Physical mechanisms in the spectral range of Broadband Dielectric Spectroscopy -

dielectric relaxation, (ionic) charge transport and electrode polarisation

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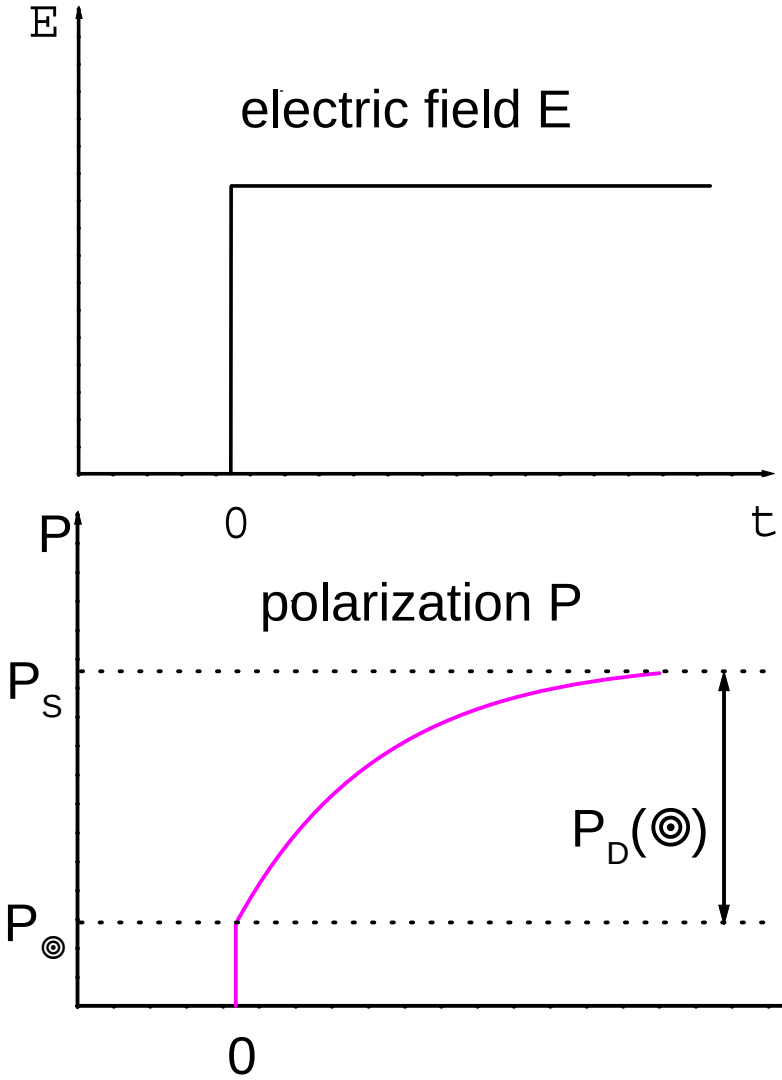
1. **Dielectric relaxation**

