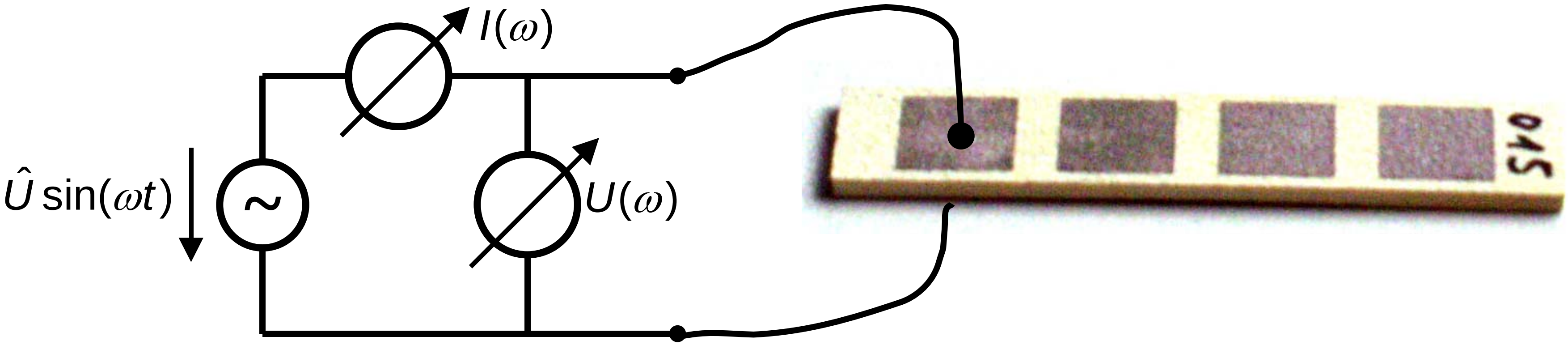
New CNLS software for analysis of impedance spectra
Outline

- Motivation
  - Impedance spectroscopy on thermal barrier coatings (TBC)
  - Insertion: RQ-element
  - thermally activated conductivity
- New CNLS software MVCNLS
  - Introduction
  - Comparison with standard CNLS software
  - fit problem from practice

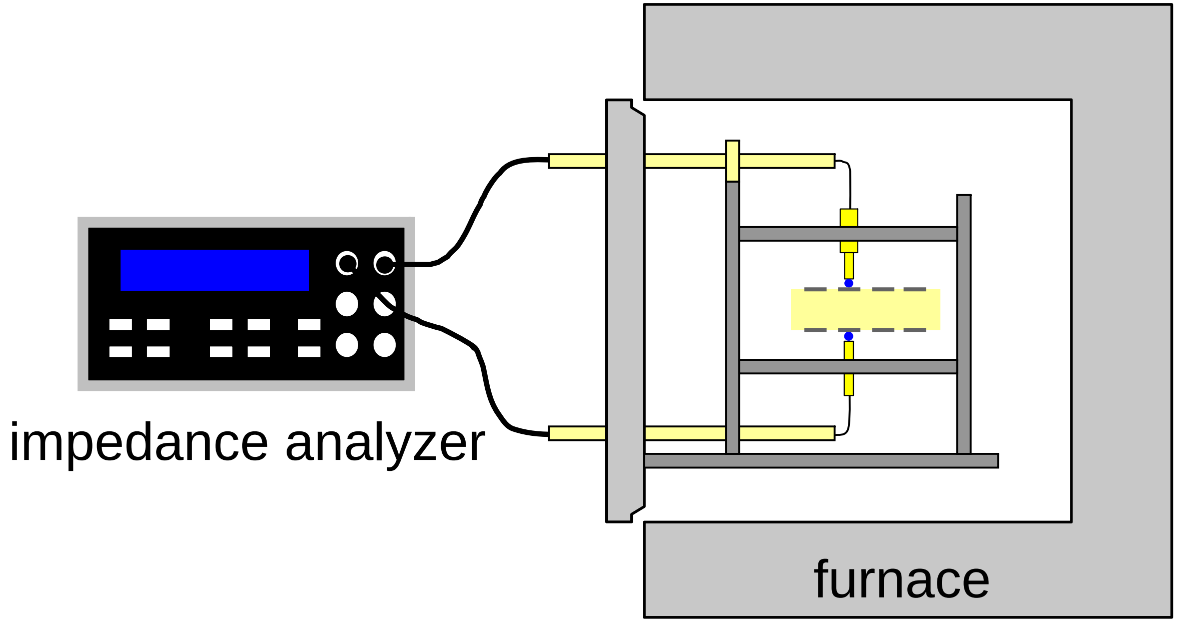
- Summary and Outlook

Motivation
Measurement setup for impedance spectroscopy (IS)

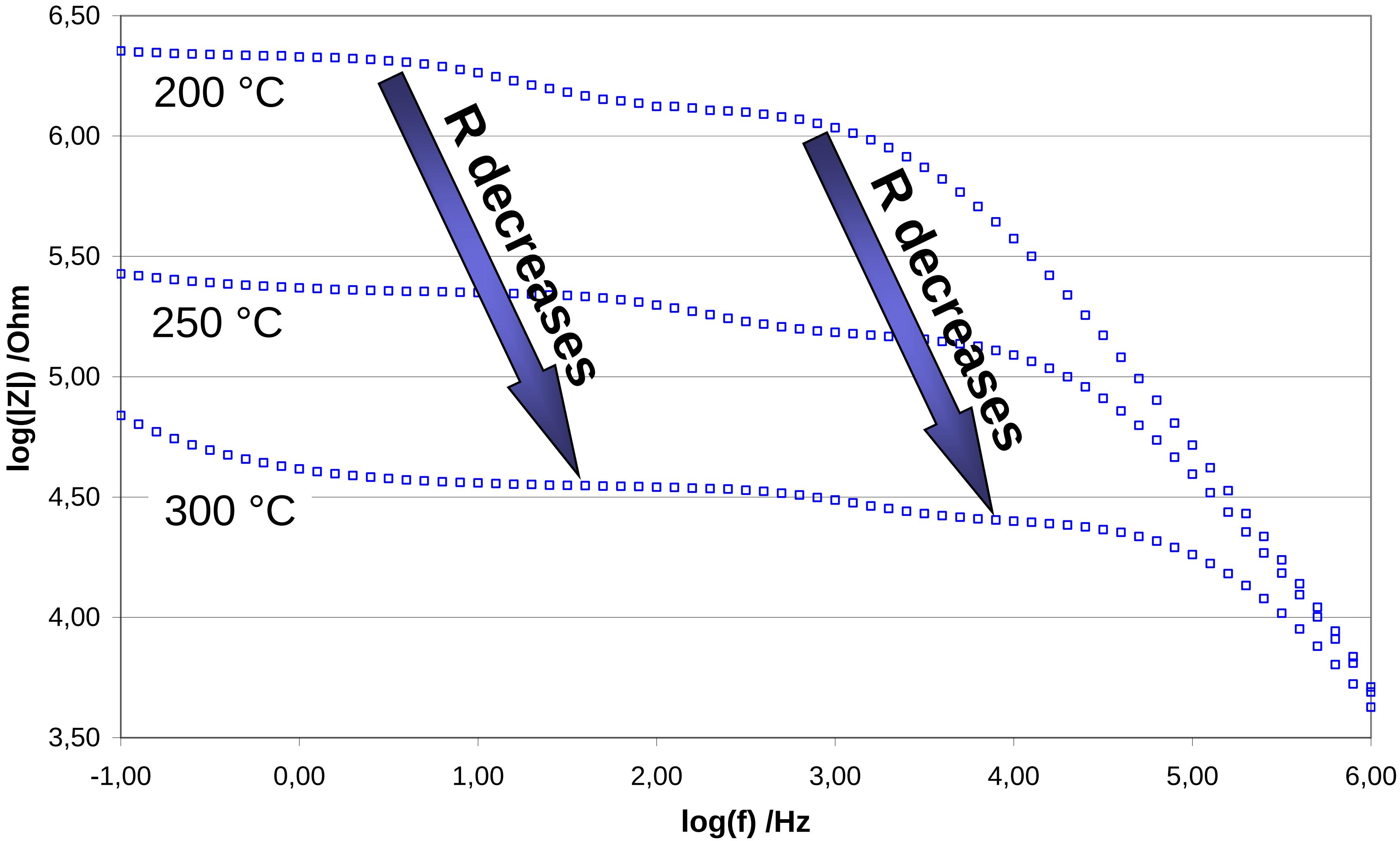


$$Z(\omega) = \frac{U(\omega)}{I(\omega)}$$

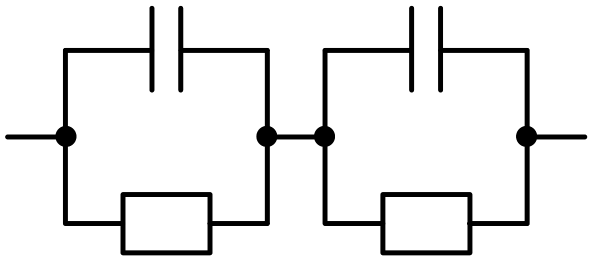
IS measurementsn
between 200 °C and 500 °C
from 10 mHz to 1 MHz

