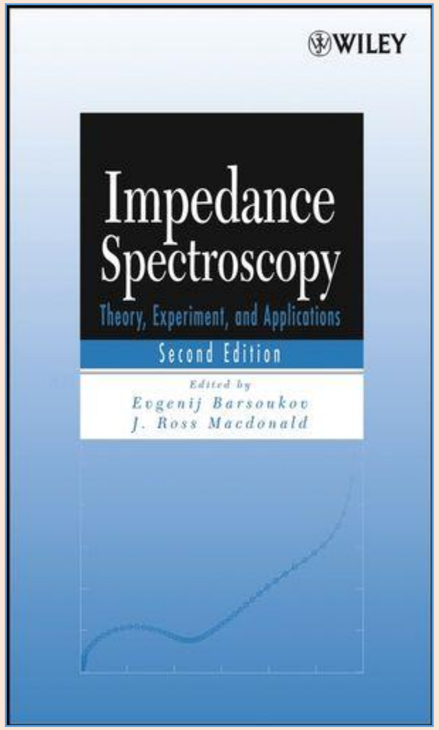
Impedance Spectroscopy

Using the Matlab program

ZfitGUI



Theory and other things may be found in the Macdonal book and here :
https://sites.google.com/site/jeanlucdellis
(in the « programmes Matlab » and in the « Spectroscopie d'Impédance» repertories)

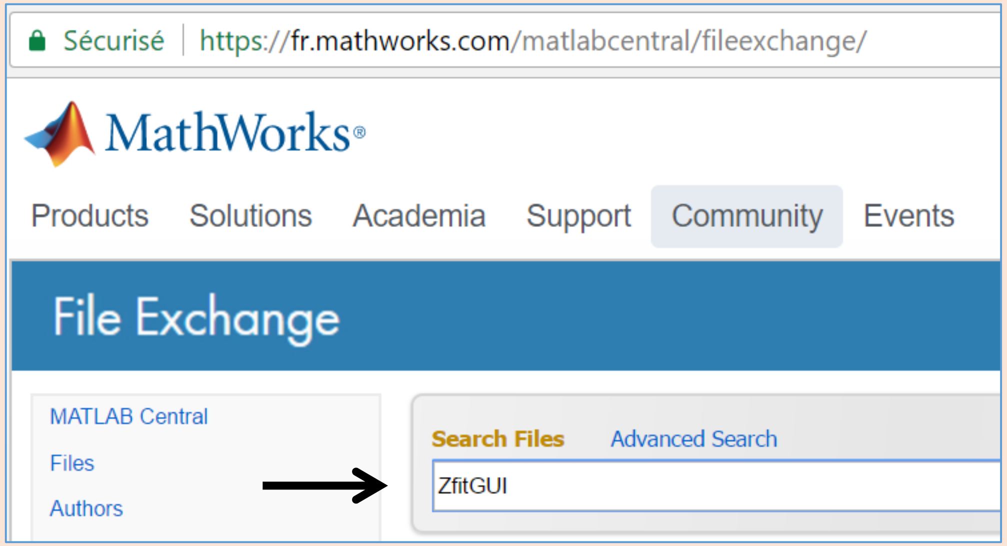
Download the Matlab program ZfitGUI

Z fit GUI

Impédance Z

Fit : search for the best parameters of an Equivalent Circuit

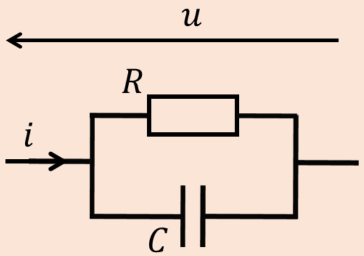
Graphical User Interface

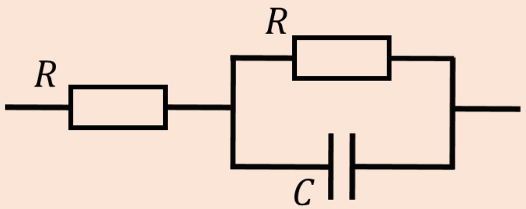


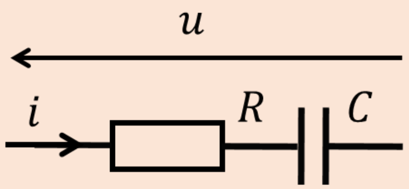
Preambule

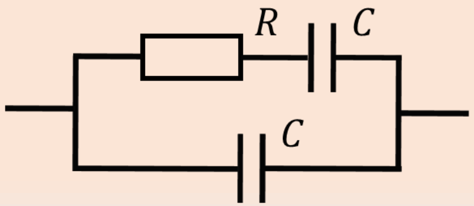
Impedance is a complex number $Z = Z_r + jZ_i$ which is frequency dependent as are the related immitances like for instance, the complex capacitance : $C = \frac{1}{jZ\omega}$. The curve $Z_i = f(Z_r)$ is called spectrum as well as $C_i = f(C_r)$. To model these data, one may use equivalent circuit (EC). The spectra have usually one or more semi-circle loops whose analysis allows to separate intrinsic phenomena of those arising from the electrodes, the wires or even the apparatus effects.

- If a semi-circle is found in the Z-representation, one may use the parallel model p(R1,C1). It means that when the EC is submitted to a voltage, the current comes from 2 additive contributions. One is dissipative $i_1 = \frac{u}{R}$ when the other is conservative $i_2 = C\frac{du}{dt}$. If the semi-circle was shifted along the real Z axis, just add a resistor in series to fit the spectrum. In the same vein, note that the series EC s(p(R1,C1), p(R1,C1)) will give 2 successive semi-circles, less or more overlapped.









- If the semi-circle was found in the C-representation, the right EC is the serial Debye model s(R1,C1) with only one current usually attributed to the material polarization and which equilibrium is delayed by the resistor. If the semi-circle was shifted along the real C axis, just add a capacitor in parallel to fit the data. Here also, we may find 2 successive semi-circles but the model would be : p(s(R1,C1), s(R1,C1)) .

Download simulations and experimantal data

In Internet, search for the google web site « jeanlucdellis », navigate to the « programmes Matlab » repertory to download the files to process as trainings.

https://sites.google.com/site/jeanlucdellis/

programmes **Matlab**

Mon Drive > programmes Matlab

Nom	Propriétaire
ZfitGUI for impedance fitting	moi
Get the Slope and the Intercept of a dra...	moi
easyfit for 2D data fitting	moi

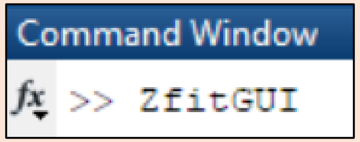
- C2Loops.mat
- circle123.mat
- circuit1.mat
- circuit2.mat
- circuit3.mat
- Legreen.mat
- Maruse.mat
- Panata.mat
- Z2Loops.mat