2. **(ionic) charge transport**

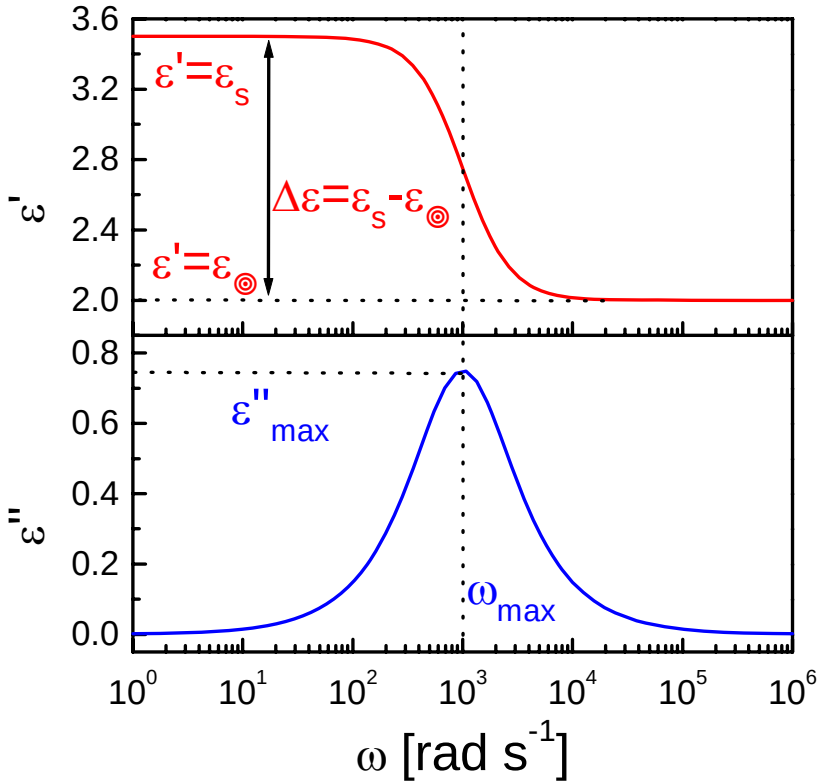
3. **Electrode polarisation**

(in all the following considerations a homogeneous system is assumed)

Dielectric spectroscopy



Debye relaxation $\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)}$



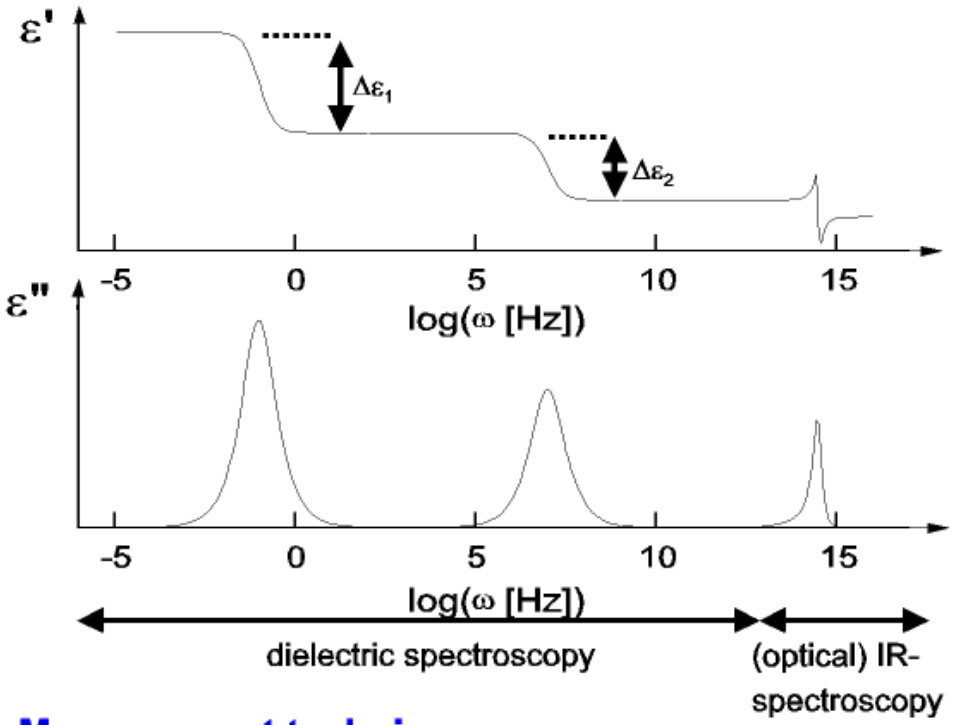
complex dielectric function $\epsilon^*(\omega, T)$

$$P(\omega, T) = (\epsilon^*(\omega, T) - 1)\, E(\omega)$$

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\ \tau)^2}$$

$$\varepsilon''(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\ \tau)^2}\omega\ \tau$$

Broadband dielectric measurement techniques



Dual-phase lock-in amplifier (SR 830) (10^{-3}Hz - 10^{5}Hz)

Impedance analyser (HP 4284 A) (20 Hz - 10^{6}Hz)

Frequency-response-analyser (SI 1260) 10^{-4}Hz - 10^{7}Hz)

