak. It behaves in the low-frequency range like a Debye peak and in the high-frequency range as a Cole-Cole peak as observable from the error calculations. Values at the characteristic frequency are best approximated by the quadratic spline ( $-0.03\%$  absolute,  $-0.2\%$  relative error), then the five-point SG ( $-0.3\%$  absolute,  $-1.7\%$  relative error), and the seven-point SG ( $-1.1\%$  absolute, and  $-5.5\%$  relative error). Close

to the peak value the five-point SG is the most accurate ( $0.2\%$  absolute,  $0.7\%$  relative error) then the quadratic spline ( $0.3\%$  absolute,  $1.1\%$  relative error) and the seven-point SG ( $0.9\%$  absolute, and  $3.9\%$  relative error). So not only the accuracy order but the direction of the difference was changed. All tested methods behave at low frequencies similar to the Debye case: 1. five-point SG ( $-2.0 \times 10^{-3}\%$  absolute,  $-15.3\%$  relative error), 2. quadratic spline ( $-5.4 \times 10^{-3}\%$  absolute,  $-40.5\%$  relative error), 3. seven-point SG ( $-1.7 \times 10^{-2}\%$  absolute, and  $-130.9\%$  relative error), and at high frequencies similar to the Cole-Cole case: 1. five-point SG ( $4.6 \times 10^{-4}\%$  absolute,  $3.2 \times 10^{-3}\%$  relative error), 2. seven-point SG ( $1.1 \times 10^{-2}\%$

absolute,  $7.2 \times 10^{-2}$  % relative error), 3. quadratic spline ( $-2.8 \times 10^{-2}$  % absolute,  $-0.2$  % relative error).

Doubling the resolution of the spectrum ( $r = 2^{1/2}$ ) rearranges the accuracy order in the Debye and the Cole-Davidson cases. At the maximum value of the Debye peak the former two best choices are interchanged: 1. five-point SG ( $-0.4$  % absolute,  $-0.5$  % relative error), 2. quadratic spline ( $0.8$  % absolute,  $1.0$  % relative error), 3. seven-point SG ( $-1.8$  % absolute, and  $-2.4$  % relative error), whereas at much lower and higher frequencies the order remains the same: 1. five-point SG ( $-4.5 \times 10^{-4}$  % absolute,  $-0.8$  % relative error), 2. quadratic spline ( $-2.9 \times 10^{-3}$  % absolute,  $-5.3$  % relative error), 3. seven-point SG ( $-3.0 \times 10^{-3}$  % absolute,  $-5.5$  % relative error). A strong decrease in the errors could be observed, especially far from the peak maximum for the quadratic spline and the seven-point SG. In the case of the Cole-Cole function the order is the same as mentioned above, but the absolute and the relative errors are so small even if we use quadratic spline ( $0.002$  % absolute, and  $0.02$  % relative error), that these are completely negligible in the evaluation of a real measurement. Since the errors decrease with increasing resolution, only the two other types of peaks are discussed below.

The best method for the Cole-Davidson function at this resolution ( $r = 2^{1/2}$ ) is the five-point SG with the highest absolute error of  $0.03$  % ( $0.35$  % relative error) in the peak area, and  $-5.4 \times 10^{-5}$  % ( $-0.8$  % relative error) in the low-frequency range. The second best choice is the quadratic spline with an absolute error of  $0.12$  % ( $0.54$  % relative error) near the maximum and  $-3.5 \times 10^{-4}$  % ( $-5.3$  % relative error) at low frequencies. The absolute error for the seven-point SG at the maximum is under  $1$  % ( $0.17$  % absolute,  $0.77$  % relative error) and is close to the absolute error of the spline in the low-frequency regime ( $-3.6 \times 10^{-4}$  % abs., and  $-5.5$  % relative error). At high frequencies both the absolute and the relative errors of all three methods are much lower, practically negligible, which is the effect of the similarity to the Cole-Cole function.

