Universidade do Minho
Escola de Ciências

Dielectric Properties

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Outline

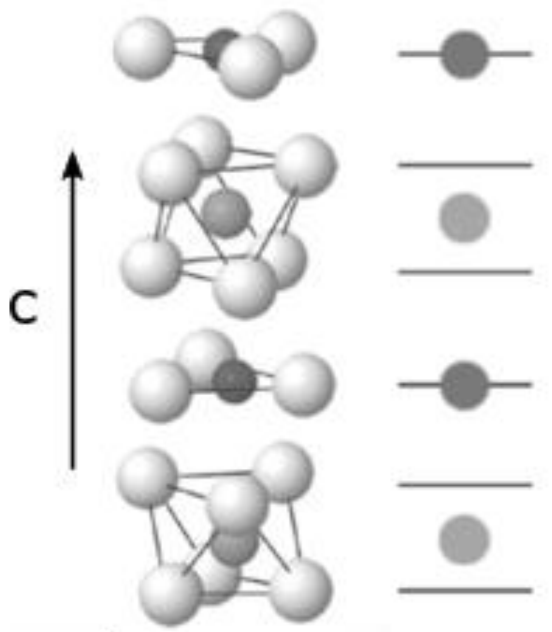
Main Objective: Fit a model to experimental data and assess its validity.

1. Brief introduction to key concepts;
2. Fitting the model in study to portions of the experimental data;
3. Performing the fit across the whole domain for both data sets individually;
4. Introducing new elements in the model;
5. Repeating the individual fits and computing a global fit to both data sets simultaneously;
6. Concluding remarks.

Introduction…

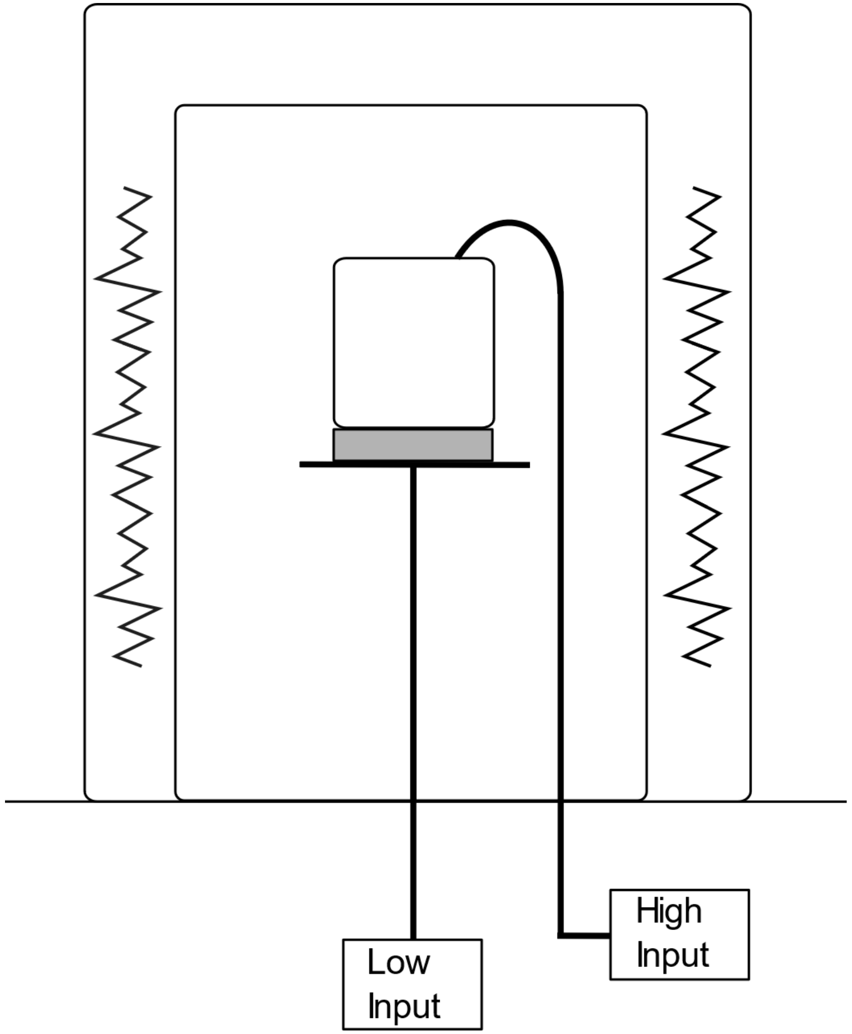
Physics Case: Lithium Niobate

- It’s a displacement ferroelectric with very usefull features;
- It shows great promise for devices such as:
  - Wave-guide optical devices;
  - SAW devices for chemical detectors;
  - FRAM and RRAM units;
  - …



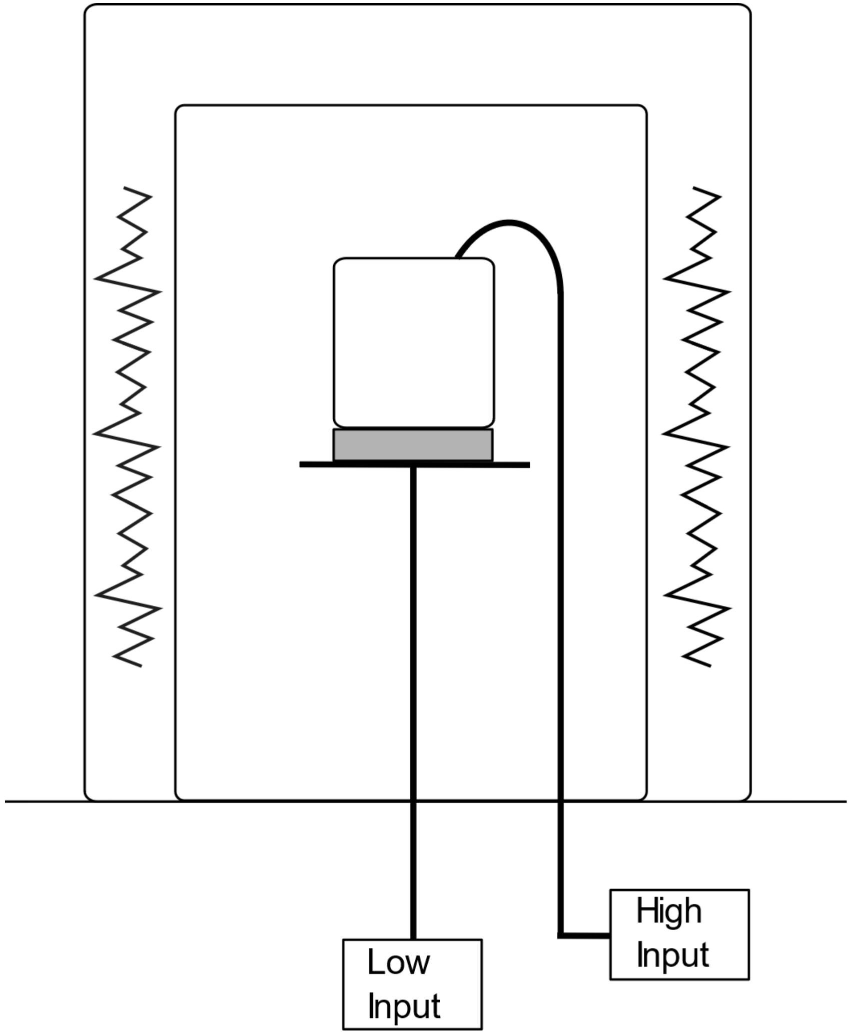
Physics Case: Experimental Method

- A **flat-faced capacitor** is made using the dielectic sample;
- Capacitive response is related to dipoles reorientation mobility → **huge amount of information**:
  a) structure of matter;
  b) ion displacement;
  c) valence cloud distortion;
  d) …



Physics Case: Experimental Method

- Different responses can be studied with a **wide range of frequencies**;
- Dipolar polarization is studied up to a range of about 10^{10} Hz;
- Different preparation conditions may lead to different responses → BDS can act as a quality control;



Initial Steps

1. Collect the data
2. Measure the area A
3. $$\epsilon' = \frac{Cd}{A}$$
4. $$\tan\delta = \frac{Z''}{Z'}$$
5. $$\tan\delta = \frac{\epsilon''}{\epsilon'}$$
6. Plot $\epsilon'(\omega)$ and $\epsilon''(\omega)$

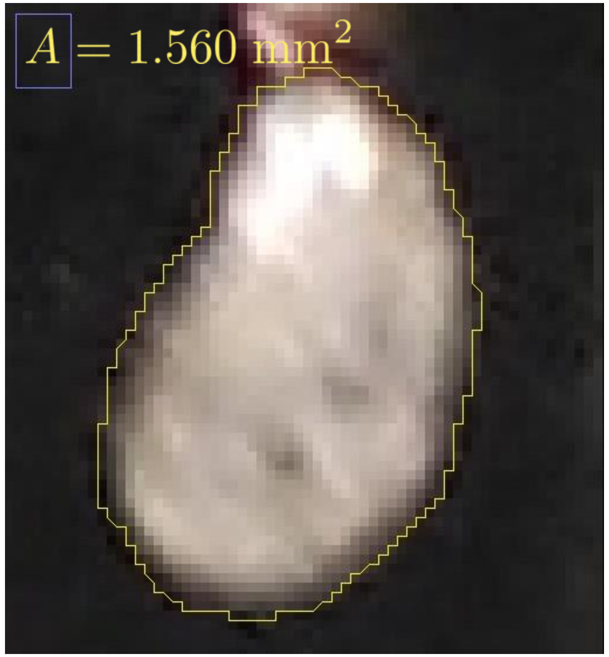
$$\epsilon = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (i\omega\tau)^\beta)^\gamma}$$

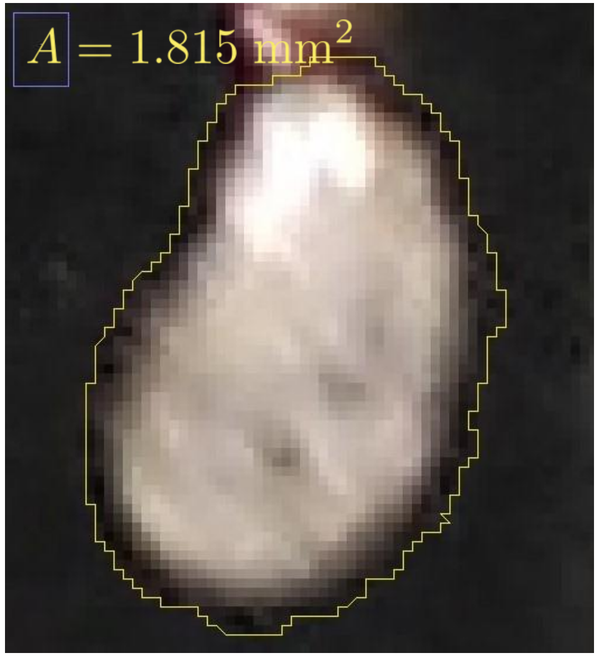
$$\epsilon'' = \frac{\sigma_{\mathrm{DC}}}{\epsilon_0 \omega^s}$$

Error Sources

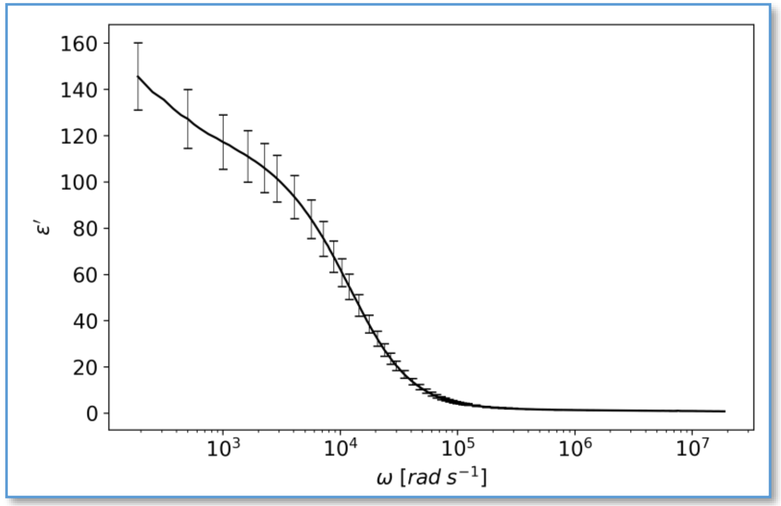
From the **experimental** procedure: 1%

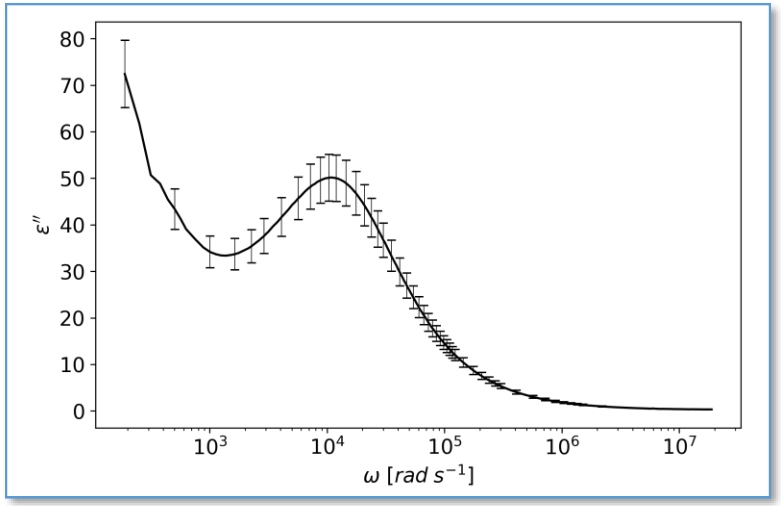
Considering the error associated with the **area measurement**, the final error is about 10%.



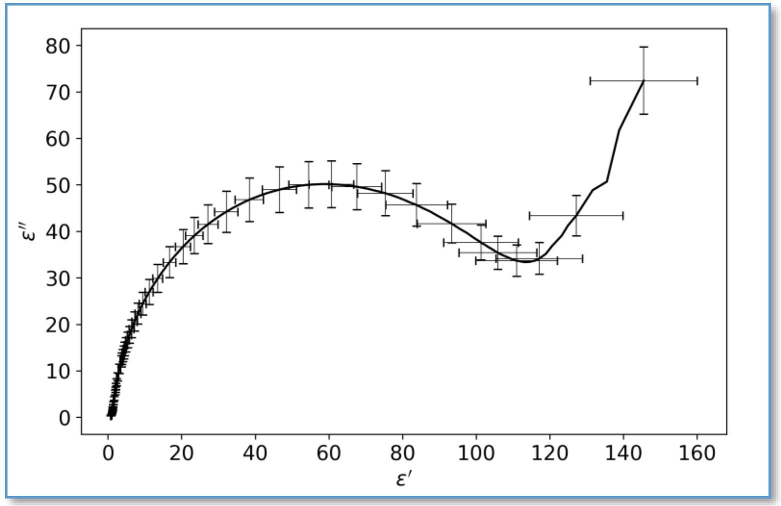


The Data





Cole - Cole



$\epsilon'(\omega)$

$\epsilon''(\omega)$

Statistical Analysis

To test the validaty of a theoretical model, comparing it with experimental data is crutial.

Fitting models to experimental data is a key part of physics.

How can we **measure the goodness of a fit**?