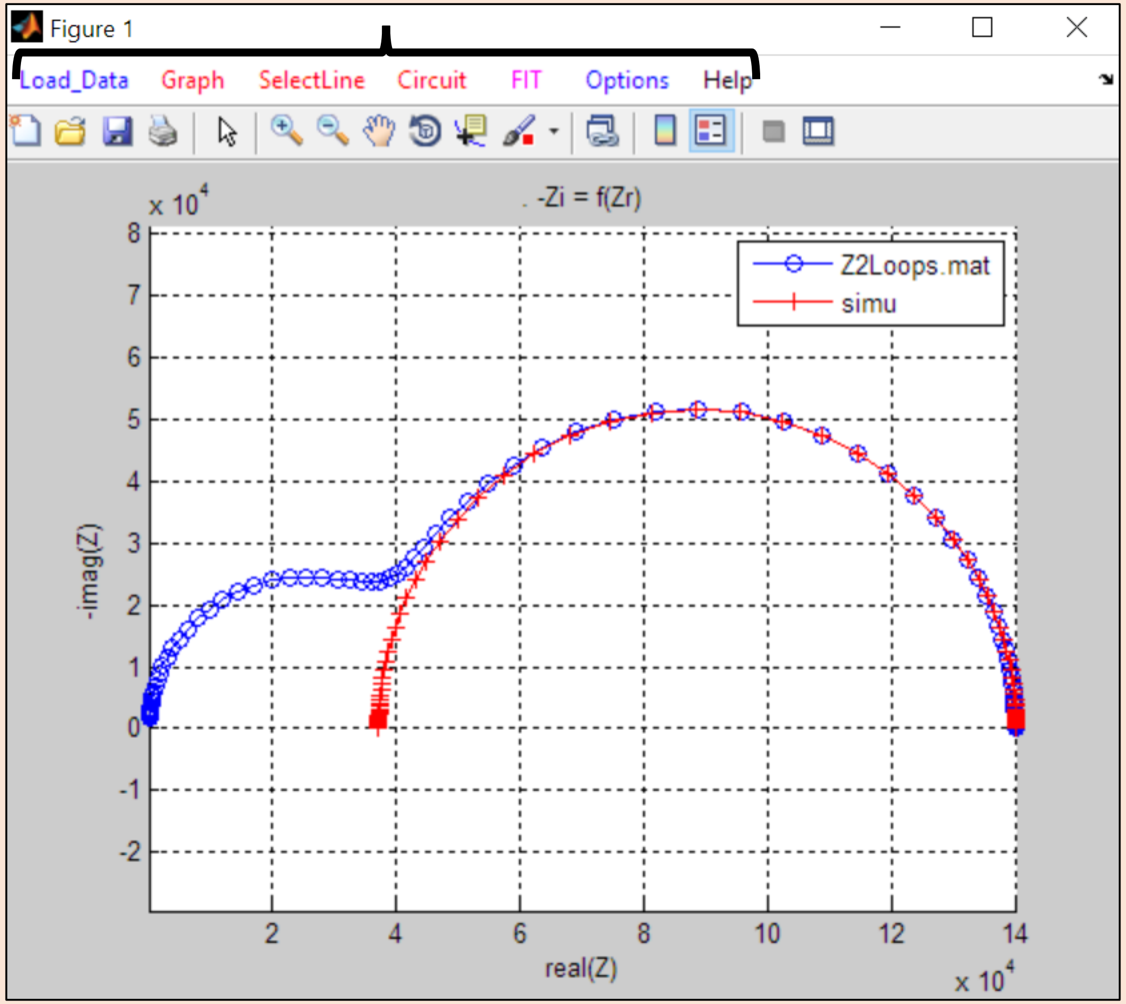
Download

- Data for the Tutorial
- U.m
- ZfitGUI.m
- ZfitGUI_Tutorial.pptx
- ZfitGUI_User_Manual.docx

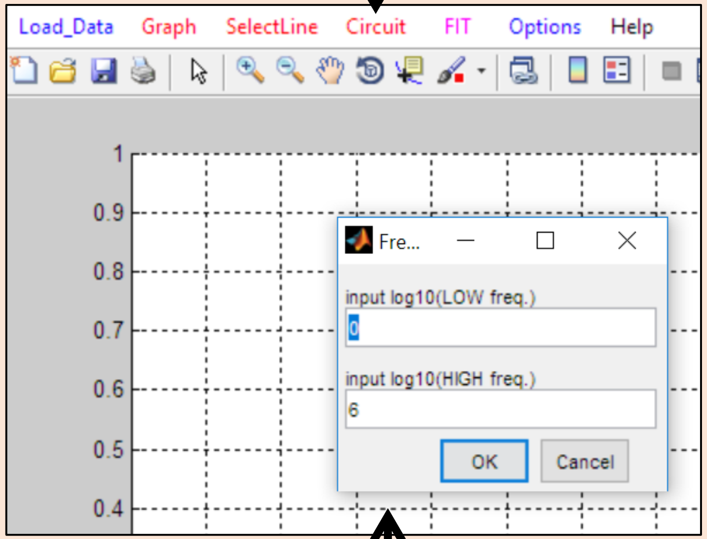
Get the function ZfitGUI, the Tutorial and the User Manual the Matlab program ZfitGUI adds UIMENUS to a figure

Type ZfitGUI without inputs :



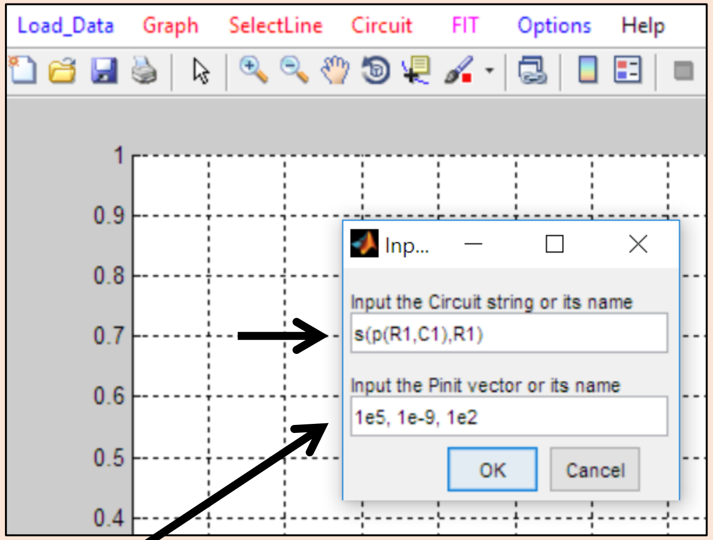


How to generate simulated Z-data

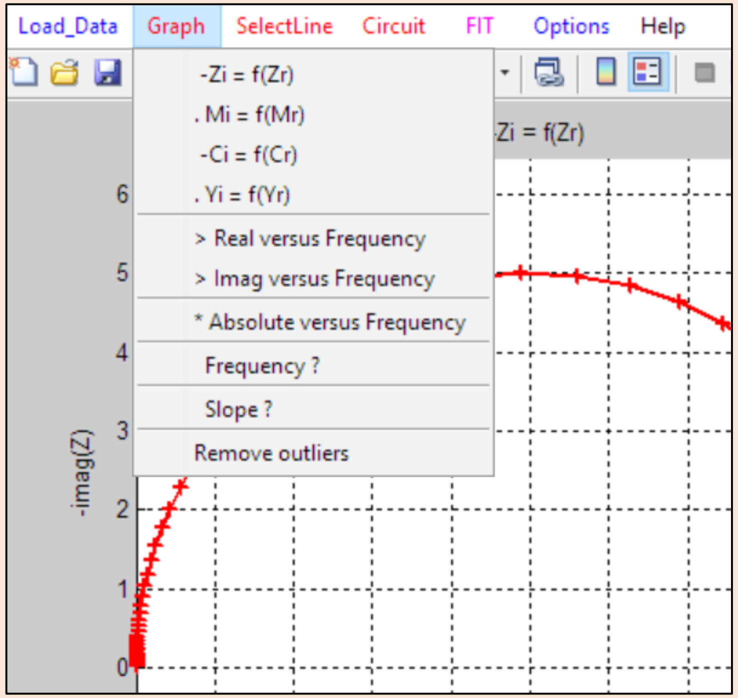


Click ‘Circuit’ to enter the frequency bounds.
Default : 1 Hz to 10^6 Hz…

… and to enter the Circuit String. Default string is : s(p(R1, C1), R1).
‘s’ stands for ‘put in series’ and ‘p’ for ‘put in parallel’. These operators must have exactly 2 arguments. The numerals beside the element letters R (resistor) and C (capacitor) are reminders about the amount of parameters they need. L1 (inductor), E2 (CPE), G2, H2 (diffusion impedances) and even user-defined element may be used. Read the User Manual of ZfitGUI to have more details about them.



