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Fitting Havriliak-Negami Equation

Outline

- Description (what is studied and how)

- Study using OriginLab (finding the best fit for the Havriliak-Negami equation with conductivity term)

- Validation using different tool (Scipy, restricting the parameters, initial guess, correlation matrix)

- Suggestions for improvement (Decreasing input errors mainly via improved Area measurements)

Context

- Study of dielectric properties of a thin film of Lithium Niobate at 100°C, used as dielectric in a capacitor subjected to AC electric field at different frequencies (impedance spectroscopy).

- Determination of complex permittivity ($\epsilon = \epsilon' - i\epsilon''$) through the following relations involving measured quantities:
  - Capacitance: $C = \epsilon' \epsilon_0 \frac{A}{d}$
  - Tangent loss: $\tan(\delta) = \frac{\epsilon''}{\epsilon'}$

Debye Model

- Dipolar polarization is the main type of polarization in the range of frequencies considered.
- D.M. describes dielectric relaxation response of dipoles to alternating electrical field $E = E_0 e^{i\omega t}$ considering a single relaxation time τ.

$$\frac{dP_d}{dt} = \frac{1}{\tau}[(\epsilon_s - \epsilon_\infty)E - P_d(t)] \longrightarrow P_d(t) = \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau}E = \frac{\Delta\epsilon}{1 + i\omega\tau}E$$

$$\epsilon = \epsilon_\infty + \frac{\Delta\epsilon}{1 + i\omega\tau}$$

ϵ_s – *stationary permittivity, low freqs.*

ϵ_∞ – *limit of permittivity for high freqs.*

Havriliak–Negami Model

Empirical modification of Debye model to account for the broadening (β) and asymmetry (γ) of dielectric dispersion curve, considering that there is a distribution of relaxation times instead of one time only.

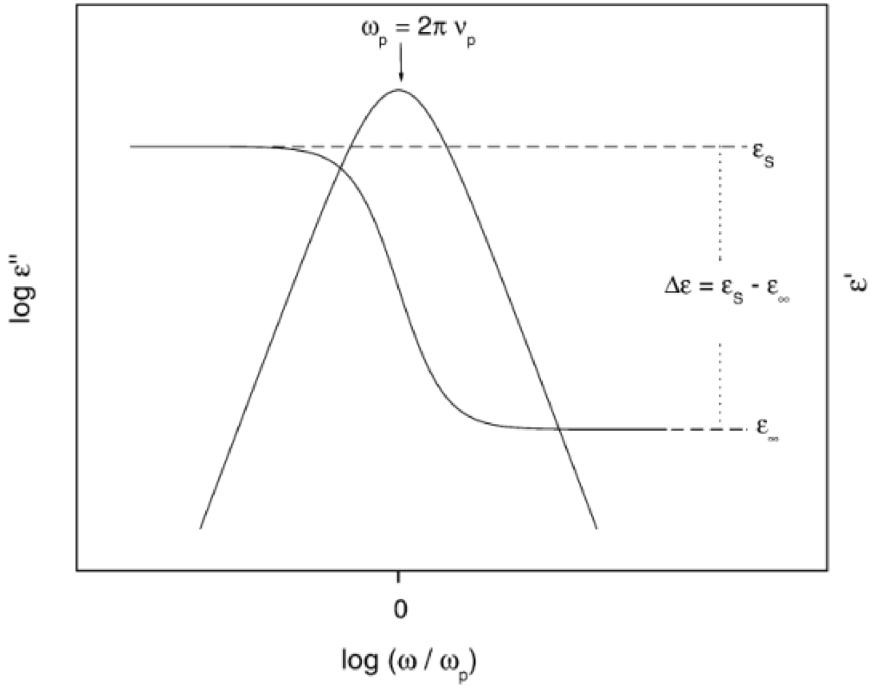


Fig. 3.2. Real ε' and imaginary part ε'' of the complex dielectric function vs normalized frequency for a Debye relaxation process

Broadband Dielectric Spectroscopy, p. 61

Debye:

$$\epsilon = \epsilon_\infty + \frac{\Delta\epsilon}{1 + i\omega\tau}$$

Havriliak-Negami

$$\epsilon = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (i\omega\tau)^\beta)^\gamma}$$

Conductive term

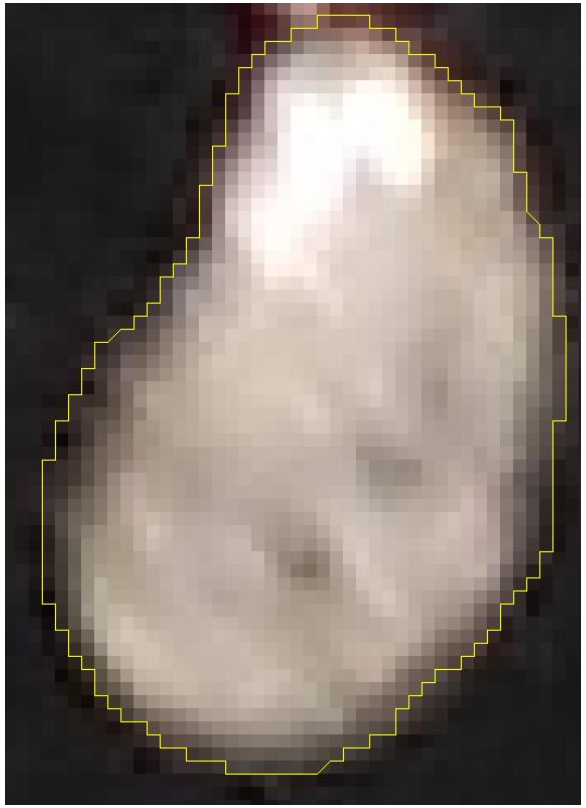
- Contributing to the dielectric function there are conductive processes alongside relaxation, which are important in low frequencies.

- Of pure electronic origin, we have a contribution for the imaginary part of ε, $\frac{\sigma_{DC}}{\varepsilon_0 \omega}$.

- To account for other contributions we add an exponent $s \leq 1$ in ω :

$$\frac{\sigma_{DC}}{\varepsilon_0 \omega^s}$$

Area Calculation



Problems:

- Limits
- Shadows
- Superficial curvature

$$Area \; = 1{,}521 \; \pm 0{,}165 \; \mu m$$

Data Error

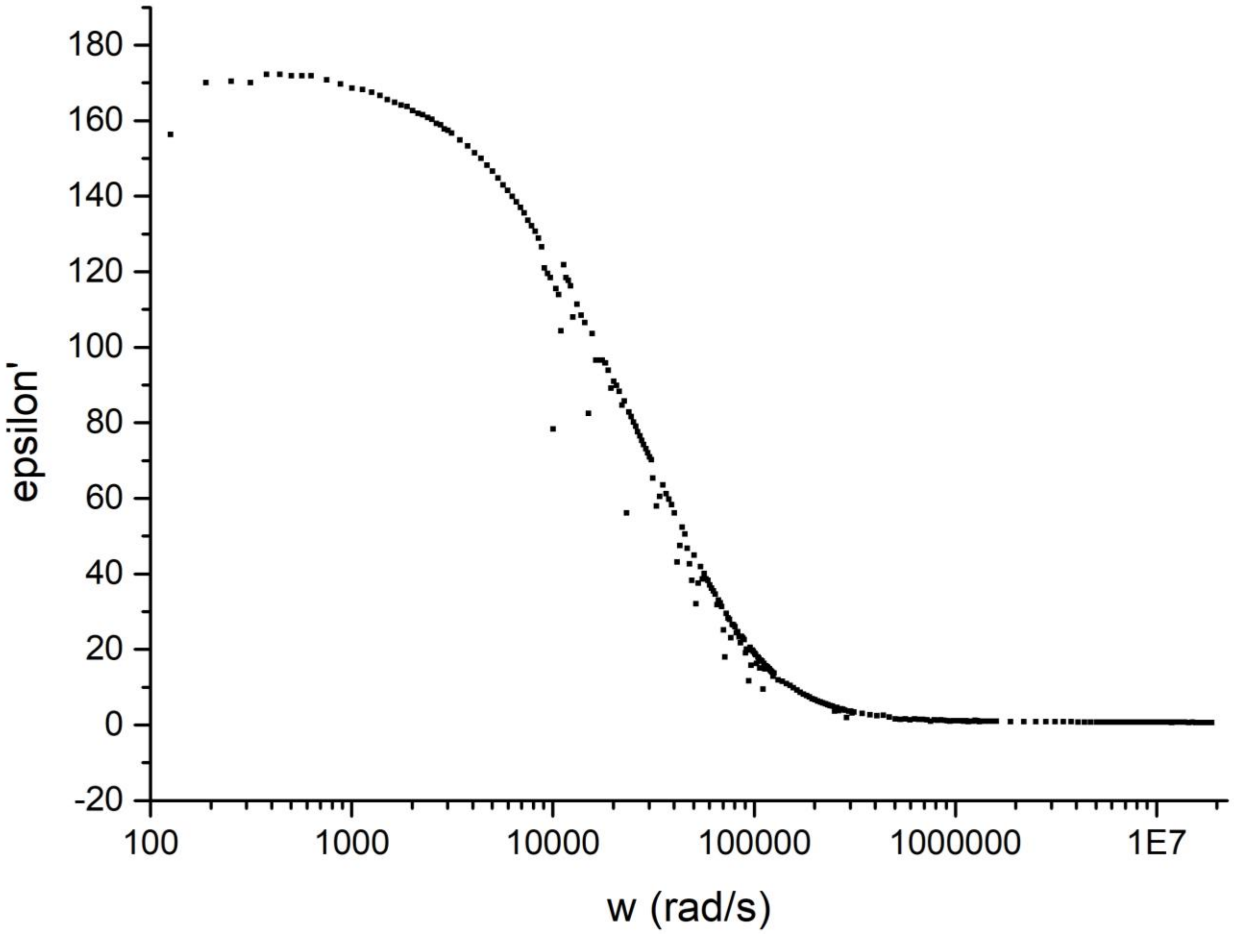
$$\delta f(x_1, x_2, \dots) = \sqrt{\left(\frac{\partial f}{\partial x_1}\right)^2 \delta {x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \delta {x_2}^2 + \cdots}$$