Coaxial line reflectometer (HP 4291 A) (10^{6}Hz - 10^{9}Hz)

(Sample amount required <5mg)

Measurement techniques:

Time-domain spectrometer

Frequency response analyser

AC-bridges

Coaxial line reflectometer

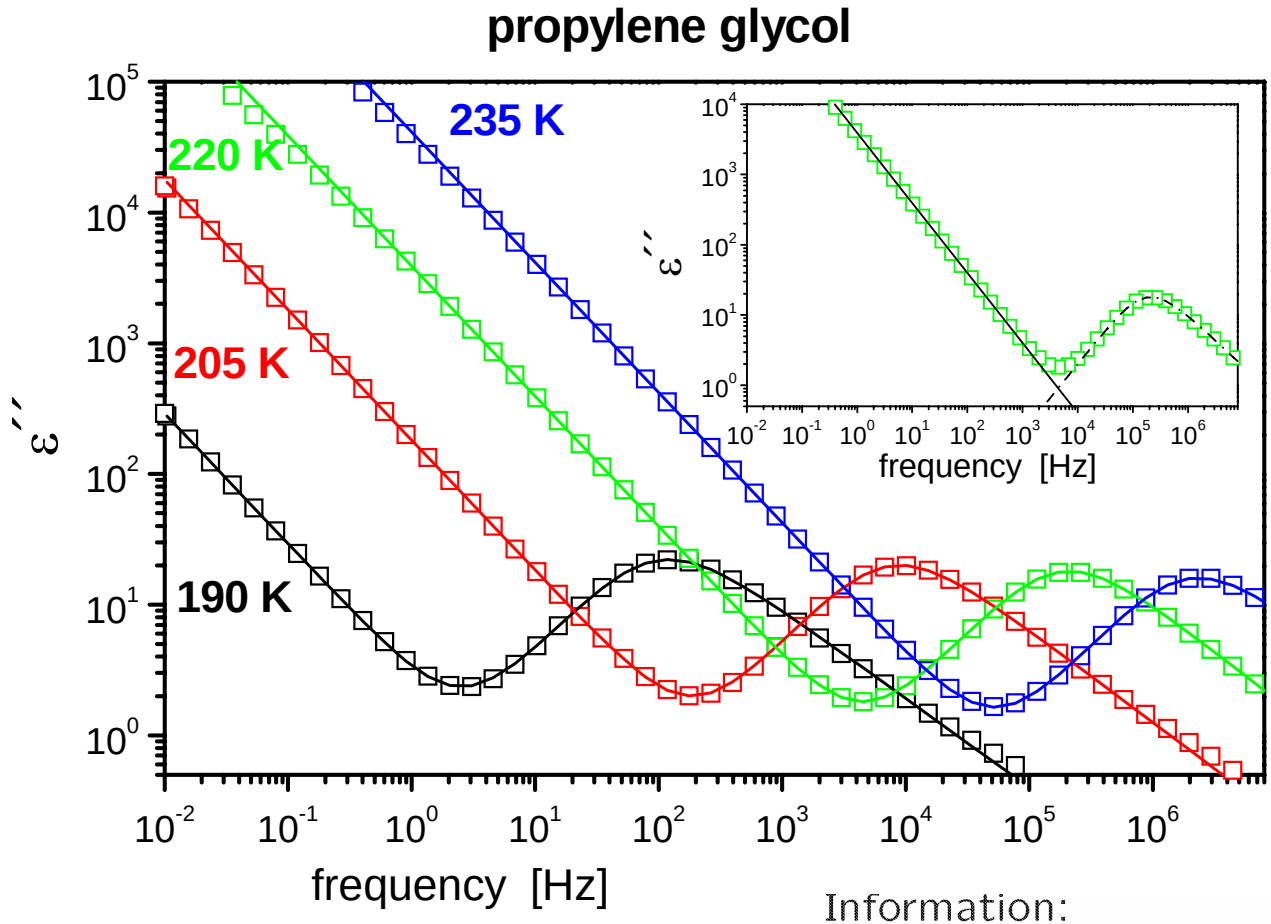
Network analyser

Wave-guides-techniquies

1. Dielectric relaxation

(rotational diffusion of bound charge carriers (dipoles) as determined from orientational polarisation)

