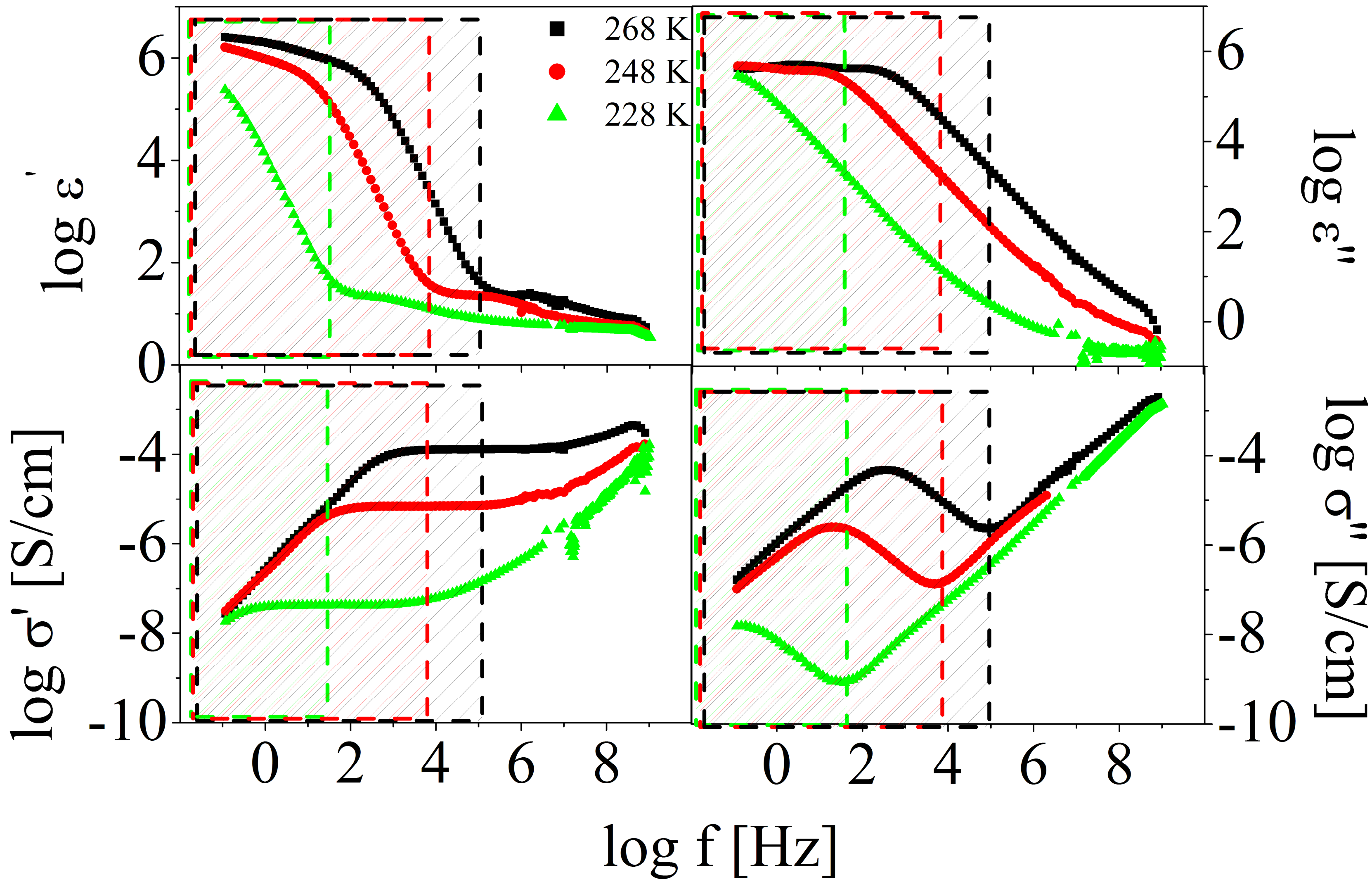
UNIVERSITÄT LEIPZIG

Electrode-polarisation and its scaling: a microscopic model

A. Serghei, J.R. Sangoro, C.Iacob and <u>F.Kremer</u>

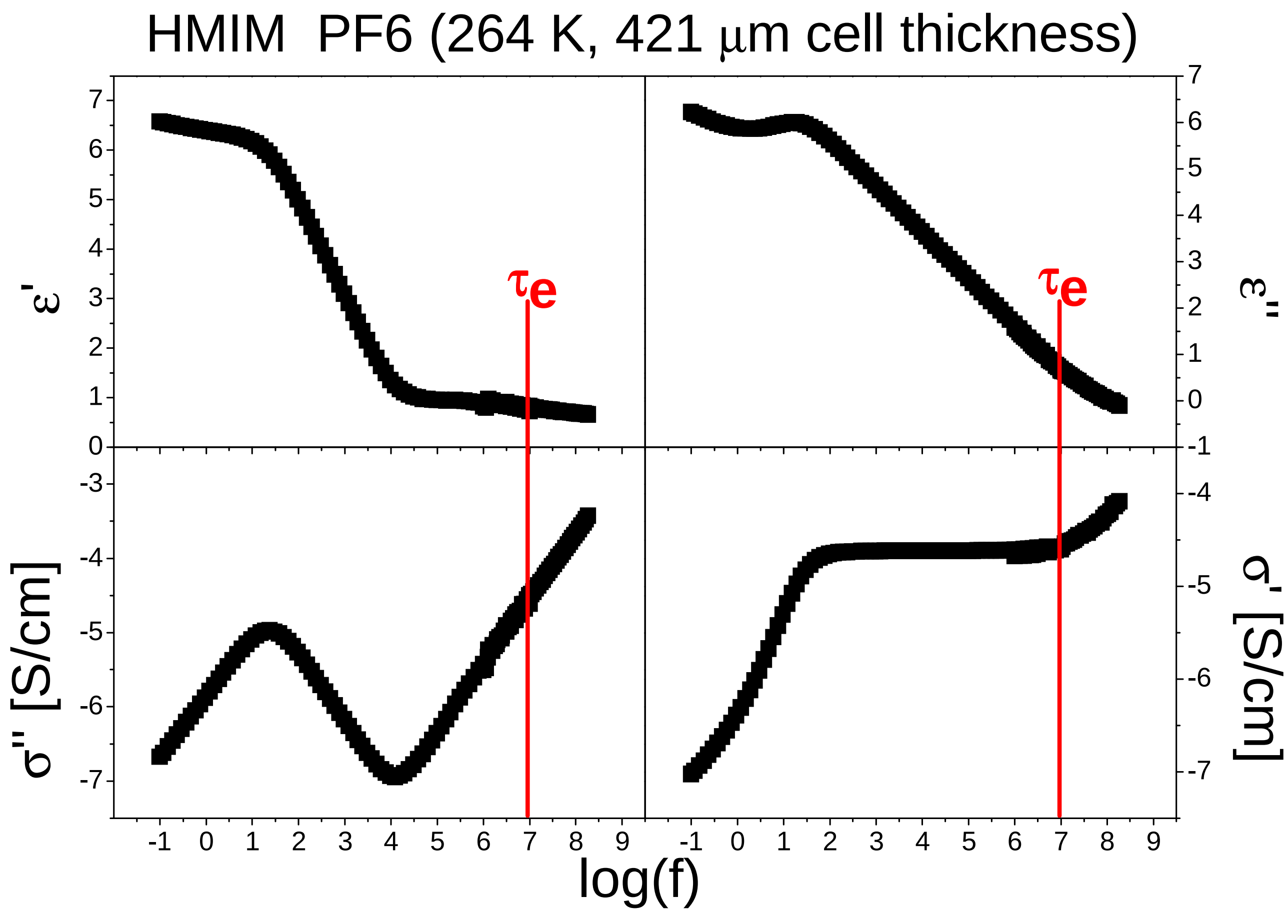
Two temperature dependent regimes: Electrode polarisation and bulk charge transport



Questions to be adressed:

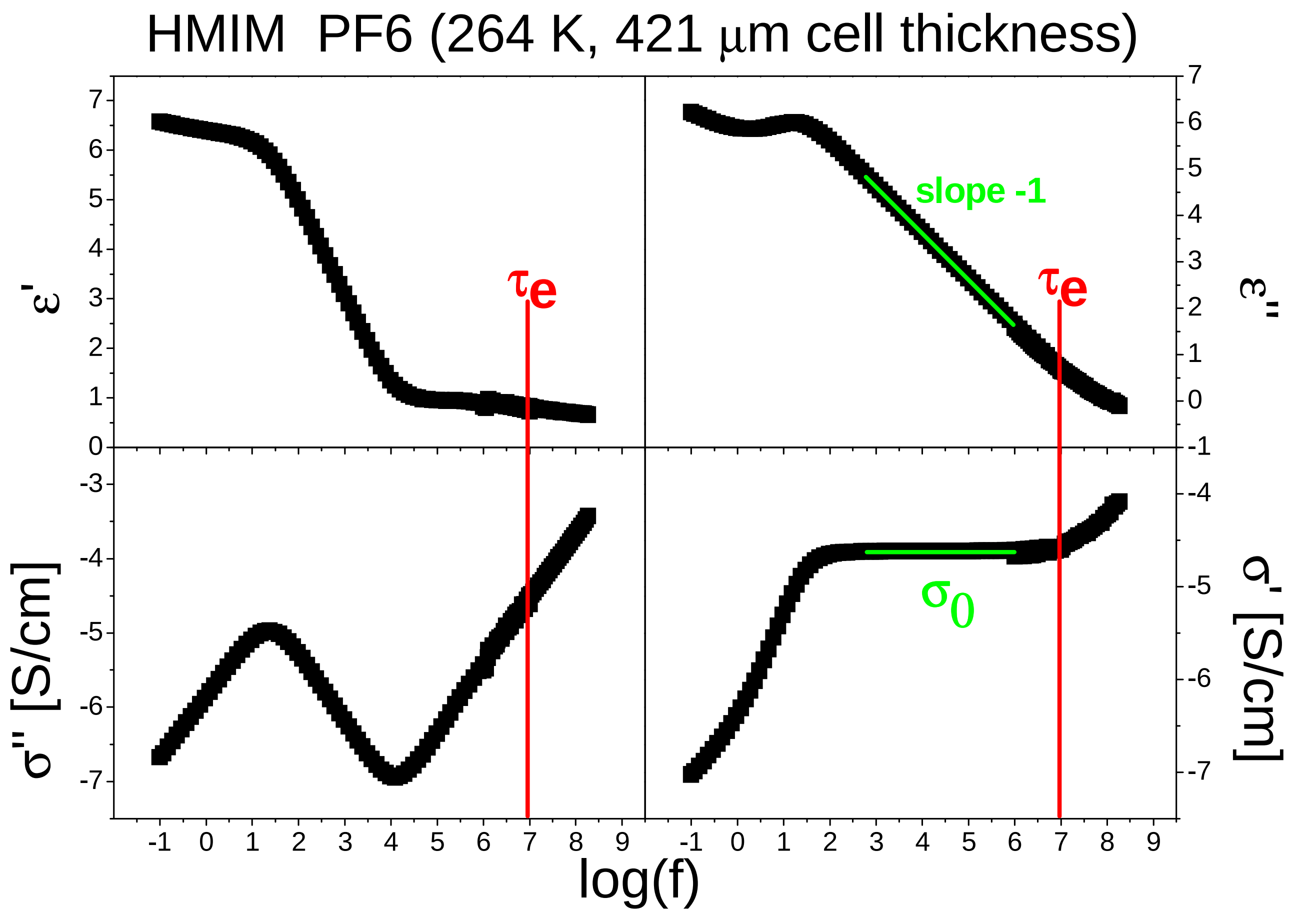
1. What is the ***signature* of electrode polarisation** in the complex dielectric function, resp. the complex conductivity?
2. What is the **scaling of electrode polarisation** with respect to frequency, temperature, concentration of charge carriers and length of the sample cell?
3. What is the **effect of different materials** of the electrode?
4. What is the ***quantitative* model** to describe EP?
5. What ***novel quantitative* information** can be deduced **from fits of electrode-polarisation**?

Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

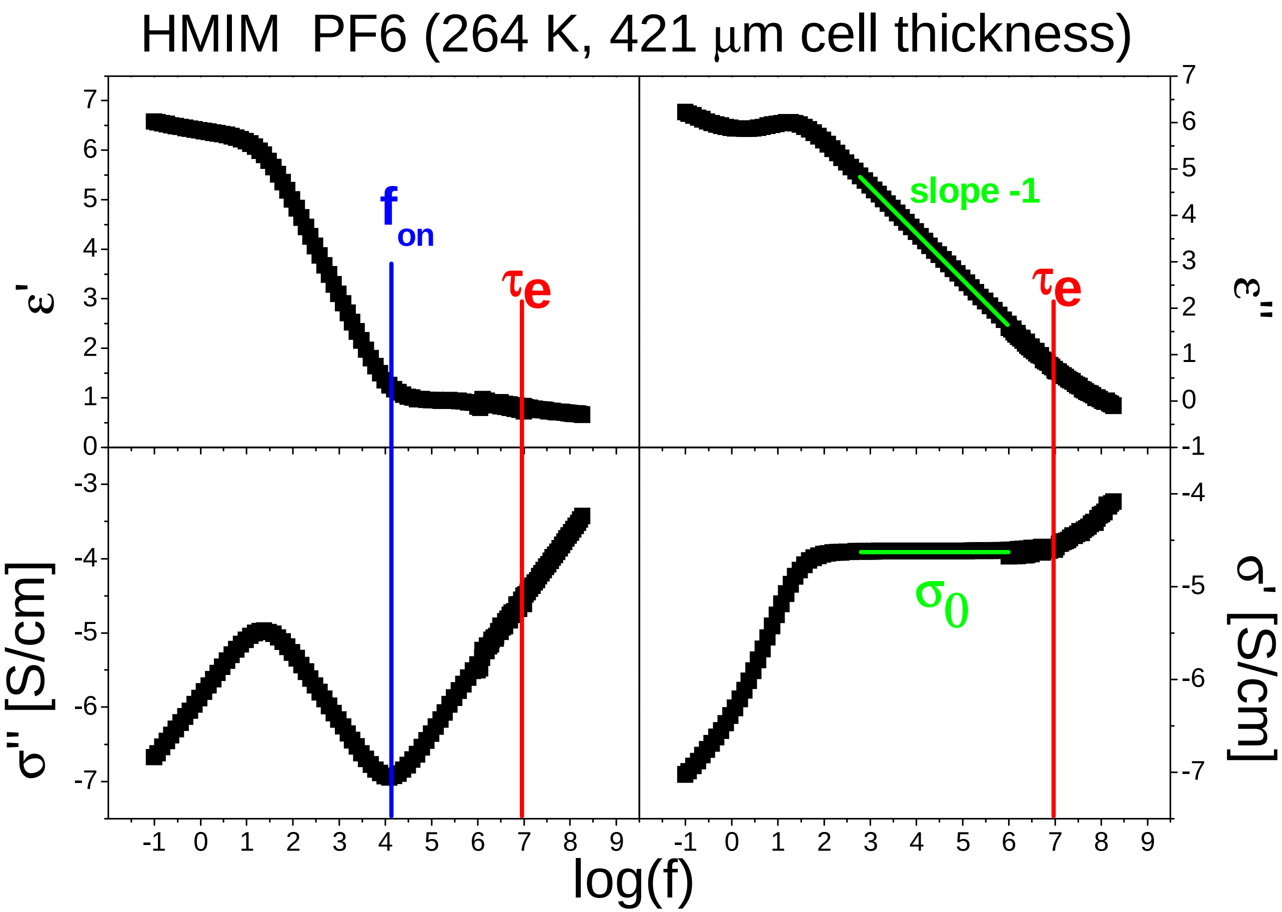
Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