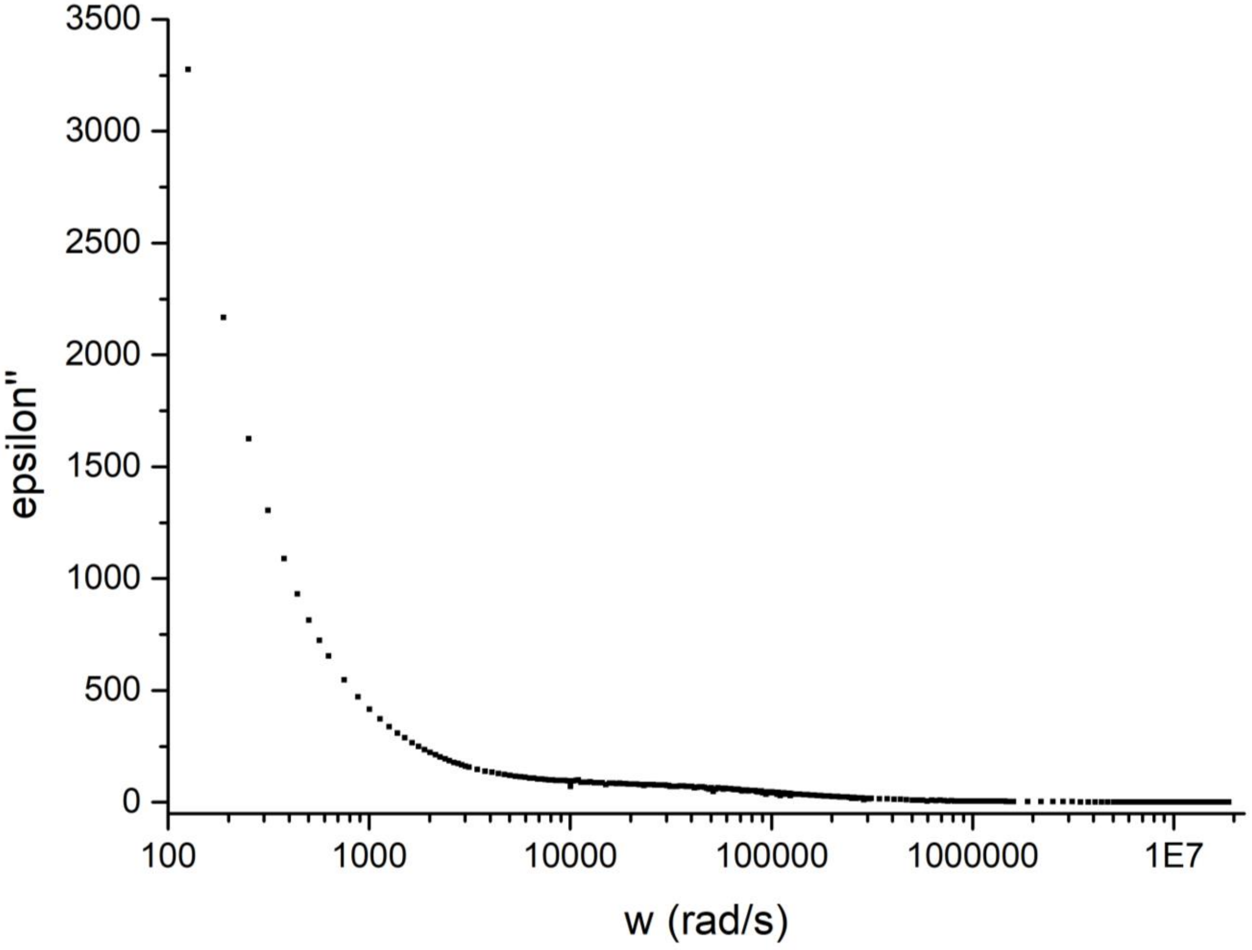
Lab Measurements error: 1%

Area error: 10,9%

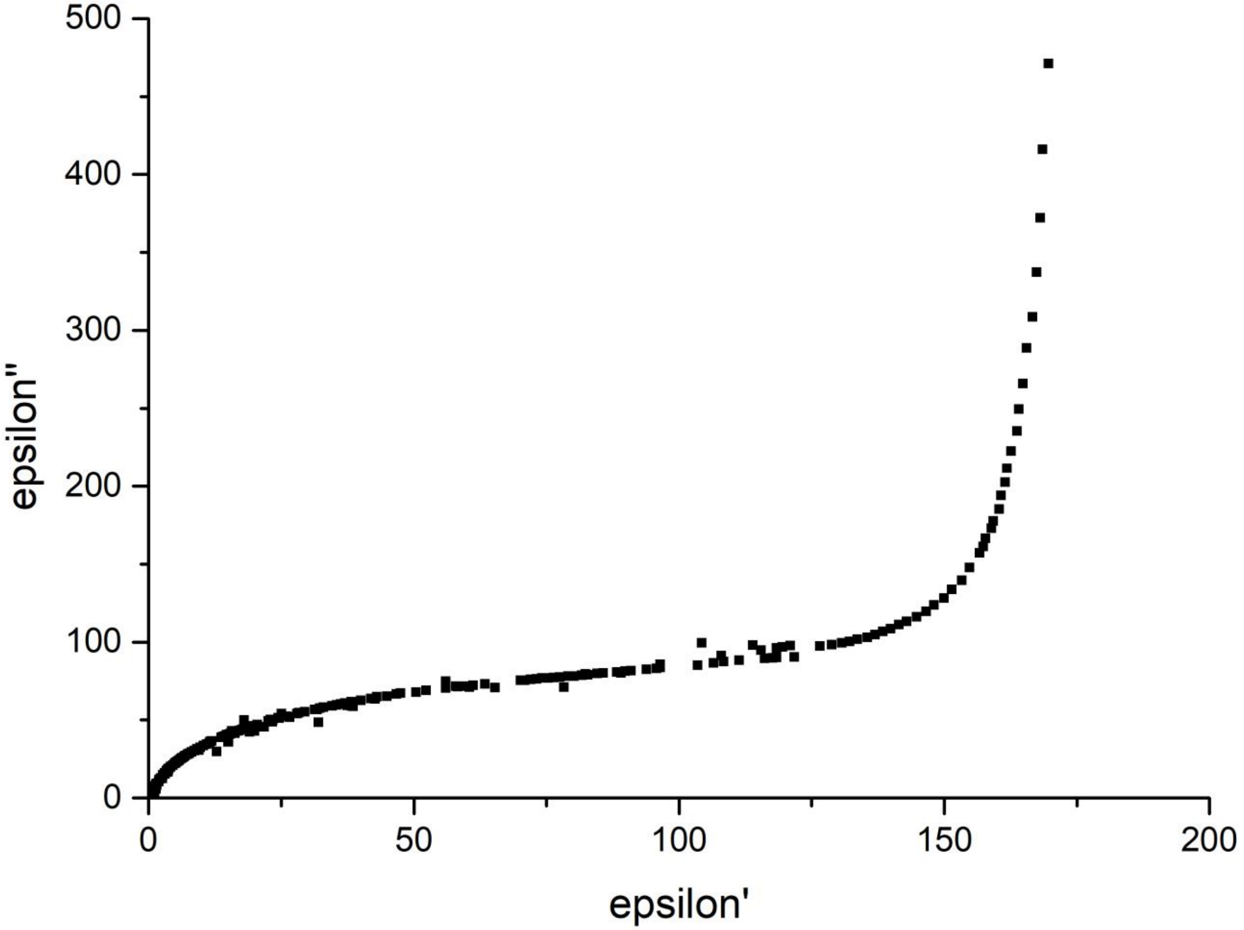
Real and Imaginary Permittivity error: 10,9%