Analysis of the dielectric data



Havriliak-Negami fit function:

$$\epsilon'' = \frac{\sigma_0}{\epsilon_0} \cdot \frac{a}{\omega^s} - \Im\left[\frac{\Delta\epsilon}{(1+(\imath\omega\tau)^\alpha)^\gamma}\right]$$

Information:

- relaxation time τ
- relaxation time distribution $g(\tau)$, parameters α and γ
- dielectric strength $\Delta\epsilon \propto n \cdot \frac{\mu^2}{3kT}$

Relaxation time distribution functions according to Havriliak-Negami

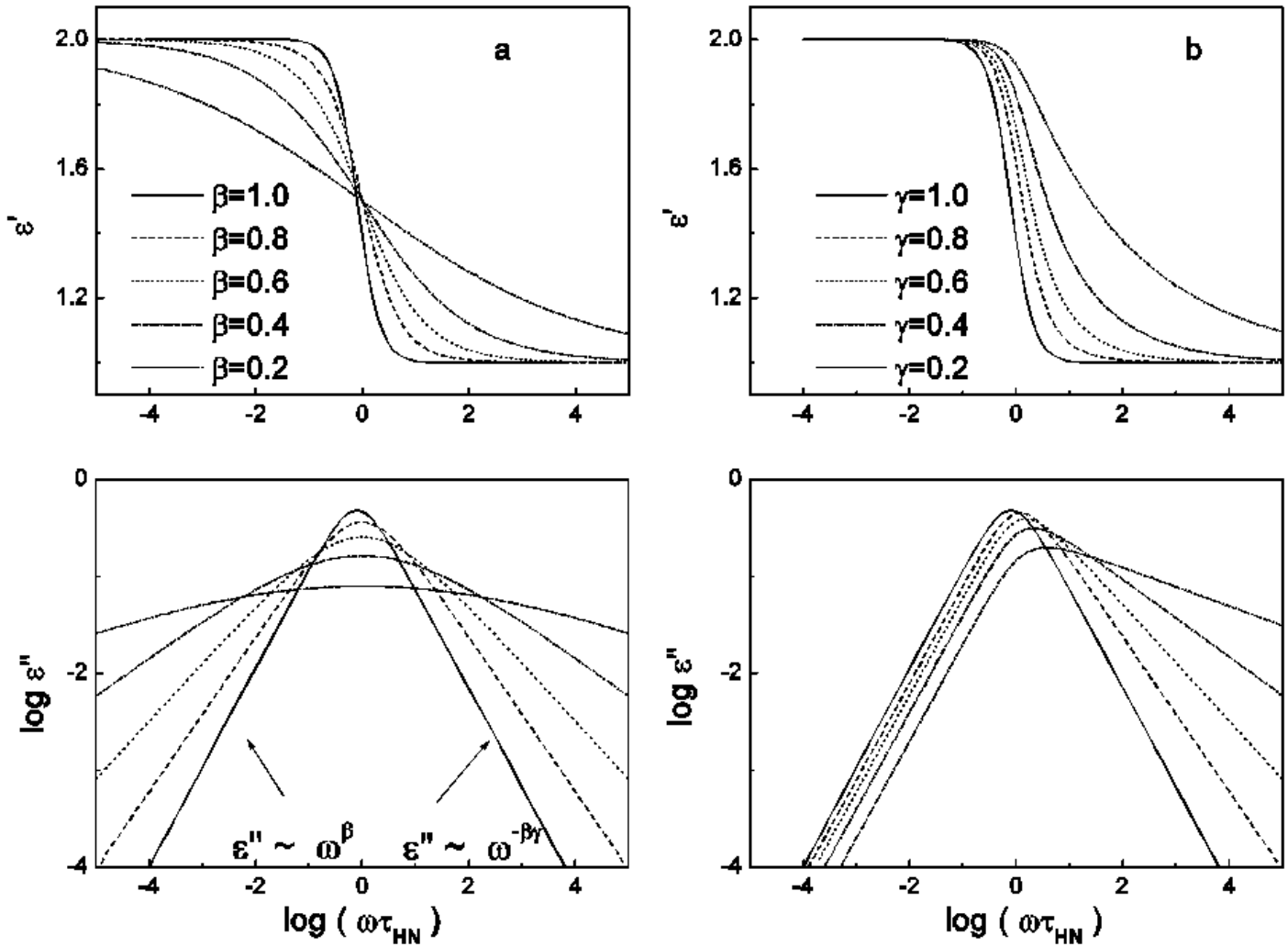
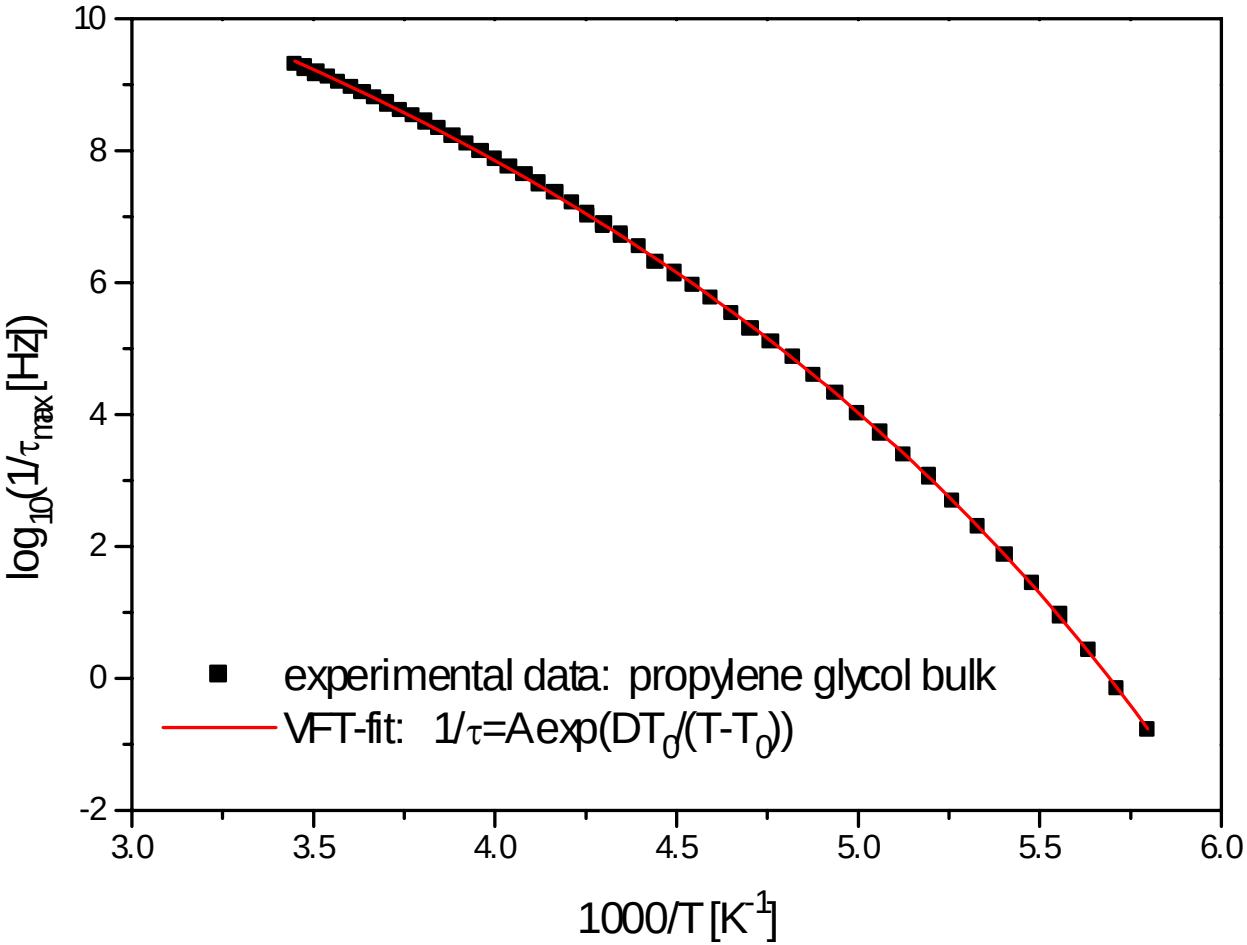