Goodness of Fit

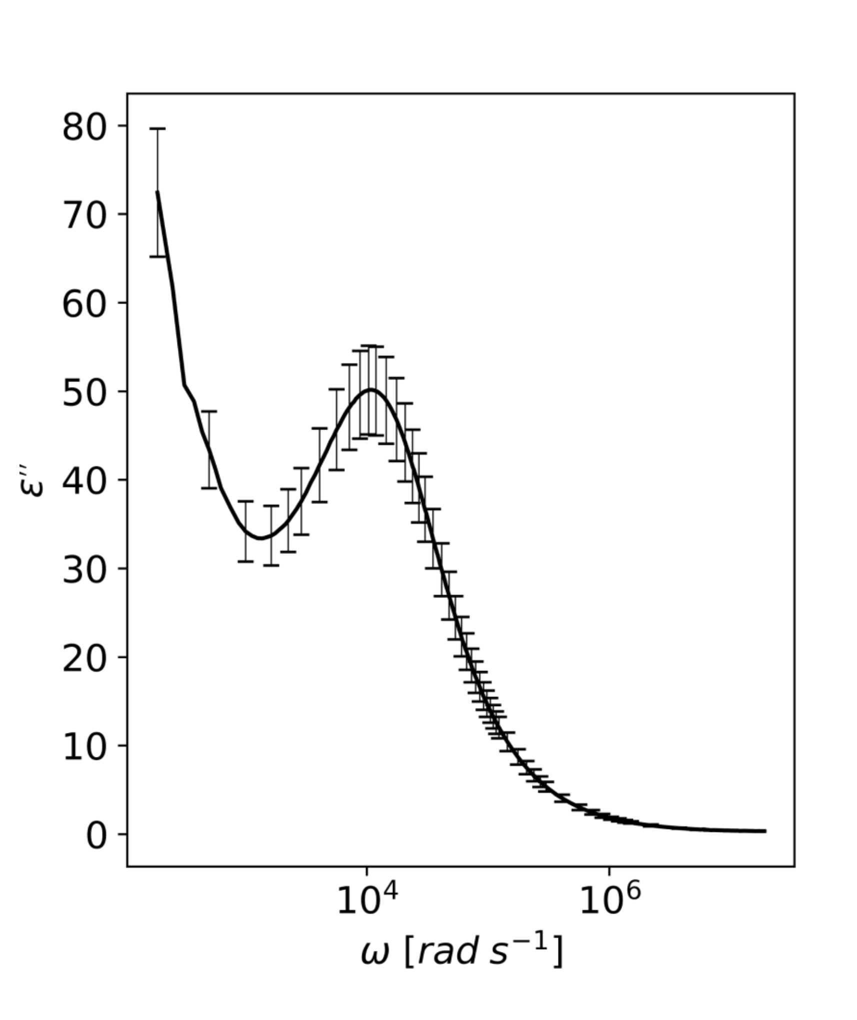
$$\chi^2 = \sum_n (E_n - O_n)^2/\sigma_n^2 \qquad (\chi^2 \sim \text{N. of bins})$$

$$\bar{\chi}^2 = \chi^2/\text{DoF} \qquad (\bar{\chi}^2 \sim 1)$$

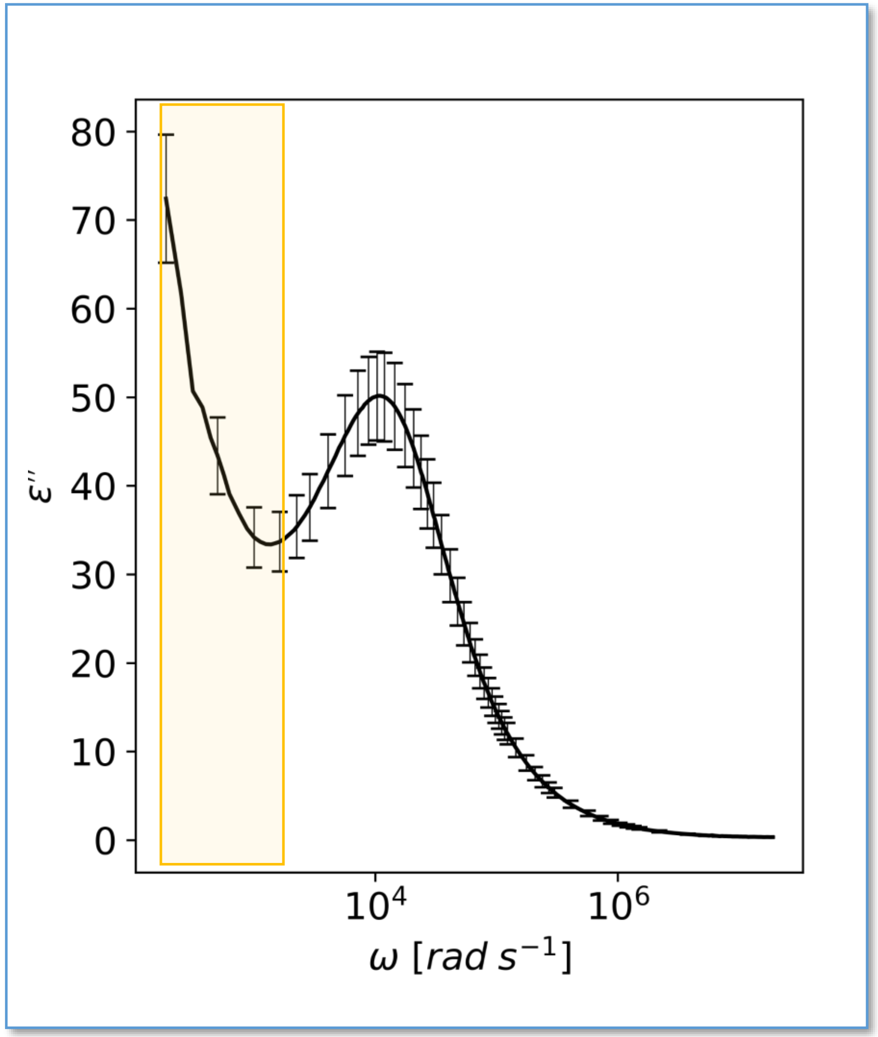
$$p-\text{value} \rightarrow \begin{cases} p.v. > 0.05 & ✓ \\ p.v. < 0.05 & ✗ \end{cases}$$

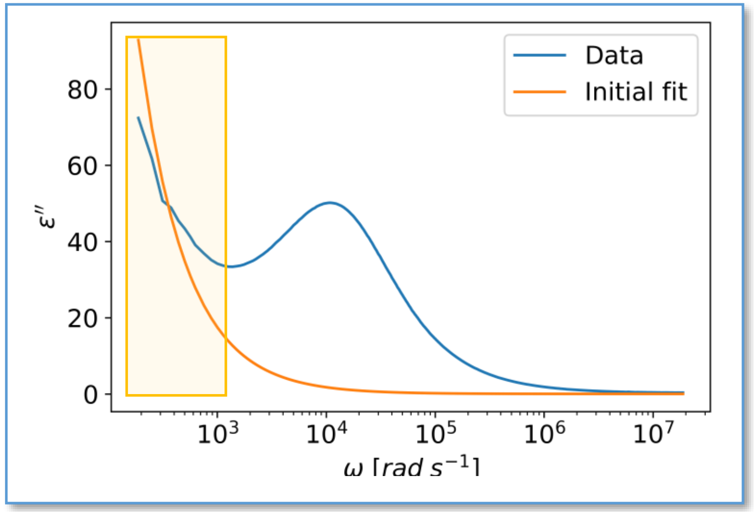
Fitting…

The Data – Imaginary Part



Fitting Portions – Imaginary Part

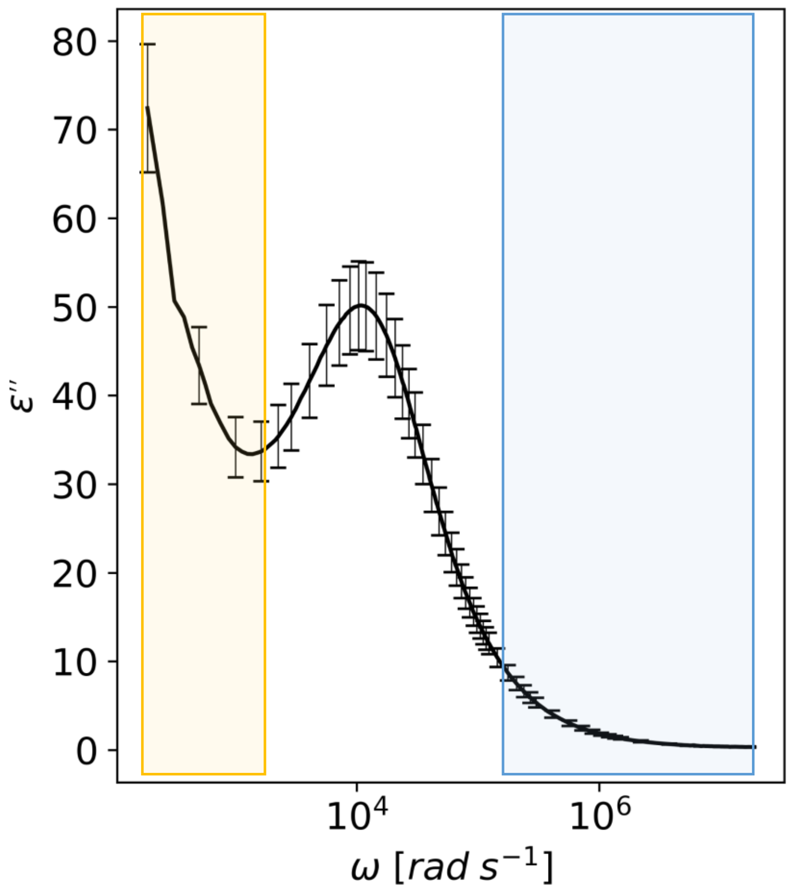


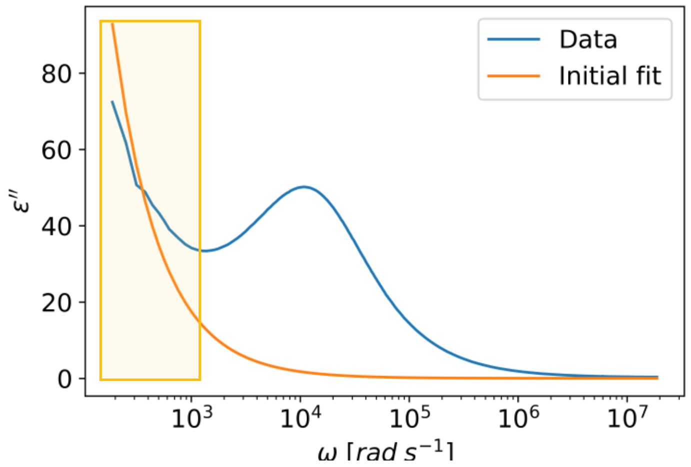


$$\epsilon'' = \frac{\sigma_{DC}}{\epsilon_0 \omega}$$

$$\sigma_{DC} = 1.5 \cdot 10^{-7}\ 1/(\Omega\mathrm{m})$$

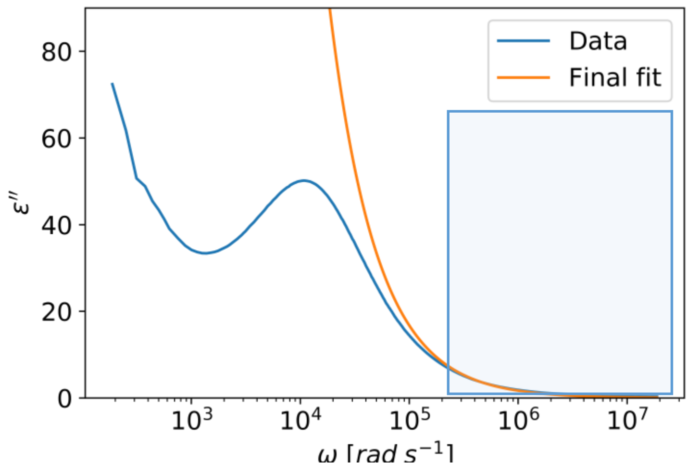
Fitting Portions – Imaginary Part





$$\epsilon'' = \frac{\sigma_{\mathrm{DC}}}{\epsilon_0 \omega}$$

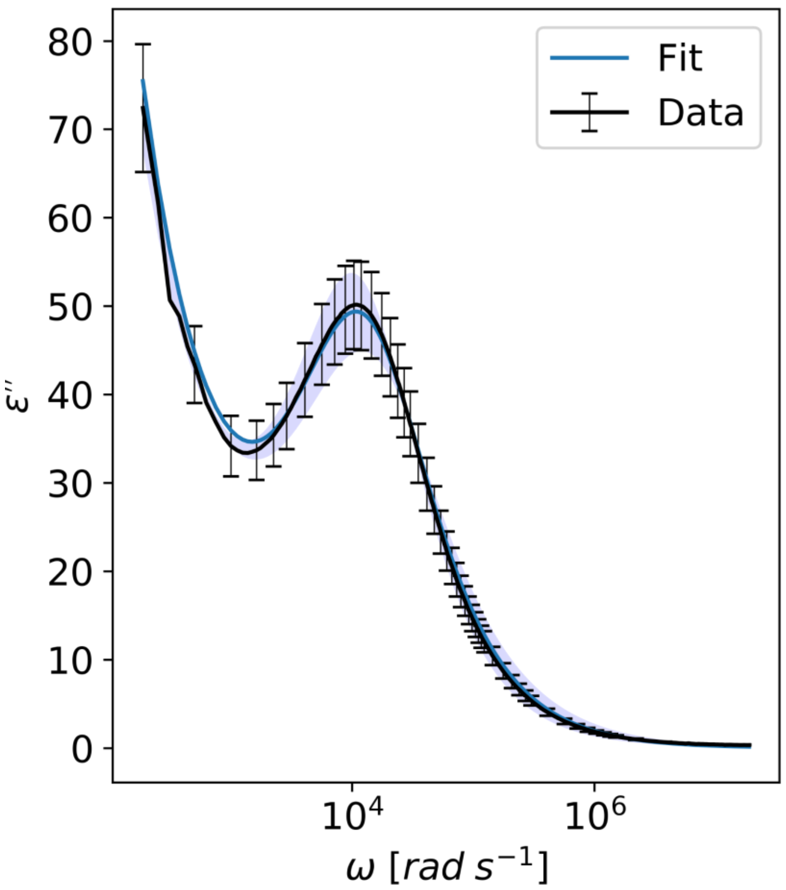
$$\sigma_{\mathrm{DC}} = 1.5 \cdot 10^{-7} \; 1/(\Omega \mathrm{m})$$



$$\epsilon'' = \frac{\sigma_{\mathrm{DC}}}{\epsilon_0 \omega}$$

$$\sigma_{\mathrm{DC}} = 1.5 \cdot 10^{-5} \; 1/(\Omega \mathrm{m})$$

Individual Fit – Imaginary Part

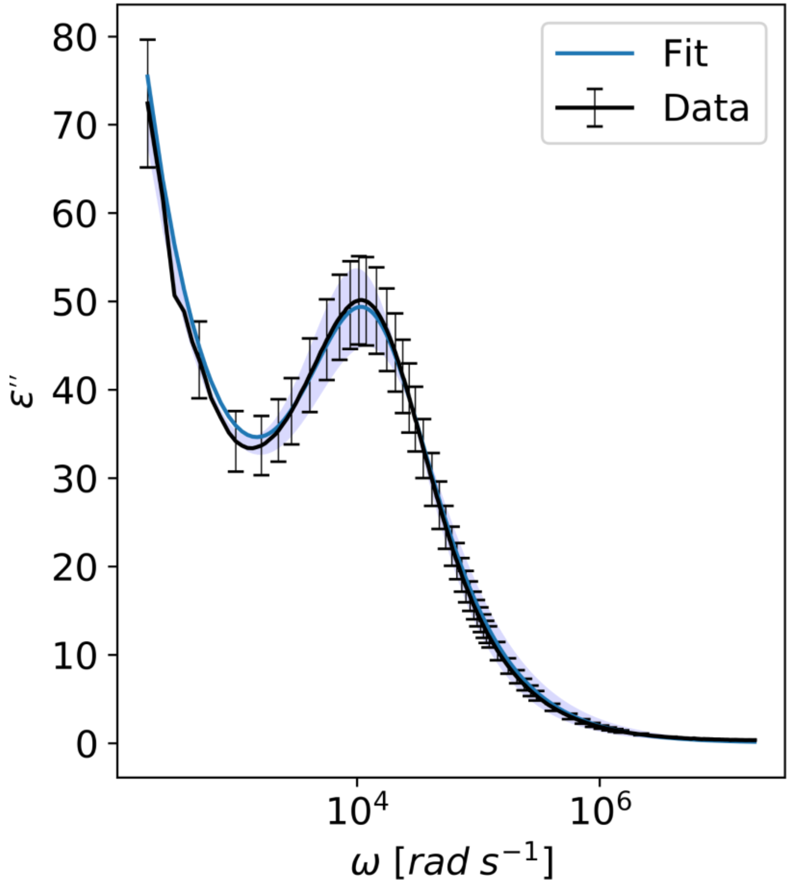


$$\epsilon'' = \mathrm{Im}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^{\beta})^{\gamma}}\right] + \frac{\sigma_{\mathrm{DC}}}{\epsilon_0 \omega^s}$$