Data: Real and Imaginary Permittivity vs Angular Frequency

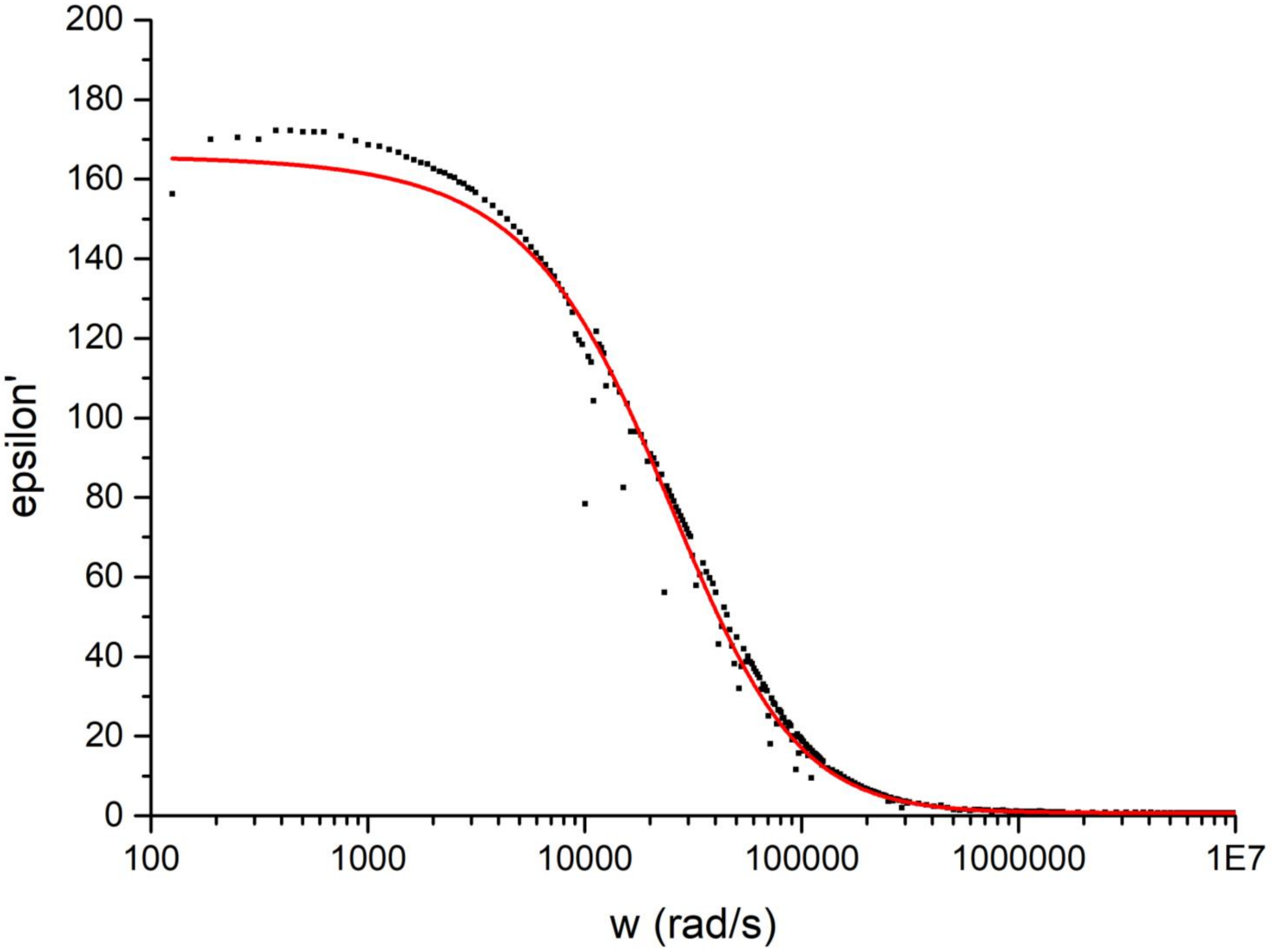




Data: Cole-Cole Diagram



Fitting Havriliak-Negami Equation: Real Part



$$\varepsilon' = \varepsilon_\infty + \Delta\varepsilon * r(\omega) * cos\big(\gamma\varphi(\omega)\big)$$

$$r(\omega) = \left[1 + 2(\omega\tau_{HN})^\beta \cos\left(\frac{\beta\pi}{2}\right) + (\omega\tau_{HN})^{2\beta}\right]^{-\gamma/2}$$

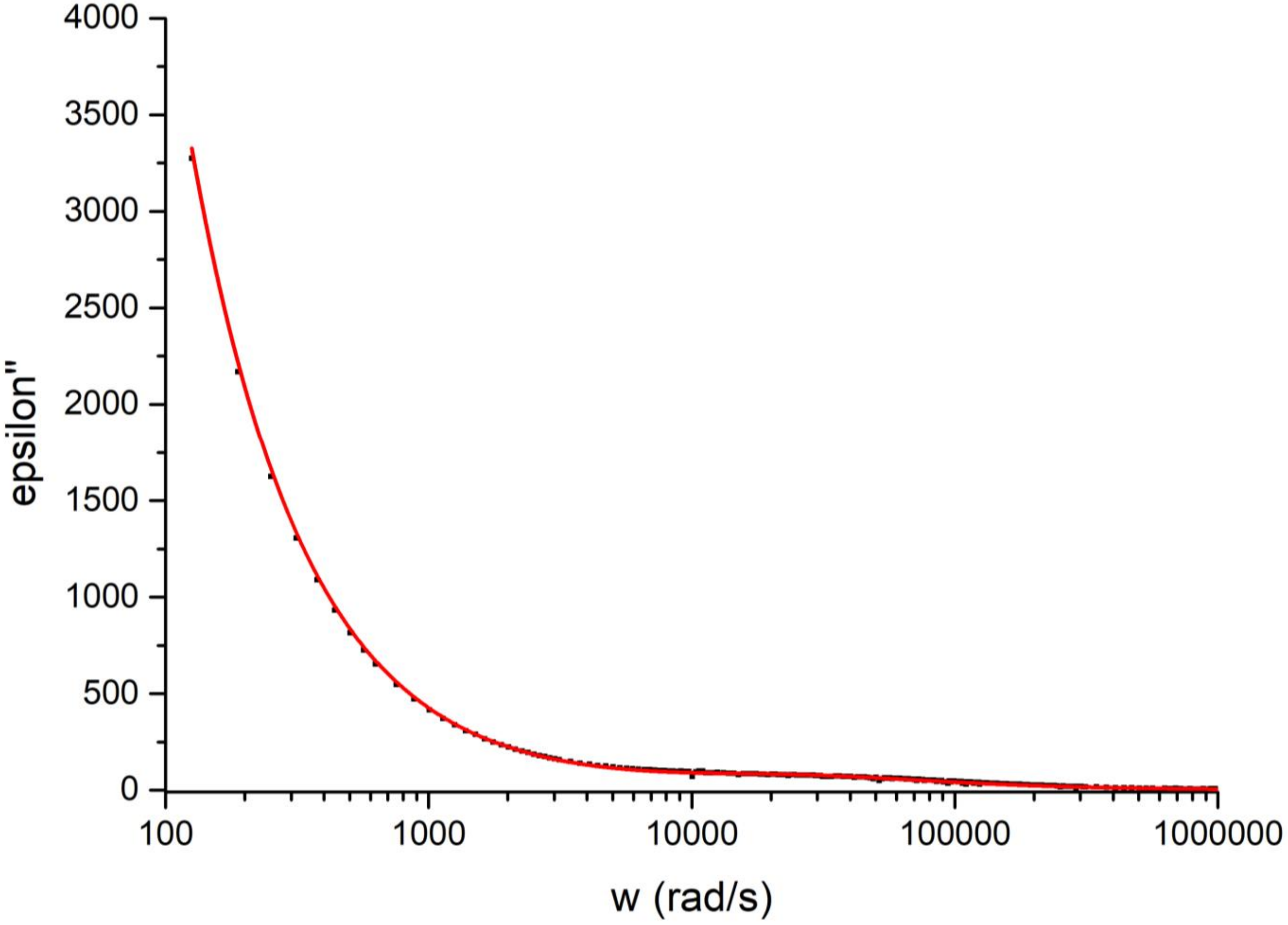
$$\varphi(\omega) = arctan\left[\frac{\sin(\beta\pi/2)}{(\omega\tau_{HN})^{-\beta}+\cos(\beta\pi/2)}\right]$$