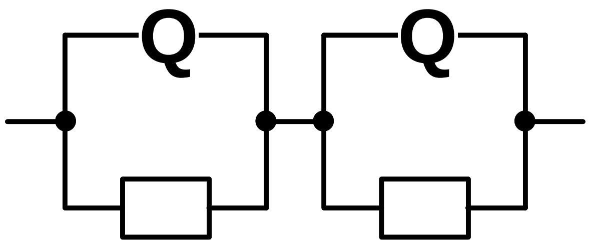


Motivation
temperatur dependance of TBC impedance spectra



Insertion
difference between RC- and RQ-elements





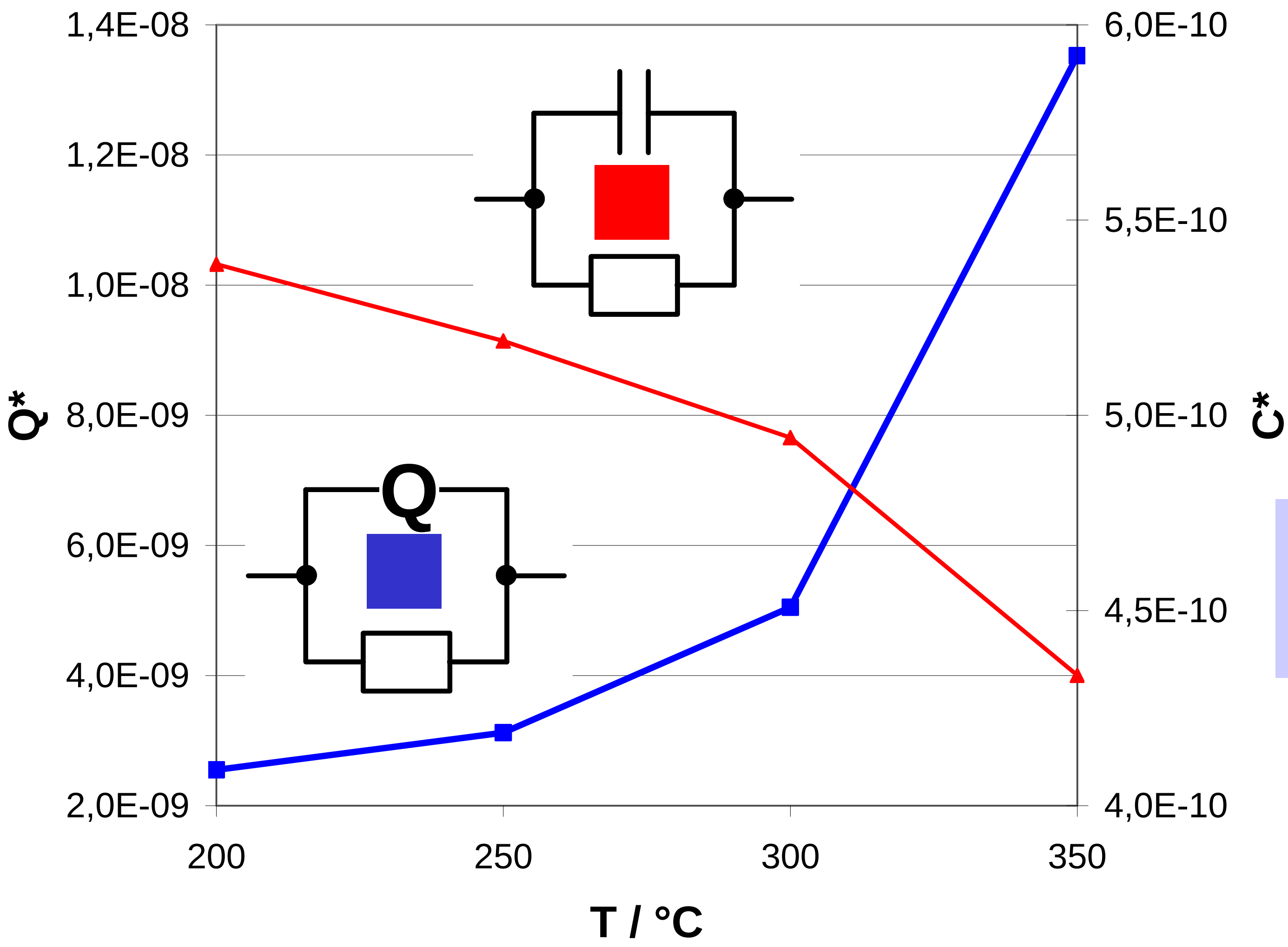
$$Z = \frac{R_1}{1 + j\omega R_1 C_1} + \frac{R_2}{1 + j\omega R_2 C_2}$$

$$Z = \frac{R_1}{1 + (j\omega)^{n1} R_1 Q_1} + \frac{R_2}{1 + (j\omega)^{n2} R_2 Q_2}$$

A Constant Phase Element (Q) is artificial.
For n=1 it is an ideal capacitor, for n=0 an resistance.
Index n is a measure for the broadness of the distribution of the electrical properties,
thus a measure for the (electrical) inhomogeneity.

„an alternative expression of our ignorance of the mechanism“ (Cole 1968)

Insertion
Constant Phase Element – temperature dependence of Q



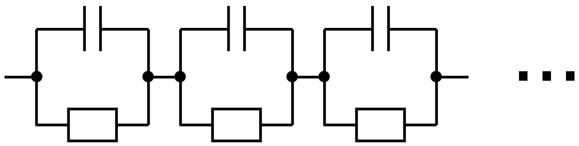
Q shows exponential temperature behaviour

for YSZ not feasible

„equivalent“ capacity shows linear or 1/T behaviour => feasible

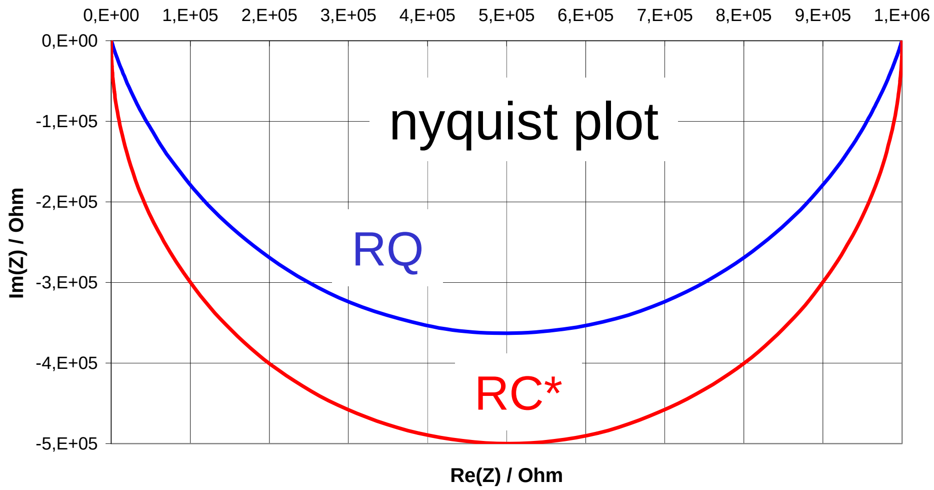
Insertion
Conversion of a RQ-element to an equivalent RC-element