	τ_{HN} [s]	β	γ	σ_{DC} $[\Omega^{-1}m^{-1}]$	s	$\Delta\varepsilon$
	7.4×10^{-5}	0.86	1.12	2.0×10^{-8}	0.65	106
$\pm$	0.6×10^{-5}	0.03	0.06	0.6×10^{-8}	0.05	4

- All the parameters present orders of magnitude close to the expected.
- $0 < \gamma\beta \leq 1$

Individual Fit – Imaginary Part

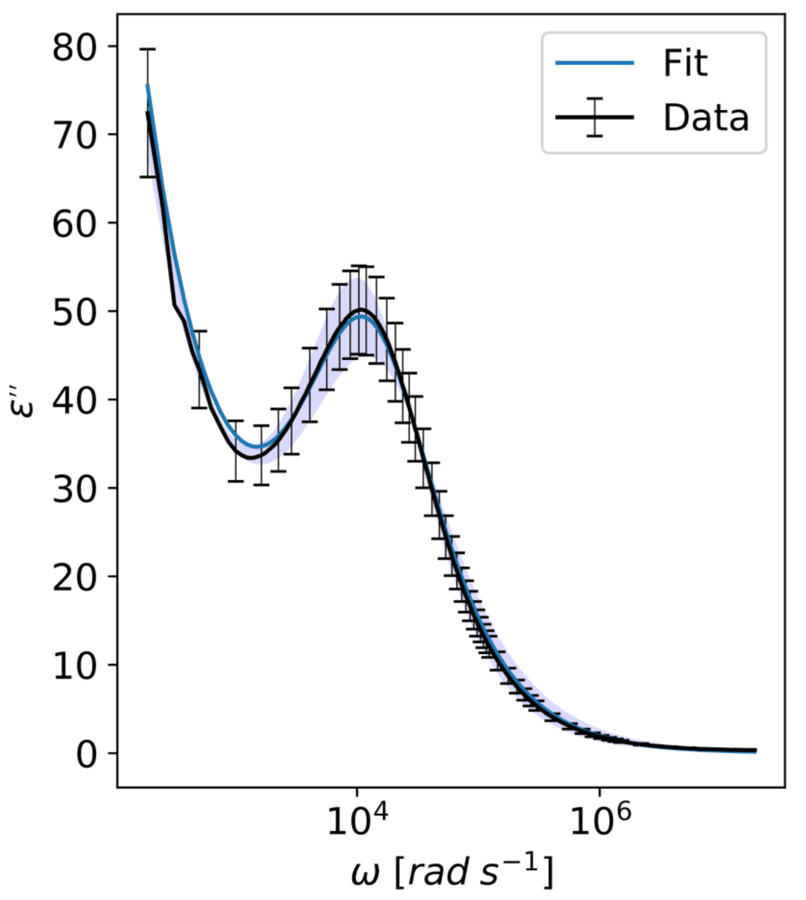


$$\epsilon'' = \mathrm{Im}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^{\beta})^{\gamma}}\right] + \frac{\sigma_{\mathrm{DC}}}{\epsilon_0\omega^s}$$

	s	$\Delta\varepsilon$	τ_{HN}	β	γ	σ/ε_0
s	0.0029	0.17	2.6e-07	0.0003	-0.0021	40
$\Delta\varepsilon$	0.17	20	1.7e-05	-0.042	-0.029	1.9e+03
τ_{HN}	2.6e-07	1.7e-05	3.6e-11	7.5e-08	-2.9e-07	0.0035
β	0.0003	-0.042	7.5e-08	0.00087	-0.0016	6.2
γ	-0.0021	-0.029	-2.9e-07	-0.0016	0.0037	-31
σ/ε_0	40	1.9e+03	0.0035	6.2	-31	4.4e-17

Colour scale: 0, 250, 500, 750, 1000, 1250, 1500, 1750

Individual Fit – Imaginary Part



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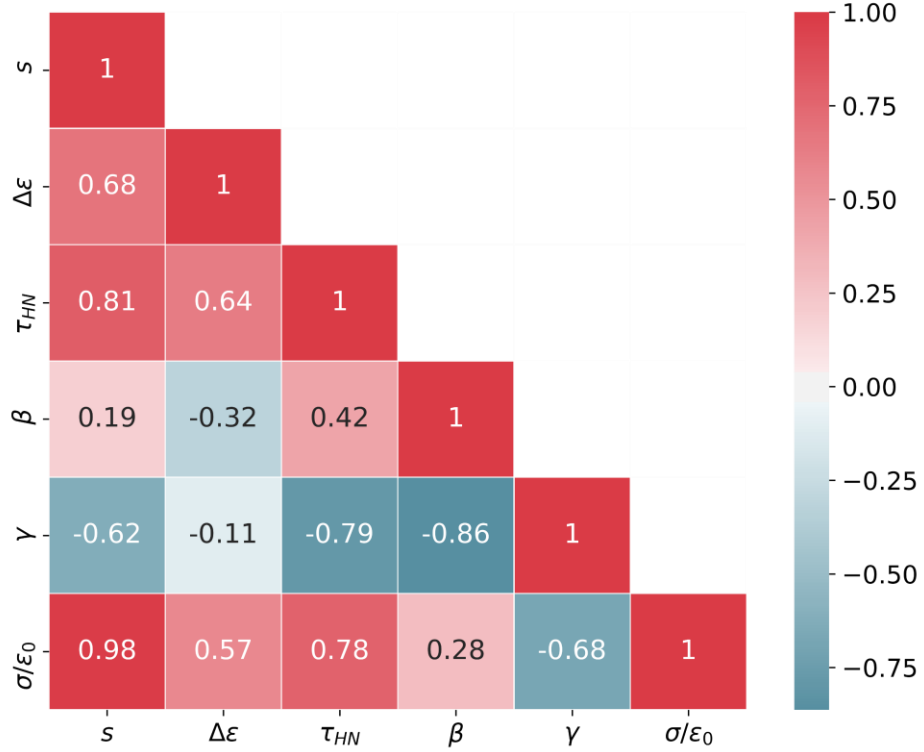
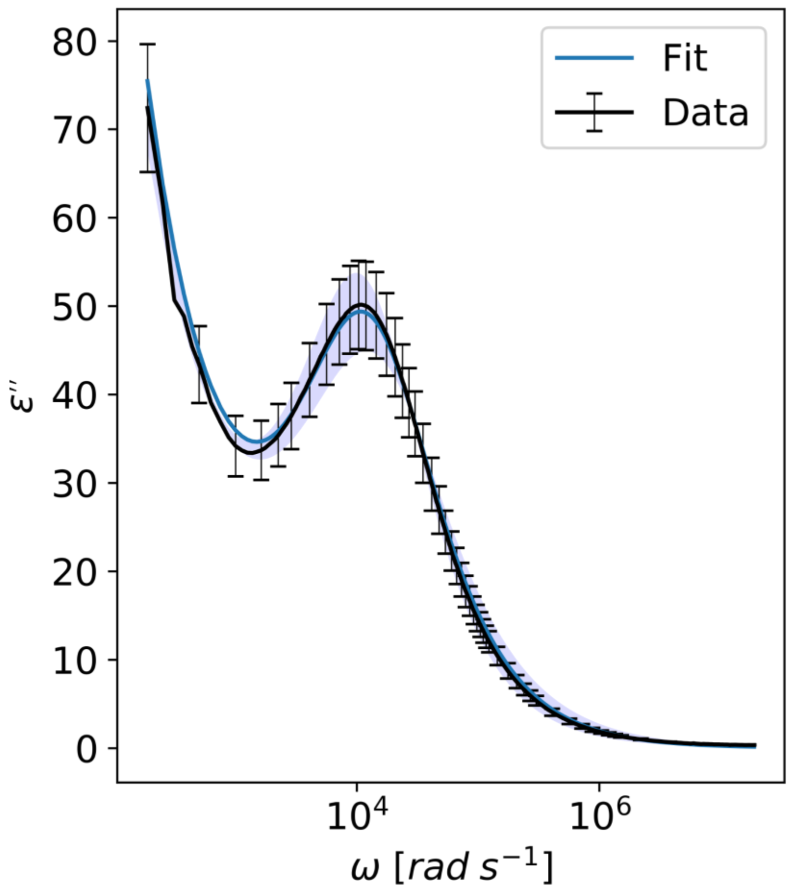


Individual Fit – Imaginary Part



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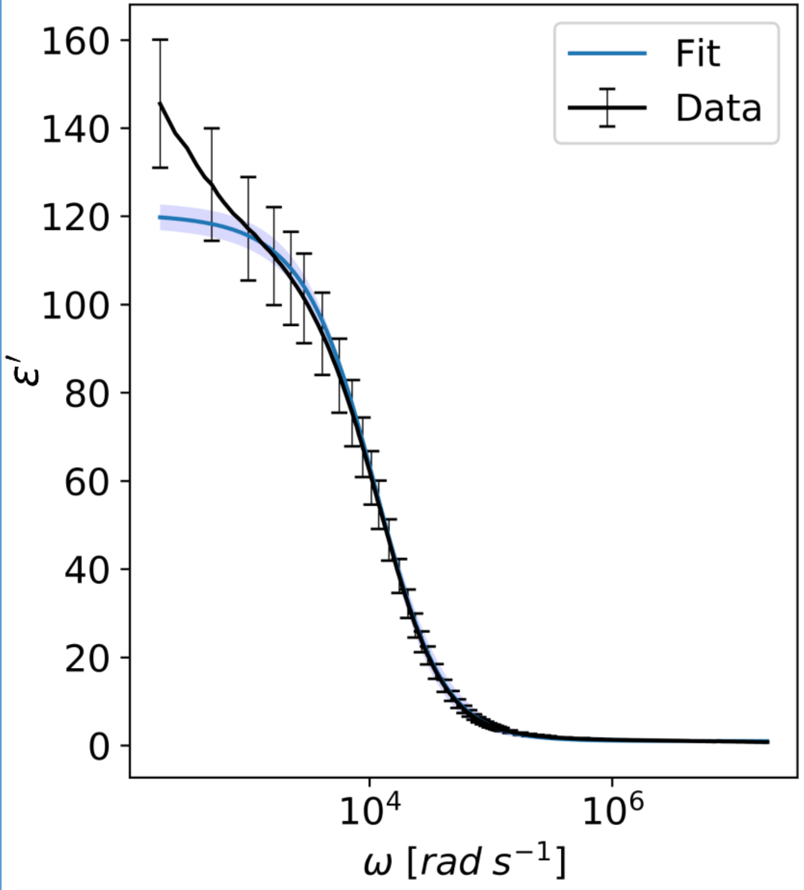
	7.4×10^{-5}	0.86	1.12	2.0×10^{-8}	0.65	106
$\pm$	0.6×10^{-5}	0.03	0.06	0.6×10^{-8}	0.05	4

Goodness of fit parameters:

$\chi^2 = 100.56$ $\overline{\chi}^2 = 0.37$ p-value $= 1.0$

Individual Fit – Real Part

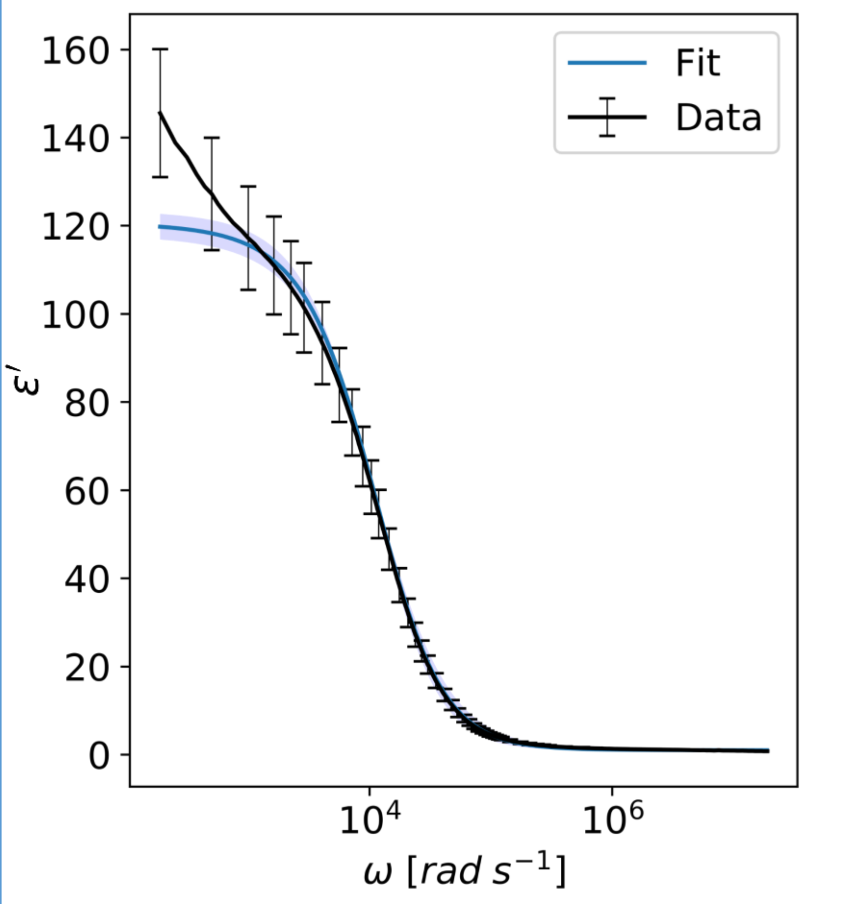


$$\epsilon' = \epsilon_\infty + \mathrm{Re}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right]$$

	τ_{HN} [s]	β	γ	ε_∞	$\Delta\varepsilon$
	8.0×10^{-5}	0.86	1.13	0.97	120
$\pm$	0.2×10^{-5}	0.02	0.03	0.01	3

- All the parameters presente orders of magnitude close to the expected.
- $0 < \gamma\beta \leq 1$
- Some diferences compared with the Im part;