Fig. 3.3

Analysis of the dielectric data



Information:

- type of thermal activation (VFT -or Arrhenius-like)

Summary concerning Broadband Dielectric Spectroscopy (BDS) as applied to dielectric relaxations

1.: BDS covers a huge spectral range of about 15 decades from THz to below mHz in a wide range of temperatures.

2.: The sample amount required for a measurement can be reduced to that of isolated molecules.

3.: From dielectric spectra the relaxation rate of fluctuations of a permanent molecular dipole and it´s relaxation time distribution function can be deduced. The dielectric strength allows to determine the effective number-density of dipoles.

4.: From the temperature dependence of the relaxation rate the type of thermal activation (Arrhenius or Vogel-Fulcher-Tammann (VFT)) can be deduced.

2. (ionic) charge transport

(translational diffusion of charge carriers (ions))

Basic relations between the complex dielectric function ε* and the complex conductivity σ*

The *linear* interaction of electromagnetic fields with matter is described by Maxwell‘s equations

$$curl \quad H = j + \frac{\partial D}{\partial t}$$

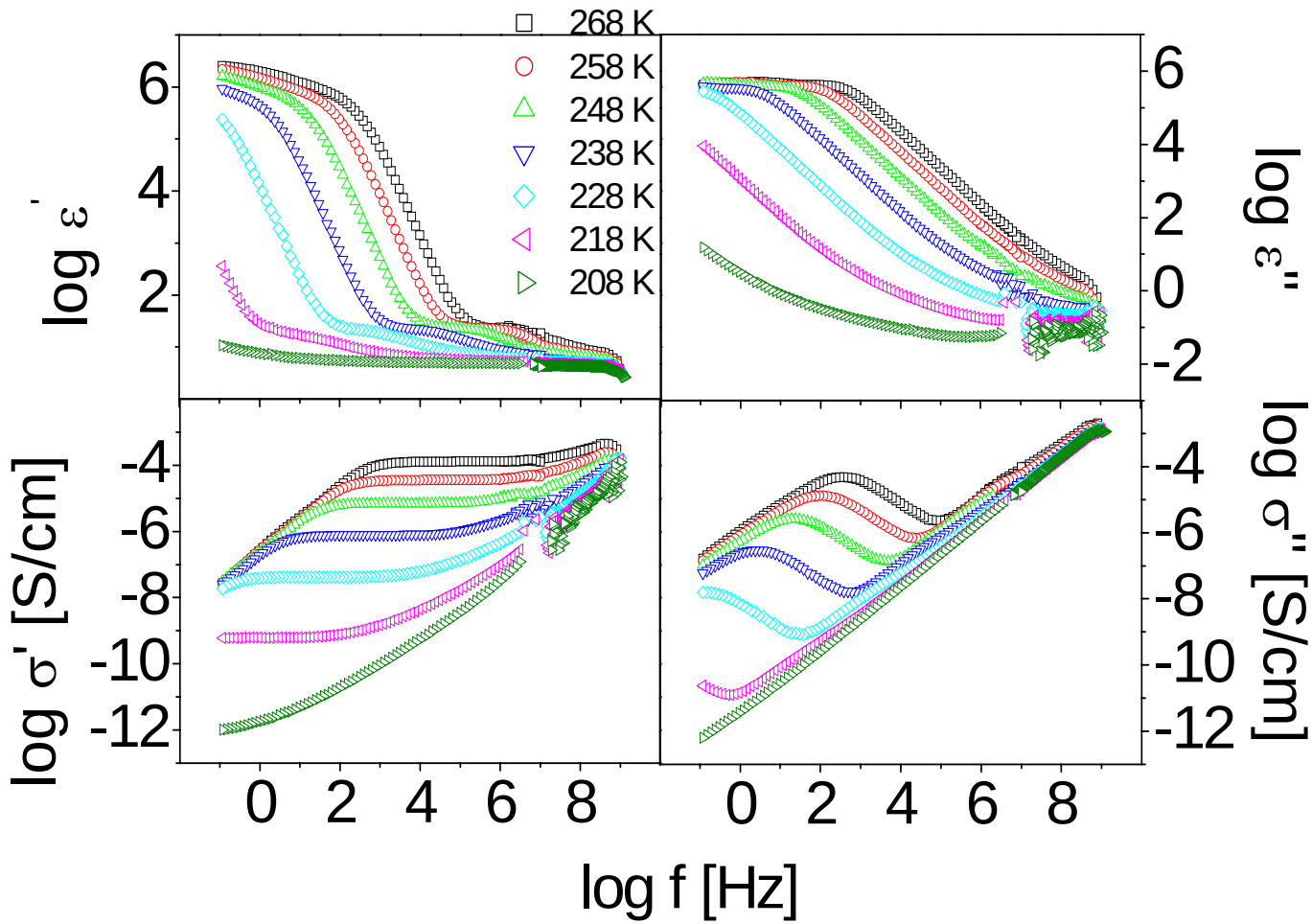
$$D = \varepsilon^* \varepsilon_0 \quad E \qquad\qquad j = \sigma^* E \qquad \text{(Ohm‘s law)}$$