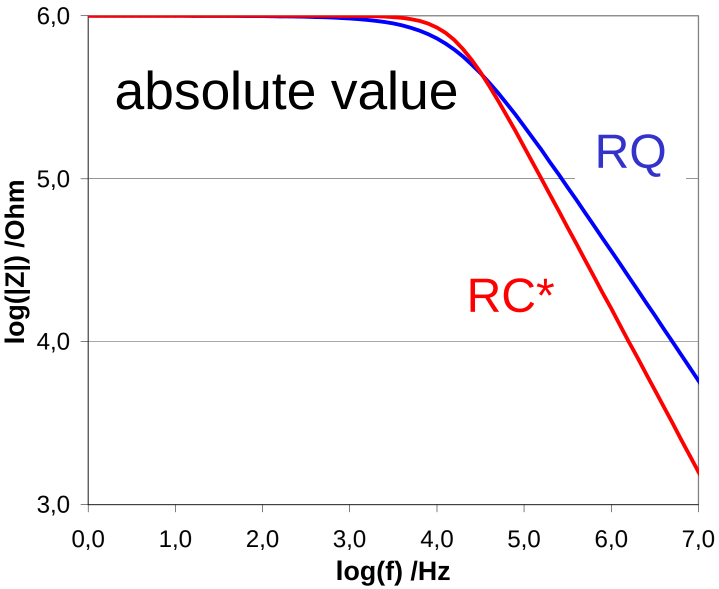
infinite number of RC-elements

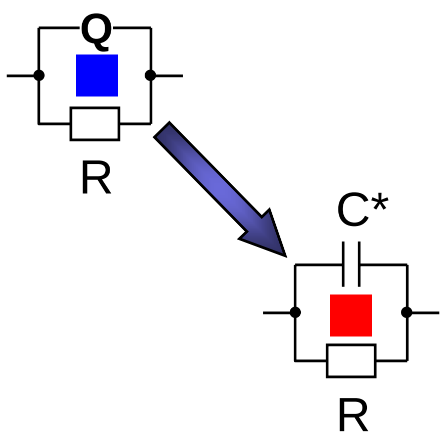


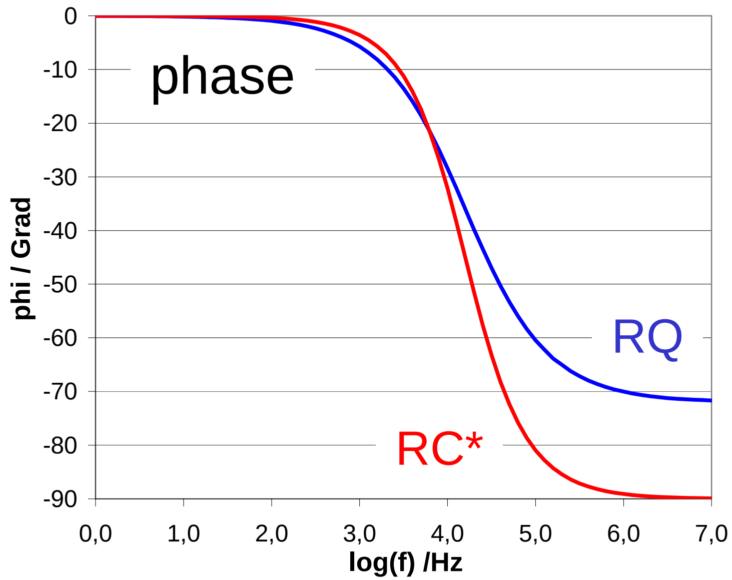
RC-element with the highest weight

$$C^* = (R^{1-n} \cdot Q)^{1/n}$$

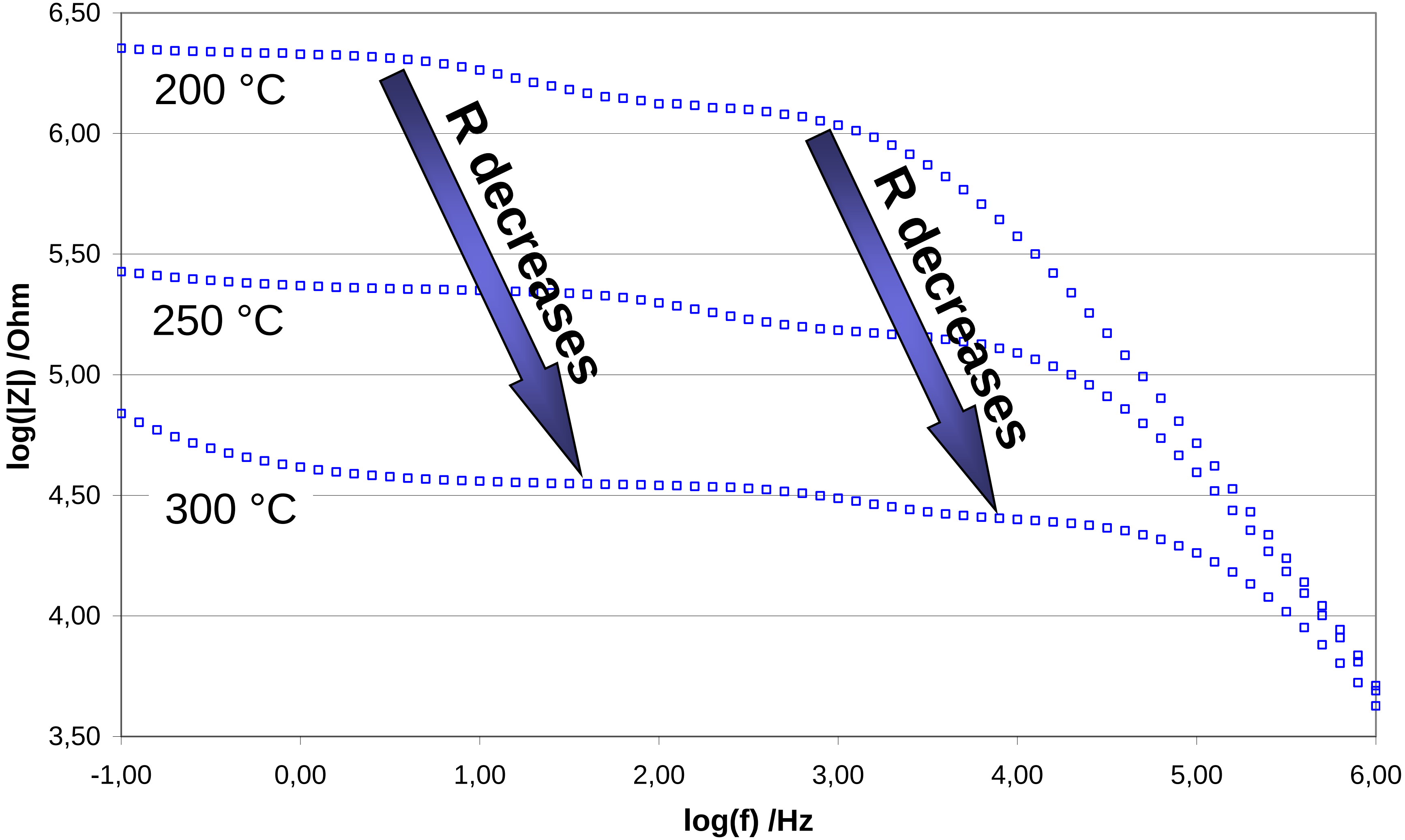




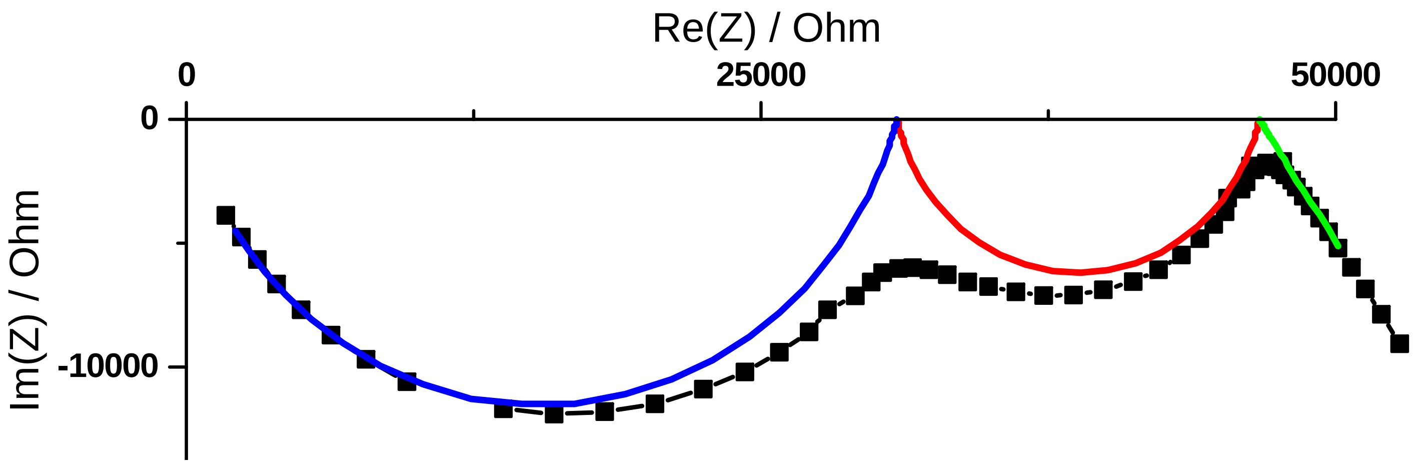


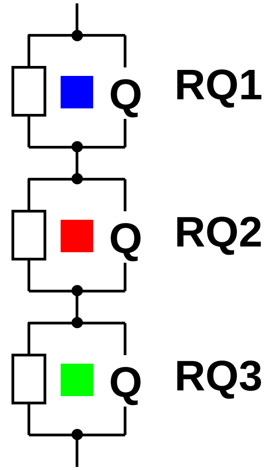


Motivation