Individual Fit – Real Part



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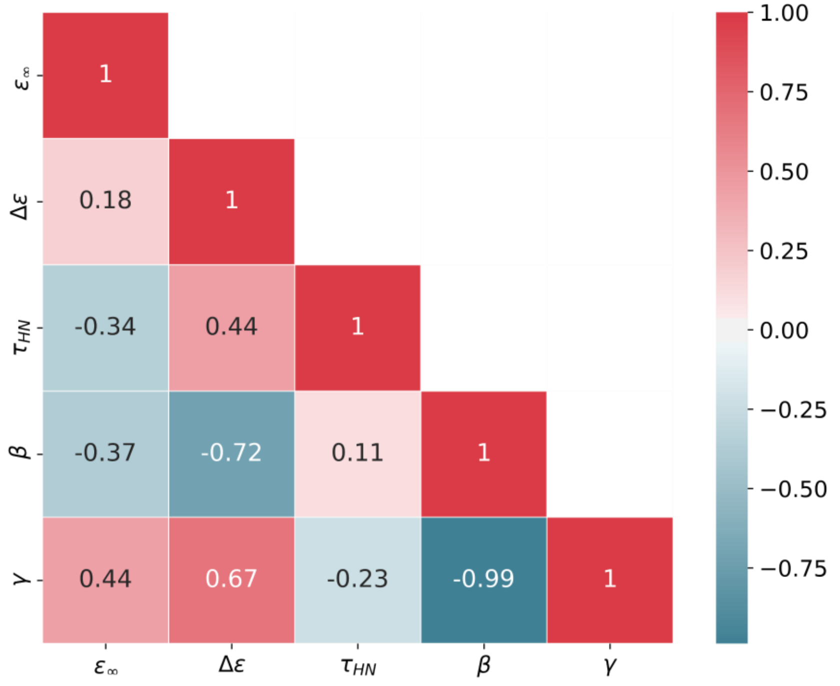
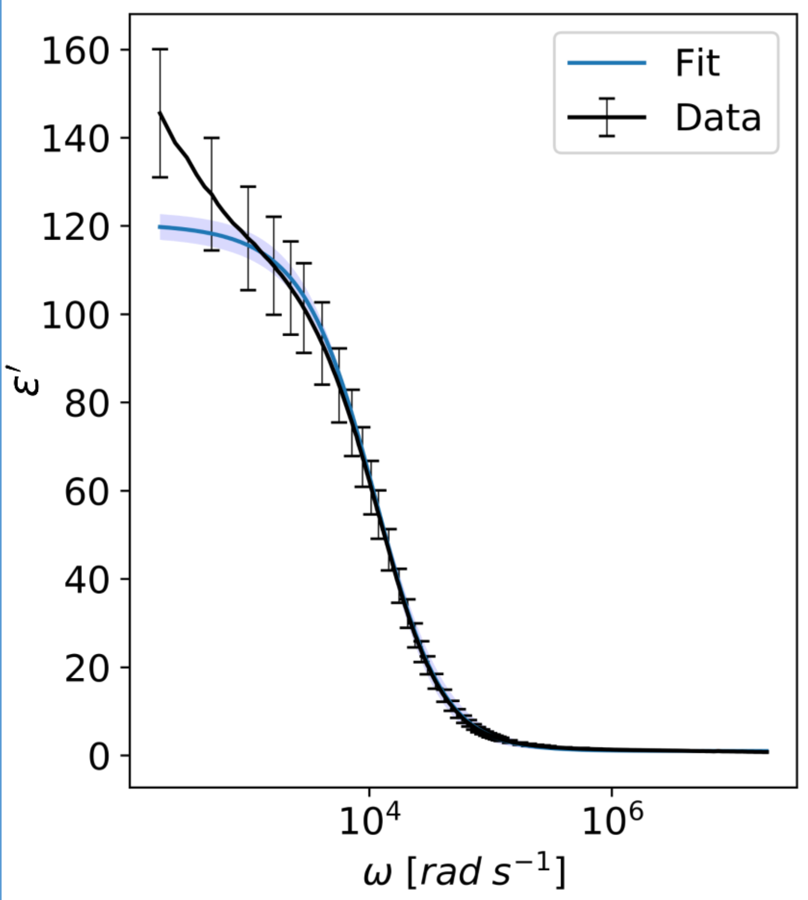


Individual Fit – Real Part



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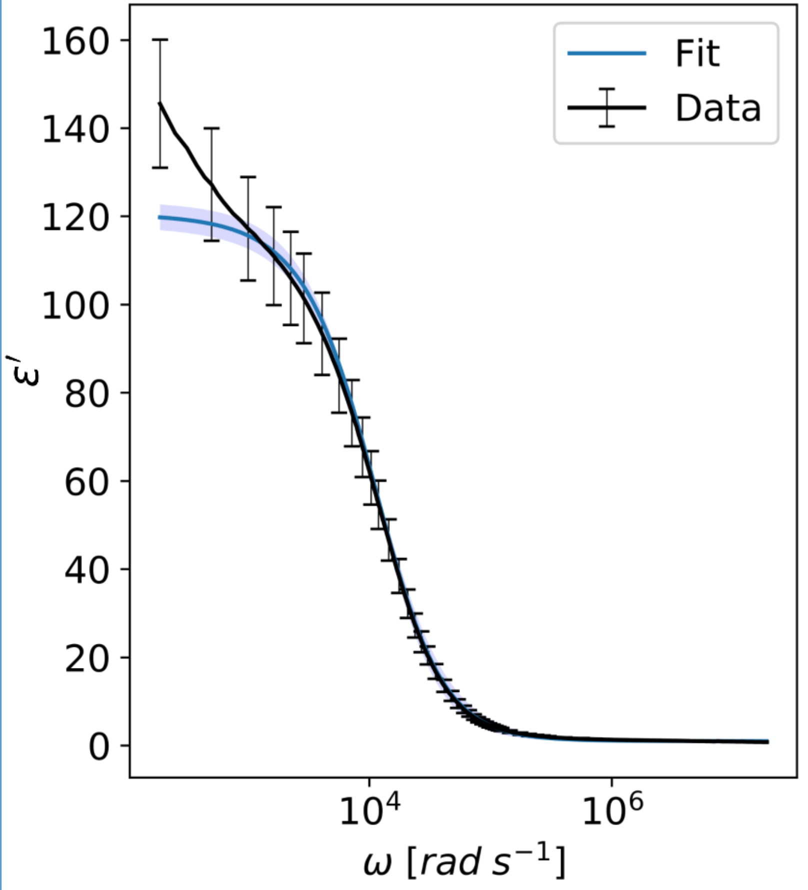
	8.0×10^{-5}	0.86	1.13	0.97	120
$\pm$	0.2×10^{-5}	0.02	0.03	0.01	3

Goodness of fit parameters:

$\chi^2 = 203.47$ $\quad \overline{\chi}^2 = 0.75$ $\quad$ p-value $= 0.95$

Real Part – What to Improve



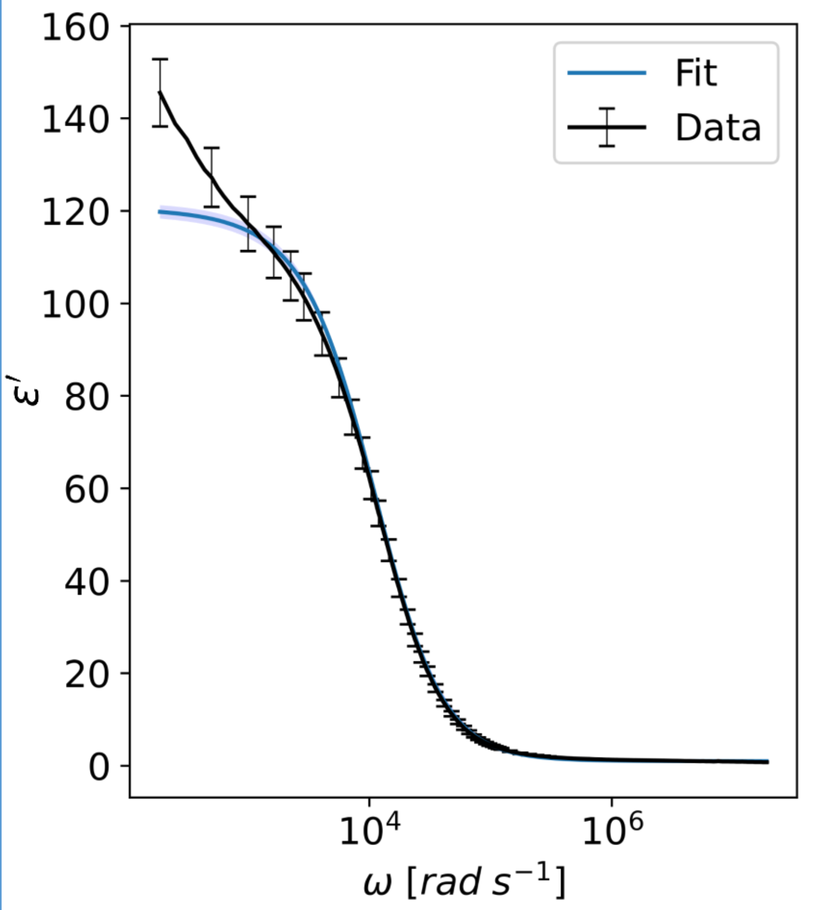
Systematic uncertainty dominates. How to reduce it?

- Improved image quality;
- Ultra thin film of a conducting metal (Au, Ag, Al…);
- Contactless measure;
- Electrode connected with spring mechanism;

With some improvements the systematic uncertainty could **be reduced to 5%**.

What's the effect of this?

Real Part – What to Improve



What's the effect of this?

The **imaginary** part stays equally good.

For the **real** part:

$$\chi^2 = 406.9 \qquad \overline{\chi}^2 = 1.49 \qquad \text{p-value} < 0.05$$

The model is no longer adequate do describe the experimental data.

How could we improve the fit?

- High frequency region is well fitted;
- Low frequency has to increase;
- This resembles: $1/x$

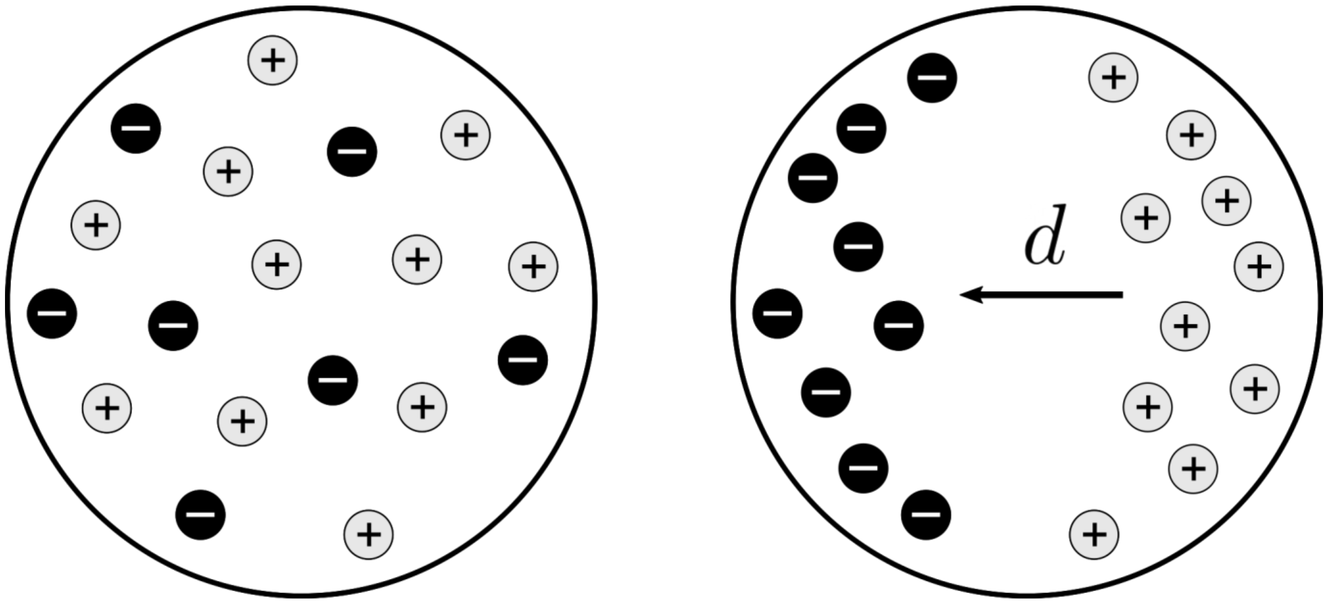
Correcting the Model...

Correcting the Model: Maxwell-Wagner

Inhomogeneous samples may lead to separation of charges.

This effect is especially noticeable for **low frequencies**.

The contribution to dielectric loss can therefore be orders of magnitude larger than other contributions.



New Model

For the **imaginary** part of the permitivity:

$$\epsilon'' = \mathrm{Im}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^{\beta})^{\gamma}}\right] + \frac{\sigma_{\mathrm{DC}}}{\epsilon_0\omega^s}$$

Havriliak-Negami Conductivity

Nothing changes for the imaginary part.

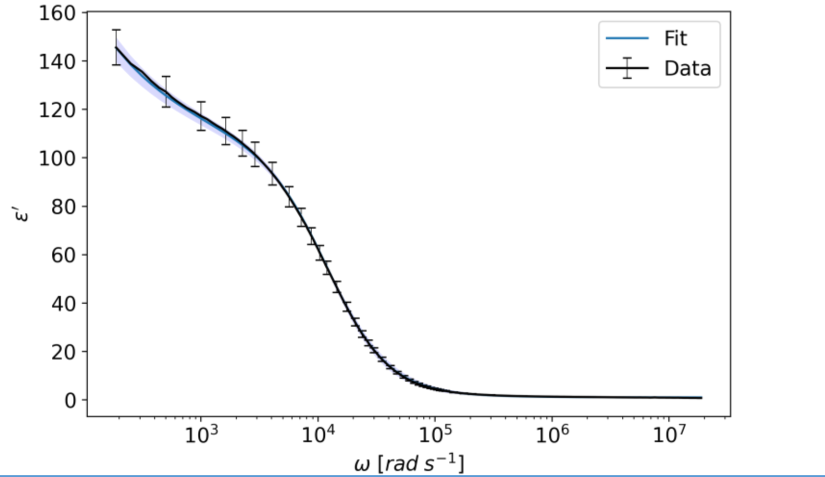
For the **real** part of the permitivity:

$$\epsilon' = \epsilon_\infty + \mathrm{Re}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^{\beta})^{\gamma}}\right] + \frac{a}{\omega^n}$$

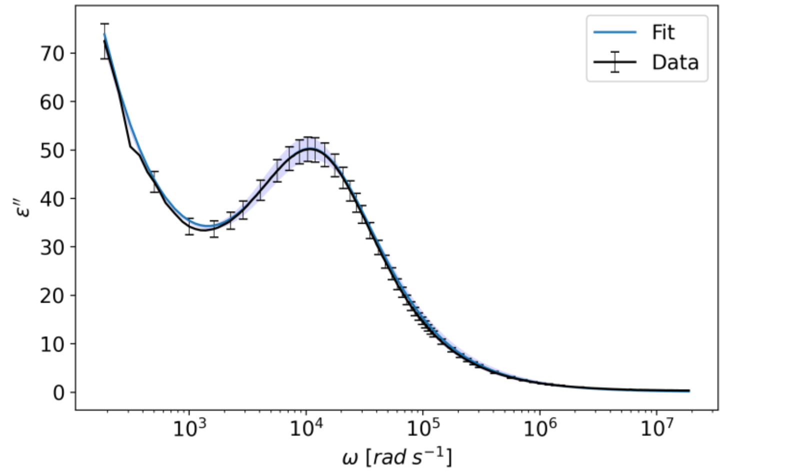
Havriliak-Negami Maxwell-Wagner

This is the type of behavior we were looking for

New Individual Fits

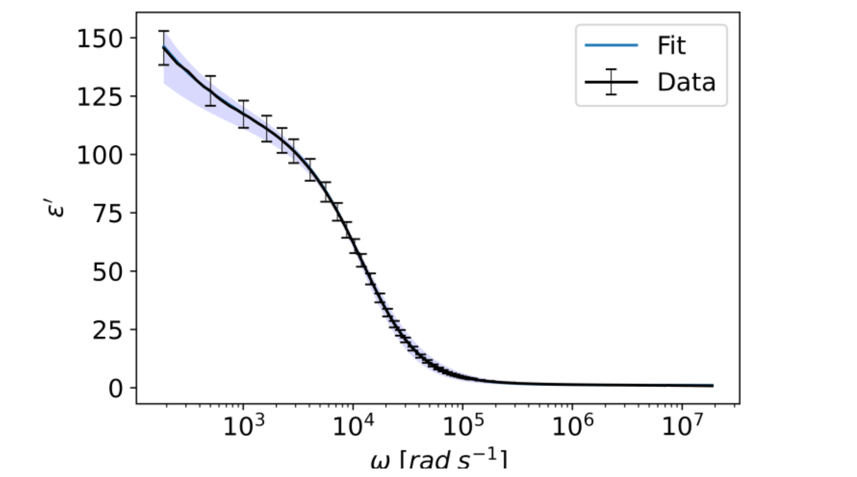


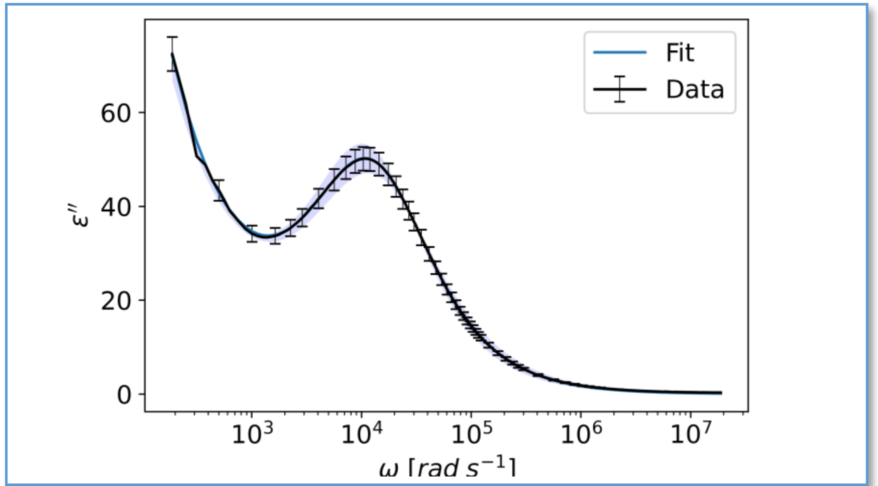
	τ_{HN} [s]	β	γ	a [$rad\ s^{-1}$]	n	ε_∞	$\Delta\varepsilon$
	7.6×10^{-5}	0.89	1.10	1086	0.62	0.94	104
$\pm$	0.3×10^{-5}	0.02	0.04	451	0.05	0.02	4