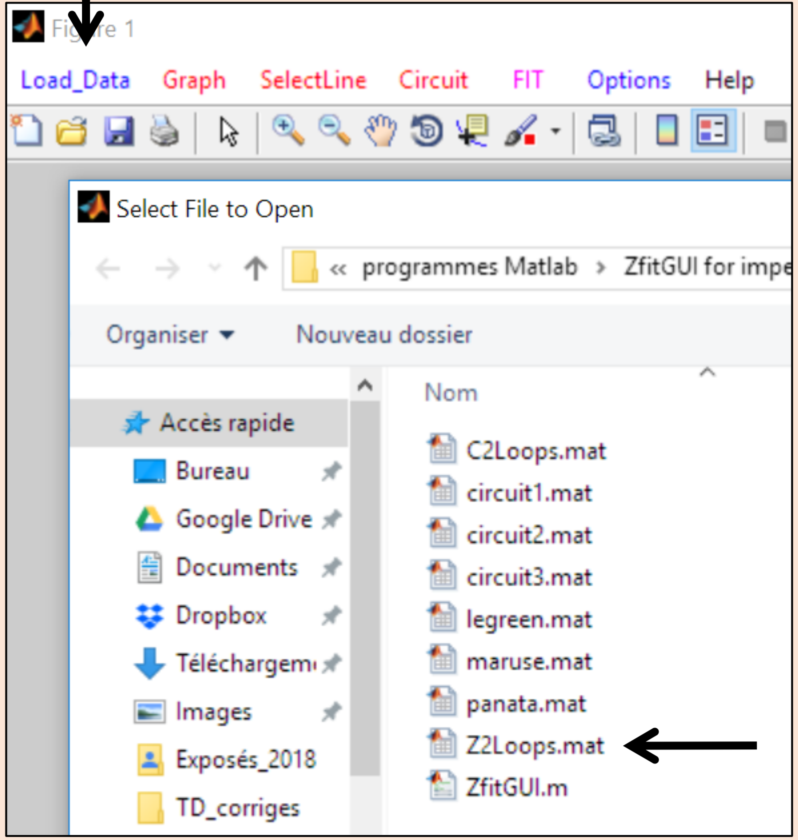
It is mandatory to enter values for the elements. Enter them as they come in the Circuit String.
Default : 5 10^4, 10^{-9}, 5 10^3

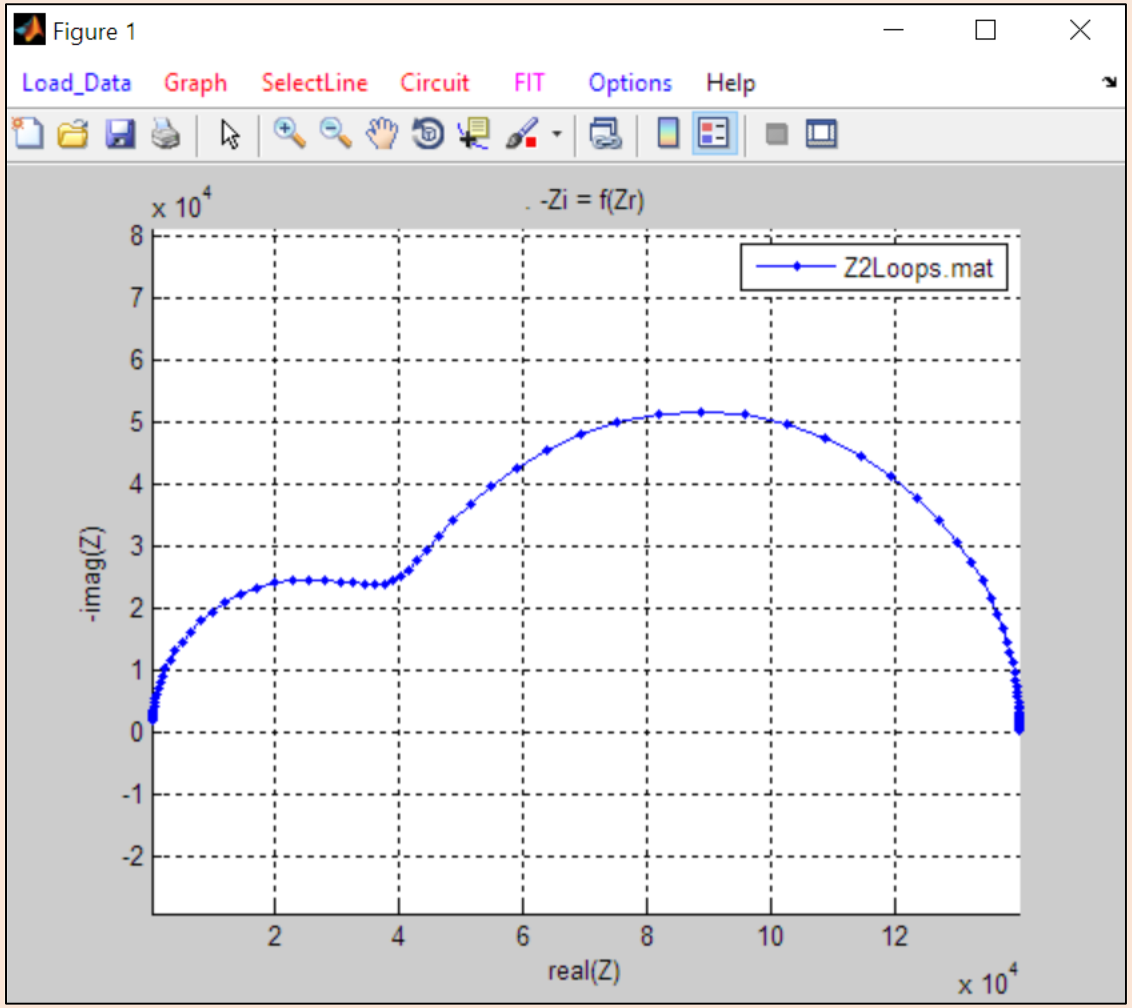


Note that ‘Graph’ contains sub-menus

Z2Loops – Fitting a simulated Data of a conductive system (A)

Click on the « Load Data » uimenu to load Z2Loops in ZfitGUI

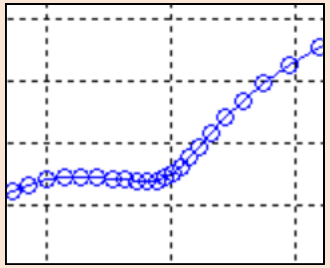




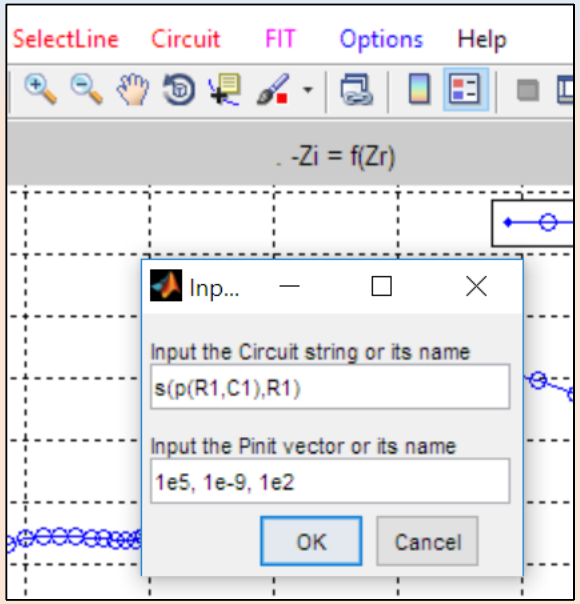
Next step is to select the curve, write a Circuit string and feed it with initial values

Z2Loops – Fitting of a simulated Data of a conductive system (B)

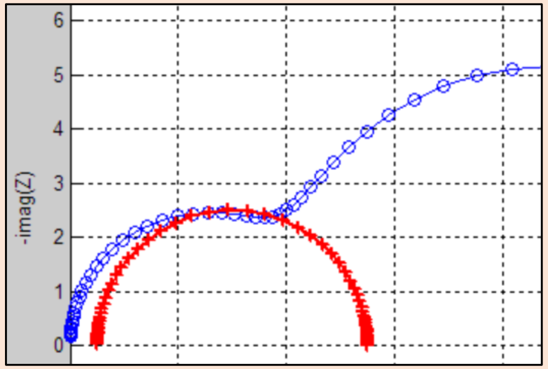
Click on «SelectLine » to process the curve