temperatur dependance of TBC impedance spectra

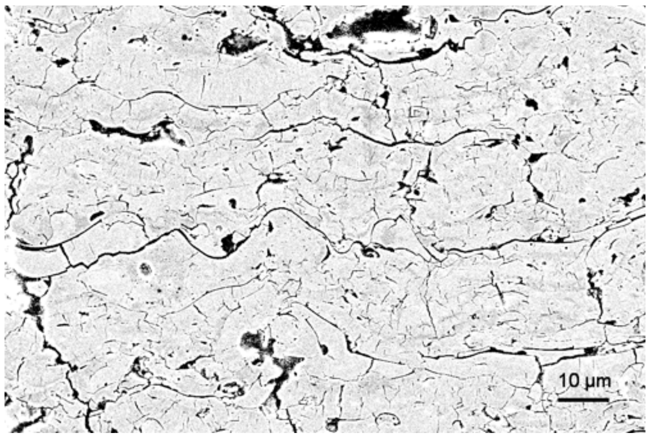


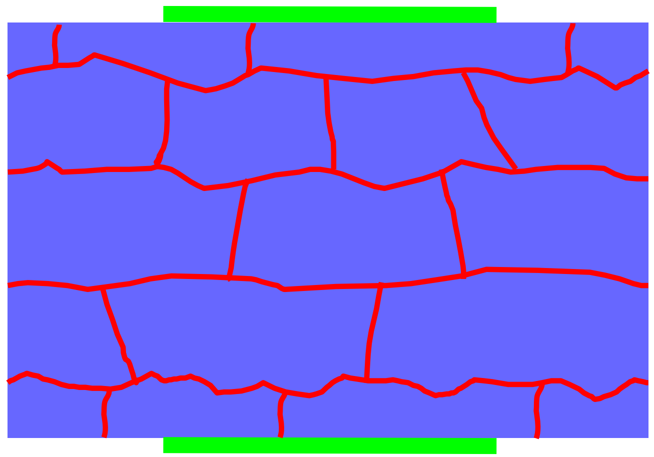
typical nyquist plot and fit model



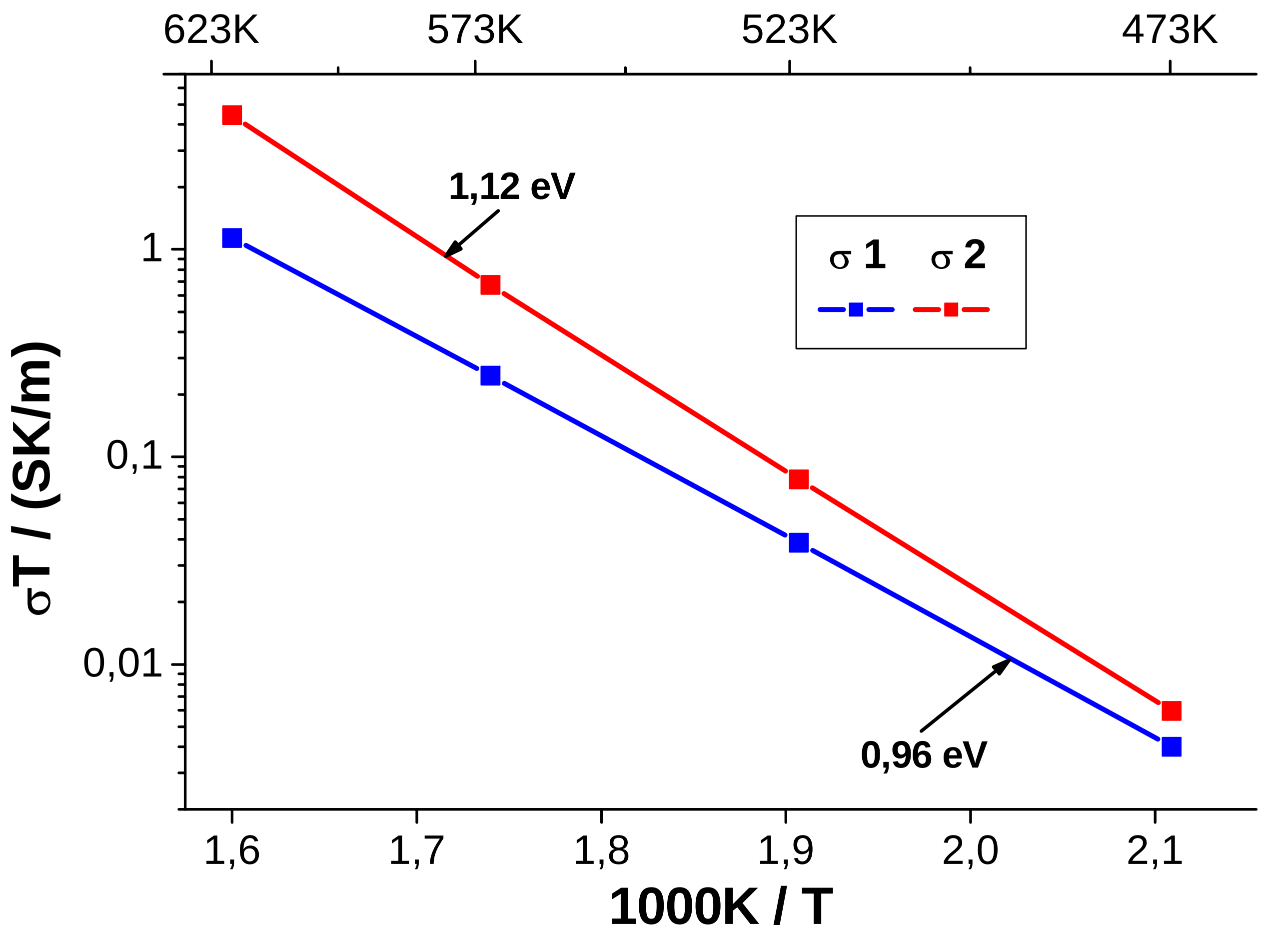


model of microstructure





Motivation
thermally activated conductivity

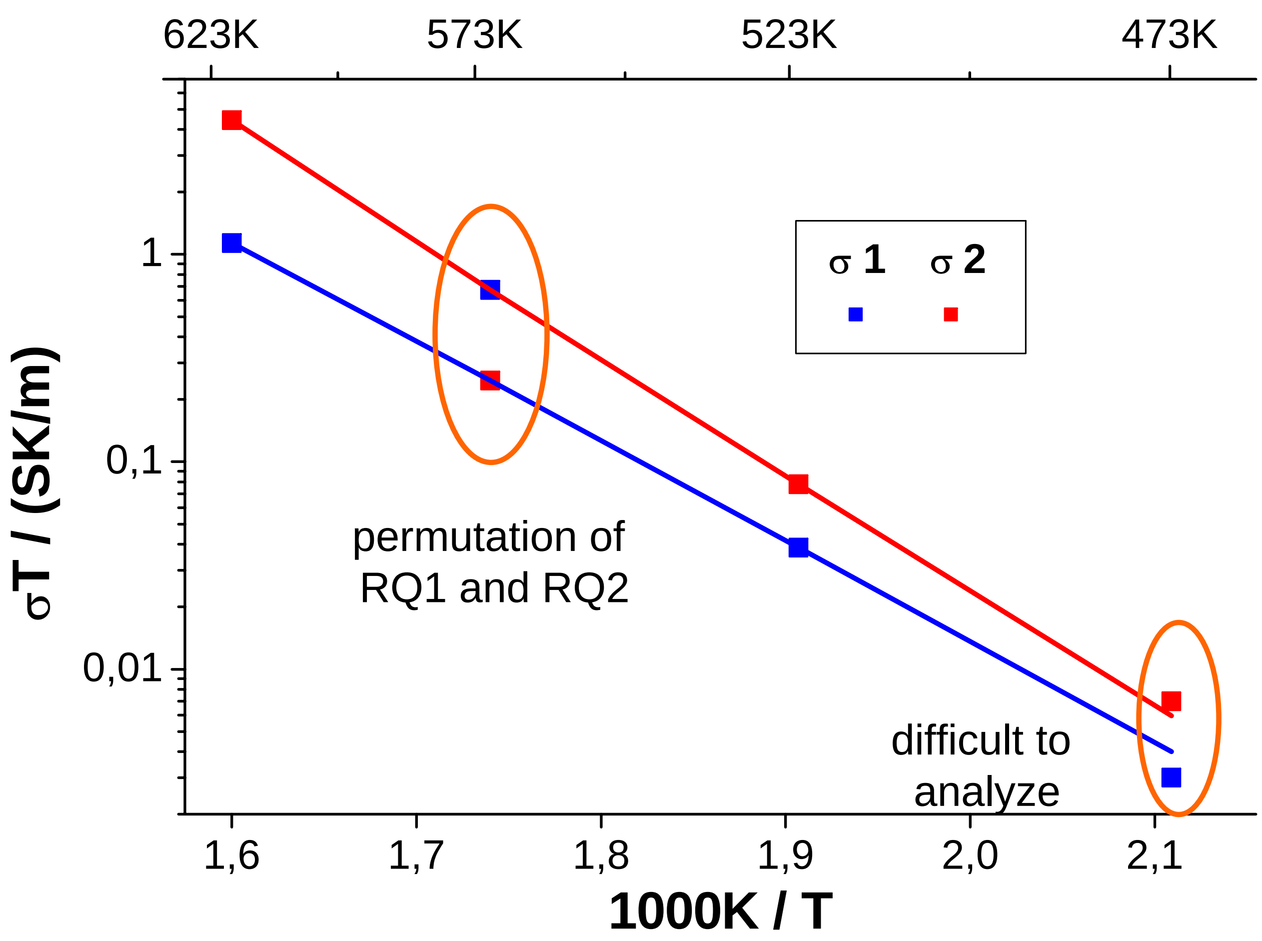


arrhenius plot

$$\sigma T = A \cdot \exp(E/kT)$$

but....