σ_0: DC conductivity

Experimental features of EP in ILs - frequency dependence

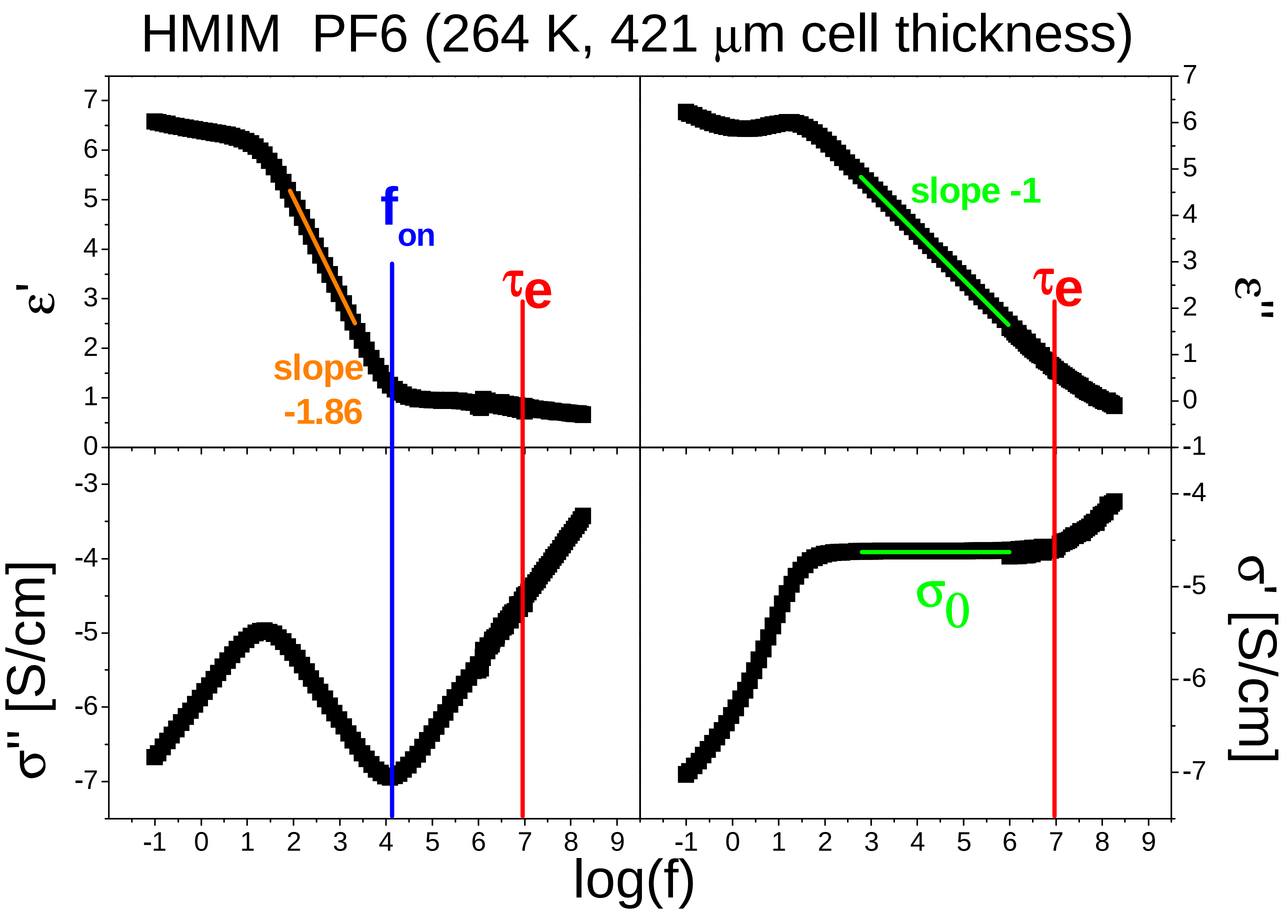


τ_e: hoping time

σ_0: DC conductivity

f_{on}: onset of electrode polarization

Experimental features of EP in ILs - frequency dependence



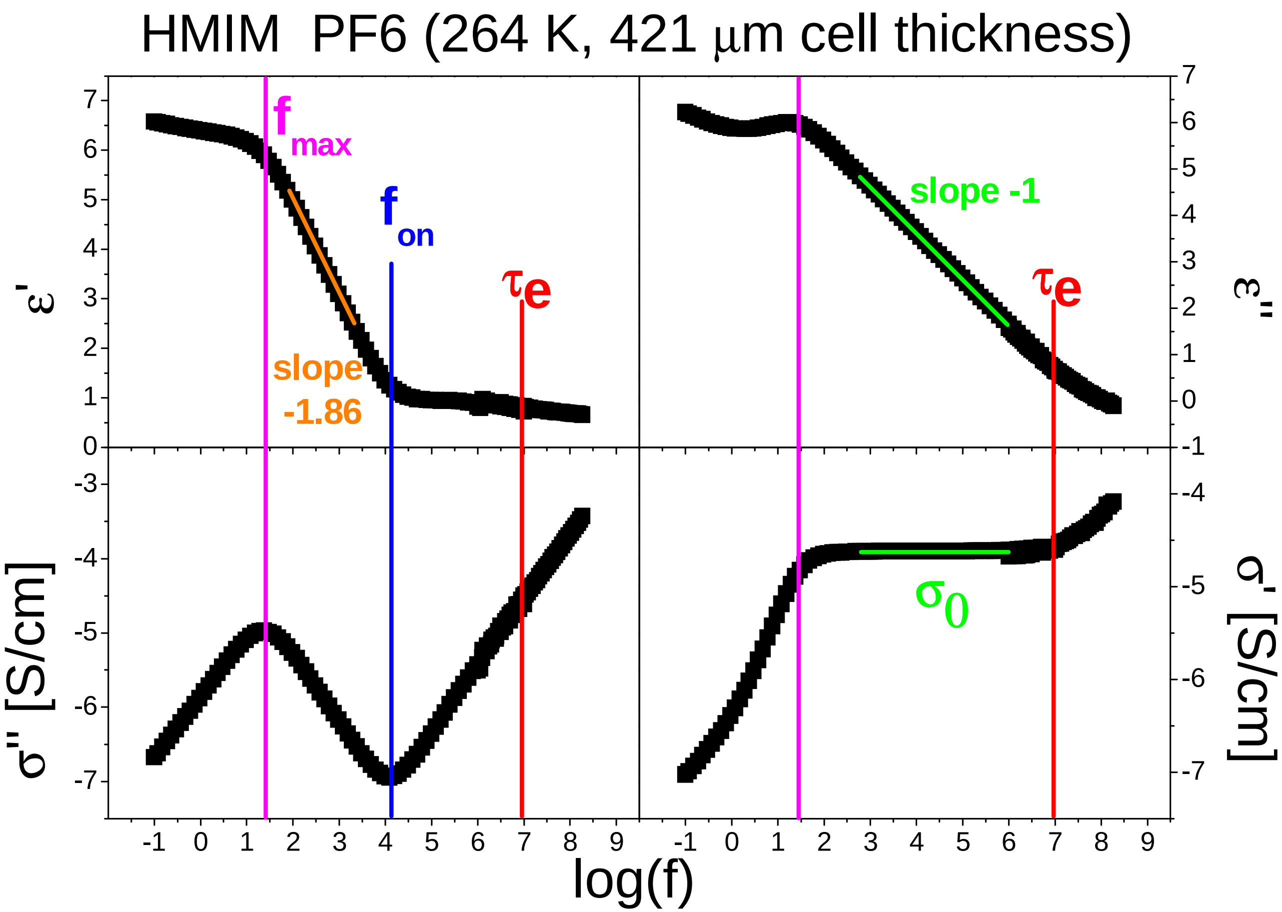
τ_e: hoping time

σ_0: DC conductivity

f_{on}: onset of electrode polarization

slope of –1.86 in ε´ for $f < f_{on}$

Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

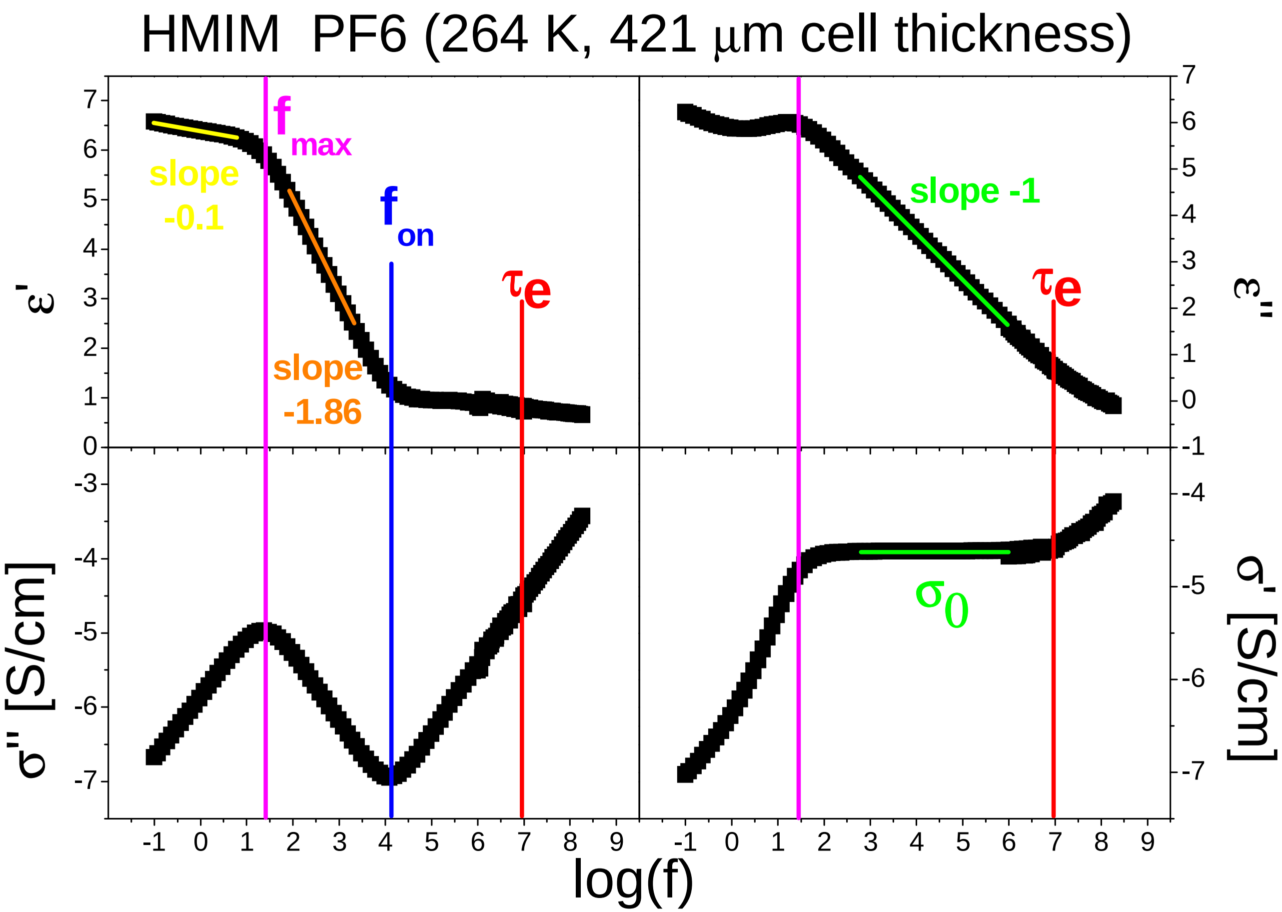
σ_0: DC conductivity

f_{on}: onset of electrode polarization

slope of –1.86 in ε´ for $f < f_{on}$

f_{max}: full development of electrode polarization

Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

σ_0: DC conductivity

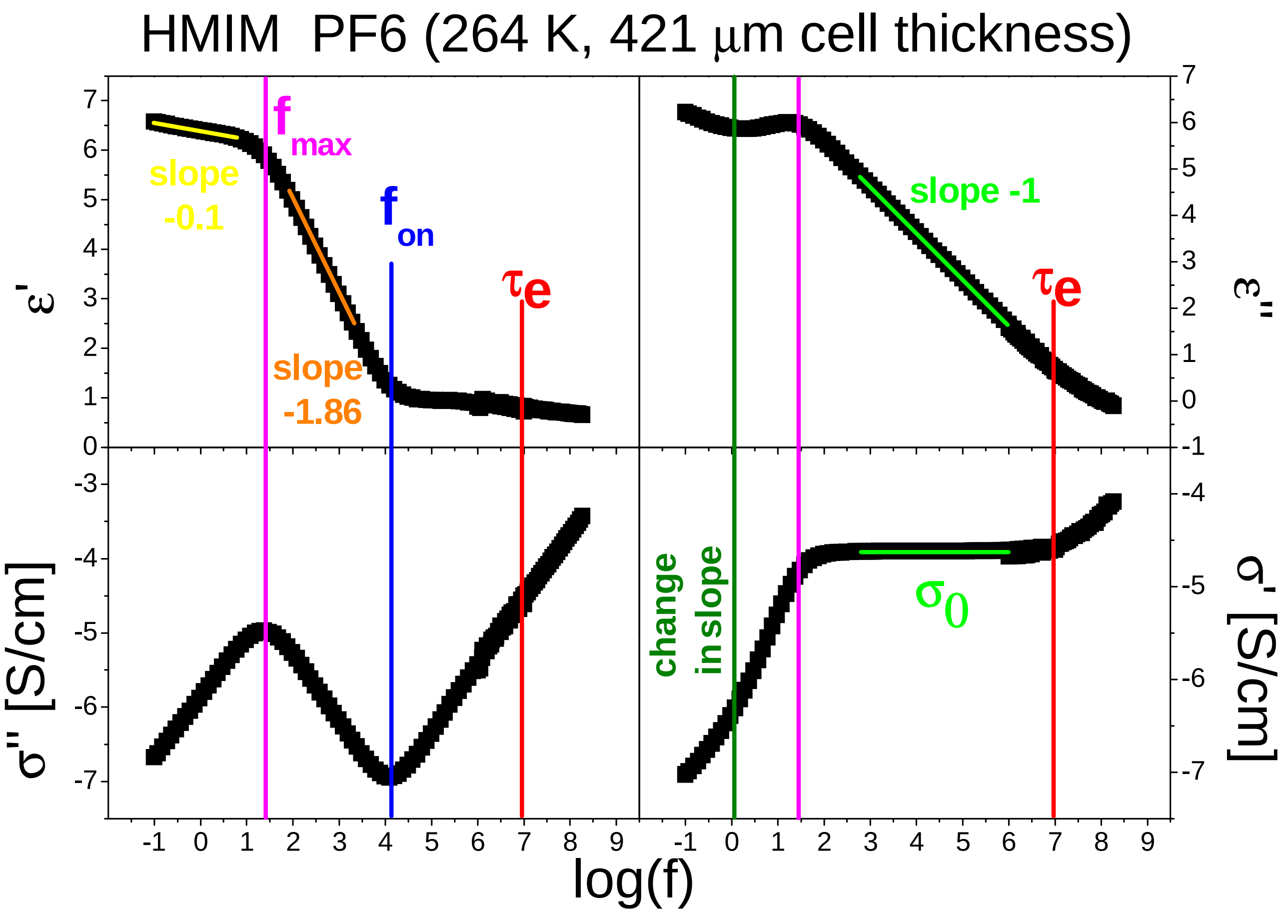
f_{on}: onset of electrode polarization

slope of –1.86 in ε´ for $f < f_{on}$

f_{max}: full development of electrode polarization

slope of –0.1 in ε´ for $f < f_{max}$