(Current-density and the time derivative of D are equivalent)

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' \qquad \sigma^*(\omega) = \sigma' + i\sigma''$$

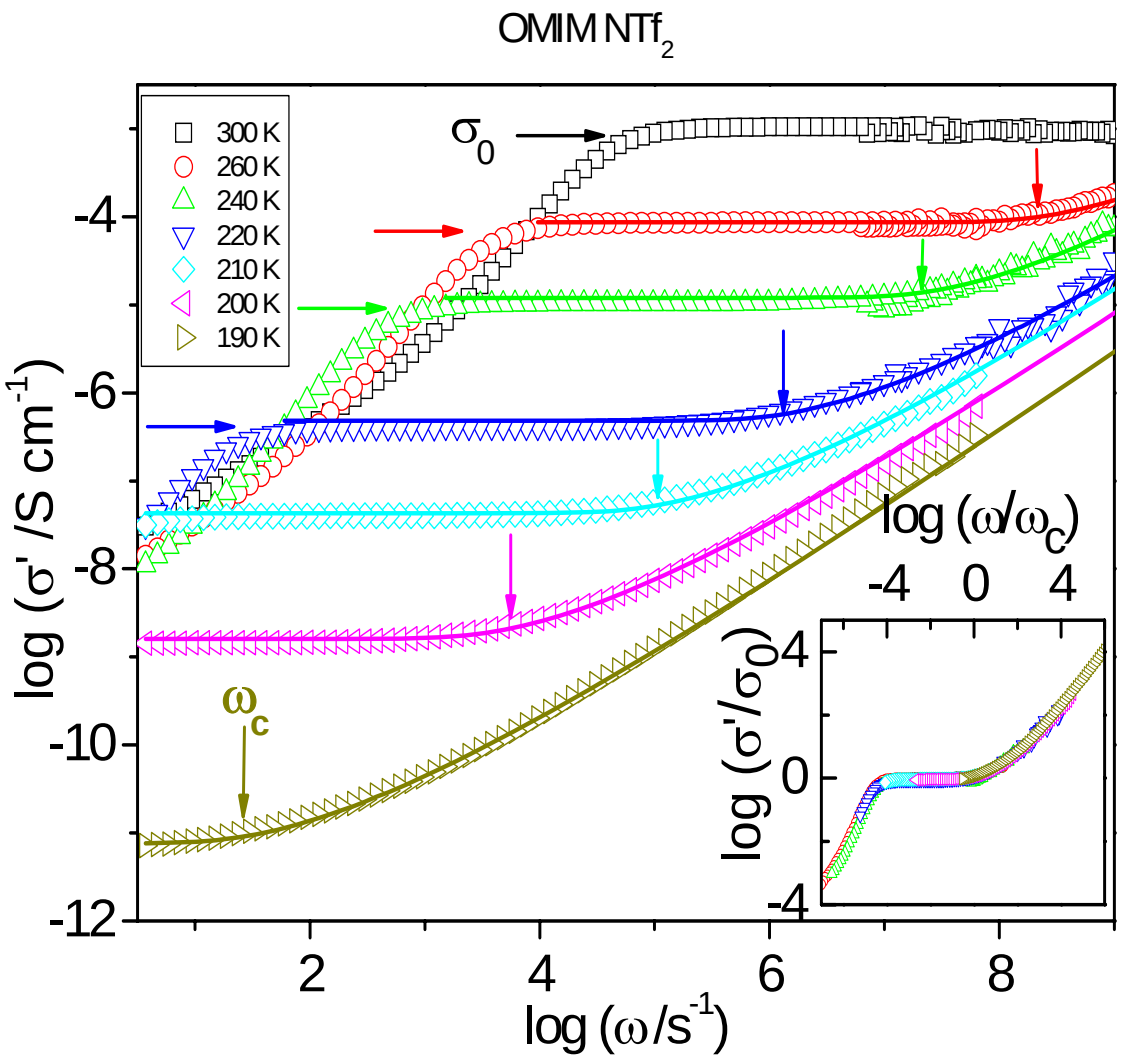
$$\boxed{\sigma^* = i\omega\varepsilon_0\varepsilon^*}$$