Motivation
thermally activated conductivity, fit problems



arrhenius plot

$$\sigma T = A \cdot \exp(E/_{kT})$$

The fit software does not know anything about the thermally activated conductivity!

Motivation
Comparison with standard CNLS software

Complex **N**onlinear **L**east **S**quares (CNLS) fit

merit function: $$S = \sum_{j=1}^{N} \frac{1}{w_j} \cdot \left| \underline{Z}_j - \underline{\hat{Z}}_j \right|^2$$

w_j: weight factors
ideal: $w_j = 1/\sigma_j^{\,2}$

relative weighting: $$S = \sum_{j=1}^{N} \frac{1}{\left|\underline{Z}_j\right|^2} \cdot \left| \underline{Z}_j - \underline{\hat{Z}}_j \right|^2$$

Z_j: measured impedance
$\hat{Z}_j$: modelled impedance

standard fit software

LEVM (Macdonald): difficult input and output files, many equivalent circuits possible, flexible weighting, many impedance representations

EquivCrt (Boukamp): grafical and interactive, good for orientation, for mass fit to slowly to operate, any equivalent circuit through CDC (Circuit Description Code) possible, only relative weighting, many impedance representations

new fit software
approach

new approach

- simultaneous fit of many impedance spectra
- consideration of assumptions regarding temperature dependance of equivalent circuit elements R, C, Q, n
- better boundary conditions for fit

requirements

- impedance spectra at all relevant temperatures can be described by the same equivalent circuit model
- impedance spectra can be modelled by (infinite) RQ-elements in series

new fit software
common temperature equation

common equation for R, C, n

$$x(T) = \underbrace{A \cdot T \cdot \exp\left(E/_{kT}\right)}_{\text{thermally activated conductivity}} + \underbrace{M \cdot T + B}_{\text{linear, constant}} + \underbrace{D \cdot T^{N}}_{\text{square root laws, 1/T, etc.}}$$

superposed effects

$$x(T) = A_1 \cdot T \cdot \exp\left(E_1/_{kT}\right) + M_1 \cdot T + B_1 + D_1 \cdot T^{N_1} +$$
$$\ldots + A_2 \cdot T \cdot \exp\left(E_2/_{kT}\right) + M_2 \cdot T + B_2 + D_2 \cdot T^{N_2} + \ldots$$

new fit software
boundary conditions

common temperature equation

$$x(T) = A \cdot T \cdot \exp(E/_{kT}) + M \cdot T + B + D \cdot T^N$$

example: thermally activated conductivity

$$R(T) = A \cdot T \cdot \exp(E/_{kT})$$

limit on equiv. crt. value

$$R_u \leq R(T) \leq R_o$$

combined limit

$$f_u \leq \frac{1}{2\pi(RQ)^{1/n}} \leq f_o$$

limit on any parameter

$$A_u \leq A \leq A_o$$

$$E_u \leq E \leq E_o$$

no other fit software supports these **necessary** multitude of boundary conditions

new fit software
command file

(easy) readable command file

the fit problem is defined by a file,
changes in starting values of boundaries
are easily possible

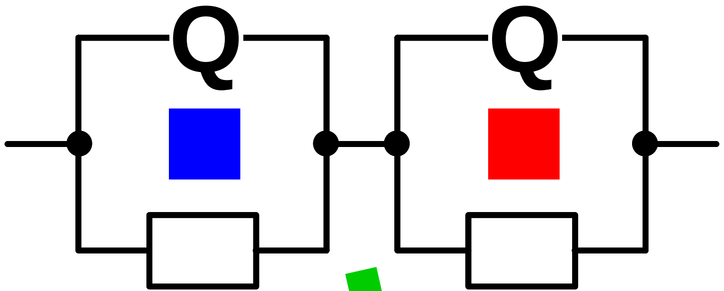
```
[FITPREFS]
GNUPlotCmd="..\gnuplot\wgnupl32.exe"
FitName="P222M07_1"

R1=f(A1,E1) A1>=1e-12 A1<=1e-5 E1>=0.8 E1<=1.3
C1=f(F)        definition of temperature
n1=f(F)          dependance of RQ1

R2=f(A1,E1) A1>=1e-12 A1<=1e-5 E1>=0.8 E1<=1.3
C2=f(F)        definition of temperature
n2=f(F)          dependance of RQ2

R3=f(A1,E1) A1>=1e-12 A1<=1e-5 E1>=0.8 E1<=1.3
C3=f(F)        definition of temperature
n3=f(F)          dependance of RQ3

f1=1
f2=5e5      start and end frequence of the fit
```

```
[ISFILE]
P222M07.258
4
250
[RQPREFS]
R1!=6,5021e+005
Q1!=6,9201e-010
n1!=0,741 >=0.5
R2!=4,1961e+005
Q2!=7,2801e-009
n2!=0,853 >=0.5
R3!=7,6072e+007
Q3!=1,0384e-008
n3!=0,739 >=0.5
[ISFILE]
P222M07.307
4
300
[RQPREFS]
R1!=7,2287e+004
Q1!=1,8819e-010
...
```

```
...
n1!=0,867 >=0.5
R2!=3,015e+004
Q2!=1,8891e-010
n2!=0,9 >=0.5
R3!=1,6852e+007
Q3!=2,2945e-008
n3!=0,674 >=0.5
[ISFILE]
P222M07.355
4
350
[RQPREFS]
R1!=2e+004
Q1!=4e-009
n1!=0,69 >=0.5
R2!=1e4
Q2!=4e-008
n2!=0,62 >=0.5
R3!=3e+006
Q3!=4e-8
n3!=0,70 >=0.5
```

Comparison with standard CNLS software
synthetic data, 2 RQ elements, same initial values