Experimental features of EP in ILs - frequency dependence



τ_e: hoping time

σ_0: DC conductivity

f_{on}: onset of electrode polarization

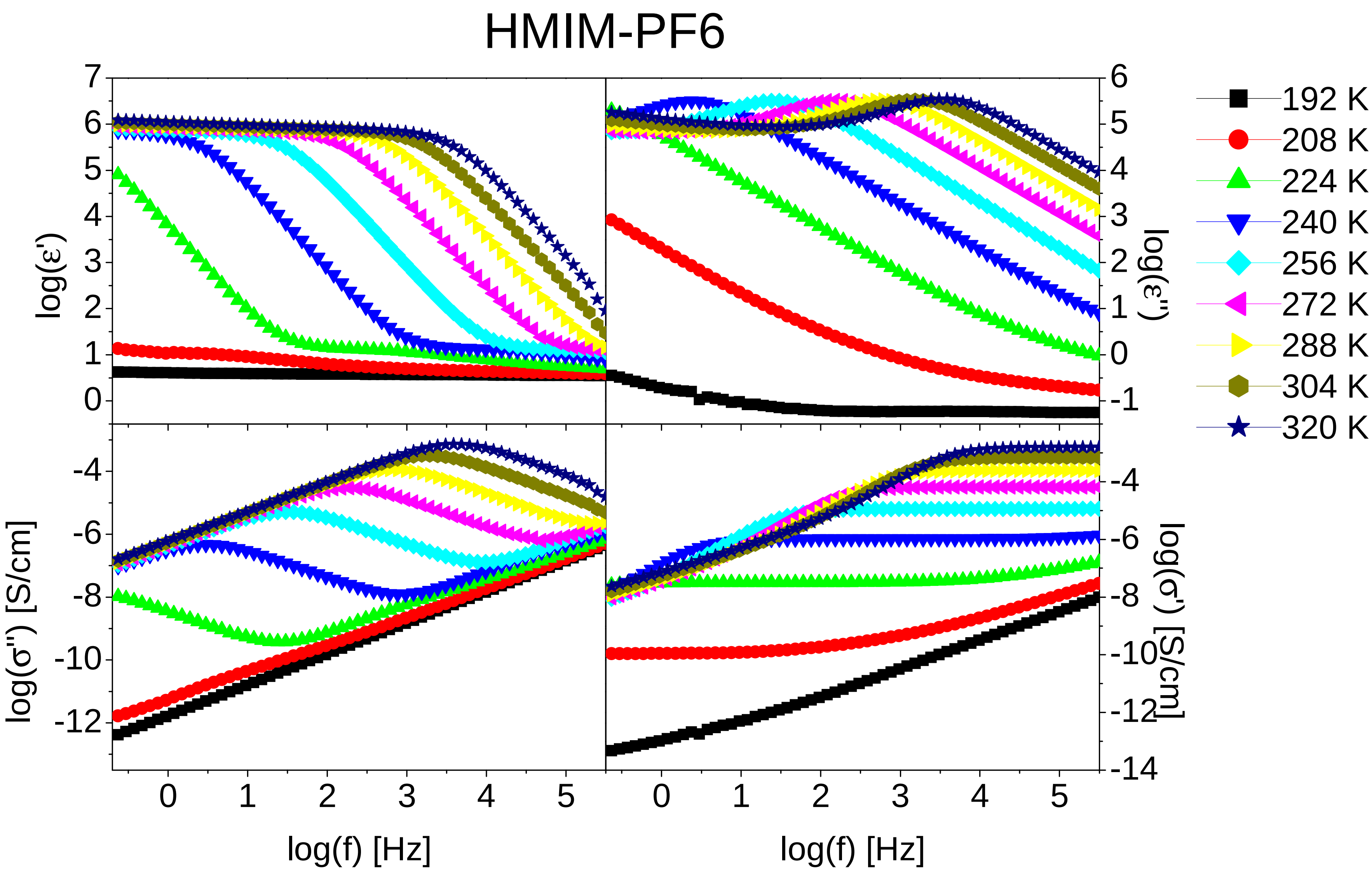
slope of –1.86 in ε´ for $f < f_{on}$

f_{max}: full development of electrode polarization

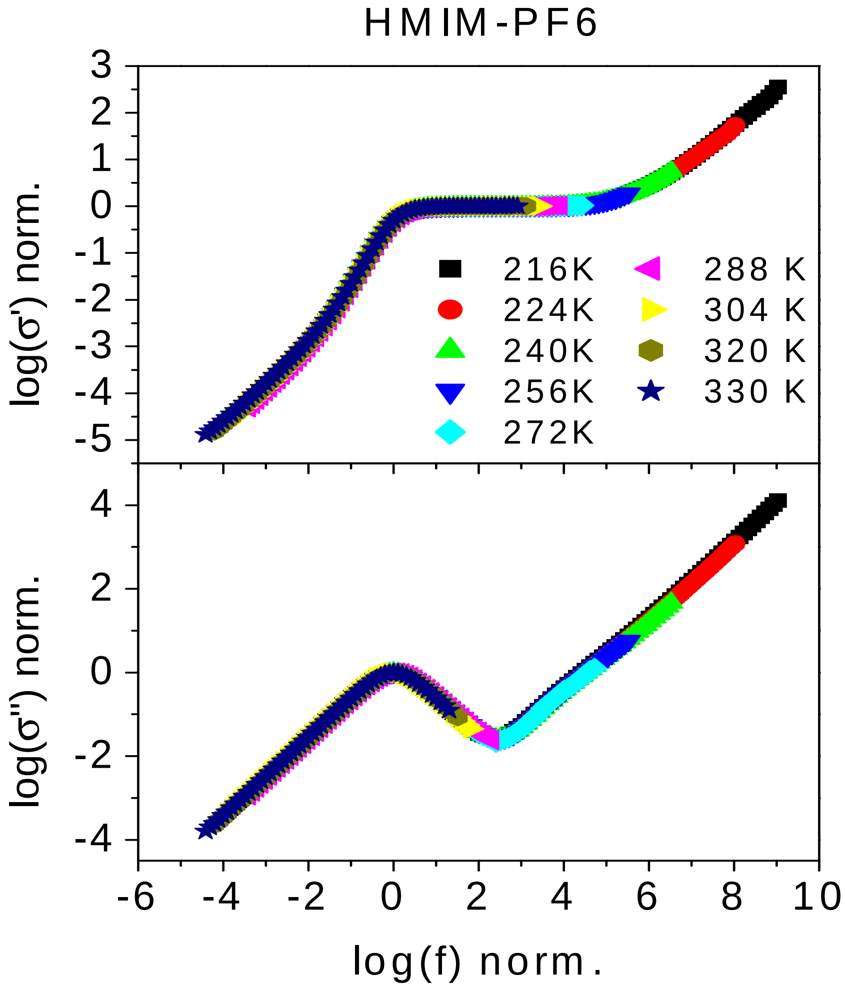
slope of –0.1 in ε´ for $f < f_{max}$

change in slope of σ´ for $f < f_{max}$

Dielectric spectra of ionic liquids
- temperature dependence (experiment) -

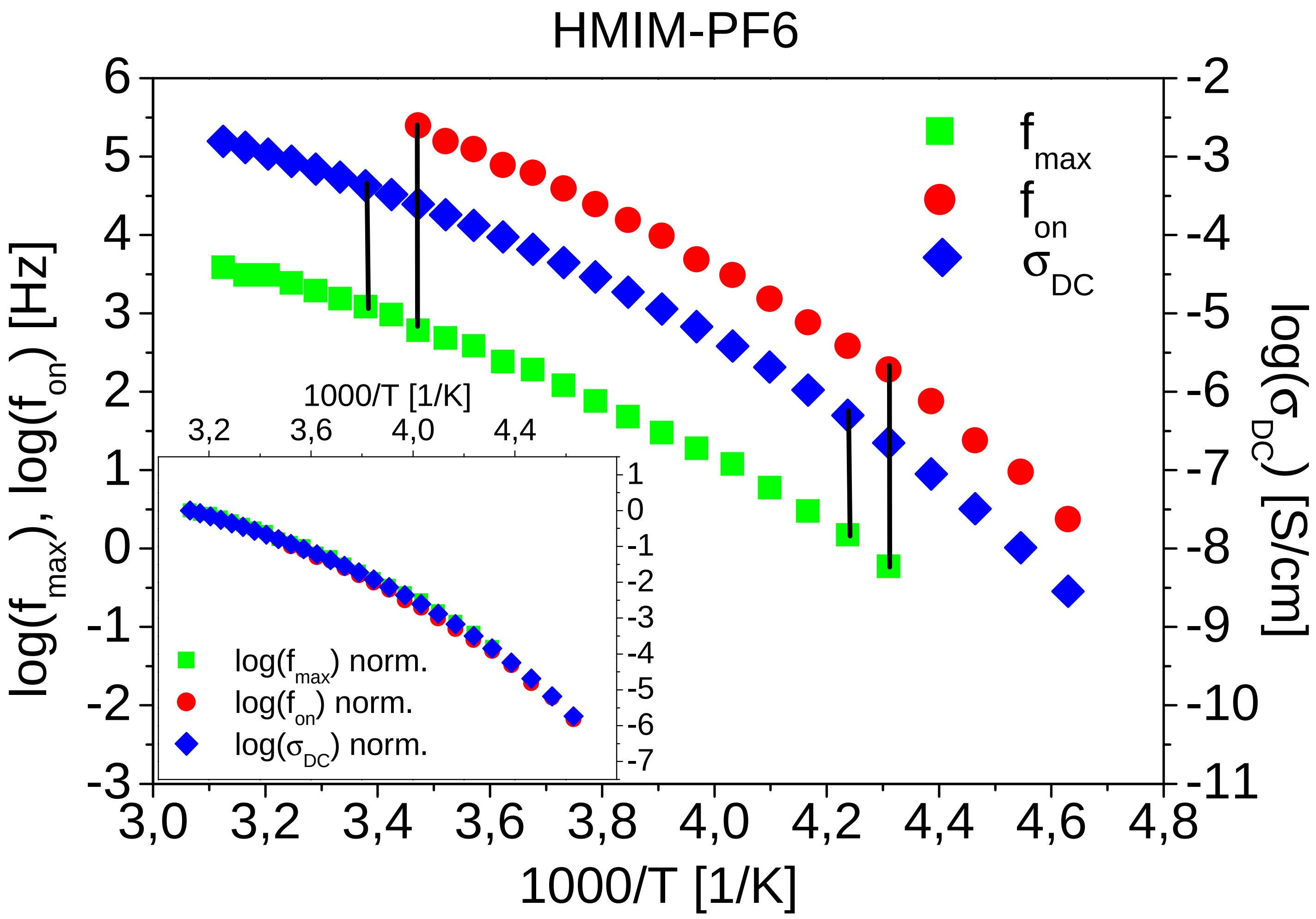


Dielectric spectra of ionic liquids
- temperature dependence (experiment) -



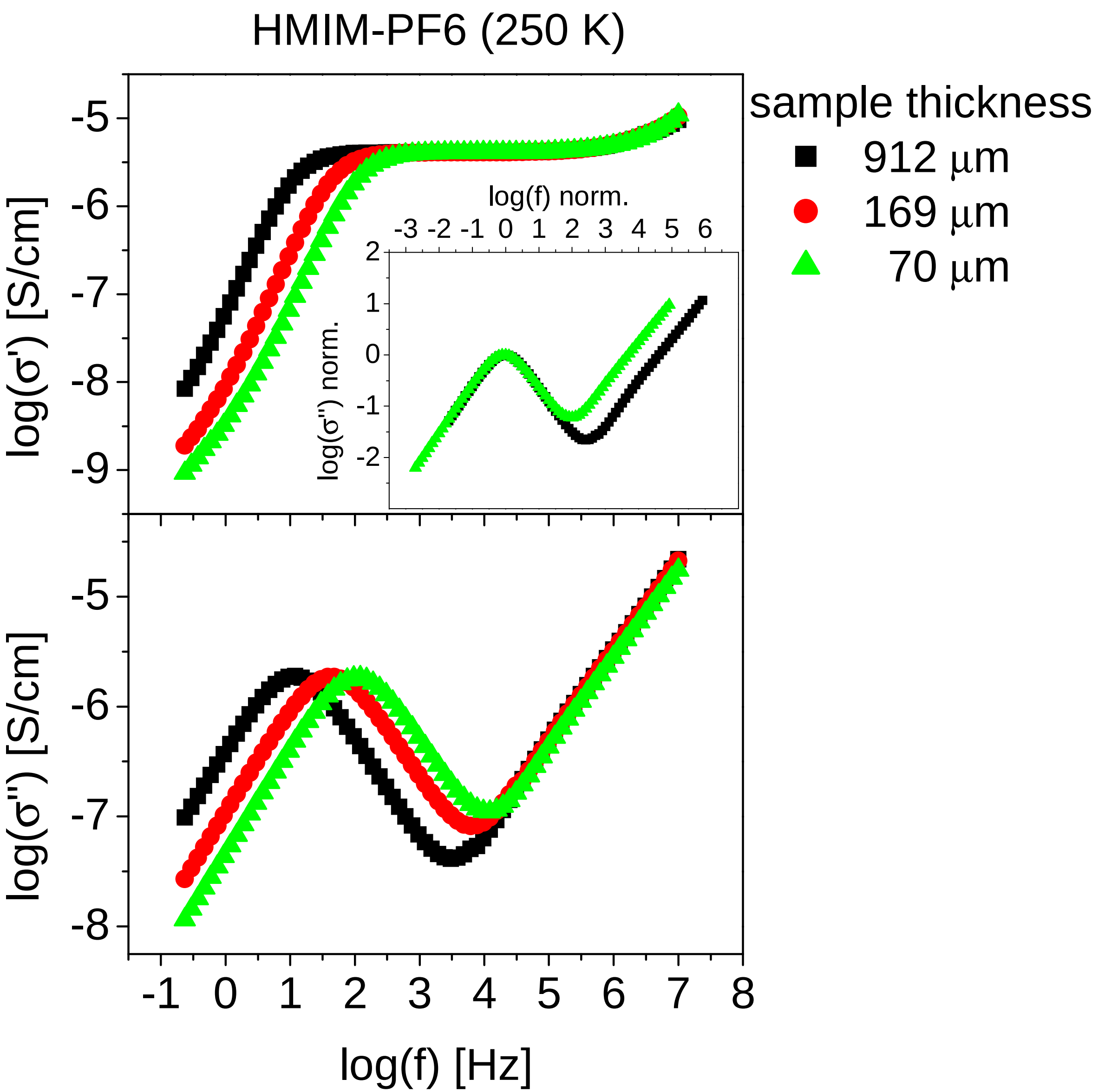
perfect scaling with temperature over many orders of magnitude in time

Dielectric spectra of ionic liquids
- temperature dependence (experiment) -

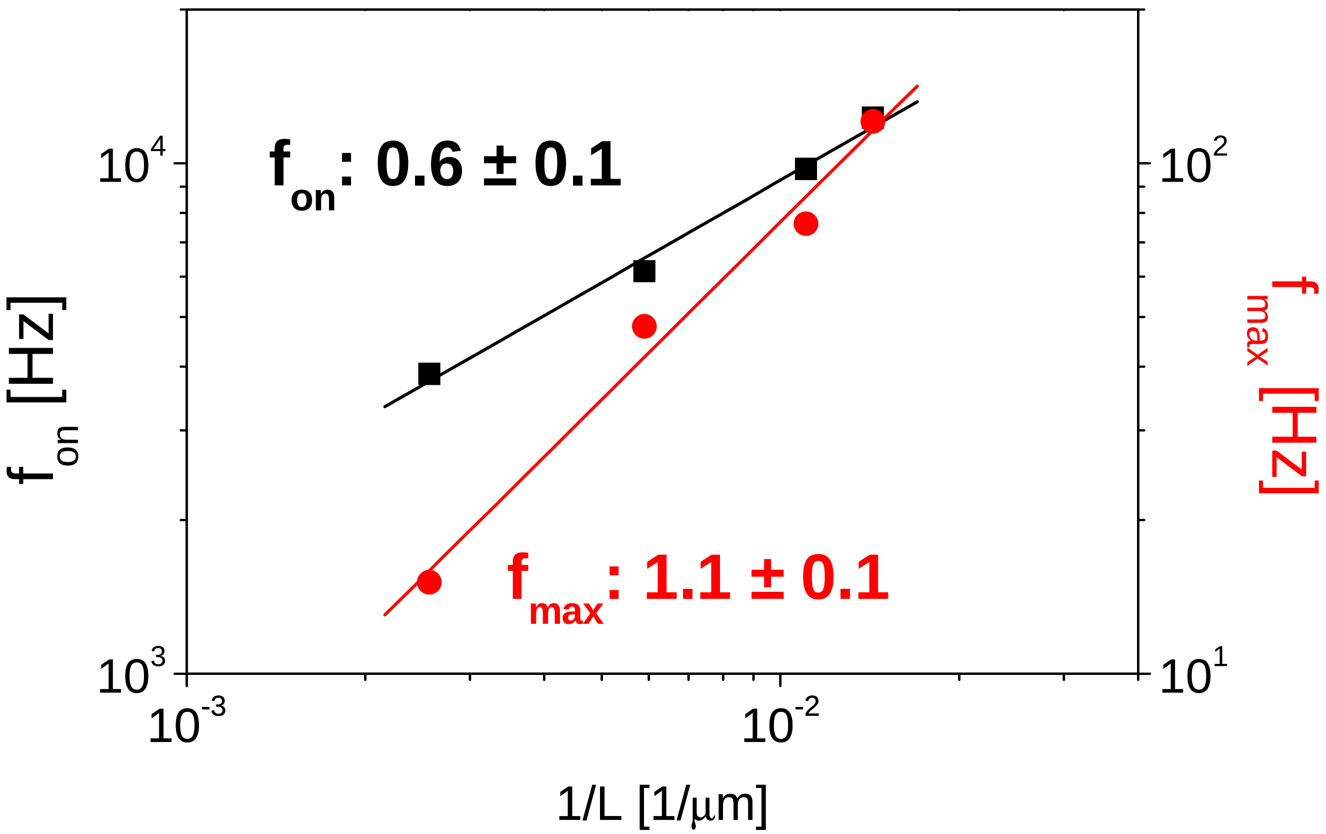


f_{max}, f_{on} and σ_{DC} scale similarly with temperature

Dielectric spectra of ionic liquids- dependence on the length of the sample cell (experiment) -