Parameters:

$$\Delta\varepsilon = 165 \pm 4$$
$$\beta = 0{,}80 \pm 0{,}02$$
$$\gamma = 1{,}25 \pm 0{,}03$$
$$\tau = 3{,}17 \pm 0{,}07\ (10^{-5})\ s$$
$$\varepsilon_\infty = 0{,}73 \pm 0{,}02$$

$$\chi^2_{red} = 138{,}59$$

Fitting Havriliak-Negami Equation with Conductivity term: Imaginary Part



$$\varepsilon'' = \Delta\varepsilon * r(\omega) * sin\left(\gamma\varphi(\omega)\right) + \frac{\sigma'}{\omega^s}$$

$$r(\omega) = \left[1 + 2(\omega\tau_{HN})^{\beta}\cos\left(\frac{\beta\pi}{2}\right) + (\omega\tau_{HN})^{2\beta}\right]^{-\gamma/2}$$

$$\varphi(\omega) = arctan\left[\frac{\sin(\beta\pi/2)}{(\omega\tau_{HN})^{-\beta}+\cos(\beta\pi/2)}\right]$$

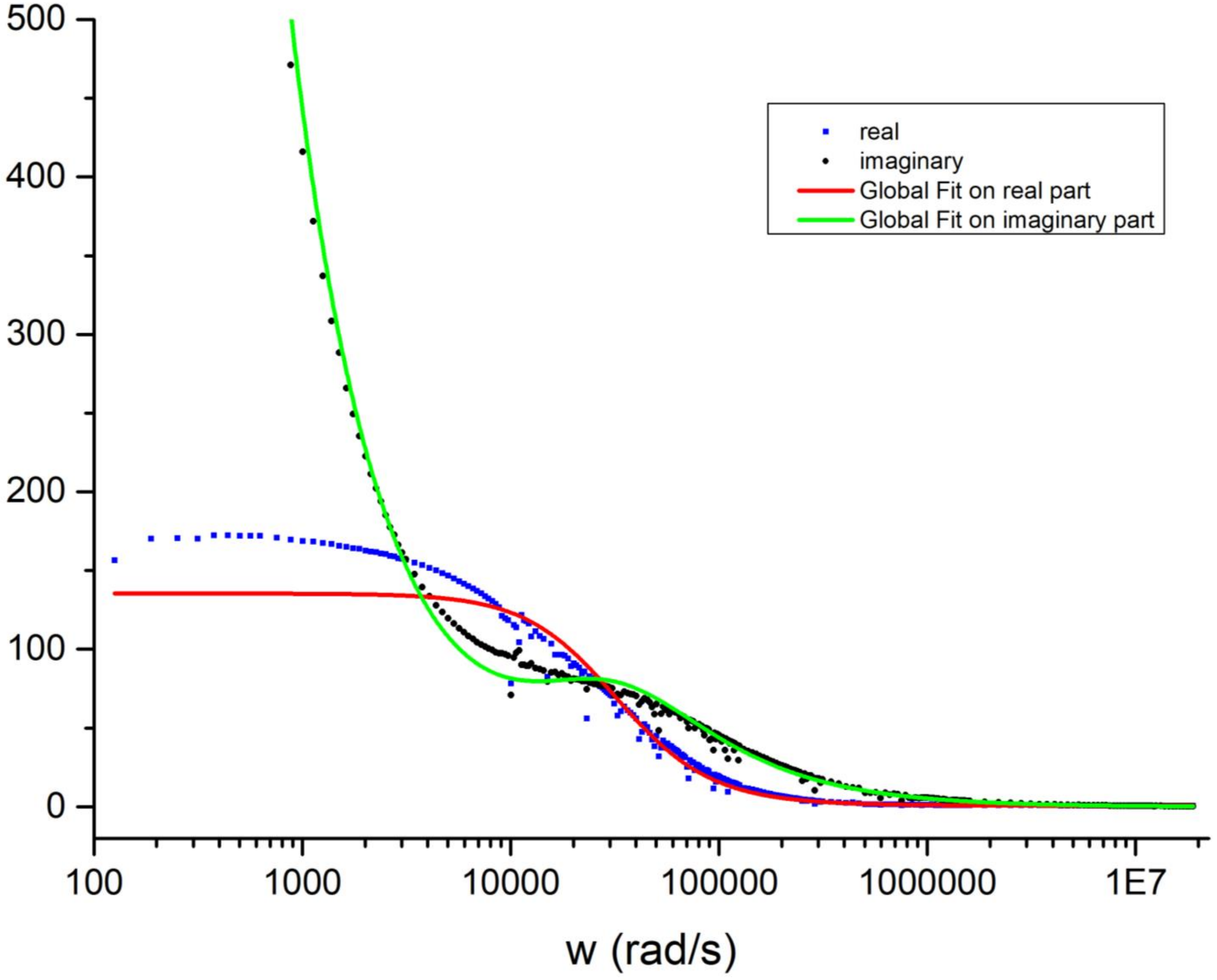
Parameters ($s = 1$):

$$\Delta\varepsilon = 152 \pm 4$$
$$\beta = 0{,}86 \pm 0{,}02$$
$$\gamma = 1{,}11 \pm 0{,}04$$

$$\tau = 3{,}46 \pm 0{,}11\ (10^{-5})\ s$$
$$\sigma' = 4{,}18 \pm 0{,}09\ (10^{5})\ \ [\Omega^{-1}m^{-1}\varepsilon_0]$$

$$\chi^2_{red} = 95{,}93$$

Global Fit: fixed *s* on conductivity term



$$\varepsilon' = \varepsilon_\infty + \Delta\varepsilon * r(\omega) * cos\big(\gamma\varphi(\omega)\big)$$

$$\varepsilon'' = \Delta\varepsilon * r(\omega) * sin\big(\gamma\varphi(\omega)\big) + \frac{\sigma}{\omega^s}$$

$$r(\omega) = \left[1 + 2(\omega\tau_{HN})^\beta \cos\left(\frac{\beta\pi}{2}\right) + (\omega\tau_{HN})^{2\beta}\right]^{-\gamma/2}$$

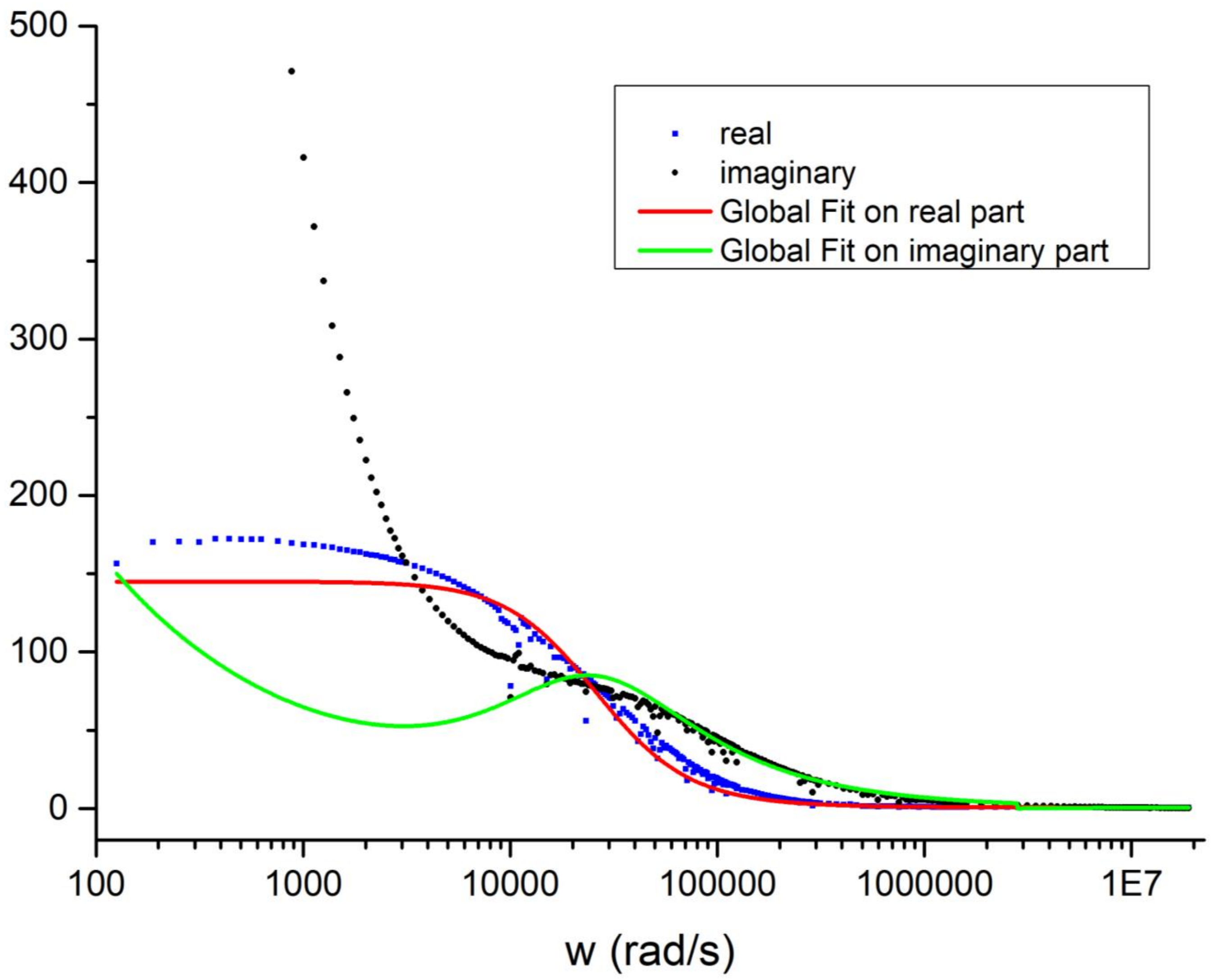
$$\varphi(\omega) = arctan\left[\frac{\sin(\beta\pi/2)}{(\omega\tau_{HN})^{-\beta} + \cos(\beta\pi/2)}\right]$$