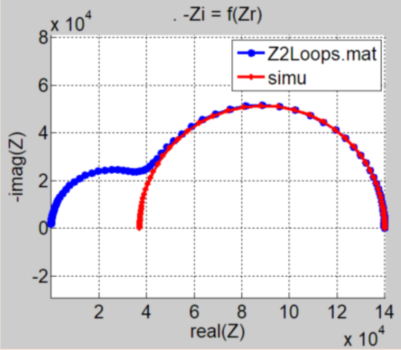


Click on « Circuit » to enter the Circuit string and the Pinit. As the spectra usually show loops, « s(p(R1,C1),R1) » is a good start because p(R1,C1) defines a semi-circle which can be translated along the real axis with the s(,R1) operator

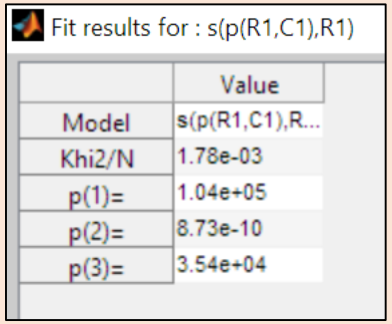


Click on «Fit», then twice on the large loop to fit it and …





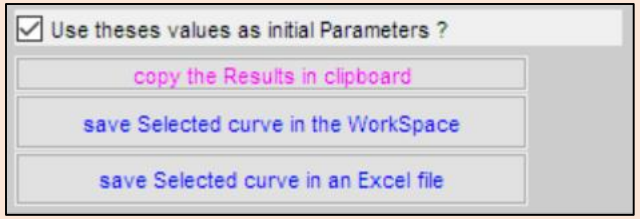
… to get the results graphically and in the Result figure:



Fit results for : s(p(R1,C1),R1)

	Value
Model	s(p(R1,C1),R...
Khi2/N	1.78e-03
p(1)=	1.04e+05
p(2)=	8.73e-10
p(3)=	3.54e+04

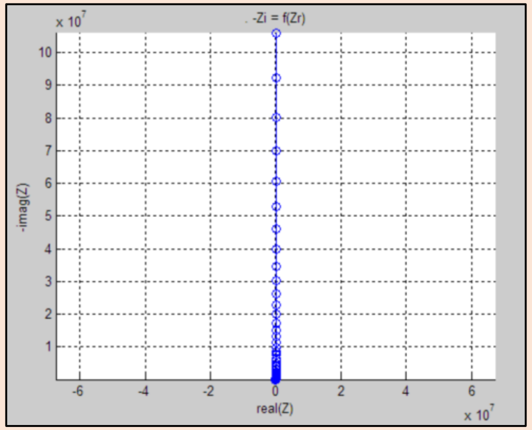
The tools in the bottom of the Result figure are very usefull :



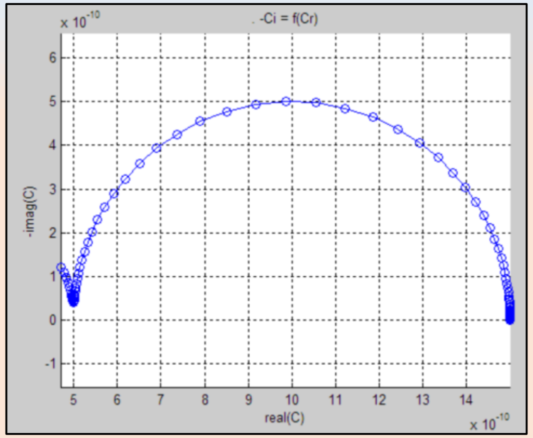
Try to fit the whole spectrum with s(p(R1,C1), p(R1,C1))

Very usefull : the values in the Value column are editable. Change them to get a better initial parameters set.

C2Loops – Fitting of a simulated Data of a dielectric system

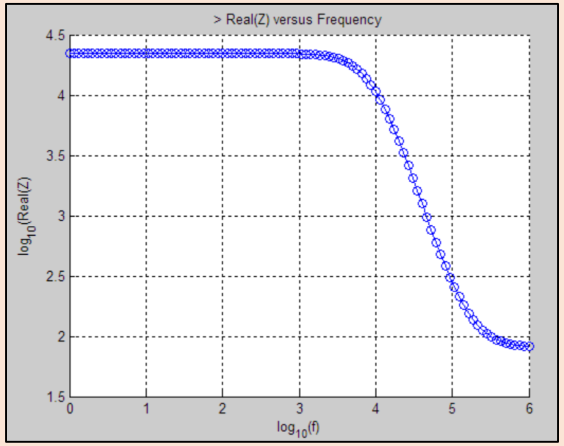


Load ‘C2Loops’. One obtains a Z-spectrum looking like the one of a capacitor, lets switch to : ‘Graph, -Ci=f(Cr)’

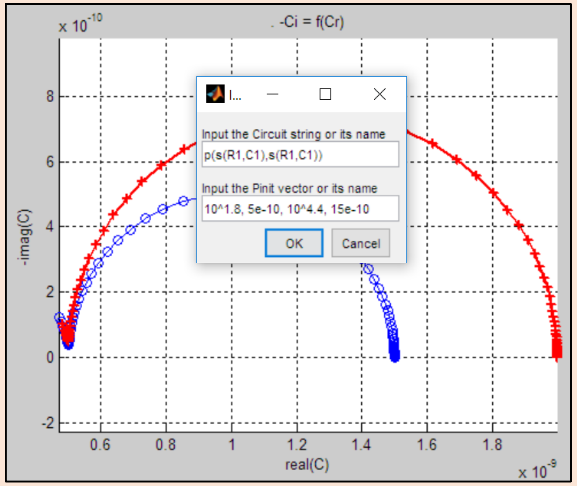


It gives a main loop and the beginning of another at HF (checked in using ‘Graph, frequency?’)

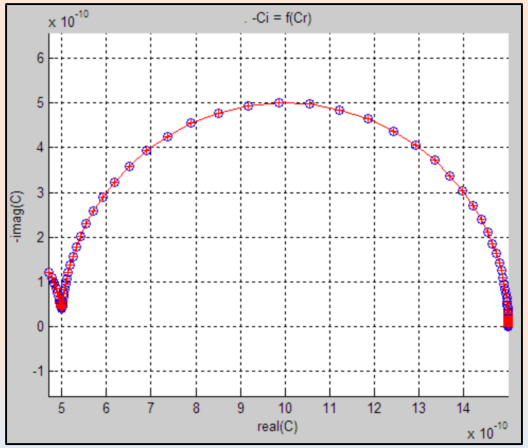
When in « C » representation, for dielectric systems, 2 successive loops correspond to 2 Debye relaxations s(R1,C1) in parallel. So here, we will use the Circuit String : p(s(R1,C1), s(R1,C1)) and from the spectrum inspection, we shall start with capacitors 5 10^{-10} F (at HF) and 15 10^{-10} F (at LF).



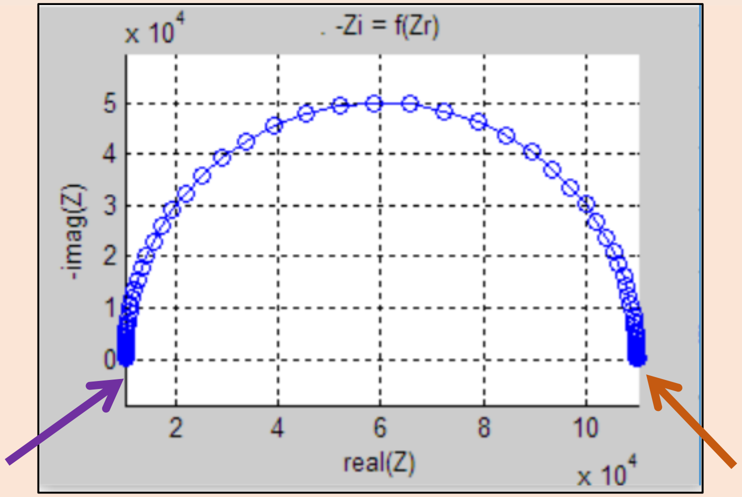
One may examine the Re(Z) = f(ω) curve to get initial values $10^{4.4}$ Ω (at LF) and $10^{1.8}$ Ω (at HF) or use « Fit » and a try and error method.