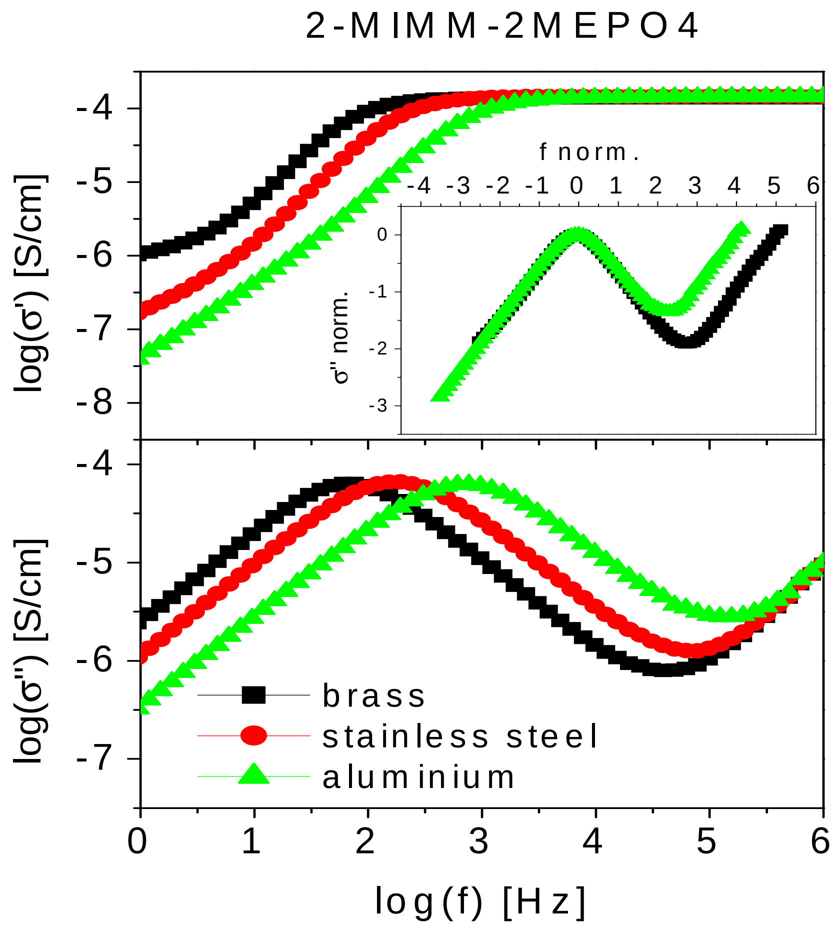


Dielectric spectra of ionic liquids- dependence on the length of the sample cell (experiment) -



No scaling of f_{on} and f_{max} with respect to 1/L !

Dielectric spectra of ionic liquids – effect of the electrode material (experiment) -



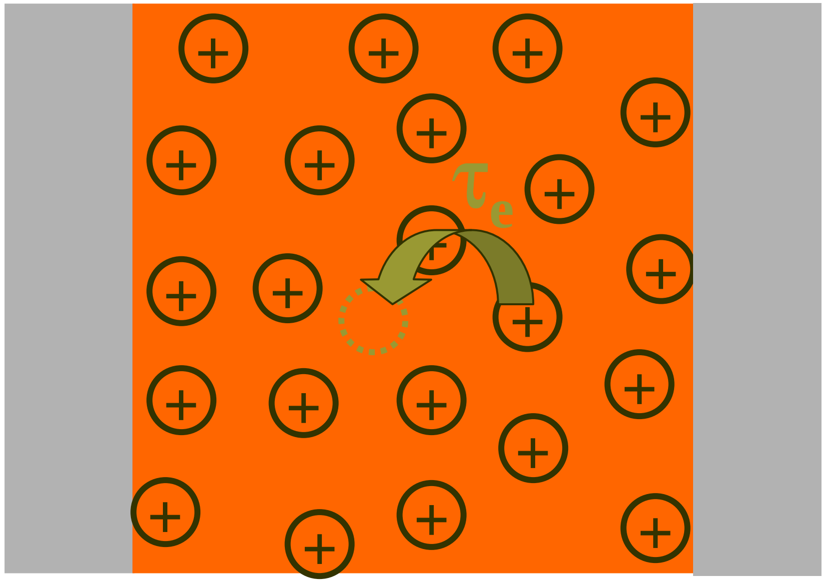
Pronounced effect of electrode material !

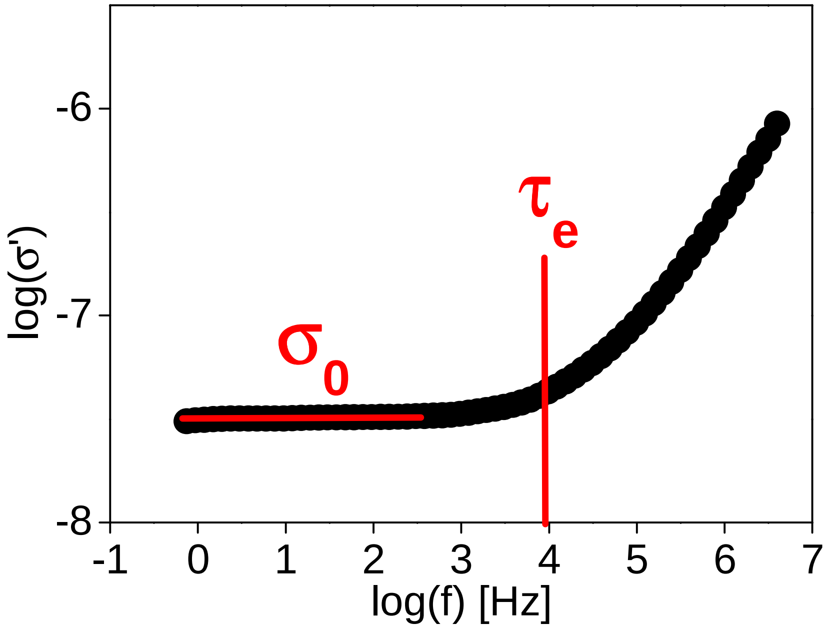
Experimental features of EP in ILs:

1. **EP shows a complex dependence on frequency, temperature, concentration, sample length, material of the electrodes.**
2. **EP does *not* depend – below a certain (low) treshold, i.e. 10 V/cm – on the applied electric field.**
3. **EP does *not* depend on the roughness of the electrodes, as long as: roughness << sample thickness**
4. **Over many decades in frequency, scaling with respect to variation of temperature and concentration**
5. ***No* scaling with respect to variation of the length of the sample cell and material of the electrodes.**

What is the microscopic mechanism of EP ?

Charge transport in the bulk



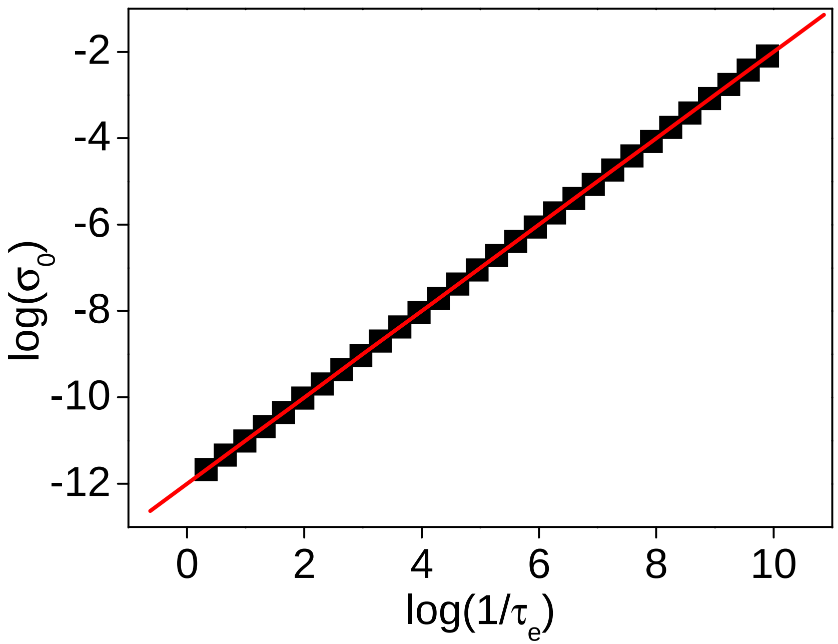


1. hoping time in bulk:

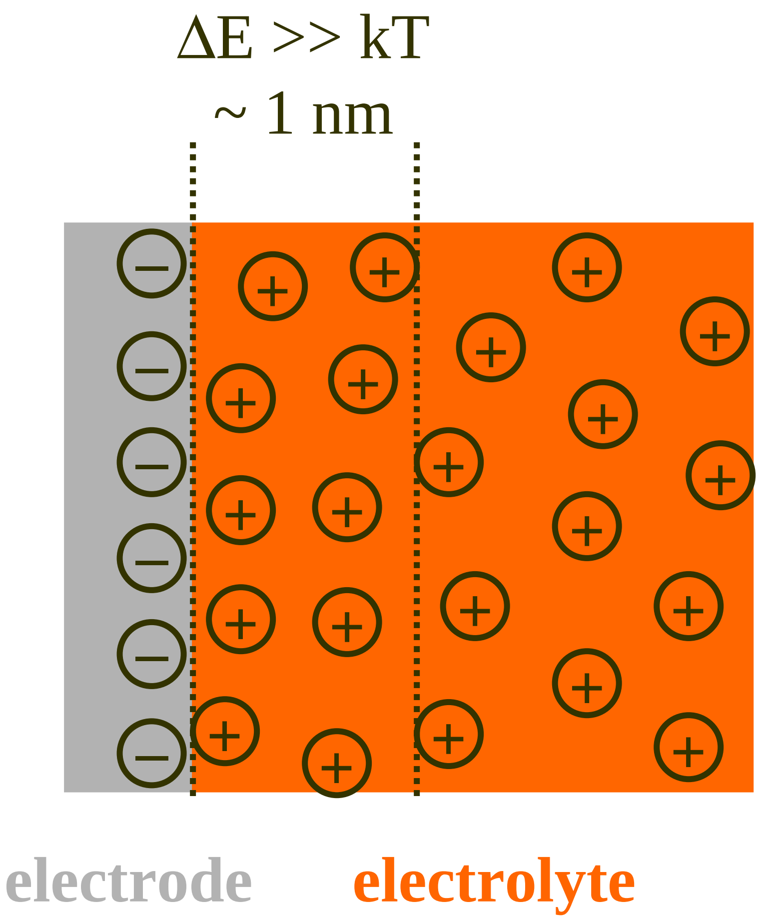
$$\tau_e = \tau_0 \exp\left(\frac{E}{kT}\right)$$

2. BNN-relation:

$$\sigma_0 \sim \frac{1}{\tau_e}$$



Charge transport at interfaces



Due to the coulombic interactions increase by many orders of magnitude in the hoping time at the interface.

hoping time at the interface:

$$E_{\mathrm{i}} \cong E_{\mathrm{b}} + \Delta E$$

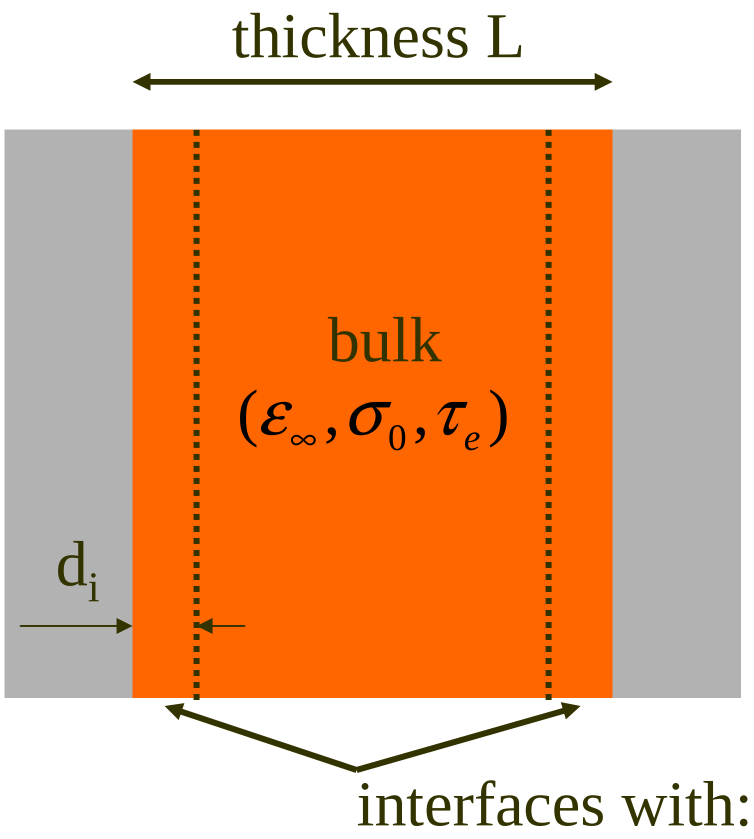
$$\frac{\tau_e(\text{interface})}{\tau_e(\text{bulk})} \approx \exp\left(\frac{\Delta E}{kT}\right) >> 1$$