	τ_{HN} [s]	β	γ	σ_{DC} [$\Omega^{-1}m^{-1}$]	s	$\Delta\varepsilon$
	7.4×10^{-5}	0.87	1.12	2.0×10^{-8}	0.66	108
$\pm$	0.6×10^{-5}	0.03	0.06	0.6×10^{-8}	0.05	4

Global Fit





$$\epsilon' = \epsilon_\infty + \mathrm{Re}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{a}{\omega^n}$$

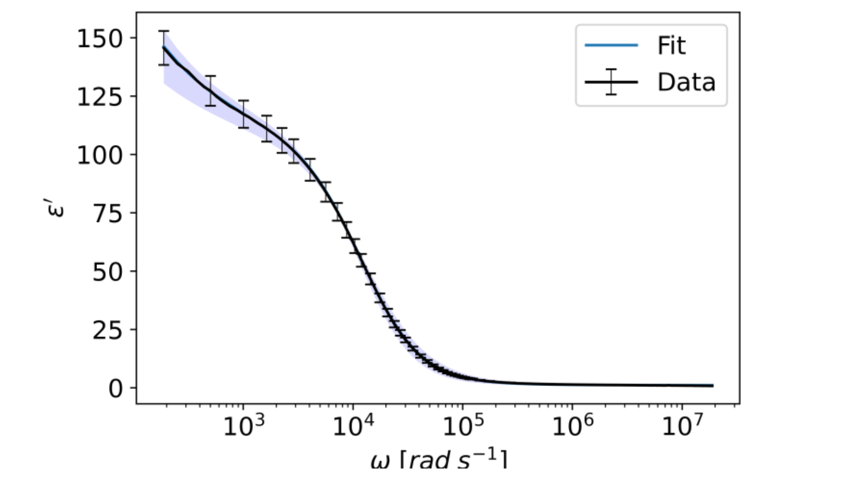
$$\epsilon'' = \mathrm{Im}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{\sigma_{\mathrm{DC}}}{\epsilon_0\omega^s}$$

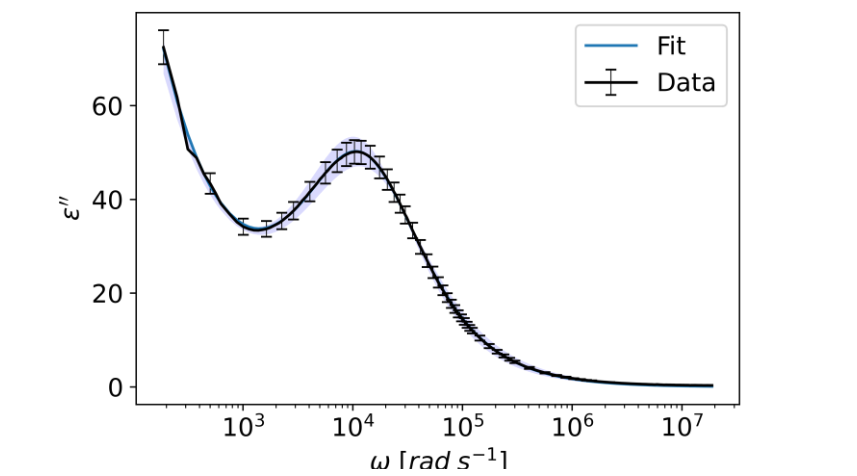
	τ_{HN} [s]	β	γ	σ_{DC} [$\Omega^{-1} m^{-1}$]	a [$rad\ s^{-1}$]	n	ε_∞	s	$\Delta\varepsilon$
	7.4×10^{-5}	0.87	1.14	2.0×10^{-8}	1061	0.63	0.98	0.66	106
±	0.4×10^{-5}	0.02	0.04	0.4×10^{-8}	536	0.06	0.03	0.03	3

Goodness of fit parameters:

$\chi^2 = 83.4$ $\quad \overline{\chi}^2 = 0.31$ $\quad$ p-value $= 1.0$

Global Fit





	τ_{HN} [s]	β	γ	σ_{DC} $[\Omega^{-1}m^{-1}]$	a $[rad\ s^{-1}]$	n	ε_∞	s	$\Delta\varepsilon$
	7.4×10^{-5}	0.87	1.14	2.0×10^{-8}	1061	0.63	0.98	0.66	106
$\pm$	0.4×10^{-5}	0.02	0.04	0.4×10^{-8}	536	0.06	0.03	0.03	3

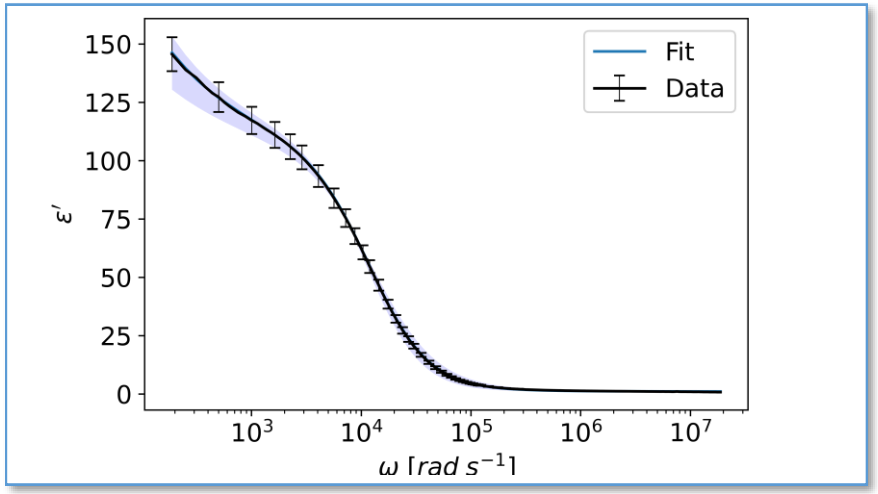
$$\sigma_{DC} = (2.0 \pm 0.4) \times 10^{-8}\ [\Omega^{-1}m^{-1}]$$

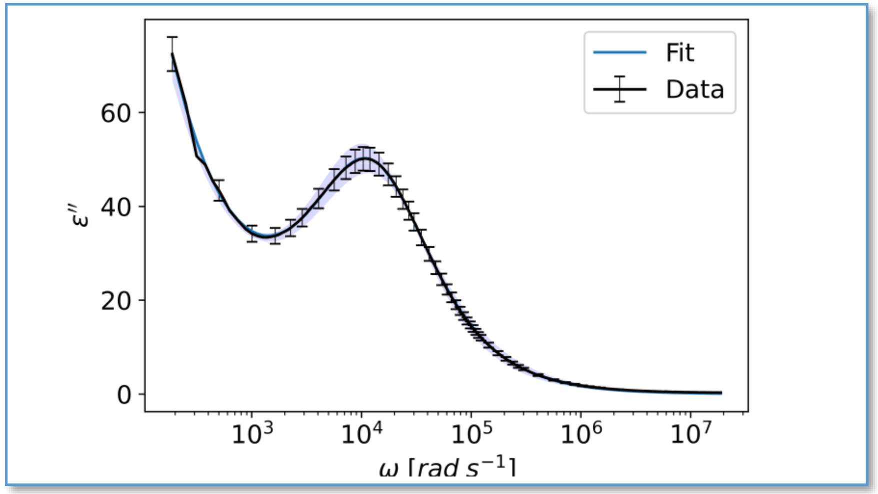
$$a\varepsilon_0 = (0.9 \pm 0.4) \times 10^{-8}\ [\Omega^{-1}m^{-1}]$$

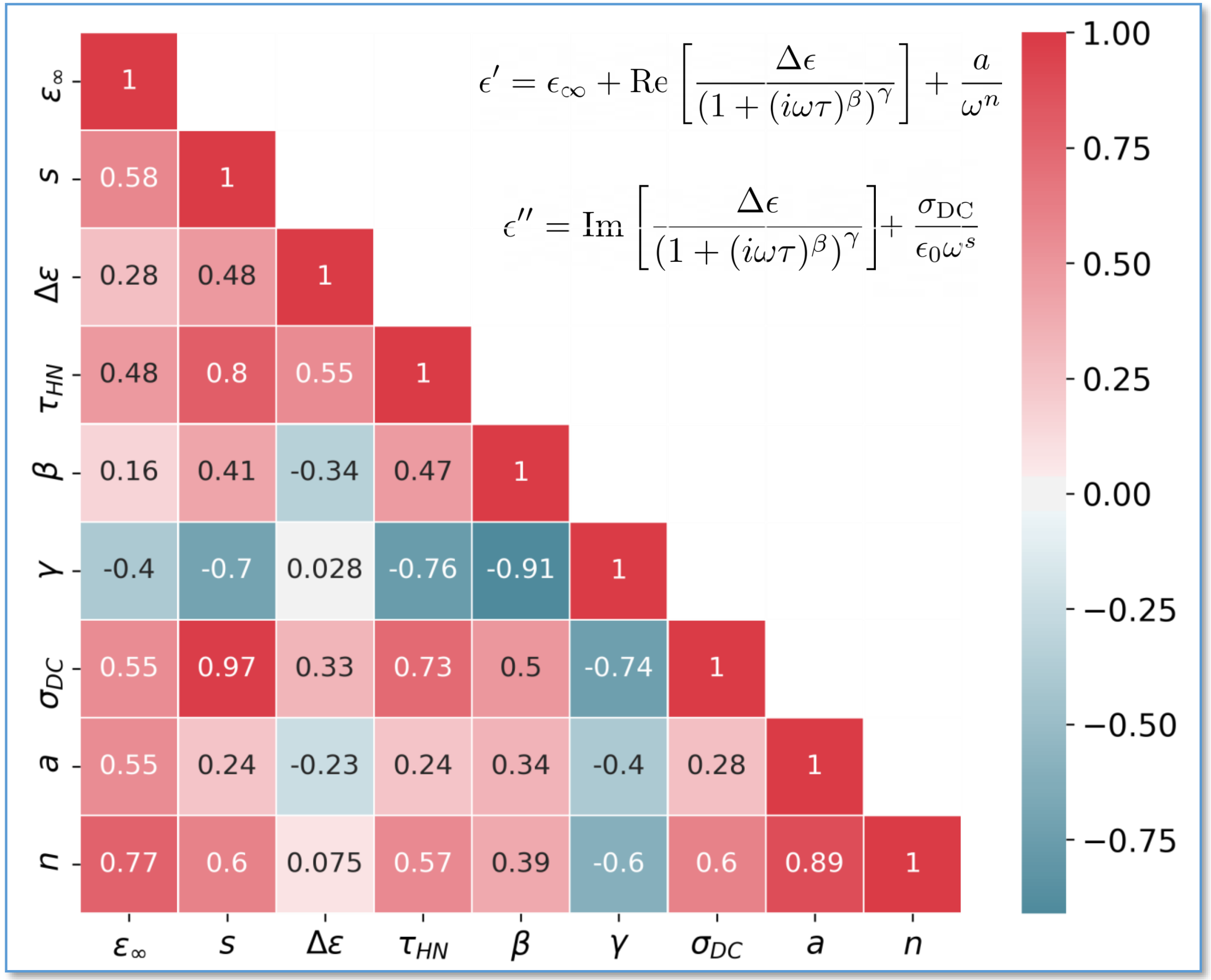
Goodness of fit parameters:

$$\chi^2 = 83.4 \qquad \overline{\chi}^2 = 0.31 \qquad \text{p-value} = 1.0$$

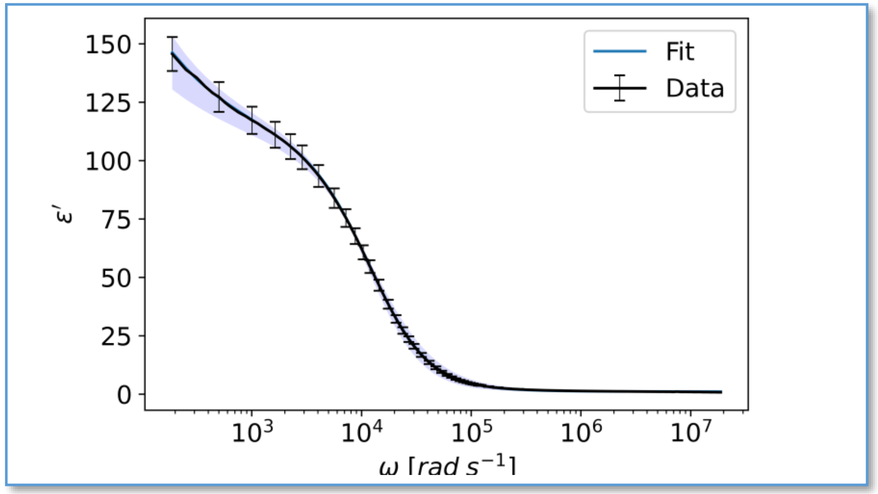
Global Fit


Fit
Data
150
125
100
75
50
25
0
ϵ'
10^3
10^4
10^5
10^6
10^7
ω [rad s^{-1}]

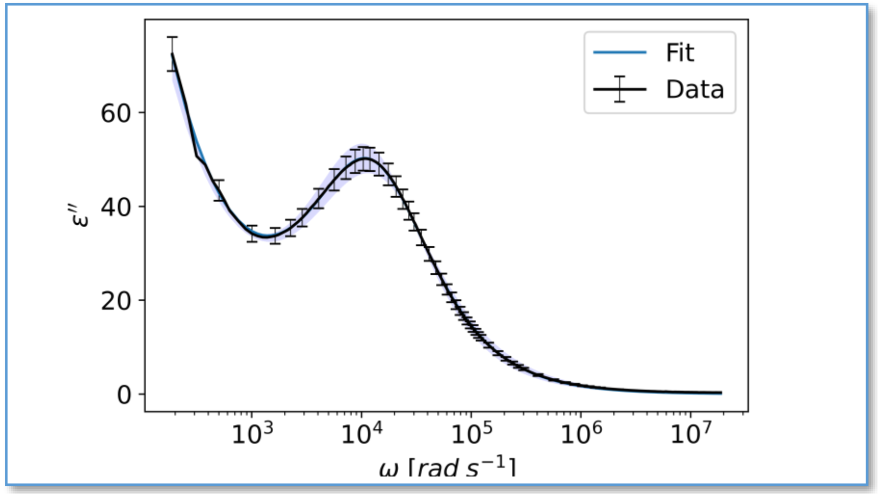

Fit
Data
60
40
20
0
ϵ''
10^3
10^4
10^5
10^6
10^7
ω [rad s^{-1}]