Parameters ($s = 1$):

$\Delta\varepsilon = 134 \pm 2$
$\beta = 0{,}996 \pm 0{,}001$
$\gamma = 0{,}955 \pm 0{,}003$
$\tau = 3{,}21 \pm 0{,}06\ (10^{-5})\ s$
$\varepsilon_\infty = 0{,}65 \pm 0{,}02$
$\sigma' = 4{,}40\ \pm 0{,}09\ (10^5)[\Omega^{-1}m^{-1}\varepsilon_0]$

$$\chi^2_{red} = 162{,}42$$

Global Fit: varying *s* on conductivity term

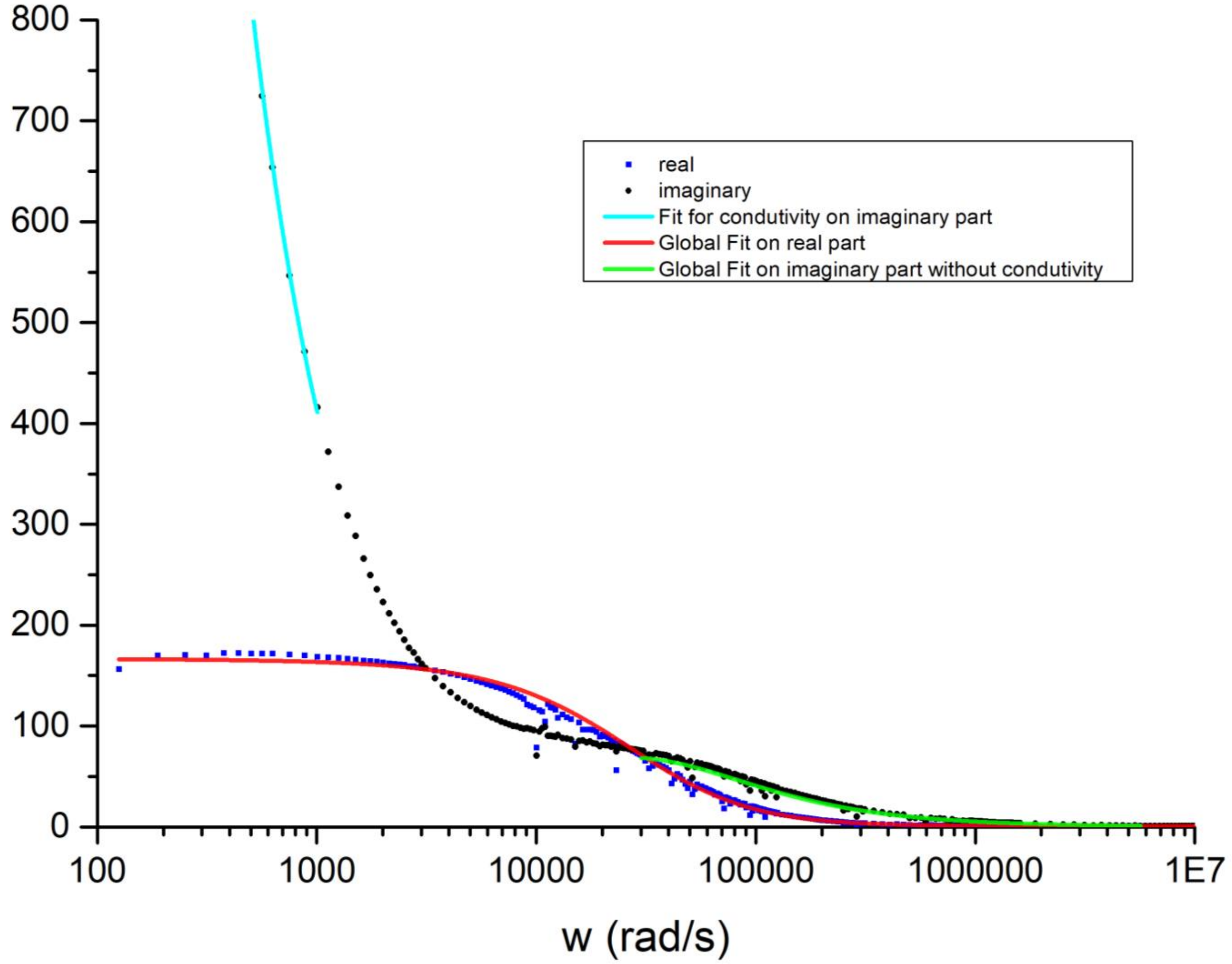


Parameters:

$$\Delta\varepsilon = 144 \pm 4$$
$$\beta = 1{,}01 \pm 0{,}01$$
$$\gamma = 0{,}940 \pm 0{,}006$$
$$\tau = 4{,}05 \pm 0{,}01\ (10^{-5})\ s$$
$$\varepsilon_{\infty} = 0{,}67 \pm 0{,}04$$
$$\sigma' = 1{,}28 \pm 0{,}42\ (10^{3})\ \ [\Omega^{-1} m^{-1} \varepsilon_0]$$
$$s = 0{,}44 \pm 0{,}02$$

$$\chi^2_{red} = 938{,}87$$

Global Fit: Separating H-N equation to Conductivity term on imaginary part



Parameters:

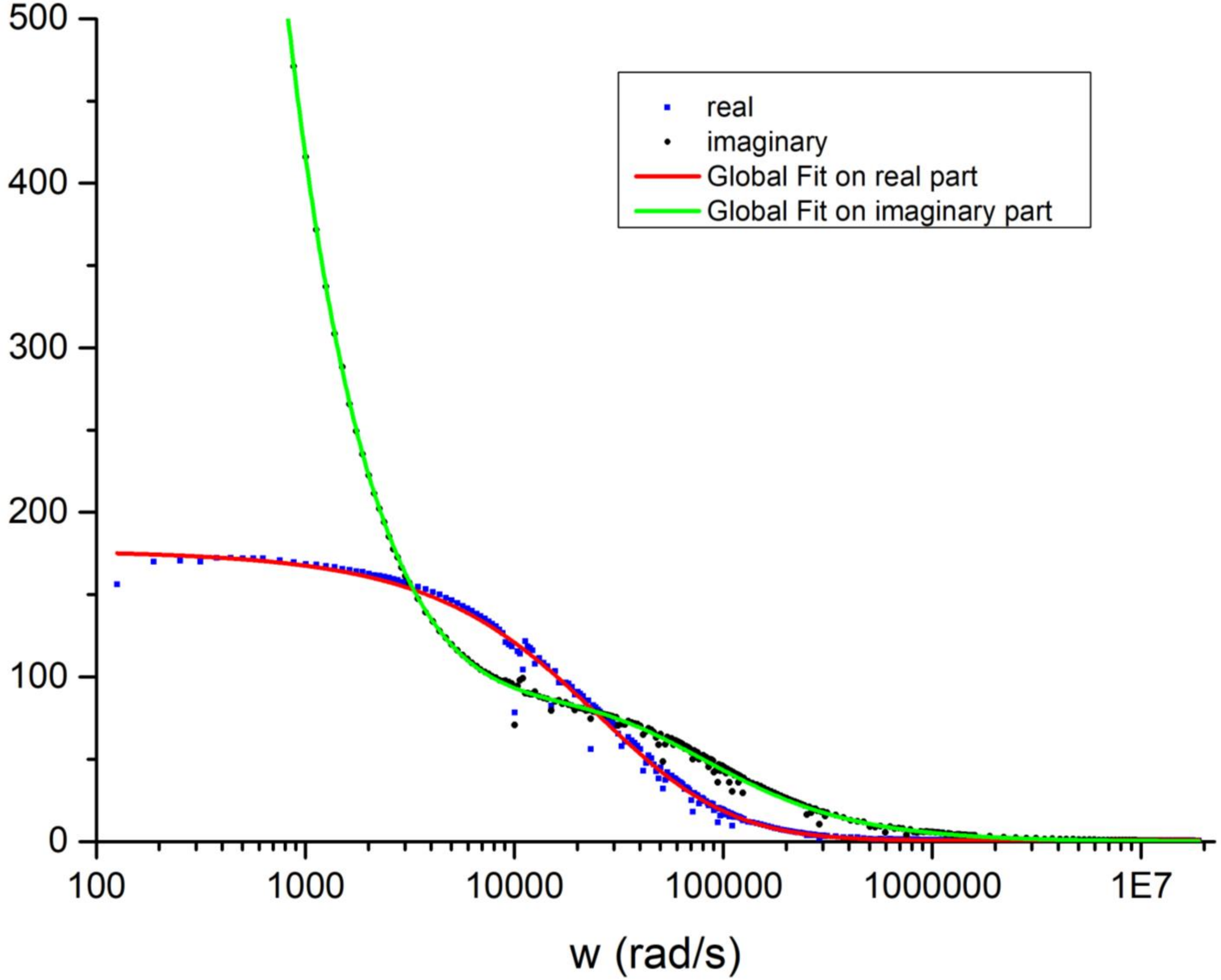
$$\Delta\varepsilon = 166 \pm 4$$
$$\beta = 0{,}84 \pm 0{,}02$$
$$\gamma = 1{,}18 \pm 0{,}03$$
$$\tau = 3{,}21 \pm 0{,}07\ (10^{-5})s$$
$$\varepsilon_\infty = 0{,}71 \pm 0{,}02$$

$$\chi^2_{red} = 152{,}06$$

$$\sigma' = 3{,}96 \pm 0{,}07\ (10^5)\ [\Omega^{-1}m^{-1}\varepsilon_0]$$
$$s = 0{,}994 \pm 0{,}003$$

$$\chi^2_{red} = 0{,}32$$

Global fit: with initial guess

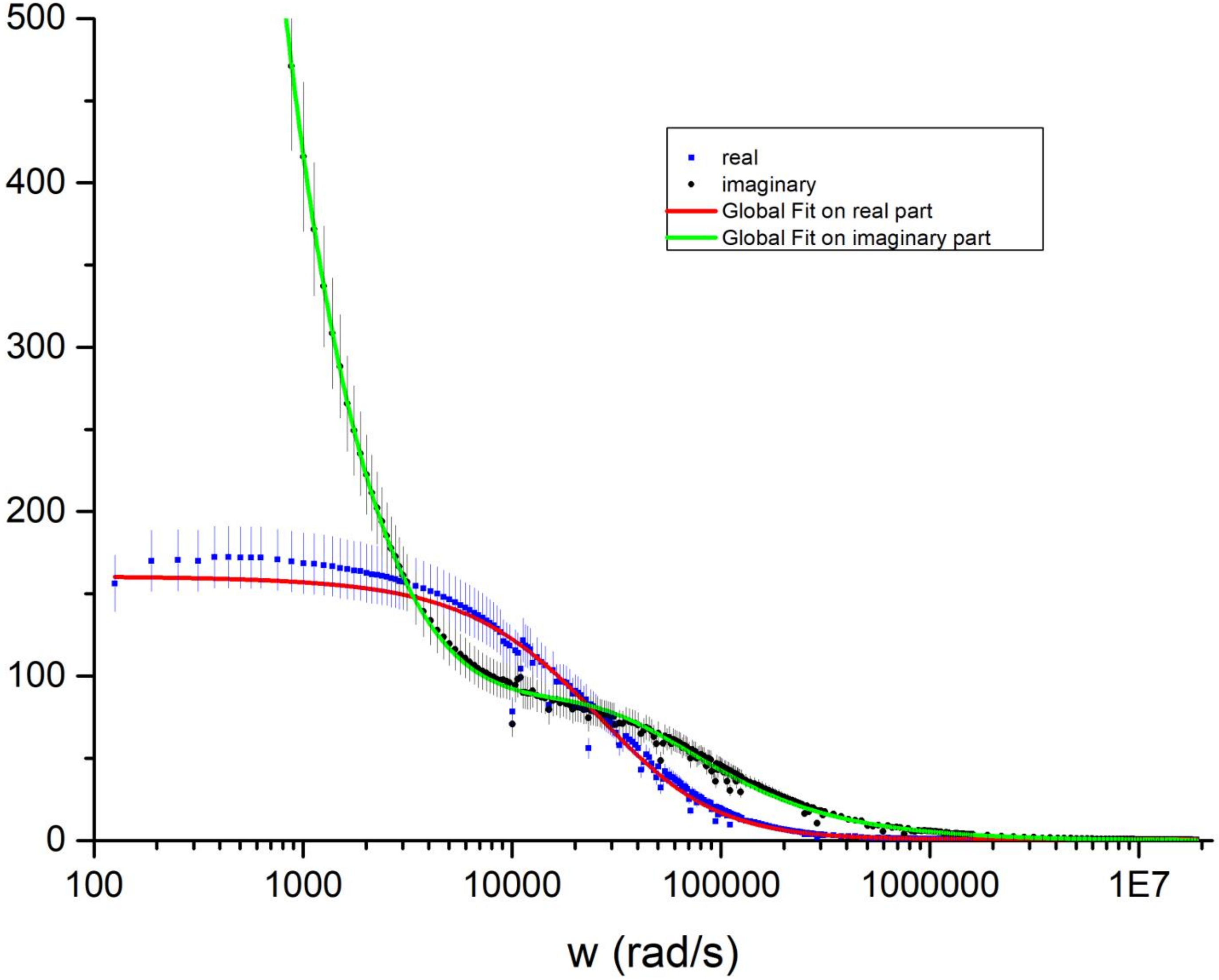


Parameters:

$$\Delta\varepsilon = 176 \pm 1$$
$$\beta = 0{,}70 \pm 0{,}010$$
$$\gamma = 1{,}56 \pm 0{,}07$$
$$\tau = 2{,}37 \pm 0{,}17\ (10^{-5})s$$
$$\varepsilon_\infty = 0{,}93 \pm 0{,}39$$
$$\sigma' = 4{,}34 \pm 0{,}03\ (10^{5})\ \ [\Omega^{-1}m^{-1}\varepsilon_0]$$
$$s = 1{,}0 \pm 0{,}01$$