The Initial parameters have little error in the C guesses but anyway, lets try « Fit »

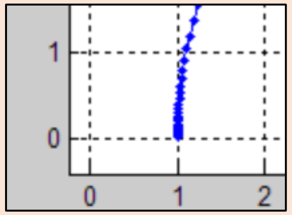


Circuit1 – Pay attention to low amplitude points

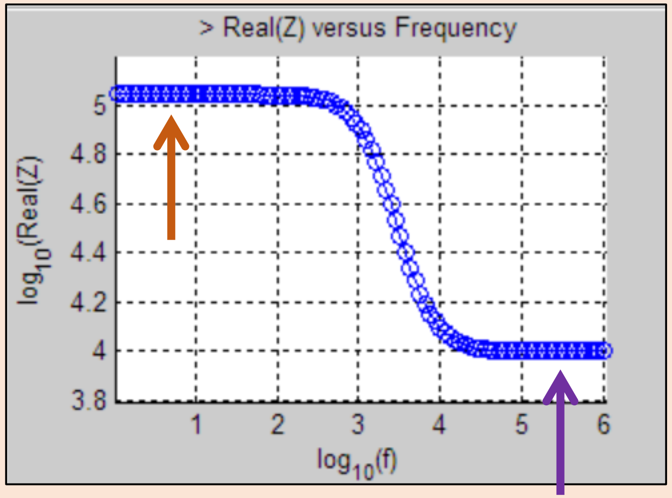


<u>Procedure :</u>

Inpect the spectrum. Here, we find with the tool  and the zoom  that the semicircle is translated along the axis of the reals:



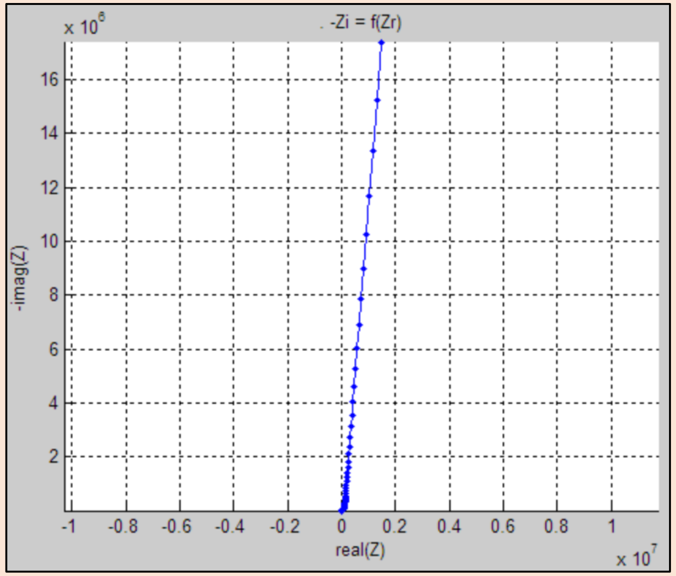
Small biases may have important consequences on the fitting success. A good strategy is to check the Re(Z) = f(ω) and the Im(Z) = f(ω) curves. One finds $\lim_{\omega\to 0} Re(Z) \approx 10^{5.05}\Omega$ and $\lim_{\omega\to\infty} Re(Z) \approx 10^{4}\Omega$.

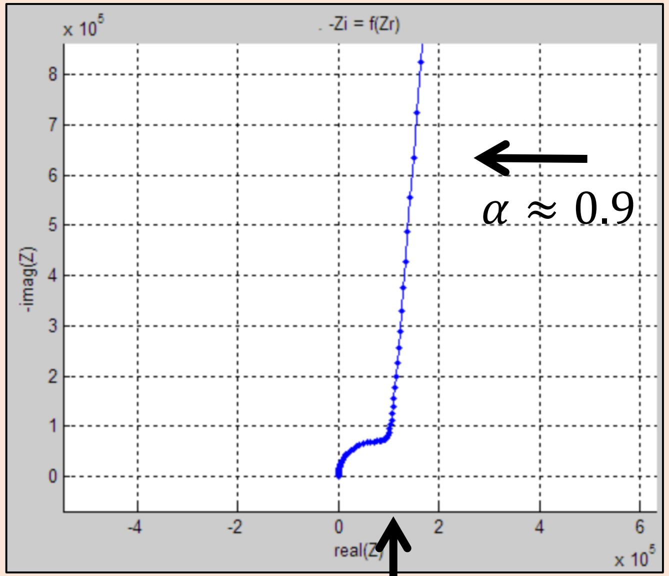


- s(R1, p(R1, C1)) is the right Circuit string.
- Enter the model string after clicking on the "Circuit" menu and initial (guessed) values
- Click on « FIT »
- Check the results

Very useful : with the « edit plot » tool (), you may delete any graphic object …

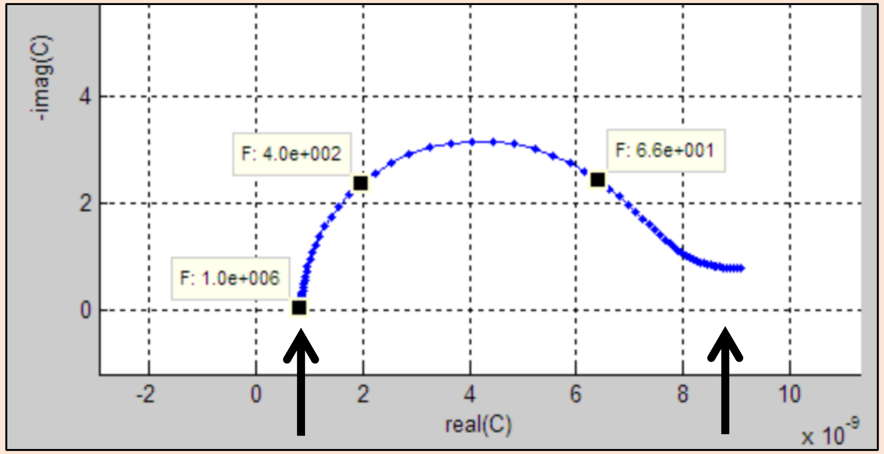
Circuit2 – Simulated Data with an CPE





$\alpha \approx 0.9$

$r \approx 1e5$



$c \approx 1e-9$ $\quad$ $A \approx 9e-9$

4 Hints :

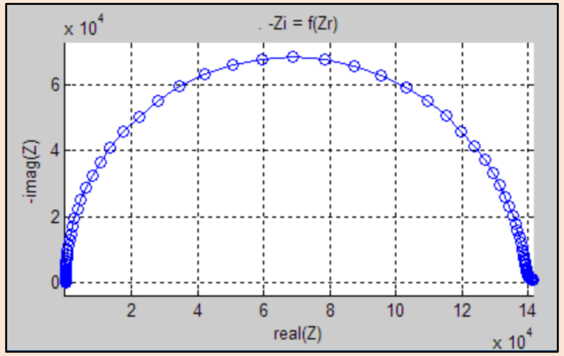
- Zoom the HF
- change graph to complex C
- use « Graph + Frequency ? »
- Remind $Z_{cpe} = \dfrac{1}{A\,(j\omega)^{\alpha}}$

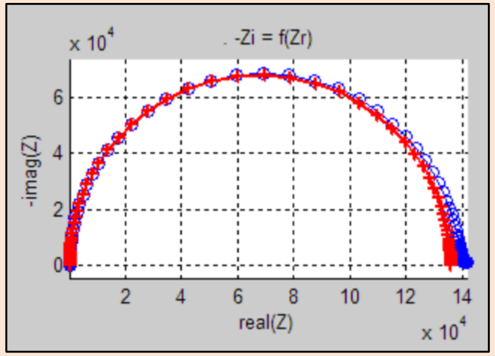
s (p (R1, C1), E2)