At  $r = 2^{1/4}$  logarithmic spacing for Debye peak the accuracy order is the following in the whole frequency range: 1. five-point SG with a highest absolute error of  $-0.04$  % and  $-0.05$  % relative error. 2. seven-point SG with maximum  $-0.2$  % absolute and  $-0.3$  % relative errors. 3. quadratic spline with maximum of  $0.3$  % absolute and  $1.1$  % relative errors. From this resolution on, all examined techniques are able to approximate the sharpest possible derived spectrum with an error (either absolute or relative) less than  $1$  % (even less than  $0.5$  %) which is an often used limit in the characterization of analytical methods.

For the Cole-Davidson peak the same order holds with very similar highest error values: 1. five-point SG ( $-0.003$  % absolute, and  $-0.05$  % relative error). 2. seven-point SG ( $-0.02$  % absolute, and  $0.3$  % relative er-

ror). 3. quadratic spline ( $0.04$  % absolute,  $1.1$  % relative error).

At  $r = 2^{1/8}$  spacing the previous order is valid for all types of peaks used to describe dielectric relaxation processes. Even if we use the least accurate one, the quadratic five-point spline, the absolute error remains below  $0.1$  %, the relative error under  $0.3$  % for a Debye peak, and below  $0.01$  % absolute, and  $0.25$  % relative error for a Cole-Davidson peak

#### IV. Conclusions

The accuracy of numerical techniques could depend on many parameters, hence we have to apply them very carefully. Here we examined the effect of the frequency, spectrum resolution and the shape of the peak on the accuracy of the so-called numerical logarithmic derivative technique, a versatile tool in the evaluation of dielectric relaxation spectroscopy measurements. A well-known numerical method, the Savitzky-Golay convolution method for differentiation was chosen for the calculations.

Synthetic dielectric data were generated in the  $10^{-3}$ – $10^7$  Hz frequency range with four different resolutions ( $r = 2, 2^{1/2}, 2^{1/4}, 2^{1/8}$  logarithmic spacing). Three types of peaks were used to investigate the shape effect: the logarithmic derivative of the normalized Debye, a normalized Cole-Cole ( $\alpha = 0.2$ ), and a Cole-Davidson ( $\beta = 0.2$ ) functions. These are all empirical dielectric relaxation functions used frequently.

From visual comparison of the numerical results for the Debye peak it can be concluded, that with increasing polynomial degree or decreasing dataset width better approximations could be reached even at lower resolution (i.e. at  $r = 2$  spacing). As the resolution of the spectrum increases, all of the investigated methods give good results with an acceptable error. Although applying higher-than-third degree polynomials is not recommended in order to avoid overfitting, the use of wider dataset could be beneficial due to its stronger noise suppression capability.

A quantitative analysis of the investigated methods was also done for all the three types of peaks at the four different resolutions. In the case of the Cole-Cole function a definite order in the accuracy can be found. The best choice for the differentiation of such a symmetrically broadened peak is the five-point Savitzky-Golay method at all resolutions. In the case of Debye and Cole-Davidson functions, at lower resolutions there is a difference in the order of accuracy near the peak maximum and far from it. Generally the five-point quadratic spline approximates the peak values best, followed by the five-point SG, which is in turn the most accurate in the low and high frequency regime followed by the quadratic spline. As the resolution increases the five-point SG overtake the first place in every range of frequency for any of the peak shape, and the accuracy of the seven-point SG also increases. Hence if the spacing can be

chosen short enough, wider „windows” in the convolution procedure can be used.

Summarizing, numerical differentiation techniques for logarithmic derivative method must be chosen carefully, taking the shape of the relaxation peak, the resolution and possibly the frequency range where the approximation should be the most accurate into account. Although our results support the selection of a proper method, the best tactics is the generation of noisy synthetic dielectric data, which properties are almost the same as the measured spectrum. In that case we could be 100 % sure regarding the reliability of the applied numerical technique.

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