equivalent circuit

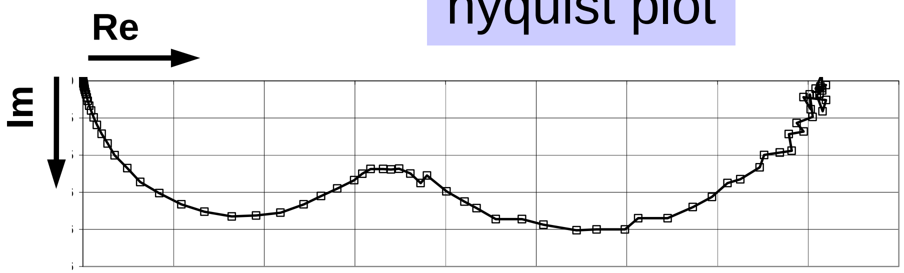


parameters

R1 = 3,11e6	R2 = 5,06e6
Q1 = 9,73e-10	Q2 = 7,45e-8
n1 = 0,9	n2 = 0,7

noise

nyquist plot



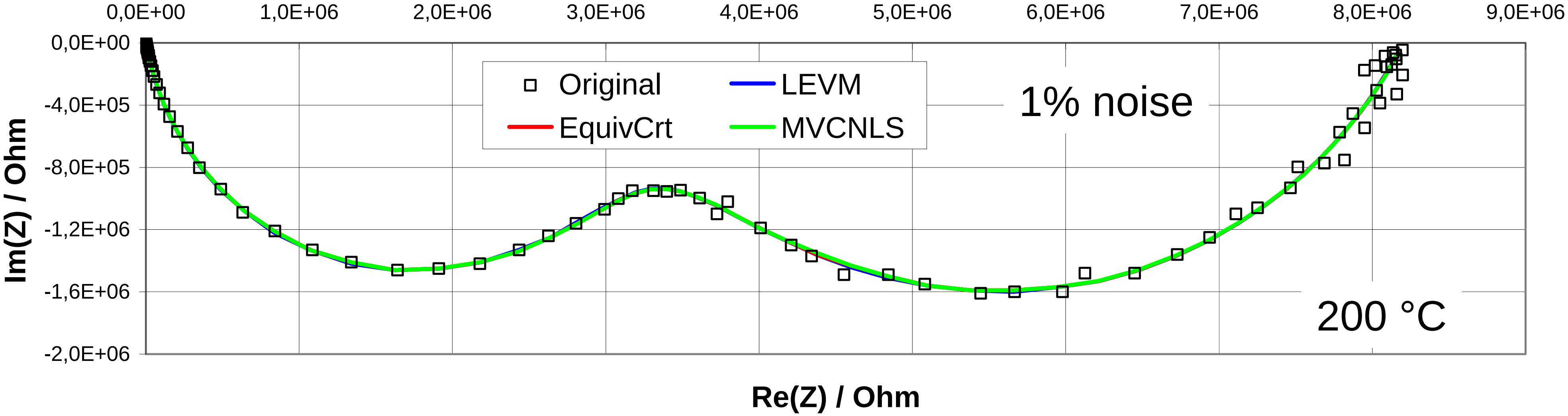
\+

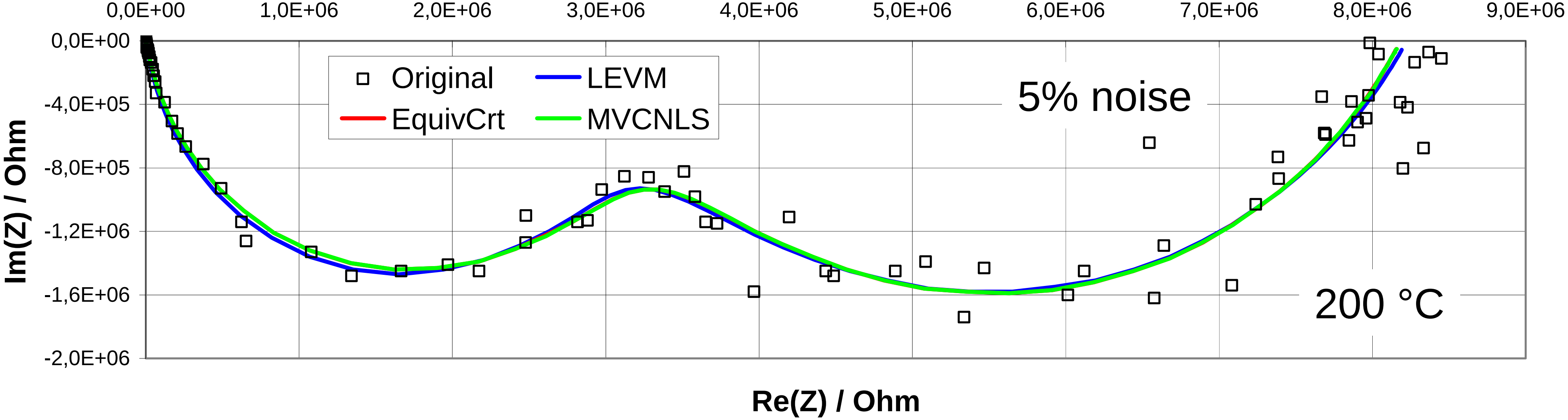
initial values

R1 = *3e6*	*R2* = *4,5e6*
Q1 = *9e-10*	*Q2* = *7e-8*
n1 = *0,88*	*n2* = *0,72*

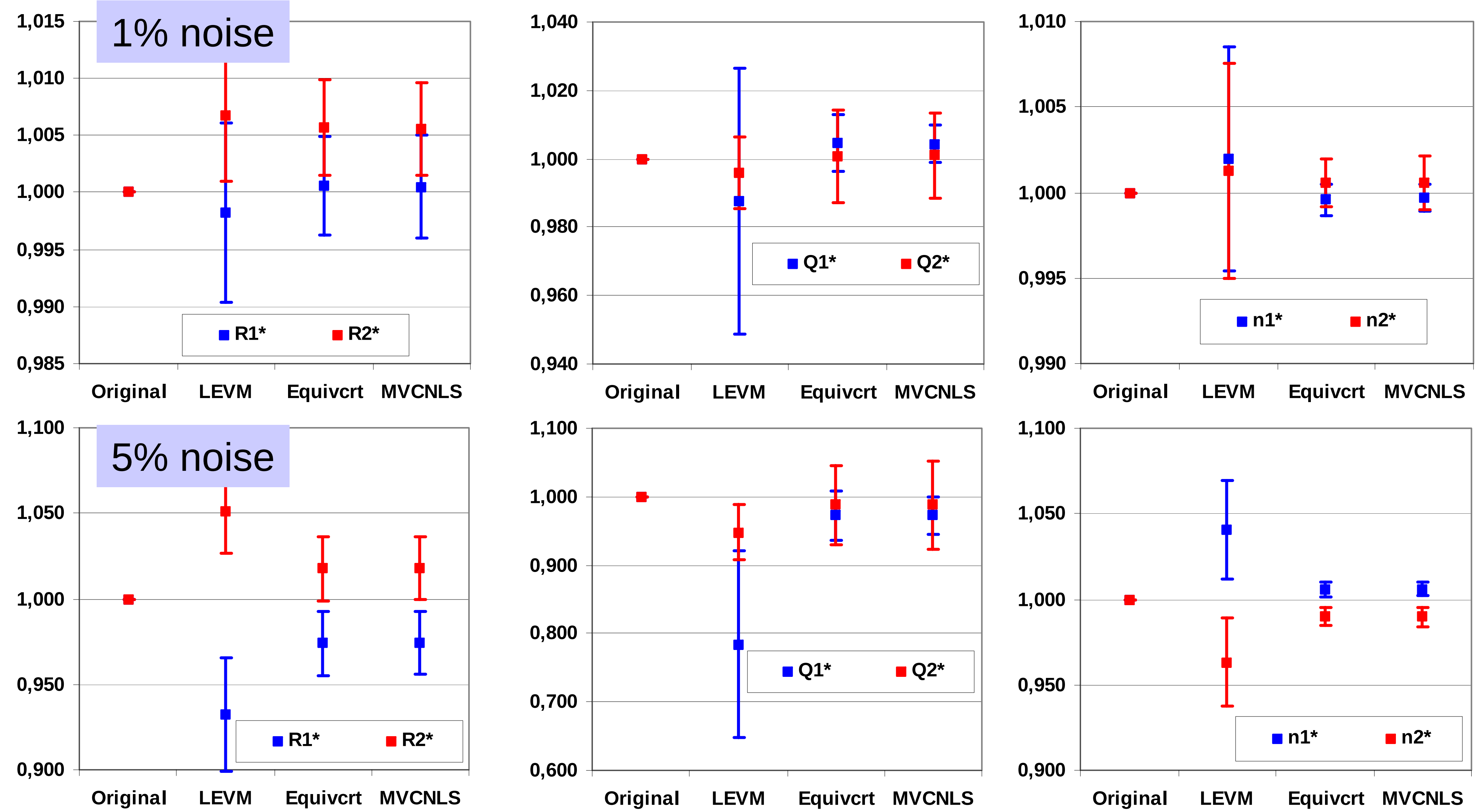
fit software

Comparison with standard CNLS software: nyquist plots synthetic data, 2 RQ elements, same initial values