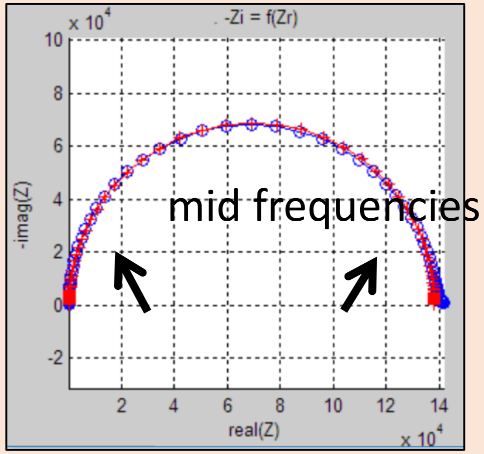
Guessed Values obtained from inspection of the graphs

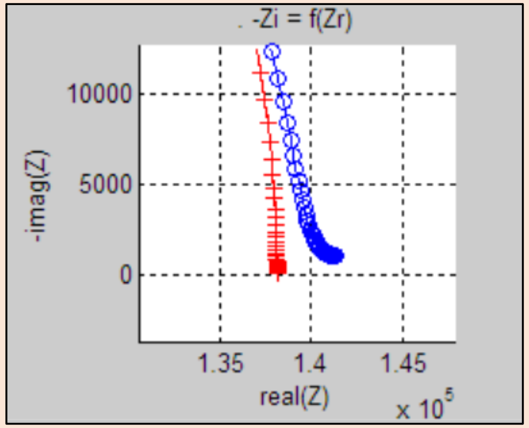
Fit …

Circuit3 – Simulated Data with low frequency dispersion





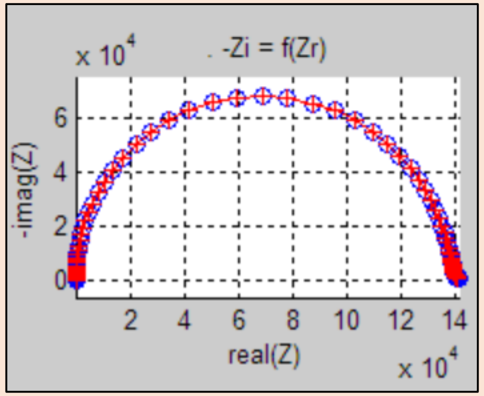




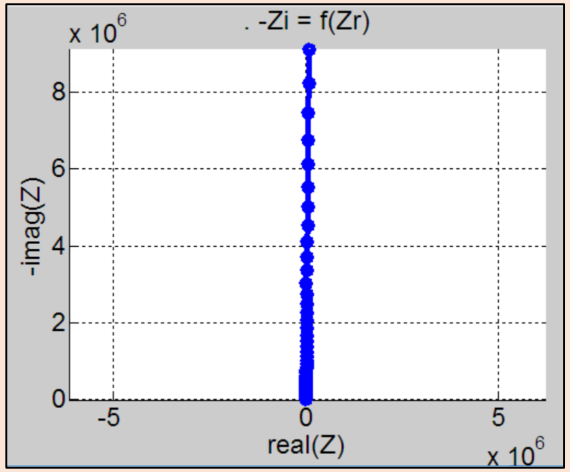
Steps (example) :

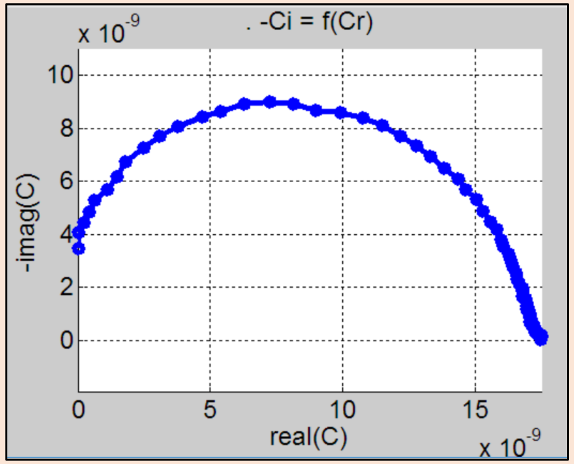
- Firstly, use a simple s(R1, p(R1, C1)) circuit.
- Use the « Fit » tool for the HF (fig2). The RC is OK for the HF but it looks like there is anoher relaxation at LF ⇒ s(p(R1,C1),p(R1,C1)).
- The fit on the mid frequencies (fig3) seems enough good.
- To go further, a zoom for the LF revealed that the experimental Z came on the real axis with a different slope compared to the RC model in red (fig4) ⇒ try s(p(R1,C1),p(E2,C1)) using the initial values from fig4 (adding an exponent of 0.01 for the CPE which mimics a 'dispersive' resistor)