Since: $\sigma_0 \sim \dfrac{1}{\tau_e}$ **(BNN relation)**

this implies:

$$\sigma_0(\text{interface}) << \sigma_0(\text{bulk})$$

Microscopic model of sample cell



$$\frac{\tau_e(\text{interface})}{\tau_e(\text{bulk})} \approx \frac{\sigma_0(\text{bulk})}{\sigma_0(\text{interface})} >> 1$$

$$\frac{L}{\varepsilon^*_{meas}} = \frac{2d_\mathrm{i}}{\varepsilon^*_\mathrm{i}} + \frac{L-2d_\mathrm{i}}{\varepsilon^*_\mathrm{b}}$$

$$\varepsilon^*_\mathrm{b} = f\left(\varepsilon_\infty, \sigma_0^\mathrm{bulk}, \tau_0^\mathrm{bulk}\right)$$

$$\varepsilon^*_\mathrm{i} = f\left(\varepsilon_\infty, \sigma_0^\mathrm{i}, \tau_0^\mathrm{i}\right)$$

Electrode polarization

$$\frac{L}{\varepsilon^*_{meas}} = \frac{2d_\mathrm{i}}{\varepsilon^*_\mathrm{i}} + \frac{L-2d_\mathrm{i}}{\varepsilon^*_\mathrm{b}}$$

$$\varepsilon'_\mathrm{meas} = (x+1)\left((\varepsilon'_\mathrm{b})^2 + (\varepsilon''_\mathrm{b})^2\right)\frac{x\varepsilon'_\mathrm{b} + y\varepsilon'_\mathrm{i}}{(x\varepsilon'_\mathrm{b} + y\varepsilon'_\mathrm{i})^2 + (x\varepsilon''_\mathrm{b} + y\varepsilon''_\mathrm{i})^2}$$

$$\varepsilon''_\mathrm{meas} = (x+1)\left((\varepsilon'_\mathrm{b})^2 + (\varepsilon''_\mathrm{b})^2\right)\frac{x\varepsilon''_\mathrm{b} + y\varepsilon''_\mathrm{i}}{(x\varepsilon'_\mathrm{b} + y\varepsilon'_\mathrm{i})^2 + (x\varepsilon''_\mathrm{b} + y\varepsilon''_\mathrm{i})^2}$$

where: $x = \frac{L-2d_\mathrm{i}}{2d_\mathrm{i}}$ $\quad y = \frac{(\varepsilon'_\mathrm{b})^2 + (\varepsilon''_\mathrm{b})^2}{(\varepsilon'_\mathrm{i})^2 + (\varepsilon''_\mathrm{i})^2}$

with

$\varepsilon^* = \frac{\sigma^*}{i\varepsilon_0\omega}$ and $\sigma^*(\omega) = \sigma_0\left[\frac{i\omega\tau_e}{\ln(1+i\omega\tau_e)}\right]$ Dyre functions

EP - consequences of the model

$$\frac{d}{d\omega}\left(\sigma''_{meas}\right)=0 \quad \Rightarrow$$

$$f_{on} \cong \frac{\sigma_0}{\varepsilon_0}\frac{1}{\sqrt{\varepsilon'_b \varepsilon'_i}}\sqrt{\frac{2d_i}{L}}$$

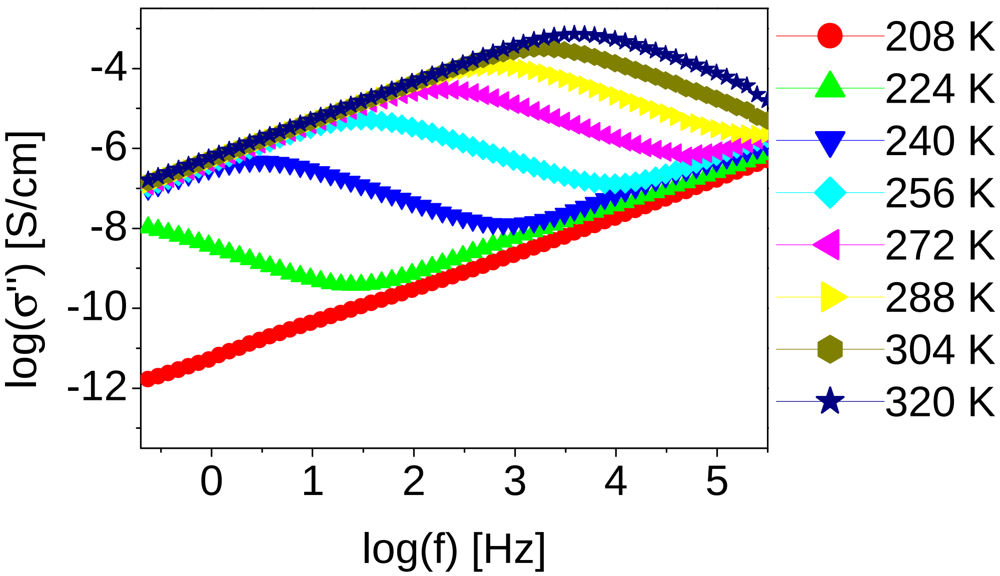
$$f_{max} \cong \frac{\sigma_0}{\varepsilon_0}\frac{1}{2\pi\varepsilon'_i}\frac{2d_i}{L}$$

Consequences:

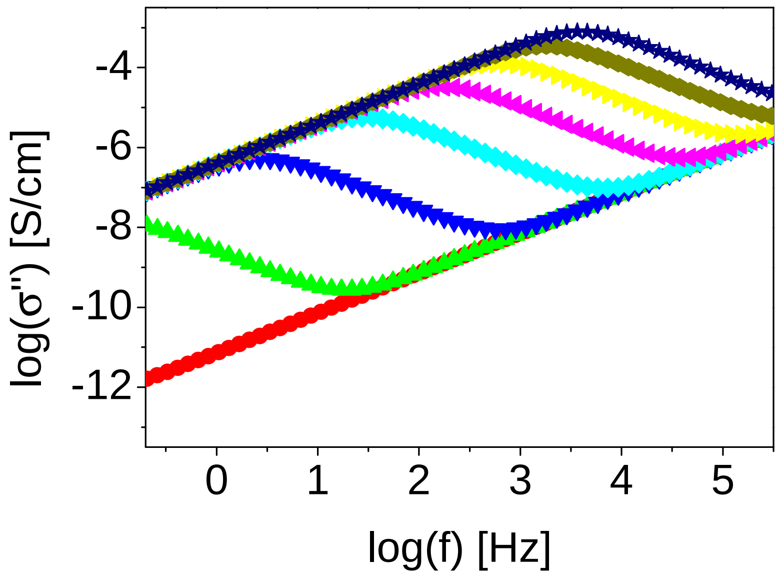
1. $f_{on} \sim f_{max} \sim \sigma_0$
2. $f_{on} \sim \frac{1}{\sqrt{L}}$, while $f_{max} \sim \frac{1}{L}$
3. $f_{on} \sim \sqrt{d_i}$, while $f_{max} \sim d_i$
4. $f=f_{max}$ solution for both $\frac{d\left(\sigma''_{meas}\right)}{d\omega}=0$ and $\frac{d\left(\varepsilon''_{meas}\right)}{d\omega}=0$
5. $\sigma_0 = 2\pi\varepsilon_0\varepsilon_S \frac{\left(f_{on}\right)^2}{f_{max}}$

Comparison of experiment and calculations - dielectric spectra of ionic liquids

experiment



calculations



Comparison of experiment and calculations - dielectric spectra of ionic liquids

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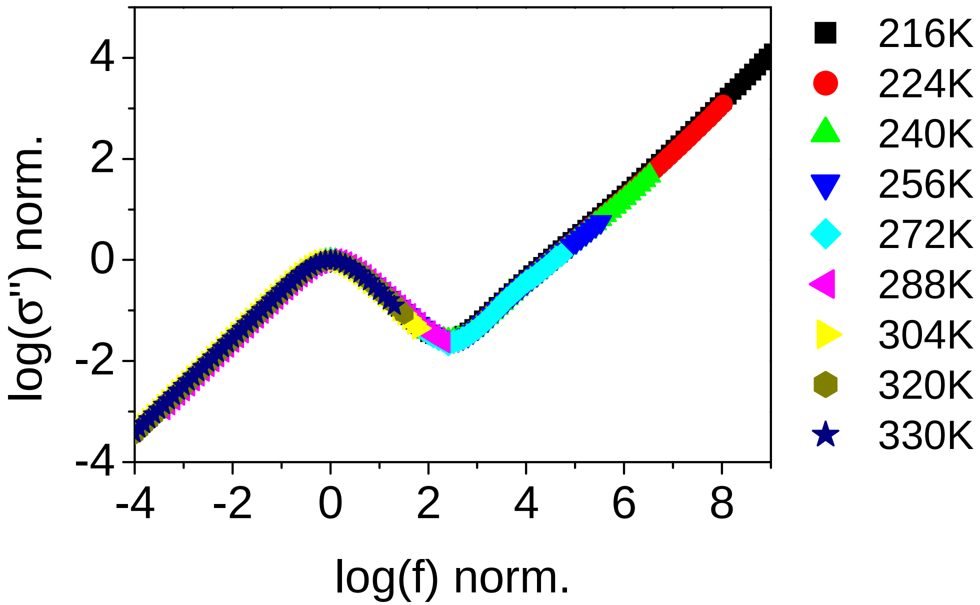
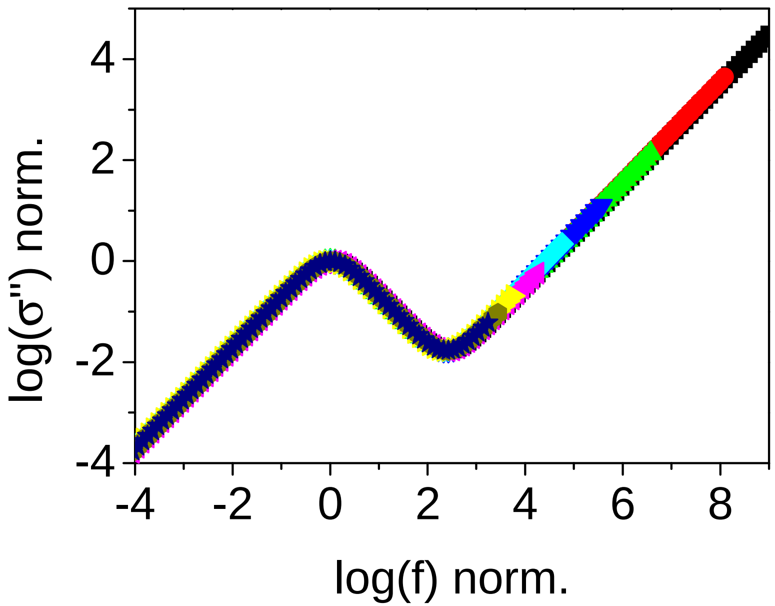
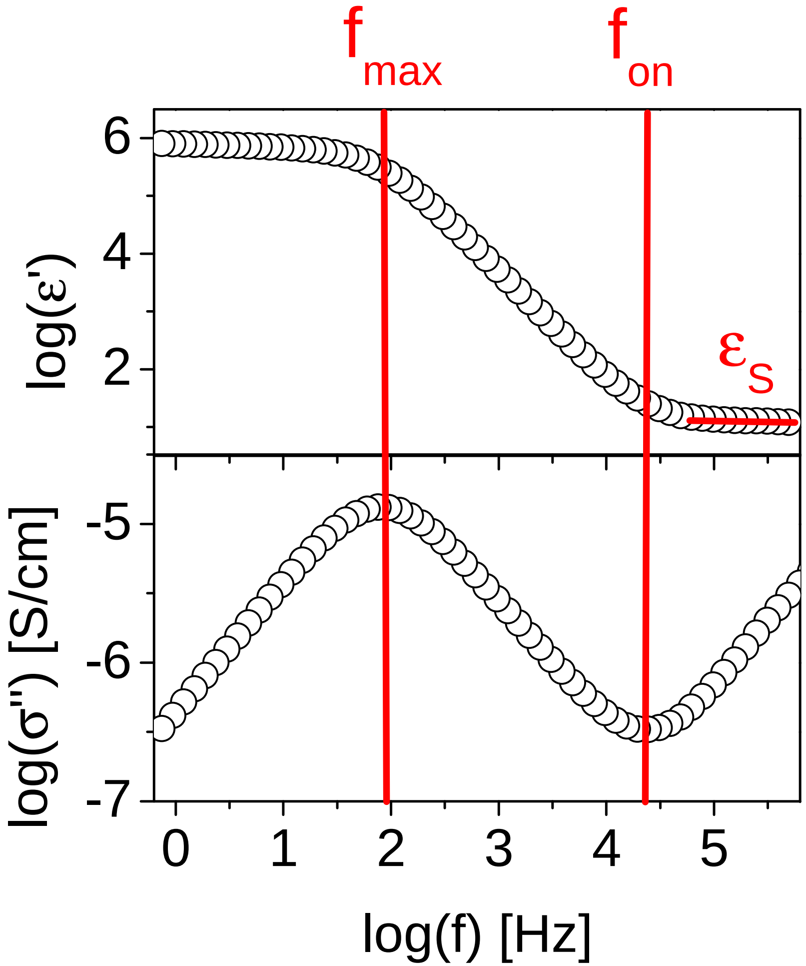


calculations



What information can be deduced from EP – a novel formula.