$$\chi^2_{red} = 11{,}68$$

Global Fit: with errors



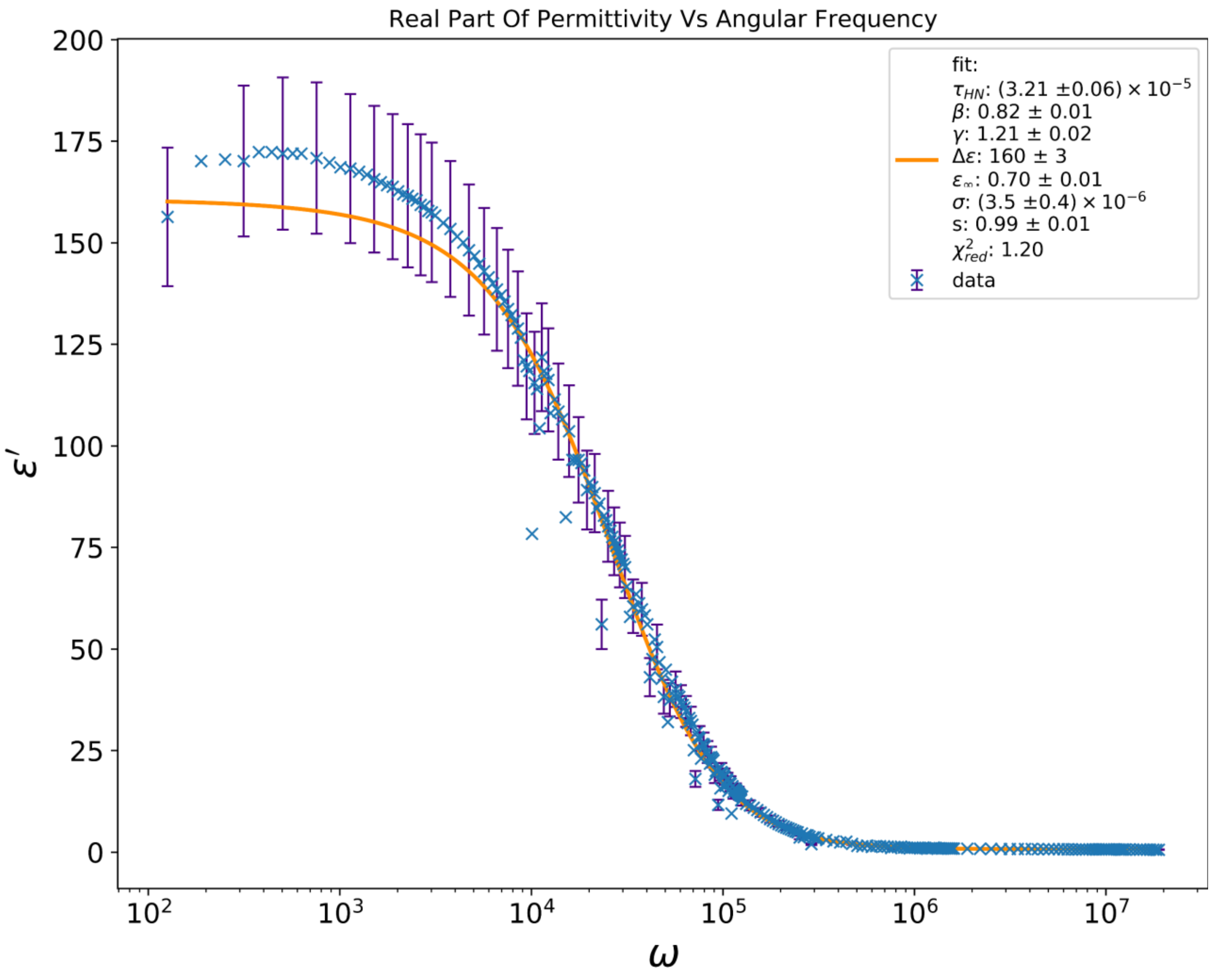
Parameters:

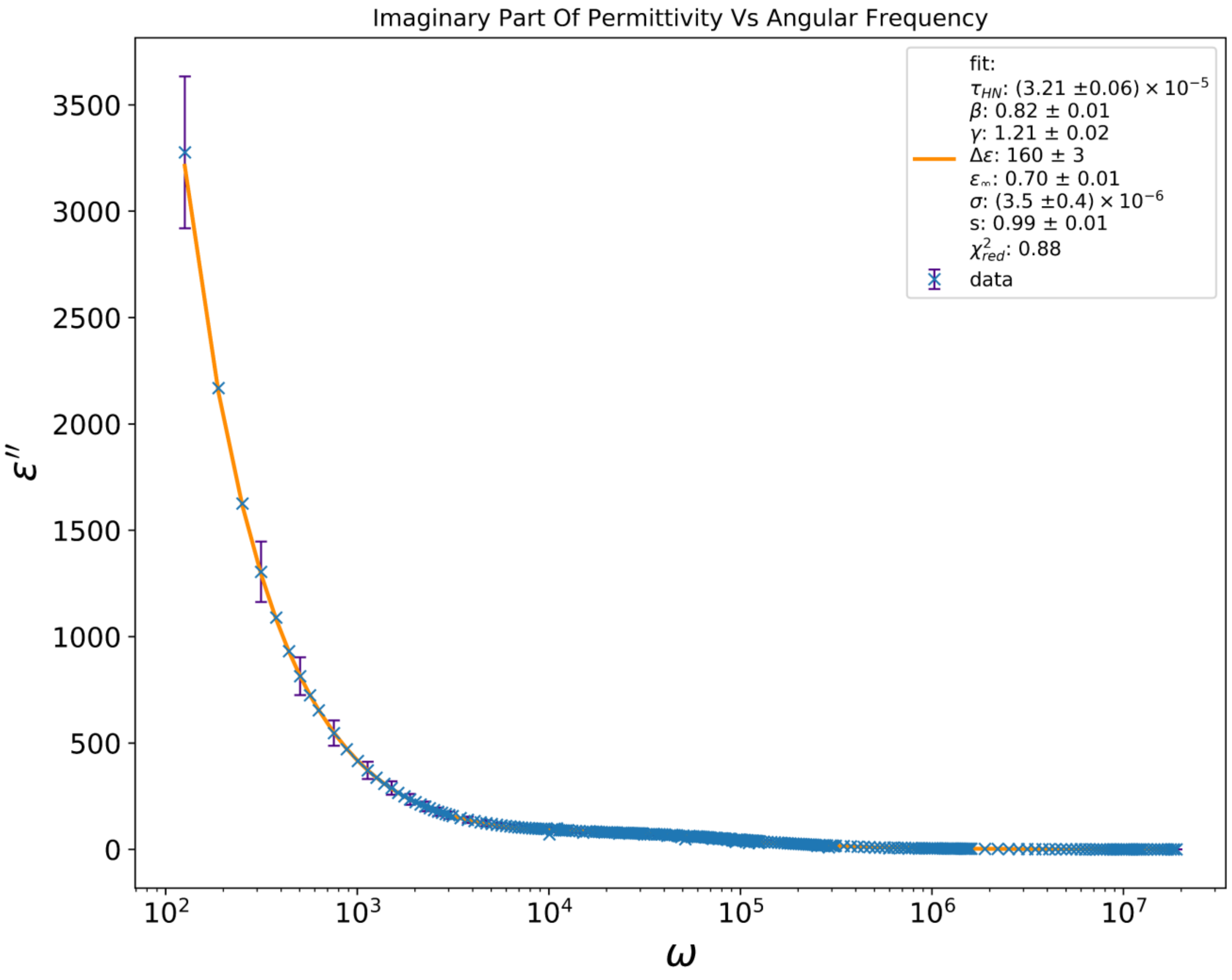
$$\Delta\varepsilon = 160 \pm 3$$
$$\beta = 0{,}82 \pm 0{,}01$$
$$\gamma = 1{,}21 \pm 0{,}02$$
$$\tau = 3{,}21 \pm 0{,}06\ (10^{-5})s$$
$$\varepsilon_\infty = 0{,}70 \pm 0{,}01$$
$$\sigma' = 3{,}94 \pm 0{,}42\ (10^{5})\ [\Omega^{-1}m^{-1}\varepsilon_0]$$
$$s = 0{,}99 \pm 0{,}02$$