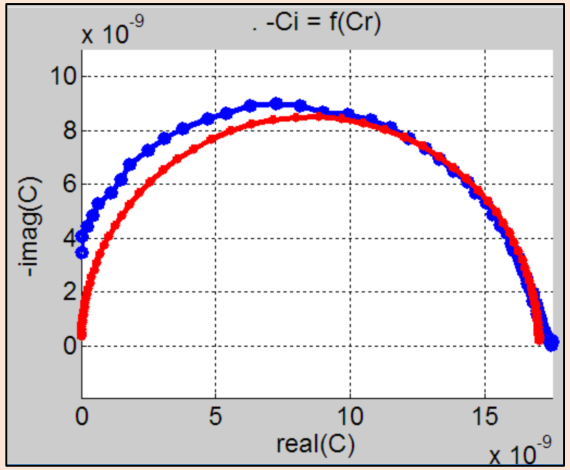
Fit …

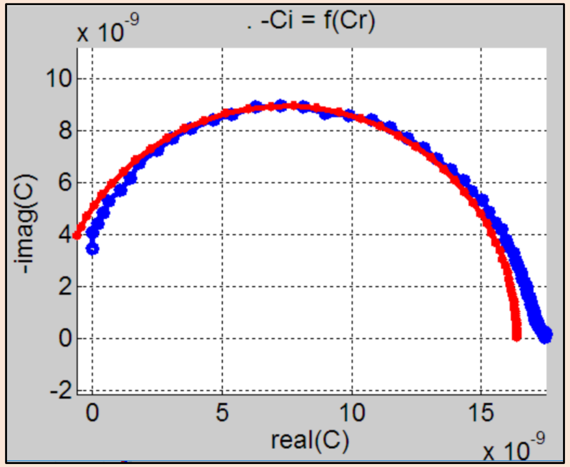


Maruse – Experimental Data



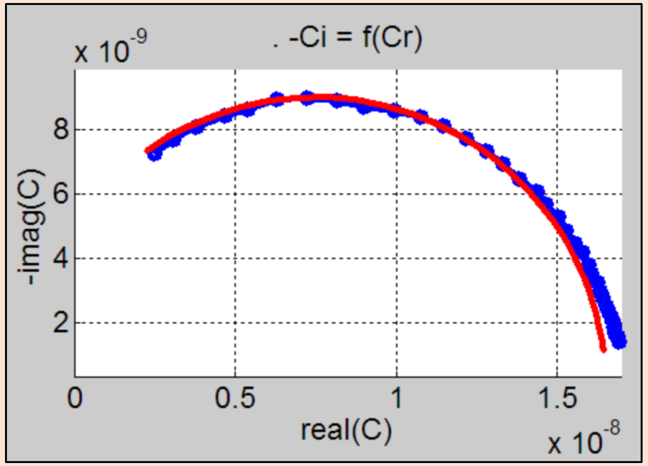




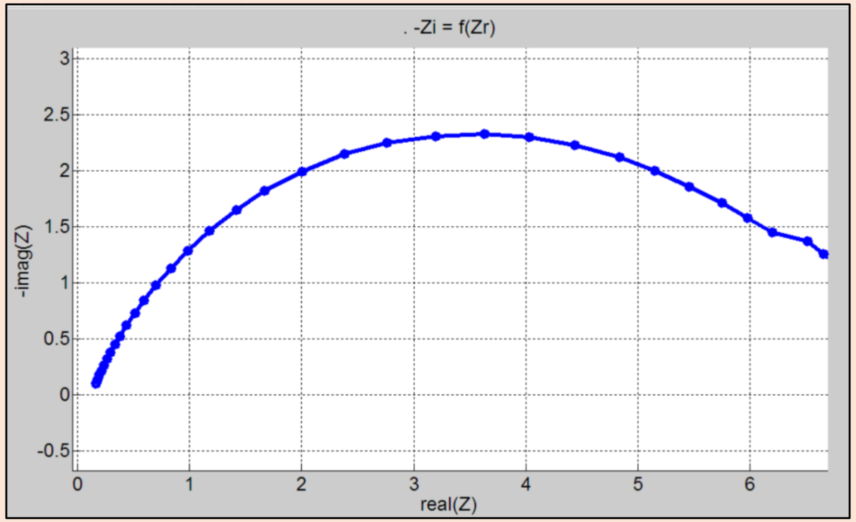


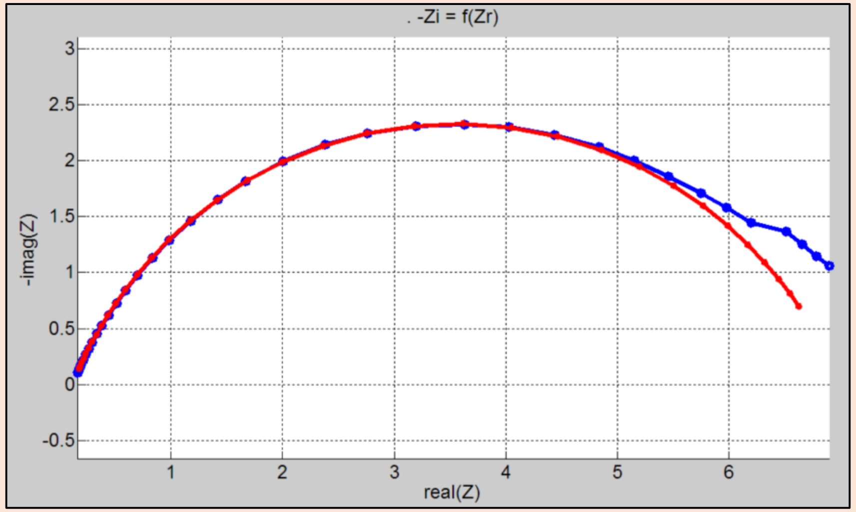
Steps (example of corrupted data) :

- The experimental HF part of the loop of fig3 (model used : s(R1,C1)) would extrapolate to negative value ! ⇒ p(C1,s(R1,C1)) with the first C<0 initialized to -1e-9.
- fit the mid frequencies (fig4) or remove the outliers from the « Graph » menu (fig5) or search if CPE or diffusion impedances could improve the fitting if interressed in the LF side of the system (= refine the model).



Panata – Experimental Data





Steps (example of corrupted data) :

- Remove the HF outliers (with positive Zi).
- Note that there is a small translation of the spectrum of $r \approx 0.1\ \Omega$ (fig1).
- A semi-circle whose the center is located under the real axis can be related to a p(R1,E2) circuit when in Z-representation. Adding the little resistor r, one tries s(R1,p(R1,E2))
- The initial values are guessed from the Z and the C representations

Fit …

model : s(R1,p(R1,E2))

Khi2 of fit: 2.08e-3

P1 = 1.17e-1

P2 = 6.87e+0

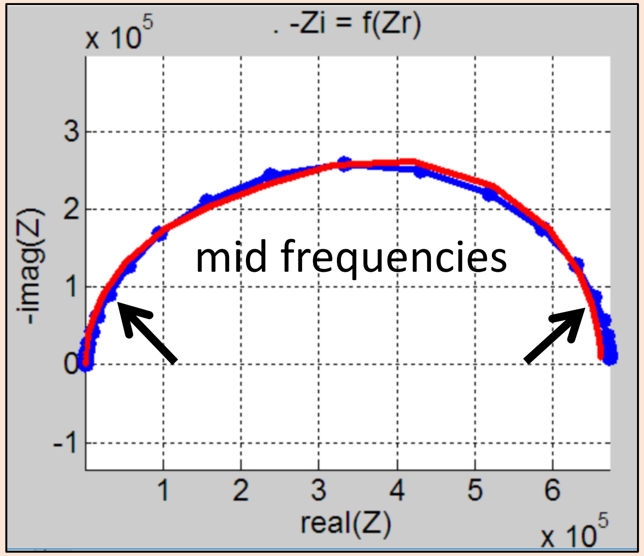
P3 = 1.27e-3

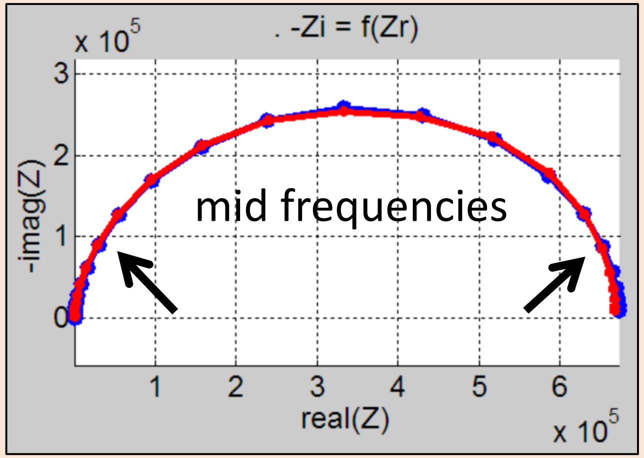
P4 = 7.58e-1

Khi2 is a measure of the distance experimental/model

Because Khi2 depends on the amount N of points taken in the fit, the normalized Khi2/N is displayed in the result figure.

Legreen – Experimental Data – a difficult case



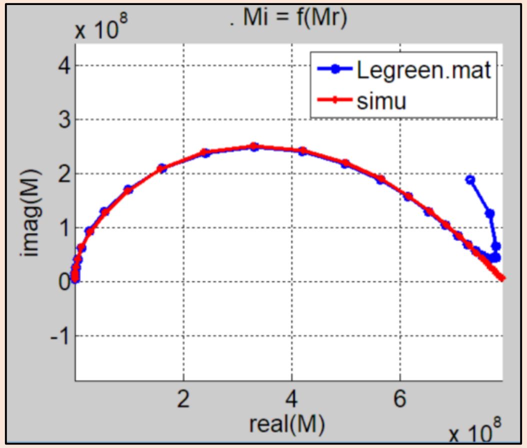


- Using the model s(p(R1,C1),p(R1,C1)) and « Fit » on the mid frequencies gave fig1 with

  'model : s(p(R1,C1),p(R1,C1))'
  'Khi2 of fit: 2.37e-2'
  'P1 = 2.18e5'
  'P2 = 2.19e-9'
  'P3 = 4.43e5'
  'P4 = 5.97e-9'

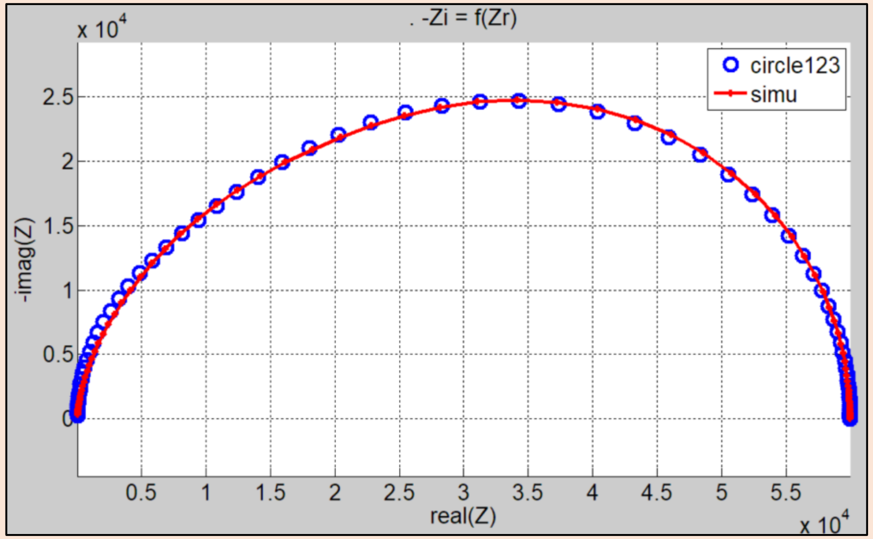
- Further investigations leads to use a model with a Finite Length Warburg with SHORT Circuit "G2" and a much better result altought using the same amount of parameters (4) :