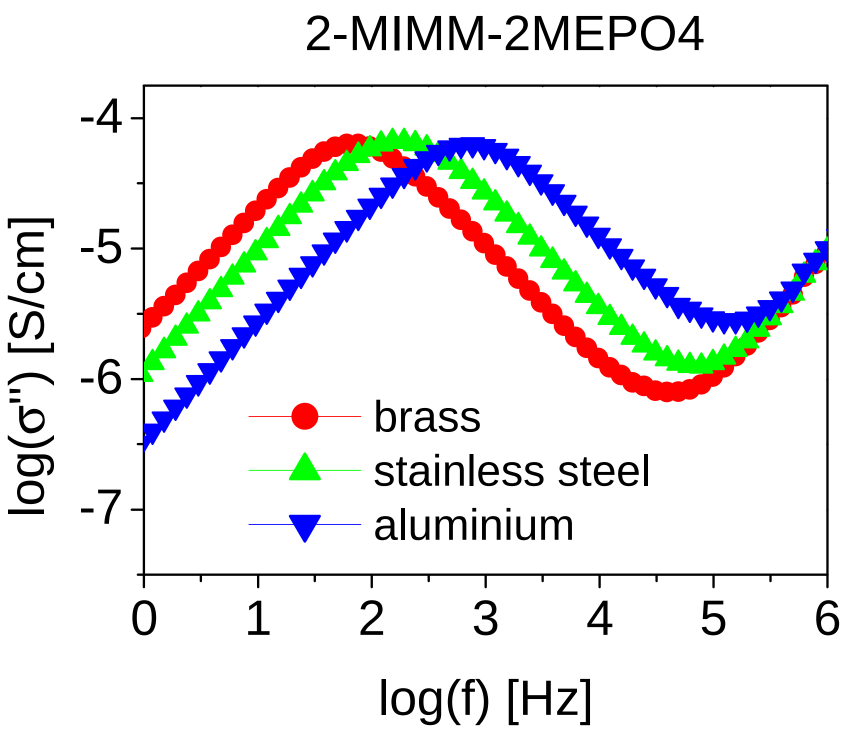
$$\sigma_0 = ?$$

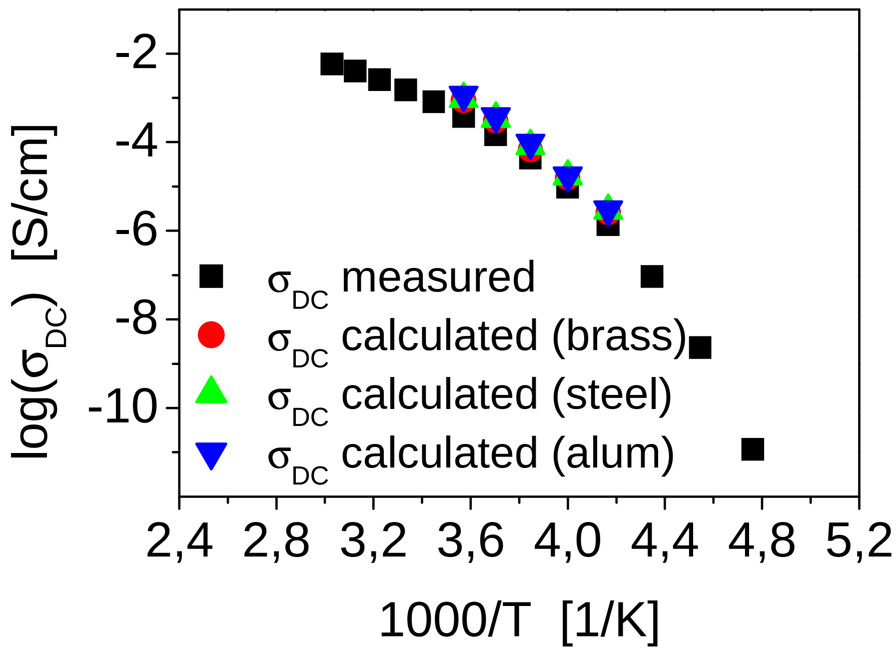
$$\sigma_0 = 2\pi\varepsilon_0\varepsilon_S \frac{\left(f_{on}\right)^2}{f_{max}}$$

Anatoli Serghei et al.

Test of the validity of the novel formula

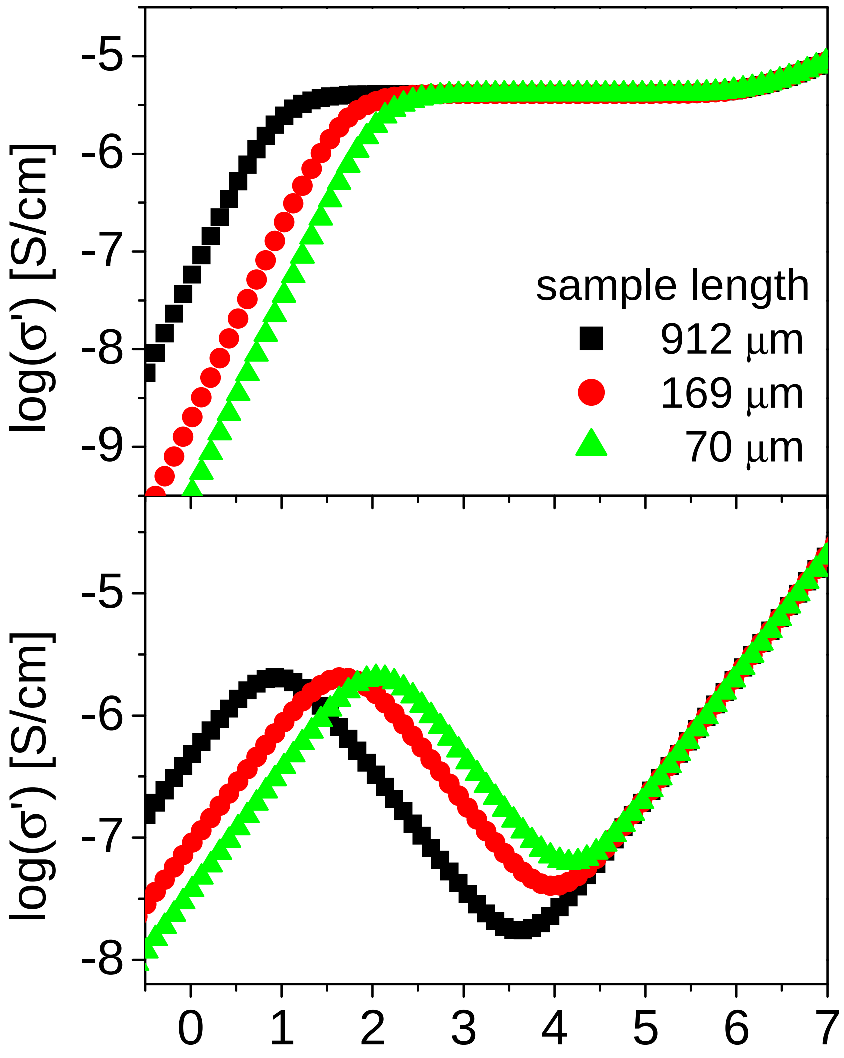
$$\sigma_0 = 2\pi\varepsilon_0\varepsilon_S \frac{(f_{on})^2}{f_{max}}$$



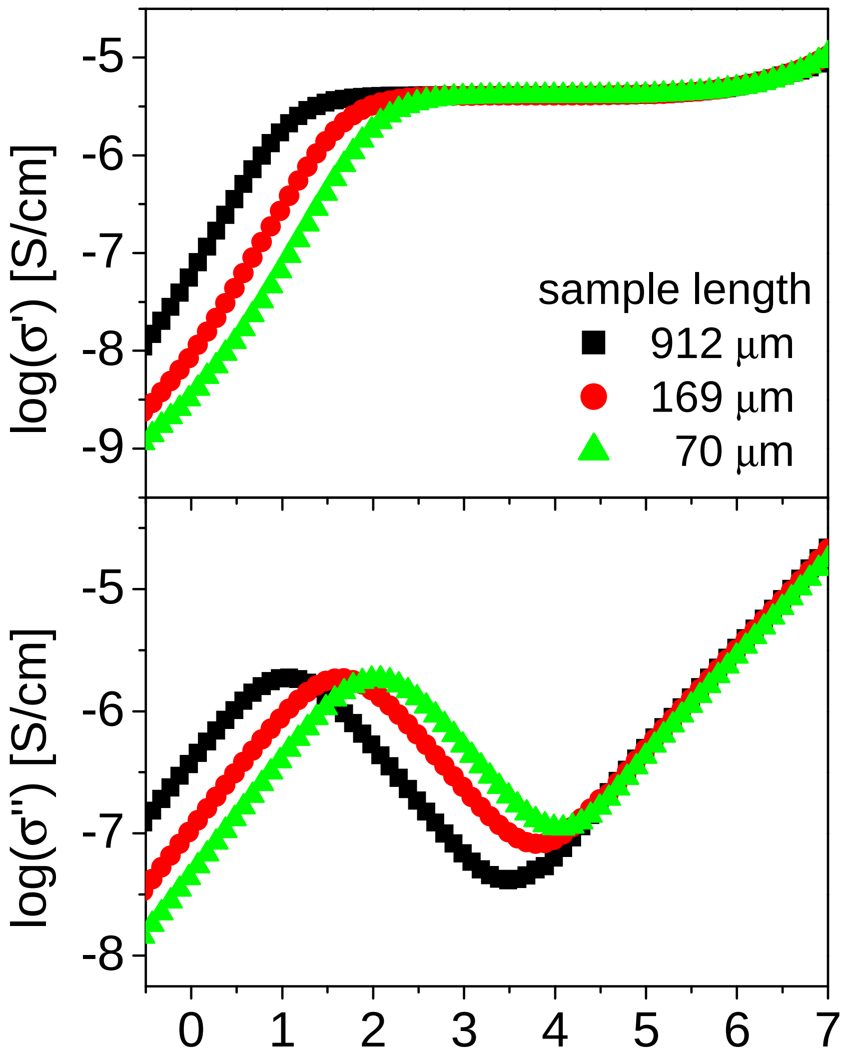


Dielectric spectra of ionic liquids - length dependence (2MIMM-2MePO4, experiment and calculations) -