$\epsilon' = \epsilon_\infty + \mathrm{Re}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{a}{\omega^n}$
$\epsilon'' = \mathrm{Im}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{\sigma_{DC}}{\epsilon_0\omega^s}$
ε_∞: 1
s: 0.58, 1
$\Delta\varepsilon$: 0.28, 0.48, 1
τ_{HN}: 0.48, 0.8, 0.55, 1
β: 0.16, 0.41, -0.34, 0.47, 1
γ: -0.4, -0.7, 0.028, -0.76, -0.91, 1
σ_{DC}: 0.55, 0.97, 0.33, 0.73, 0.5, -0.74, 1
a: 0.55, 0.24, -0.23, 0.24, 0.34, -0.4, 0.28, 1
n: 0.77, 0.6, 0.075, 0.57, 0.39, -0.6, 0.6, 0.89, 1
ε_∞ s $\Delta\varepsilon$ τ_{HN} β γ σ_{DC} a n
1.00
0.75
0.50
0.25
0.00
−0.25
−0.50
−0.75

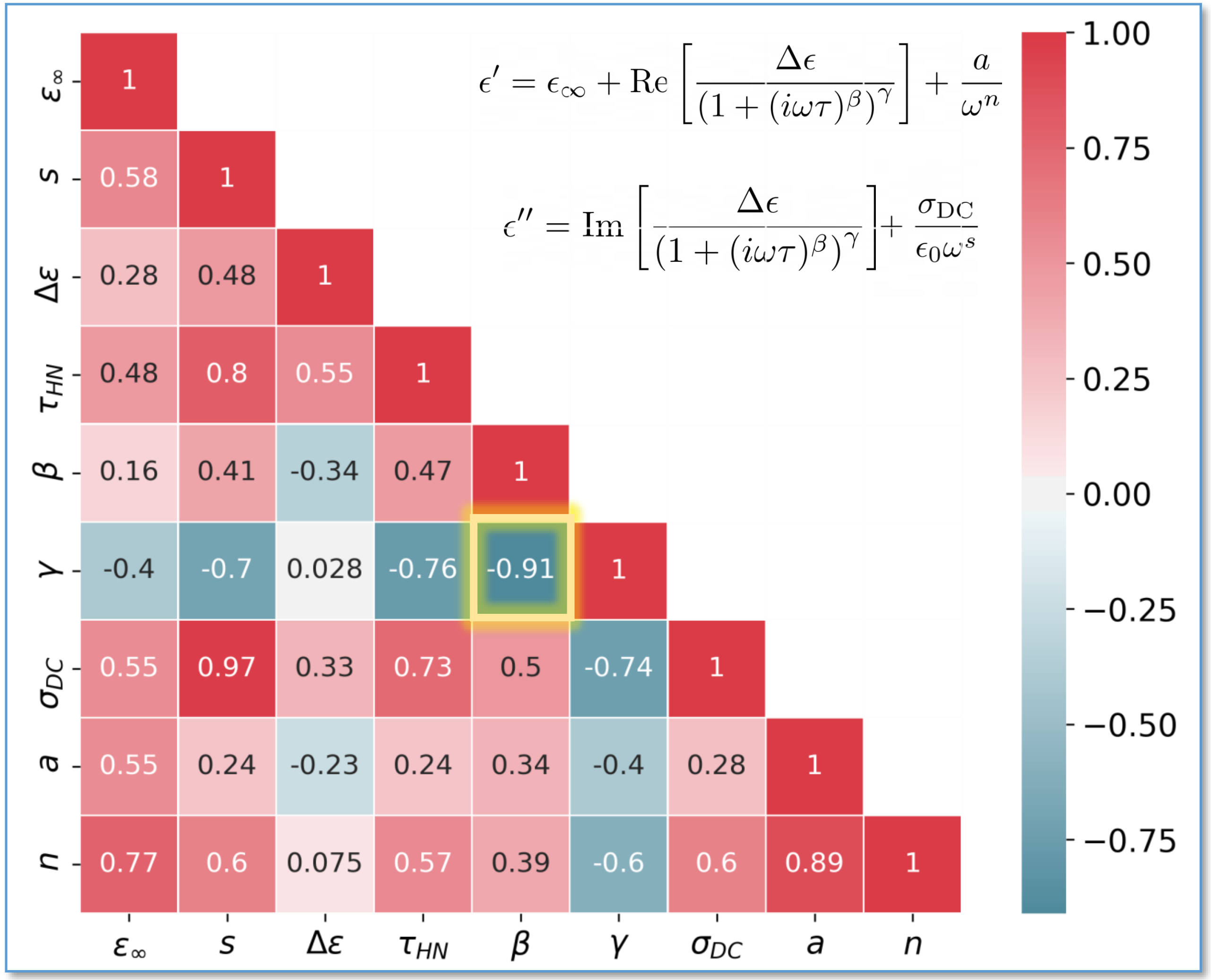
Global Fit



Fit
Data
150
125
100
75
50
25
0
ε′
10^3 10^4 10^5 10^6 10^7
ω [rad s⁻¹]

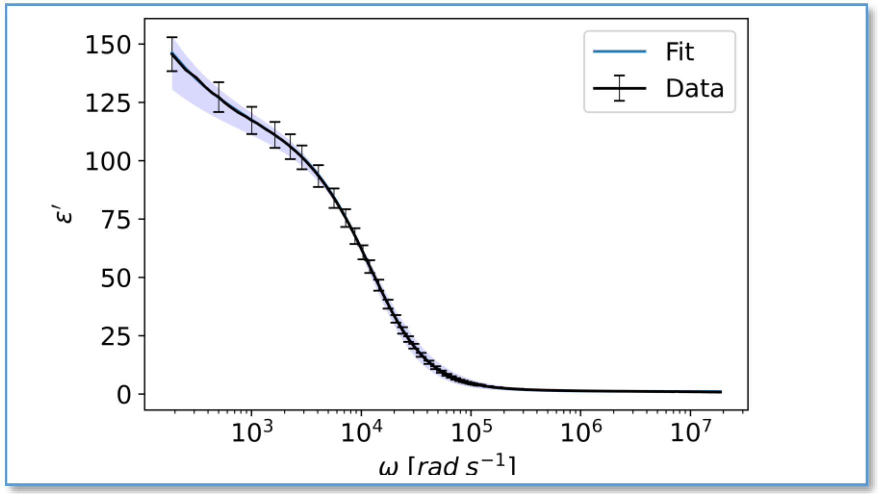


Fit
Data
60
40
20
0
ε″
10^3 10^4 10^5 10^6 10^7
ω [rad s⁻¹]

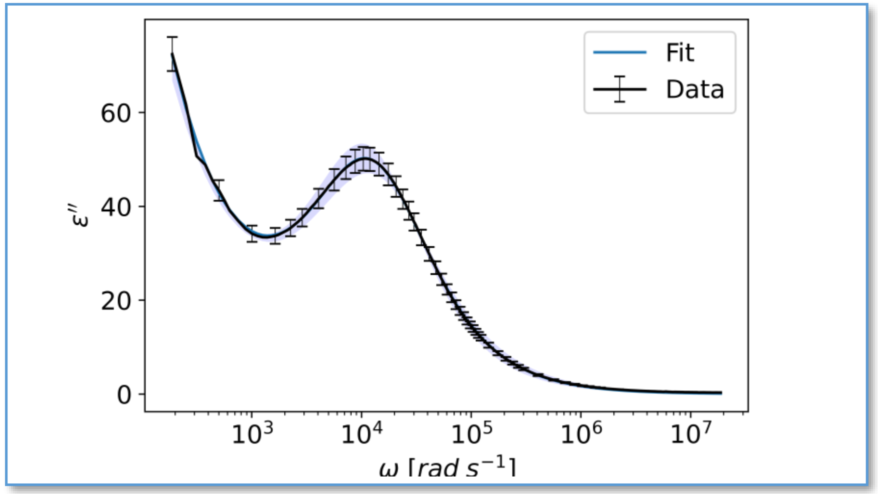


$\epsilon' = \epsilon_\infty + \mathrm{Re}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{a}{\omega^n}$
$\epsilon'' = \mathrm{Im}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{\sigma_{DC}}{\epsilon_0\omega^s}$
ε∞ 1
s 0.58 1
Δε 0.28 0.48 1
τHN 0.48 0.8 0.55 1
β 0.16 0.41 -0.34 0.47 1
γ -0.4 -0.7 0.028 -0.76 -0.91 1
σDC 0.55 0.97 0.33 0.73 0.5 -0.74 1
a 0.55 0.24 -0.23 0.24 0.34 -0.4 0.28 1
n 0.77 0.6 0.075 0.57 0.39 -0.6 0.6 0.89 1
ε∞ s Δε τHN β γ σDC a n
1.00
0.75
0.50
0.25
0.00
−0.25
−0.50
−0.75

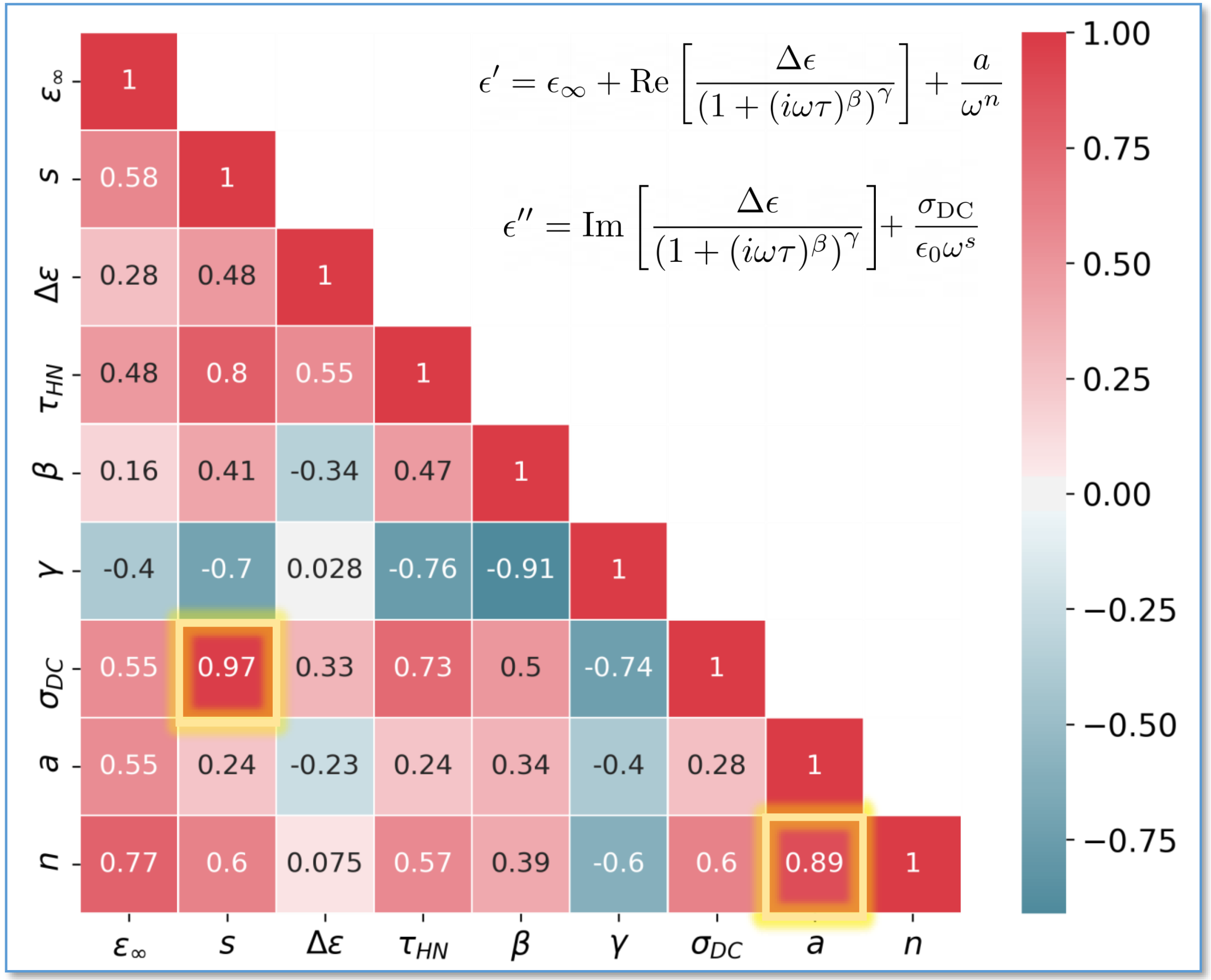
Global Fit



Fit
Data
ε′
150
125
100
75
50
25
0
10^3 10^4 10^5 10^6 10^7
ω [rad s^{-1}]

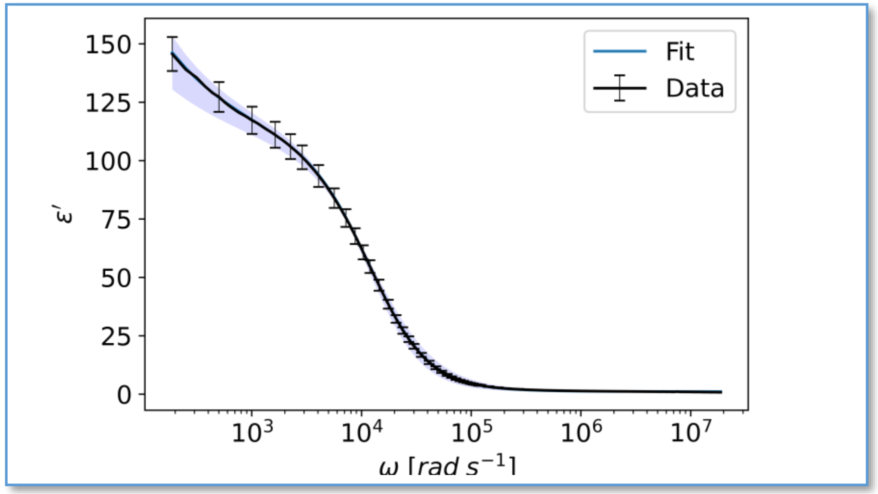


Fit
Data
ε″
60
40
20
0
10^3 10^4 10^5 10^6 10^7
ω [rad s^{-1}]