'model : p(p(R1,C1),G2)'
'Khi2 of fit: 9.43e-4'
'P1 = 7.89e5'
'P2 = 1.29e-9'
'P3 = 3.55e-8'
'P4 = 1.55e-1'



In M representation, the result is very good except at the high frequencies where there is an abnormal behavior with Mr decreasing in the experimental data. Maybe due to the apparatus …

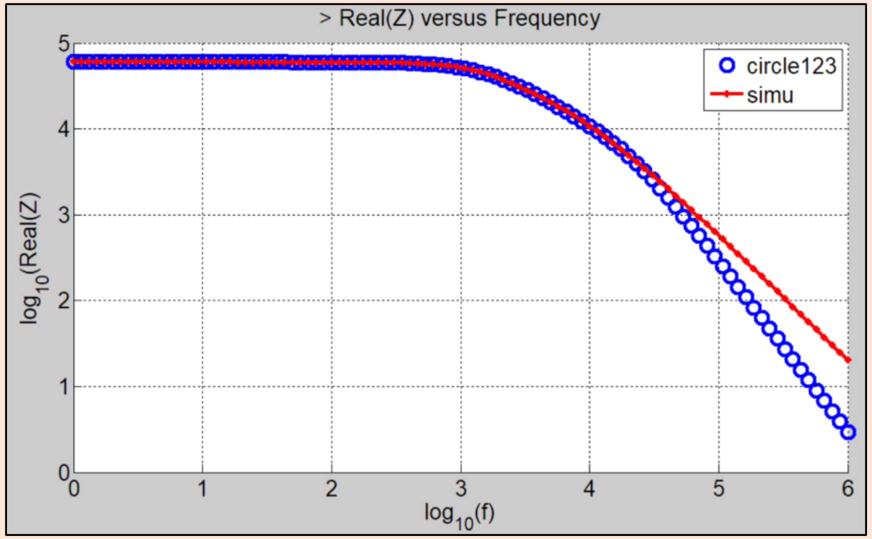
Ambiguïty of the models

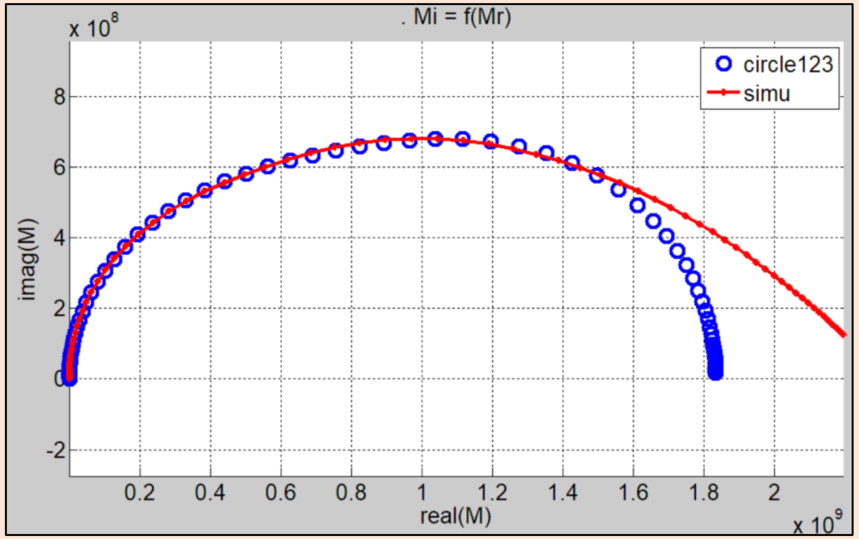


- The blue curve named « circle123 » are very similar to the experimental data processed above with a Finite Length Warburg with SHORT Circuit :

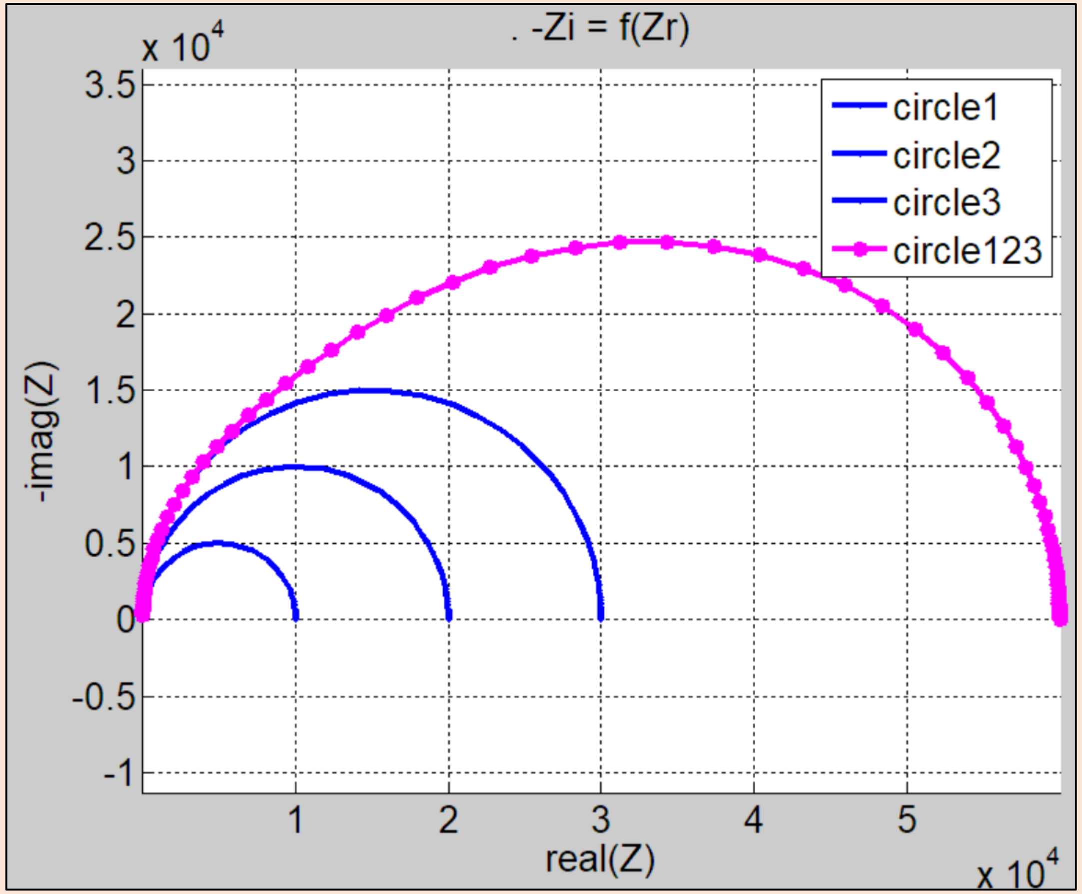
  p(p(R1,C1),G2)

- Try to find the parameters giving the red line which at first glance seems statisfying.
- However, watching the real Z-part gave the figure 2 where one can state a gap at the high frequencies. It is also visible when using the M-representation (figure 3).
- Read the next slide to know from where circle123 comes…





Producing simulated data



- Using the model p(R1,C1) in « circuit », we produced circles 1, 2 and 3. The parameters were successivly :
  p(1) = 1e4 then 2e4 and 3e4
  p(2) = 1e-9 then 2e-9 and 3e-9

- To produce the spectrum of these impedances all put in series « circle123 », the model was :
  s(s(p(R1,C1),p(R1,C1)),p(R1,C1))
  with :
  1e4,1e-9,2e4,2e-9,3e4,3e-9
- Try this model on the Legreen data …