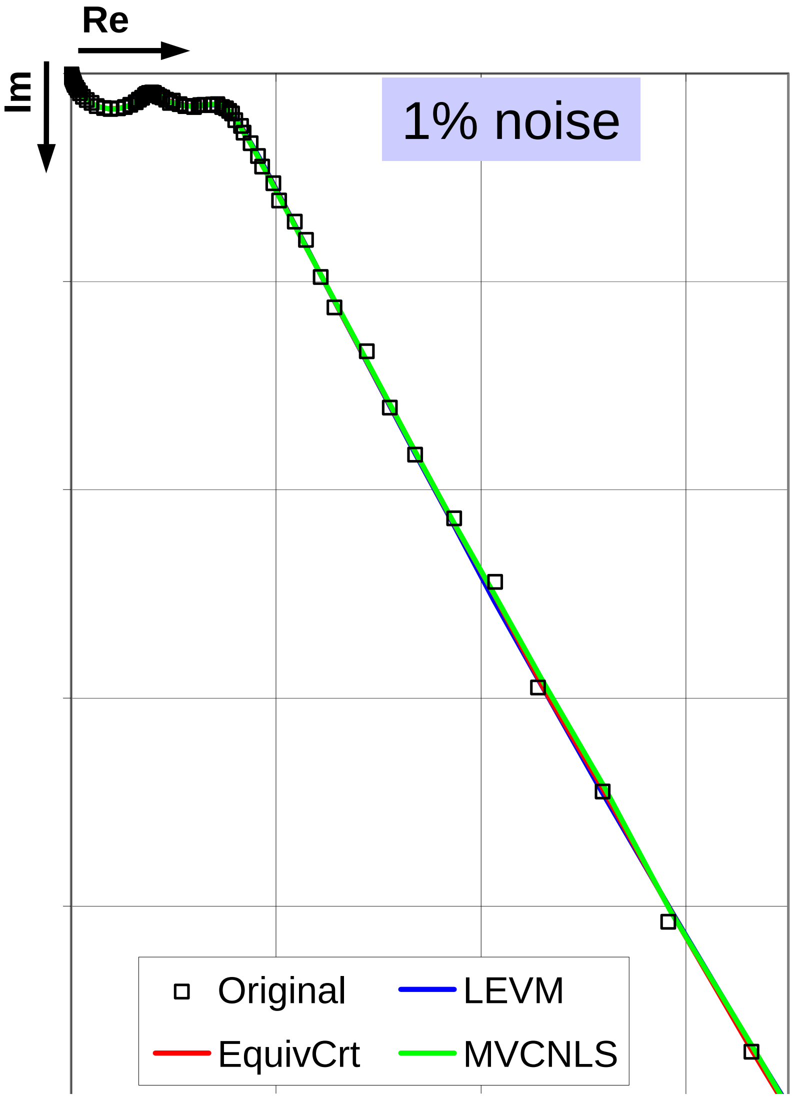




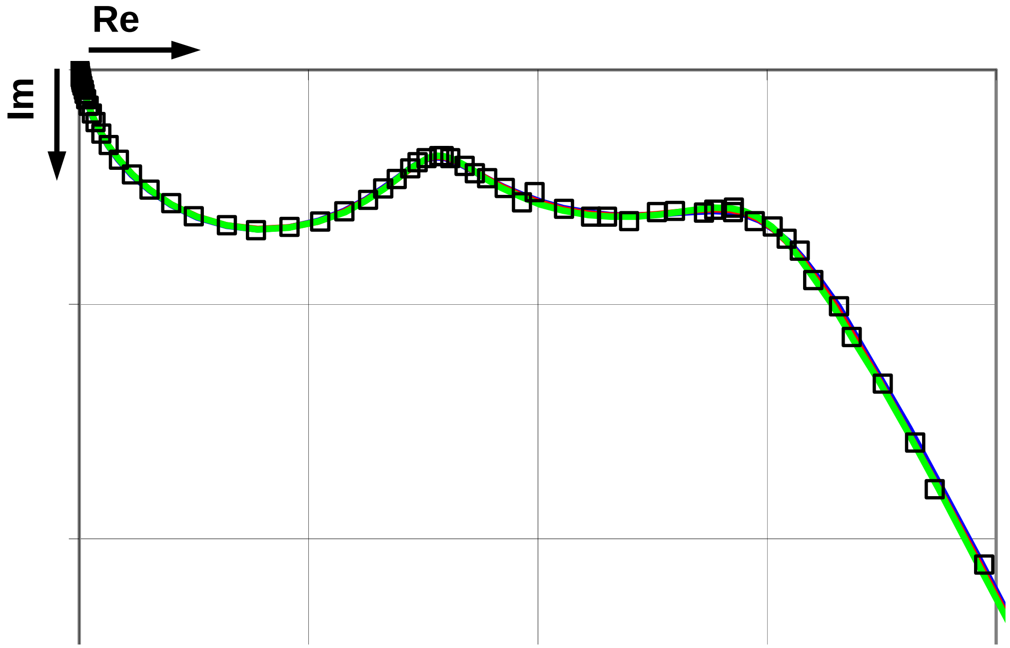
Comparison with standard CNLS software: fit results synthetic data, 2 RQ elements, same initial values



Comparison with standard CNLS software: fit results
synthetic data, 3 RQ elements, same initial values

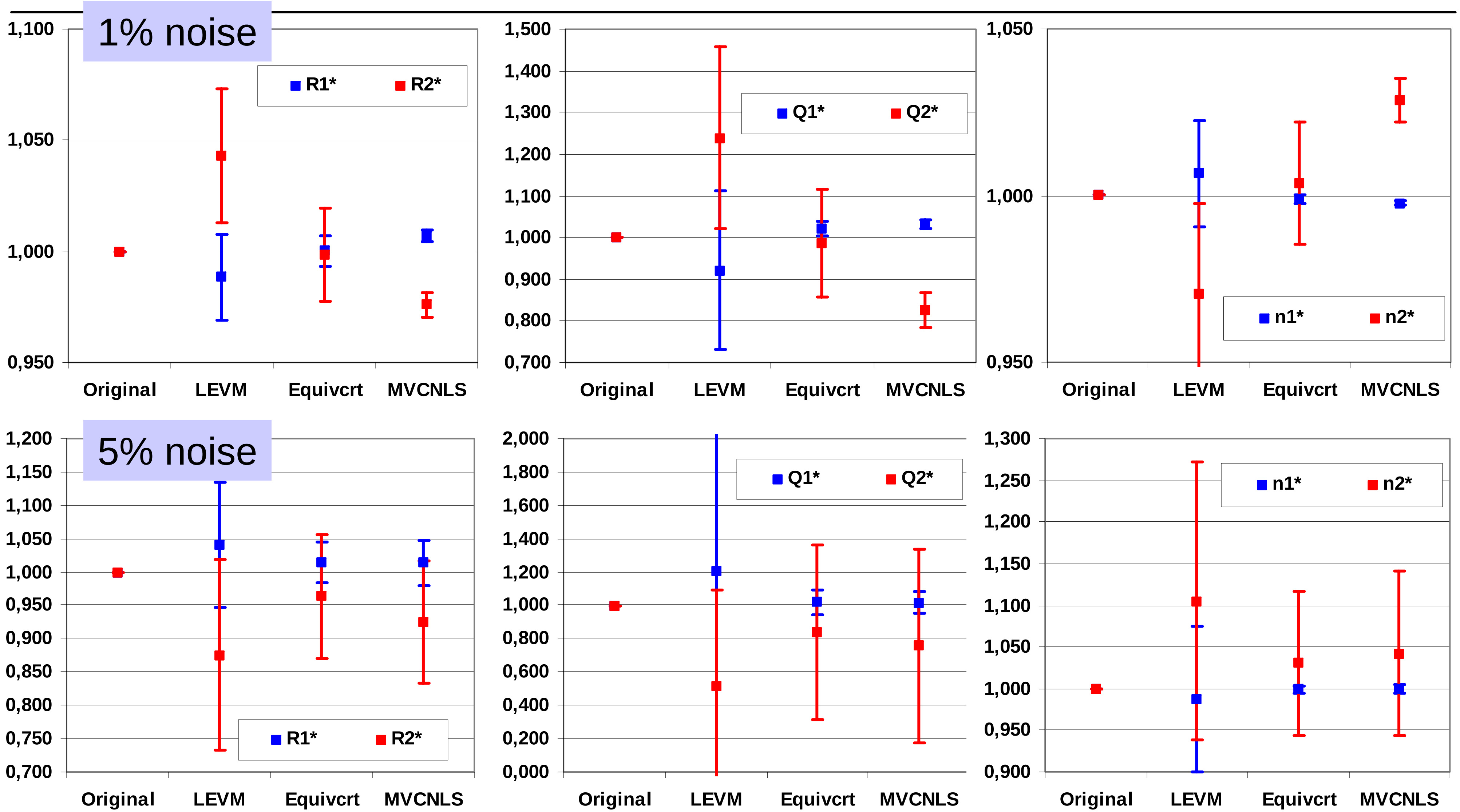


3. RQ element only partial
in measured frequency range



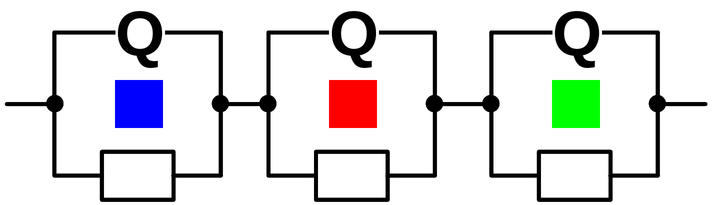
fit is ok,
but the errors ...