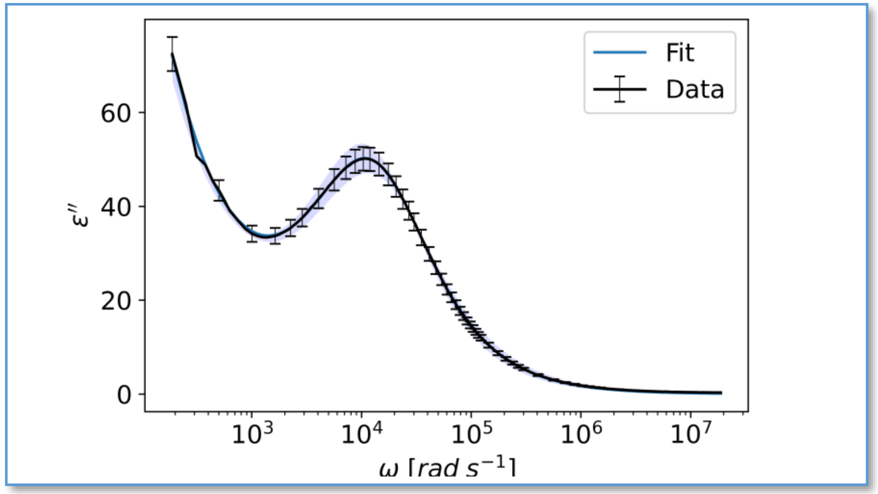


$\epsilon' = \epsilon_\infty + \mathrm{Re}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{a}{\omega^n}$
$\epsilon'' = \mathrm{Im}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{\sigma_{DC}}{\epsilon_0\omega^s}$
ε_∞: 1
s: 0.58, 1
$\Delta\varepsilon$: 0.28, 0.48, 1
τ_{HN}: 0.48, 0.8, 0.55, 1
β: 0.16, 0.41, -0.34, 0.47, 1
γ: -0.4, -0.7, 0.028, -0.76, -0.91, 1
σ_{DC}: 0.55, 0.97, 0.33, 0.73, 0.5, -0.74, 1
a: 0.55, 0.24, -0.23, 0.24, 0.34, -0.4, 0.28, 1
n: 0.77, 0.6, 0.075, 0.57, 0.39, -0.6, 0.6, 0.89, 1
ε_∞ s $\Delta\varepsilon$ τ_{HN} β γ σ_{DC} a n
1.00
0.75
0.50
0.25
0.00
−0.25
−0.50
−0.75

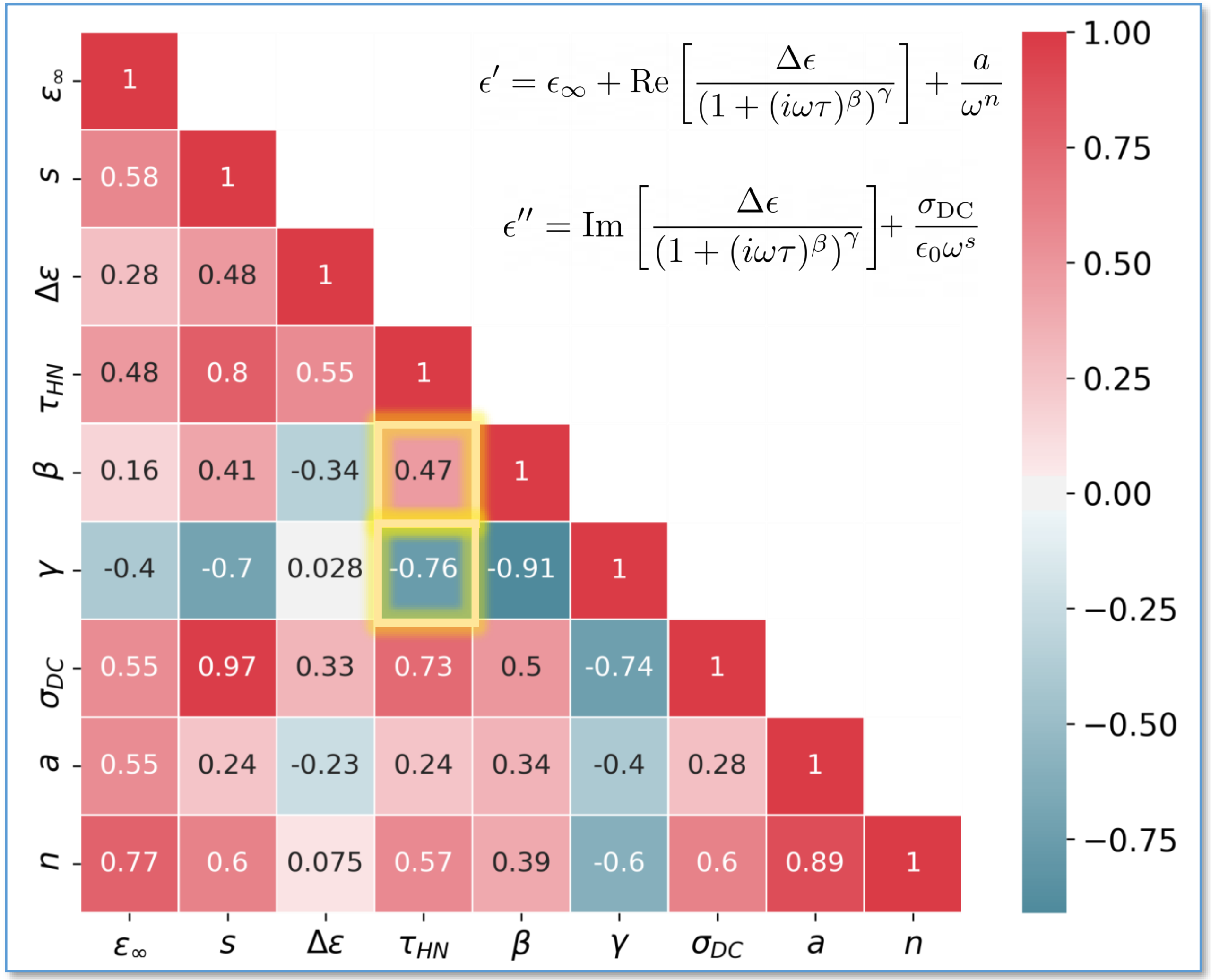
Global Fit



Fit
Data
150
125
100
75
50
25
0
ε′
10^3 10^4 10^5 10^6 10^7
ω [rad s⁻¹]



Fit
Data
60
40
20
0
ε″
10^3 10^4 10^5 10^6 10^7
ω [rad s⁻¹]



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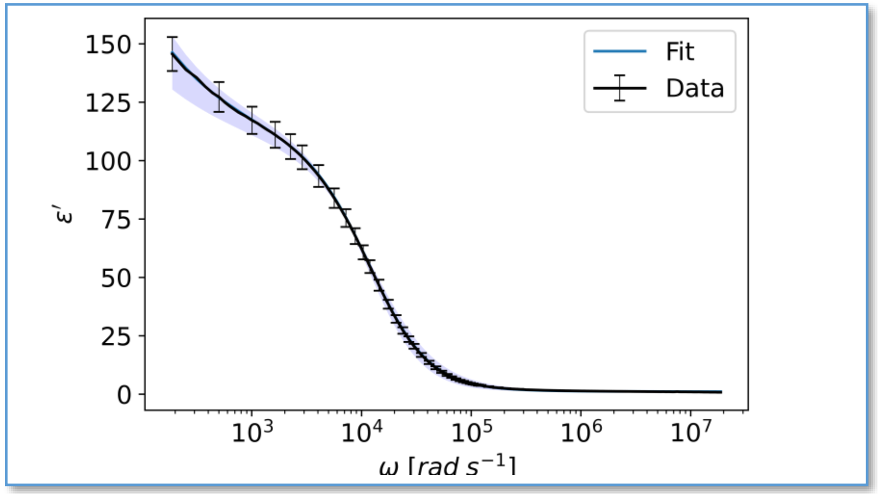
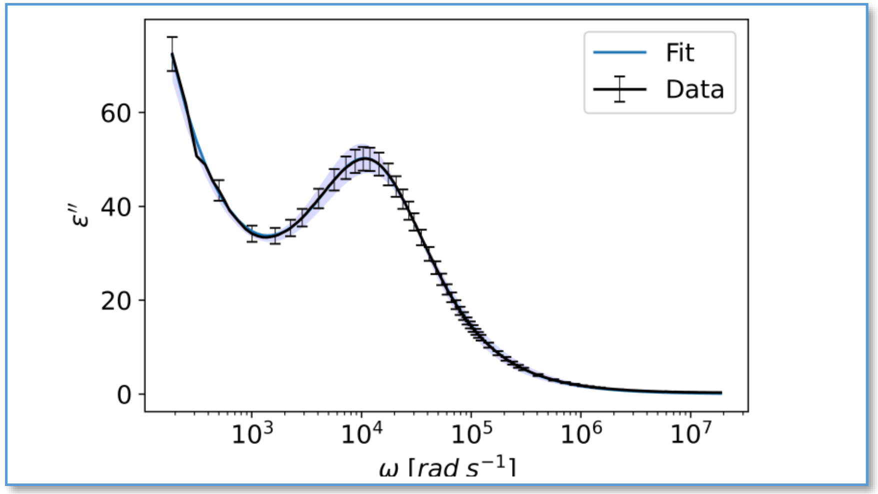
ε∞ 1
s 0.58 1
Δε 0.28 0.48 1
τHN 0.48 0.8 0.55 1
β 0.16 0.41 -0.34 0.47 1
γ -0.4 -0.7 0.028 -0.76 -0.91 1
σDC 0.55 0.97 0.33 0.73 0.5 -0.74 1
a 0.55 0.24 -0.23 0.24 0.34 -0.4 0.28 1
n 0.77 0.6 0.075 0.57 0.39 -0.6 0.6 0.89 1
ε∞ s Δε τHN β γ σDC a n
1.00
0.75
0.50
0.25
0.00
−0.25
−0.50
−0.75

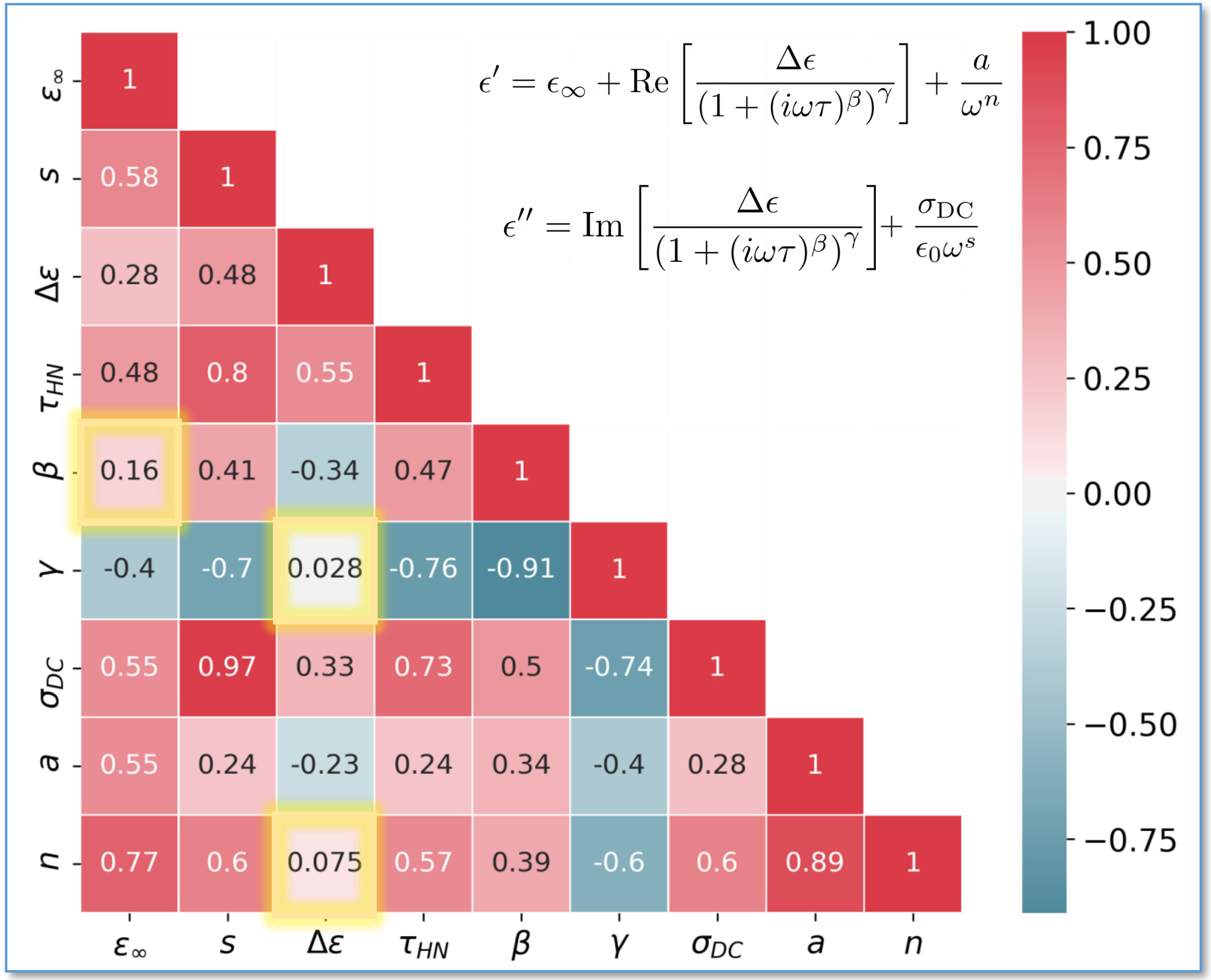
Global Fit



Fit
Data
150
125
100
75
50
25
0
ε′
10^3
10^4
10^5
10^6
10^7
ω [rad s⁻¹]



Fit
Data
60
40
20
0
ε″
10^3
10^4
10^5
10^6
10^7
ω [rad s⁻¹]



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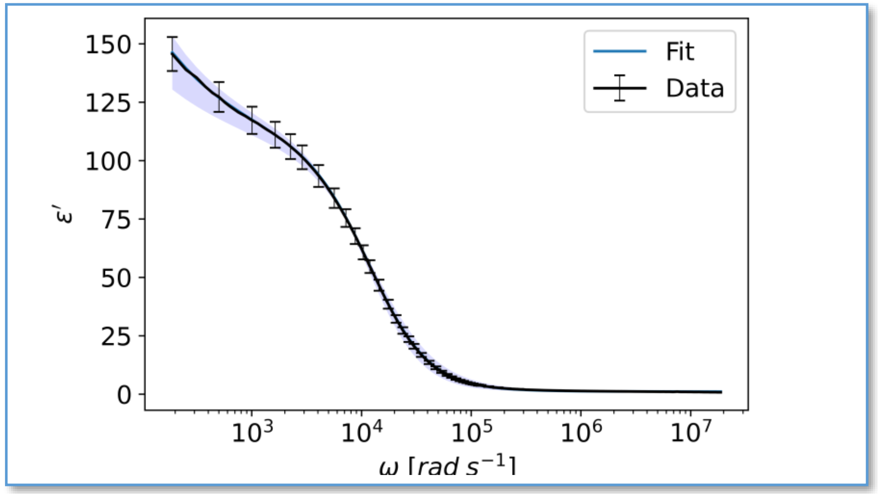
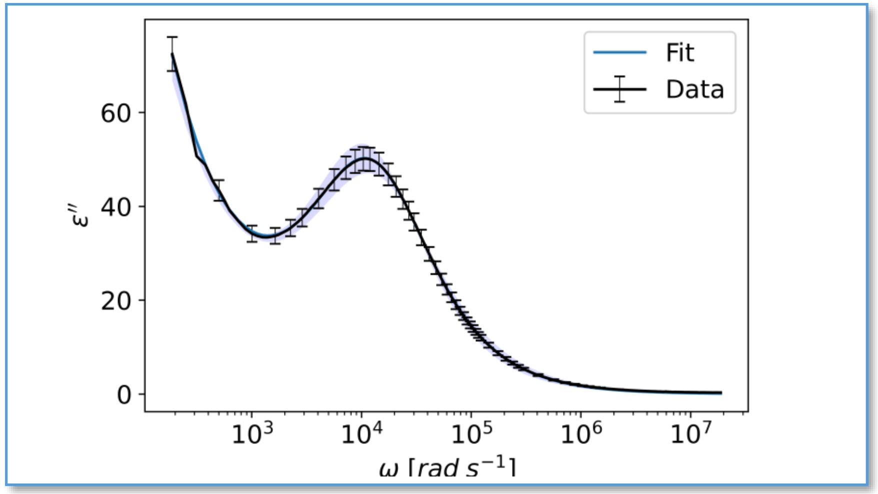
$\Delta\varepsilon$ 0.28 0.48 1
τ_{HN} 0.48 0.8 0.55 1
β 0.16 0.41 -0.34 0.47 1
γ -0.4 -0.7 0.028 -0.76 -0.91 1
σ_{DC} 0.55 0.97 0.33 0.73 0.5 -0.74 1
a 0.55 0.24 -0.23 0.24 0.34 -0.4 0.28 1
n 0.77 0.6 0.075 0.57 0.39 -0.6 0.6 0.89 1
ε_∞ s $\Delta\varepsilon$ τ_{HN} β γ σ_{DC} a n
1.00
0.75
0.50
0.25
0.00
−0.25
−0.50
−0.75