Calculations

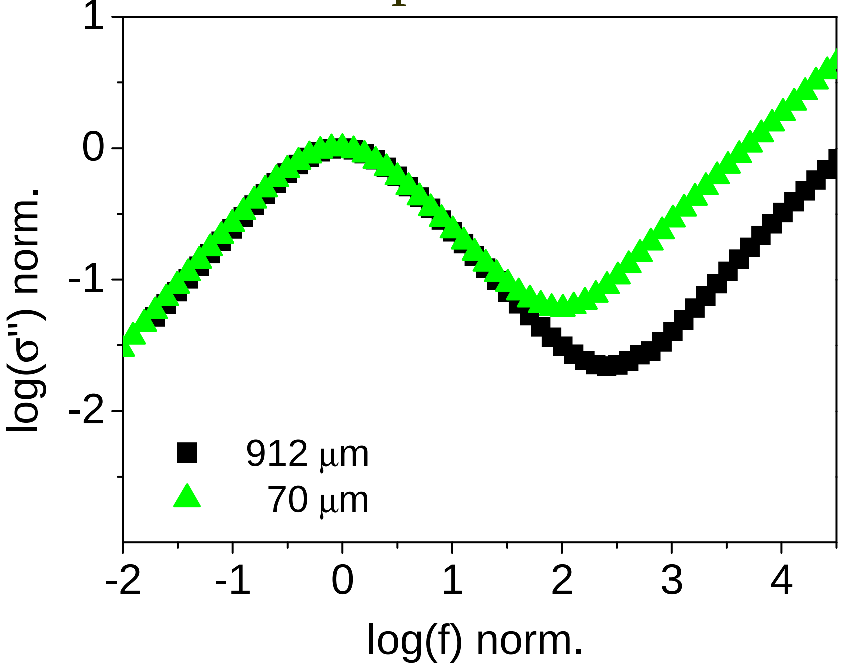


experiment

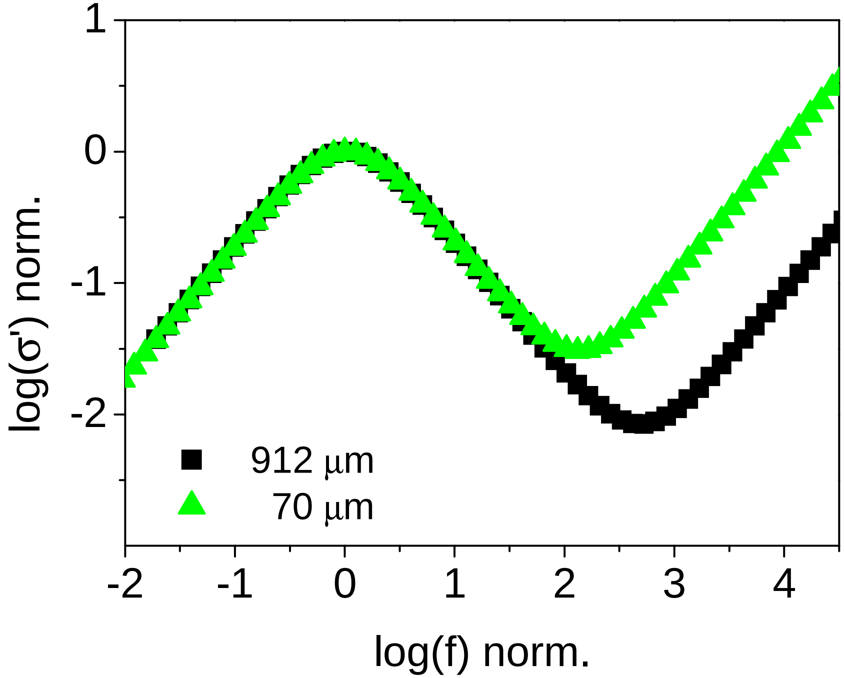


Dielectric spectra of ionic liquids
- length dependence, scaling -

experiment



calculations

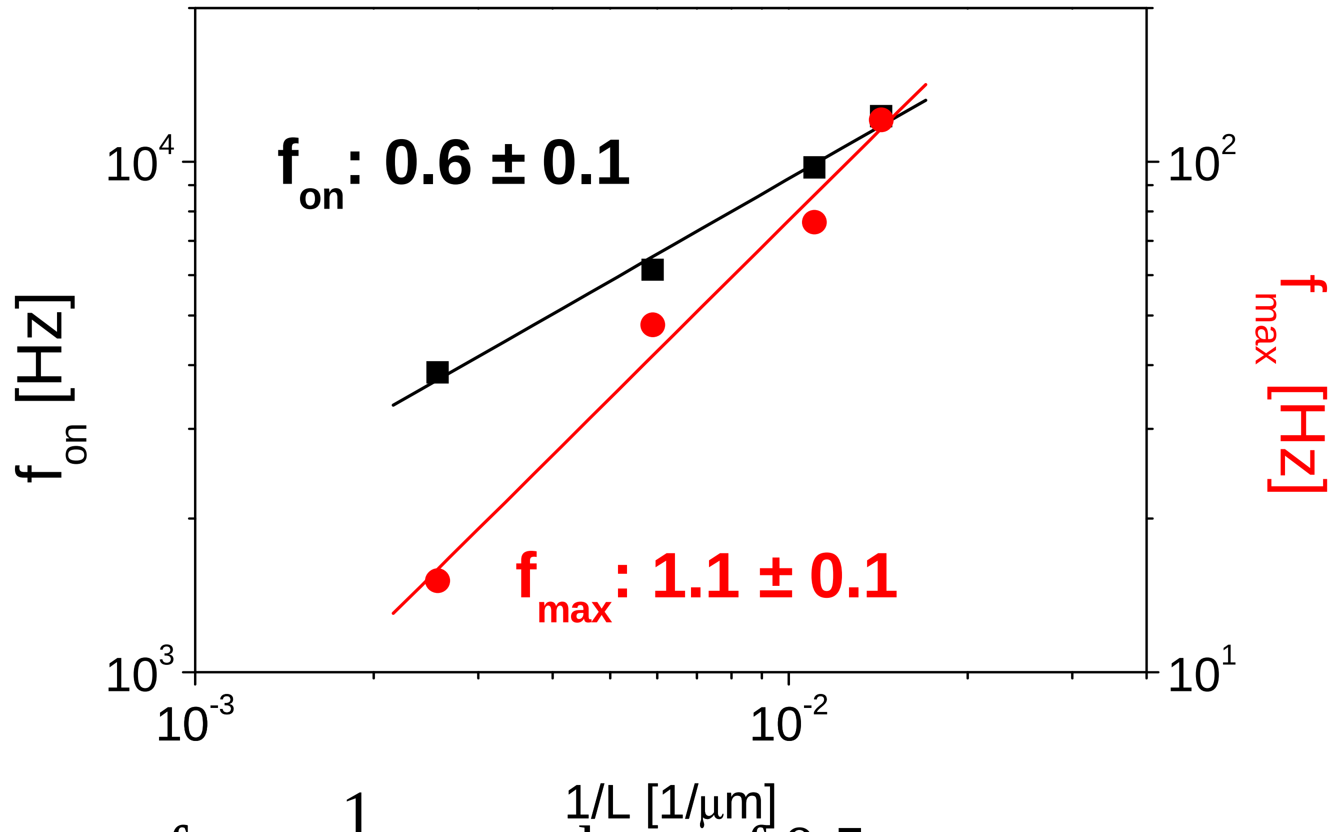


$$\frac{d}{d\omega}\left(\sigma''_{meas}\right)=0 \Rightarrow f_{on} \cong \frac{\sigma_0}{\varepsilon_0}\frac{1}{\sqrt{\varepsilon'_b\varepsilon'_i}}\sqrt{\frac{2d_i}{L}} \text{ and } f_{max} \cong \frac{\sigma_0}{\varepsilon_0}\frac{1}{2\pi\varepsilon'_i}\frac{2d_i}{L}$$

$$f_{on} \sim \frac{1}{\sqrt{L}}, \text{ while } f_{max} \sim \frac{1}{L}$$

Dielectric spectra of ionic liquids
- length dependence, scaling -

experiment



$$f_{on} \sim \frac{1}{\sqrt{L}} \Rightarrow \text{slope of } 0.5$$

$$f_{max} \sim \frac{1}{L} \Rightarrow \text{slope of } 1.0$$

Summary

$\omega \to 0$

$\left|Z_i^*\right| >> \left|Z_b^*\right|$

$f = f_{max}$

$\left|Z_i^*\right| = \left|Z_b^*\right|$

$f = f_{on}$

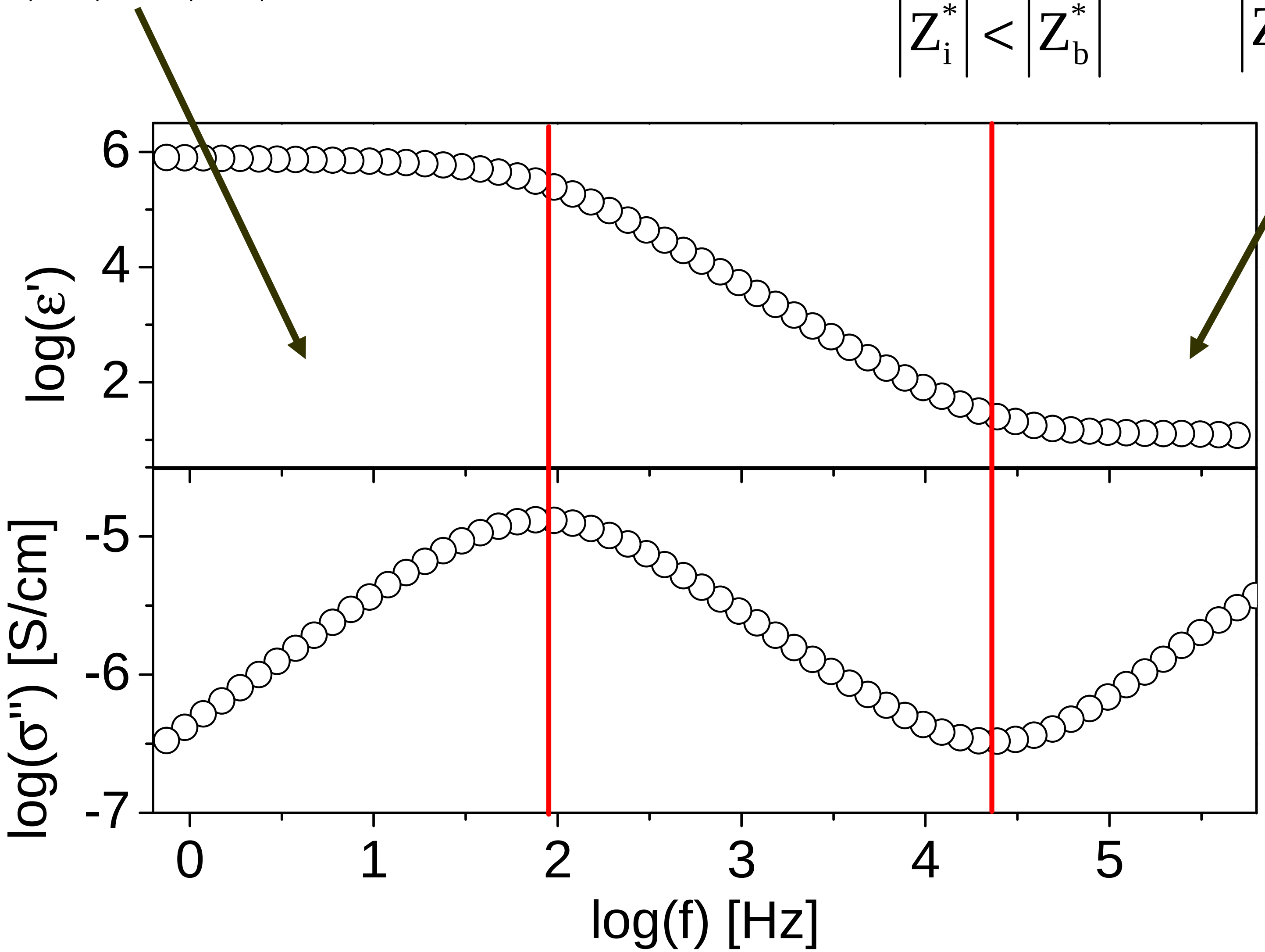
$Z_i'' = Z_b''$

$\left|Z_i^*\right| < \left|Z_b^*\right|$

$\omega \to \infty$

$Z_i'' << Z_b''$

$\left|Z_i^*\right| << \left|Z_b^*\right|$



Summary for EP

1. **What is the *signature* of electrode polarisation (EP) and how can it be analysed *quantitatively*?**
   EP has a peculiar signature in the complex dielectric function and conductivity but as well the length of the sample cell.
2. **What *quantitative* information can be deduced from fits of the EP?**
   With a novel formula discovered by A. Serghei σ_0 can be deduced from f_{min} and f_{max} of $\sigma''(f)$.
3. **What is the *quantitative* model to describe EP?**
   A model adding the complex impedances at the interface and in the bulk.
4. **What information can be deduced from EP?**
   A detailed understanding of the geometry and the complex dielectric function of the interphase is in reach.

Thanks to

...DFG for finacial support and you for attention