$$\chi^2_{red} = 1{,}031$$

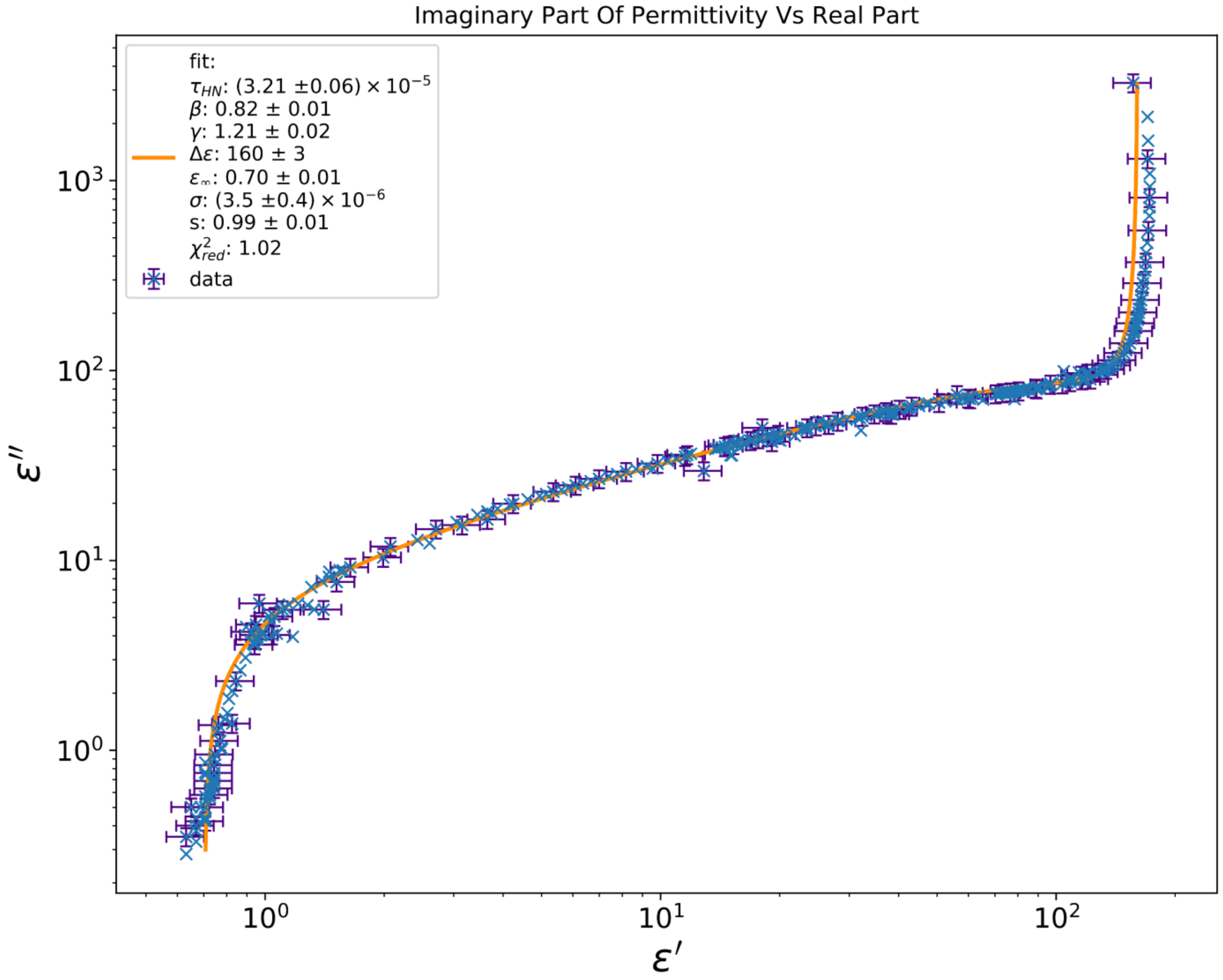
$$\sigma = 3{,}49 \pm 0{,}37\ (10^{-6})\ [\Omega^{-1}m^{-1}]$$

Scipy (curve_fit)





Scipy



$Goodness\ of\ fit$: $\chi^2_{red} = 1.02$

Results:

τ_{HN} : $(3.21 \pm 0.06) \times 10^{-5}$

β : 0.82 ± 0.01

γ : 1.21 ± 0.02

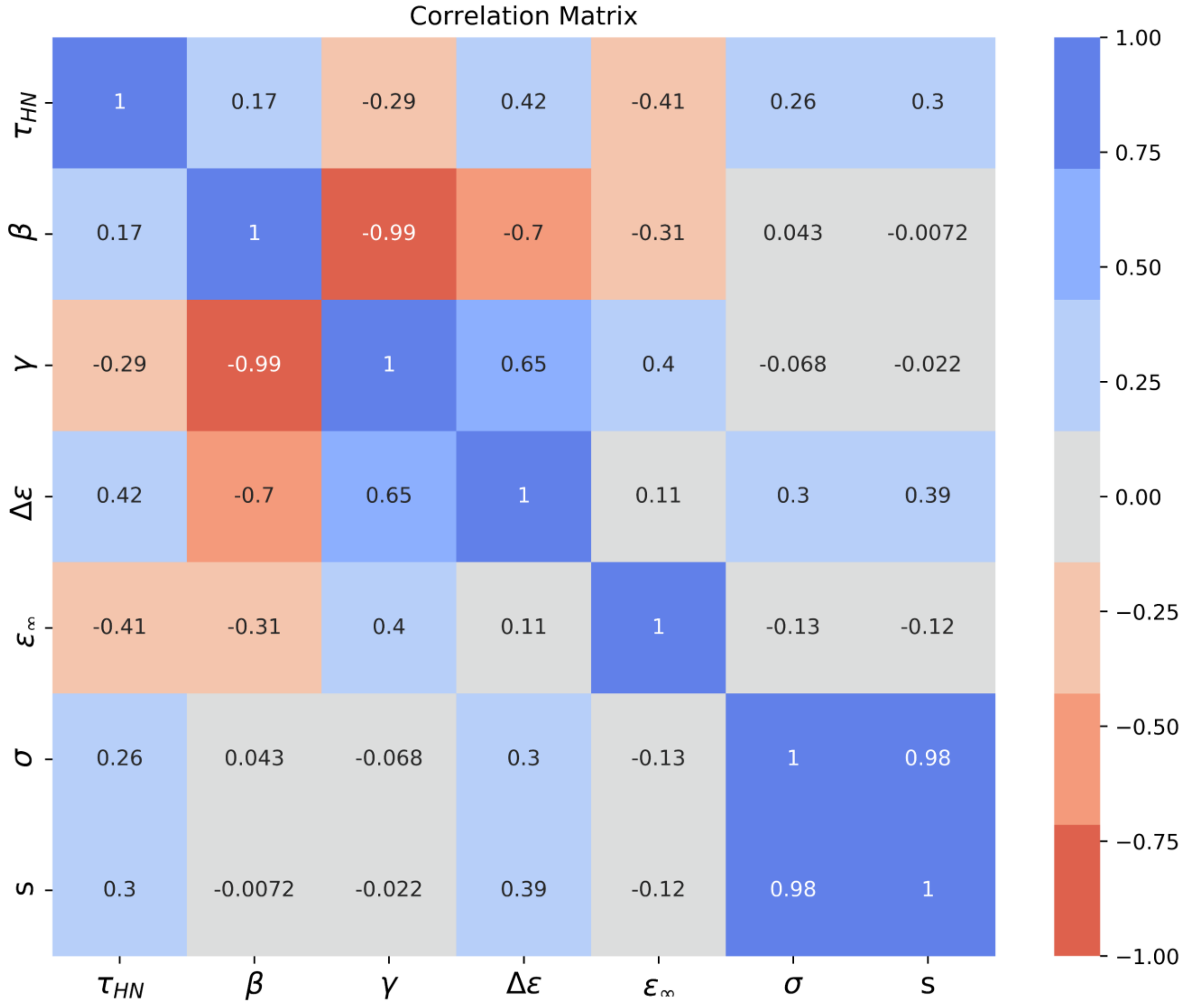
$\Delta\epsilon$: 160 ± 3

ϵ_∞ : 0.70 ± 0.01

σ : $(3.5 \pm 0.4) \times 10^{-6}$

s : 0.99 ± 0.01

Correlation matrix



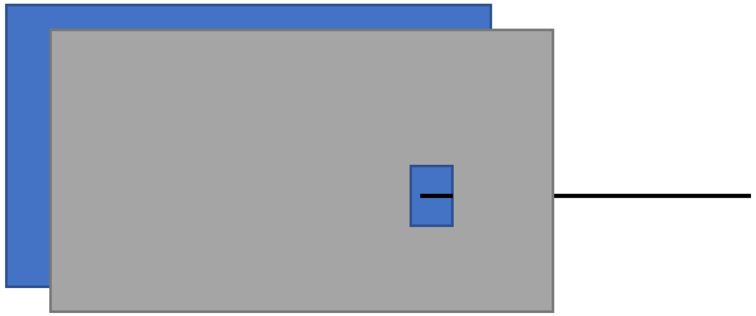
- β *and* γ are strongly anti-correlated. They obey the constraint relation: $0 < \beta\gamma \leq 1$

- DC conductivity is strongly correlated with s. Both parameters appear only in the additive term $\frac{\sigma_{DC}}{\epsilon_0 \omega^s}$

Improving Measurements:

- Measuring thickness and area with a Scanning Electron Microscope (SEM).
- Changing the way the contact is made to improve the measurement of the area and smooth the surface:
  - Changing method: laser ablation deposition or sputtering

  - Use of a mask to limit the area and fix the contact to the material



Conclusion:

- We were able to obtain a fit that describes our data;
  - Havriliak-Negami equation with the conductivity term on the imaginary part can describe our data.

- In low frequencies, because our errors are so big, there is a little deviation between the data plot and the fit.

- To get better results the measurements should be improved, and the contact should be done with a new method, for example, laser or sputtering deposition.

OriginLab: Parameter errors and χ^2_{red}

Reduced χ^2:

$$\chi^2_{red} = \frac{\chi^2}{N-p} \qquad \chi^2 = \sum_{i=1}^{N} \frac{(Y_i - f(x_i))^2}{\sigma_i^2}$$

Calculating Parameter errors:

- Derivative matrix F: $F_{ij} = \frac{\partial f(x,\theta)}{\sigma_i \partial \theta_j}$
- *Variance-Covariance Matrix:* $C = (F'F)^{-1}\chi^2_{red}$
- Standard error: $s_{\theta_i} = \sqrt{c_{ii}}$