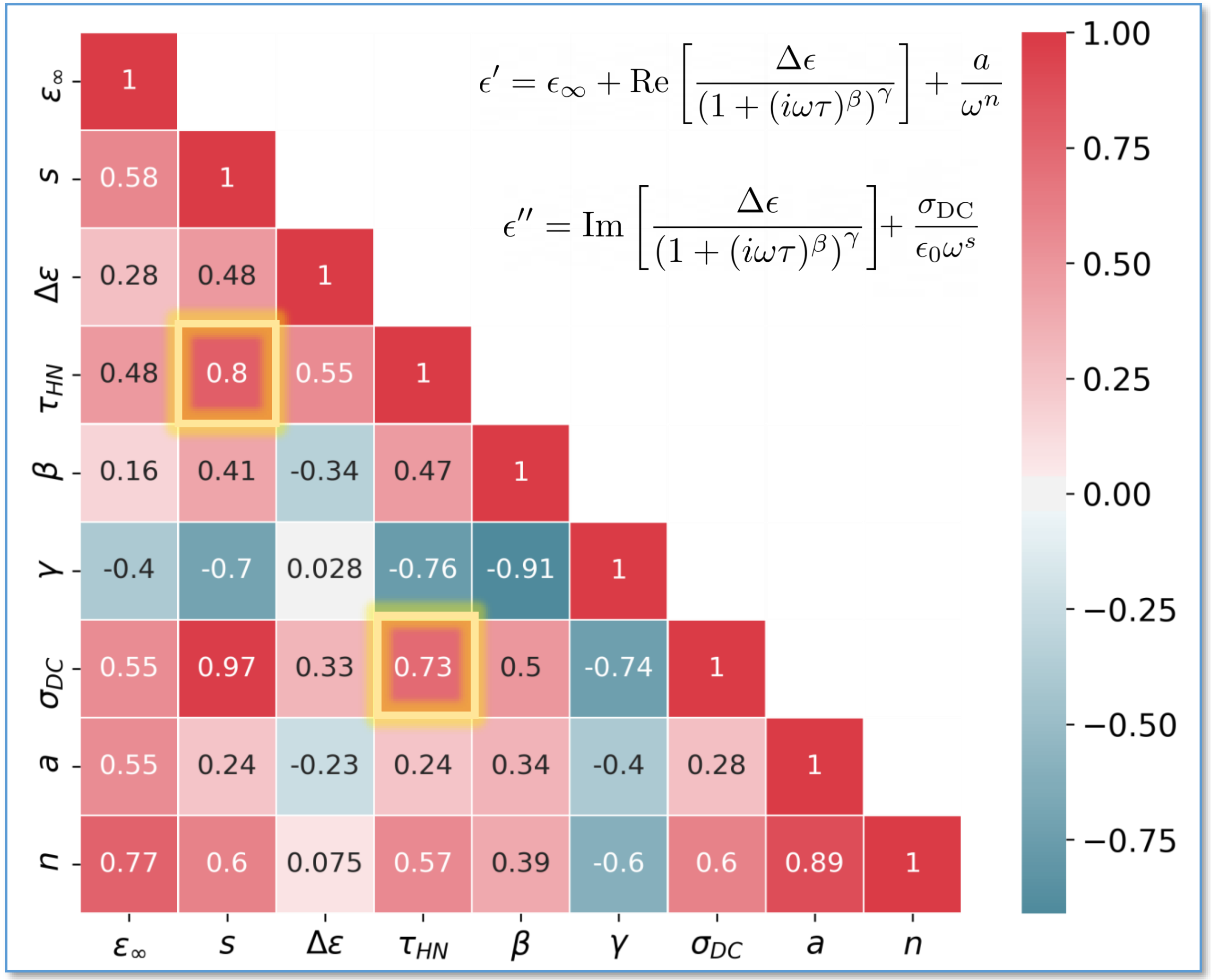
Global Fit



Fit
Data
150
125
100
75
50
25
0
ϵ'
10^3 10^4 10^5 10^6 10^7
ω [rad s^{-1}]



Fit
Data
60
40
20
0
ϵ''
10^3 10^4 10^5 10^6 10^7
ω [rad s^{-1}]



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$$\epsilon'' = \mathrm{Im}\left[\frac{\Delta\epsilon}{(1+(i\omega\tau)^\beta)^\gamma}\right] + \frac{\sigma_{DC}}{\epsilon_0\omega^s}$$
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s: 0.58 1
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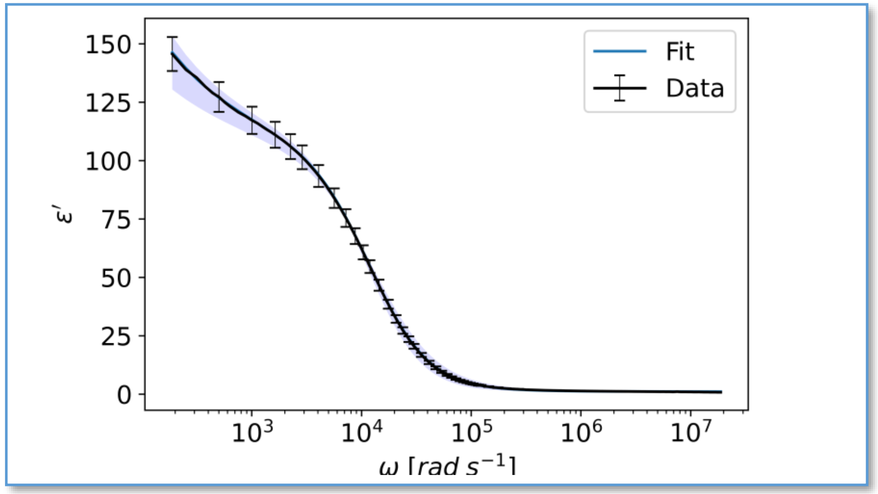
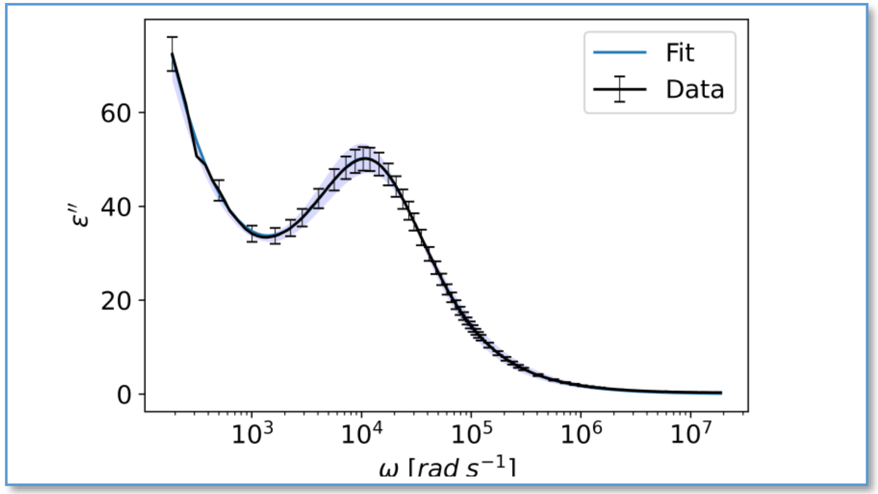
a: 0.55 0.24 -0.23 0.24 0.34 -0.4 0.28 1
n: 0.77 0.6 0.075 0.57 0.39 -0.6 0.6 0.89 1
ε_∞ s $\Delta\varepsilon$ τ_{HN} β γ σ_{DC} a n
1.00
0.75
0.50
0.25
0.00
−0.25
−0.50
−0.75

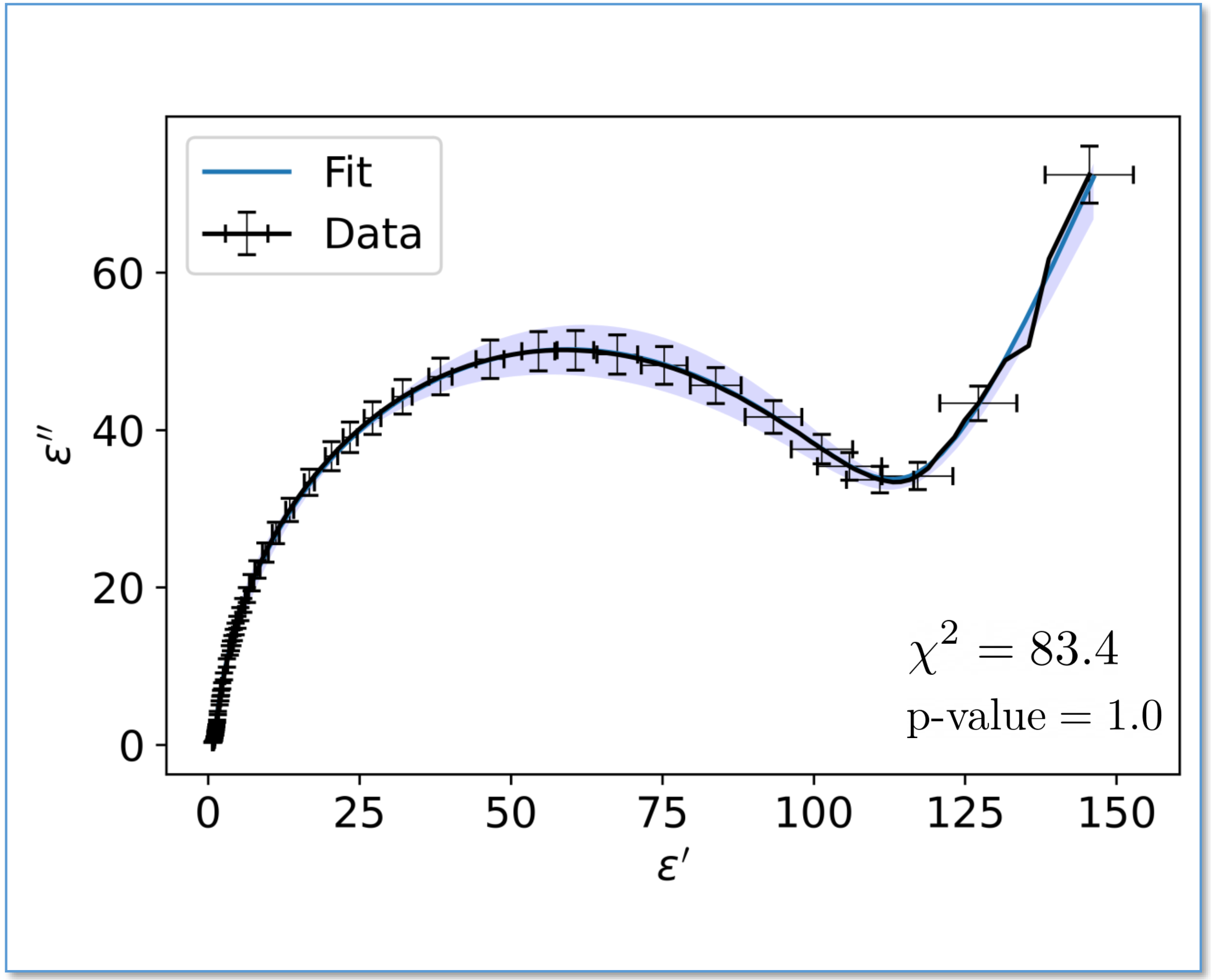
Global Fit



Fit
Data
ε′
ω [rad s⁻¹]



Fit
Data
ε″
ω [rad s⁻¹]



Fit
Data
ε″
ε′
$\chi^2 = 83.4$
p-value = 1.0

Overview

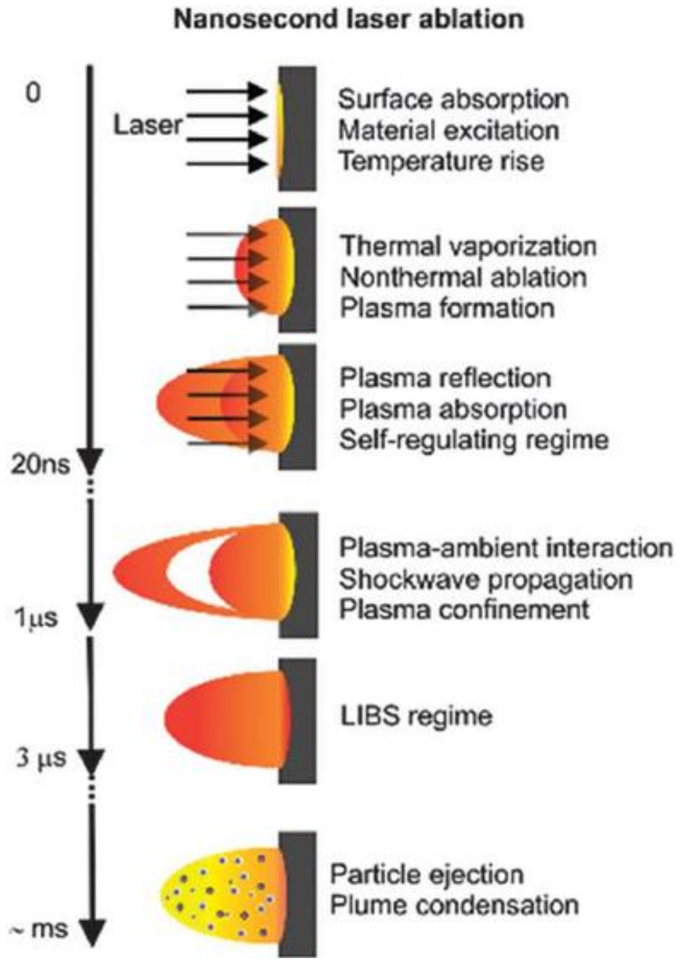
- An initial fit to portions of the data allowed us to confirm the order of magnitude;
- The individual fits showed a good agreement with the experimental data with 10% uncertainty;
- After reflecting about the experimental procedure a reduction to 5% on the uncertainty was considered;
- With 5% uncertainty the individual fit for $\epsilon'(\omega)$ did not describe the experimental data correctly;
- The Maxwell-Wagner effect was added to the initial model;
- The new model produced fits in total agreement with the experimental data.

Main conclusion: After the addition of the Maxwell-Wagner Effect the model correctly describes the physics in study even for 5% uncertainty.

Complementary Slides…

Laser Ablation

- It’s a PVD technique;
- The sample is irradiated with a pulsed laser creating a plasm plume;
- The plasma componentes expand adiabatically to reach the substrate.



Advantages and Disavantages of Laser Ablation

Advantages

- Low heat transfer;
- Environmentally friendly;
- Cost effective;
- Low energy waste;

Disavantages

- Low deposition rates;
- Requires expensive and large-dimension equipment;
- Requires great ammount of energy;

Advantages of Dielectric Spectroscopy

- Specialized staff isn’t required to use this technique;
- It’s relatively non-invasive (in terms of voltage used);
- A wide range of samples can be analized with this technique;
- It allows the use of conditions that can’t be used in other analysis;

Disadvantages of Dielectric Spectroscopy

- Some samples have a low response that can’t be detected by the equipment;
- The methods used to conect the electrodes to the sample may deteriorate the sample;
- Some interesting responses may be swamped by the response of less interesting componentes with higher intensity;

Benefits of a sputtered metal contact

- The contact area will be much more regular with the use of a mask;
- Better contact thickness and area controll;
- Uniform contact surface;
- Sample contamination is reduced when compared with silver paint contacts;