Comparison with standard CNLS software: fit results synthetic data, 3 RQ elements, same initial values

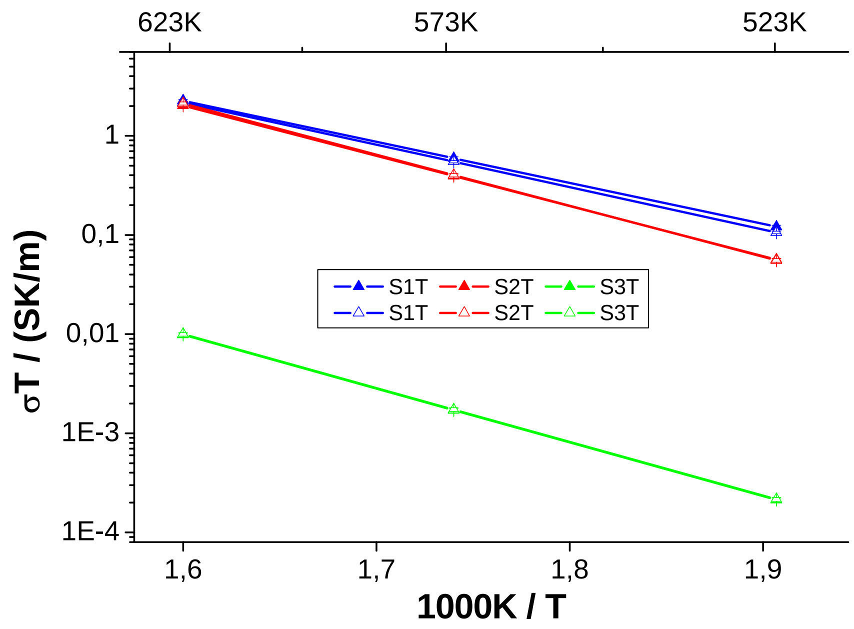


thermally cycled TBC-Systems: fit problem from practice
fit results

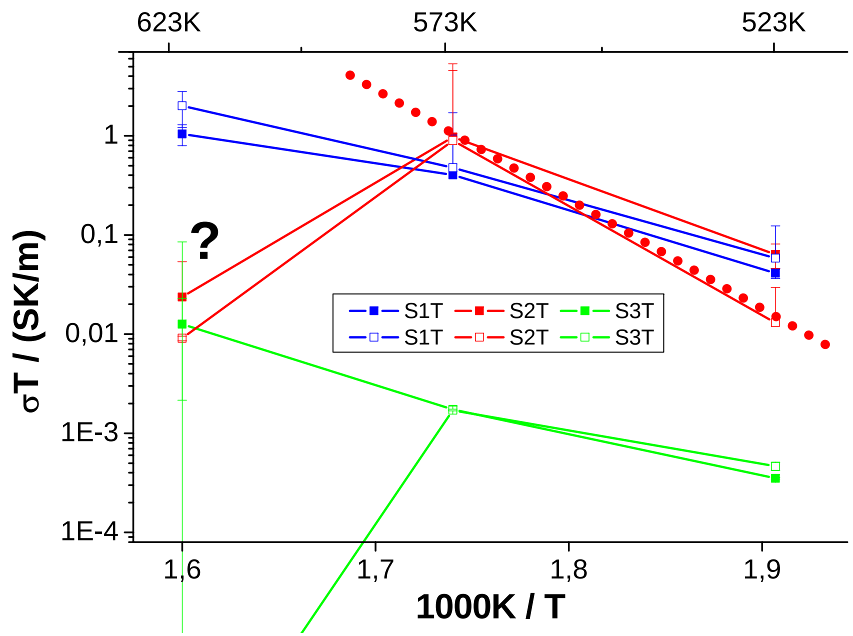
equivalent circuit of 3 RQ elements
same initial values for both
LEVM: each temperature alone
MVCNLS: 3 temperatures at once



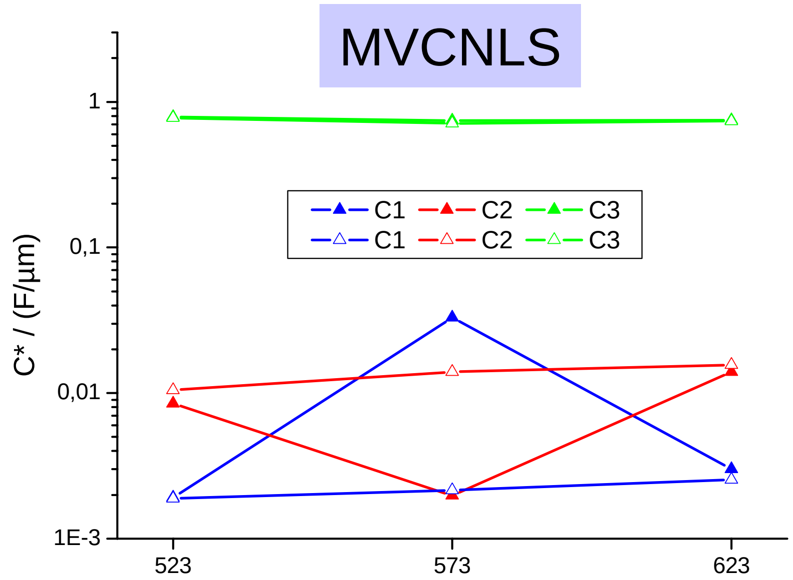
MVCNLS

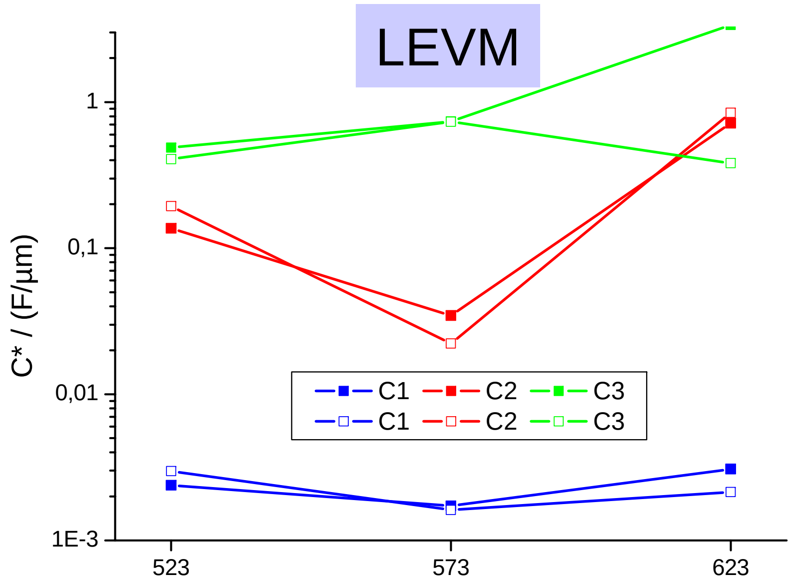


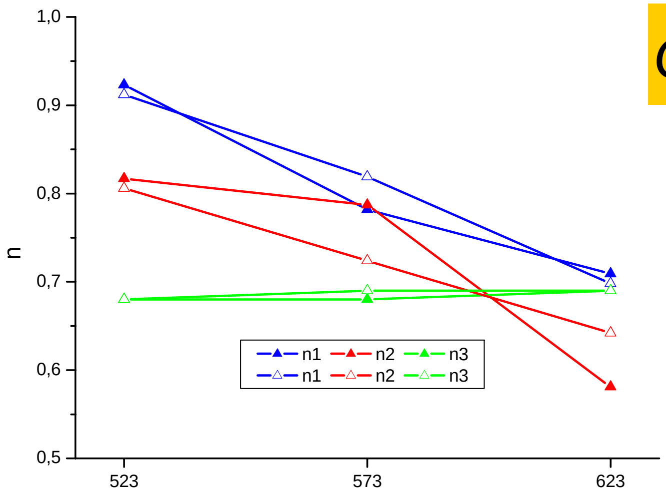
LEVM



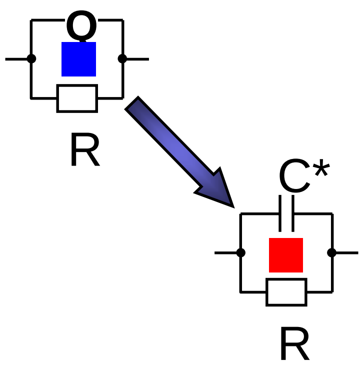
thermally cycled TBC-Systems: fit problem from practice
fit results

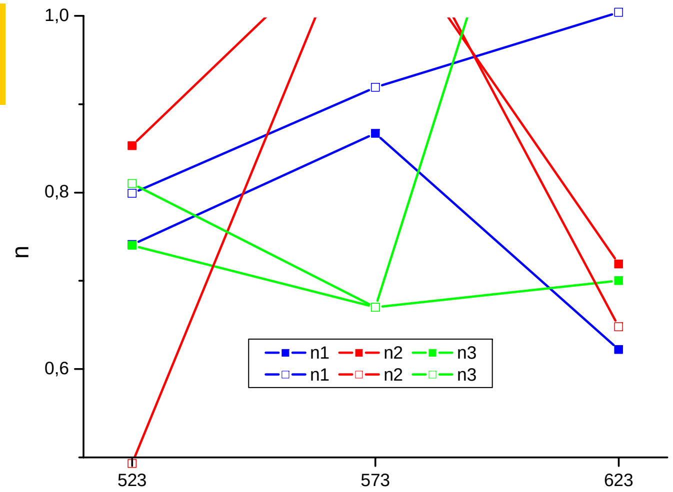






$$C^* = (R^{1-n} \cdot Q)^{1/n}$$





Summary and Outlook

- fit software for analysis of temperature depended impedance spectra
- standard CNLS fit with boundary conditions possible
- direct determination of activiation energies
- expertise can be used

- graphical interface