Dielectric spectra of MMIM Me2PO4 ionic liquid



Strong temperature dependence of the charge transport processes and electrode polarisation

$\sigma'(T,\omega)$ for the ionic liquid (OMIM NTf_2)



There are two characteristic quantities σ_0 and ω_c which enable one to scale all spectra!

Basic relations between rotational and translational diffusion

Stokes-Einstein relation:

$$D = kT/\zeta$$

D: diffusion coefficient, ζ ($=6\pi\,\eta\,a$) : frictional coefficient,T: temperature, *k*: Boltzmann constant, a: radius of molecule

Maxwell's relation:

$$\eta = \tau_\eta\, G\infty$$

G_∞: instantaneous shear modulus (~ 10^8 - 10^{10} Pa)

η: viscosity, τ_η: structural relaxation time

Einstein-Smoluchowski relation:

$$D = \frac{\lambda^2 \omega_c}{2}$$

λ : characteristic (diffusion) length

ω_c: characteristic (diffusion) rate

Basic electrodynamics and Einstein relation:

$$\sigma_0 = q\mu n = n\frac{q^2 D}{kT} \quad \Rightarrow \quad \sigma_0 \propto \omega_c$$

σ_0: : dc conductivity, μ: mobility ; q: elementary charge, n: effective number density of charge carriers

Predictions to be checked experimentally:

1.: $\omega_c = P\ \omega_\eta$

$$P = \frac{kT}{2\pi^2 G_\infty \lambda^2 a_s}$$

2.: $D = \frac{\lambda^2 \omega_c}{2}$

3.: $\sigma_0 \sim \omega_c$

ω_c: characteristic (diffusion) rate

ω_η: structural relaxation rate

G_∞: instantaneous shear modulus (~ 10^8 Pa for ILs),

a_s : Stokes‘ hydrodynamic radius ~λ,

k: Boltzmann constant,

λ: characteristic diffusion length ~ .2 nm

D : molecular diffusion coefficient

(Barton-Nakajima-Namikawa (BNN) relation)

Measurement techniques required: Broadband Dielectric Spectroscopy (BDS); Pulsed Field Gradient (PFG)-NMR; viscosity measurements;

1. Prediction: $\omega_c = P\ \omega_\eta$ **with P ~ 1**

Broadband Dielectric Spectroscopy (BDS)

Mechanical Spectroscopy

ω_c: characteristic (diffusion) rate

ω_η: structural relaxation rate

G_∞: instantaneous shear modulus (~ 10^8 Pa for ILs),

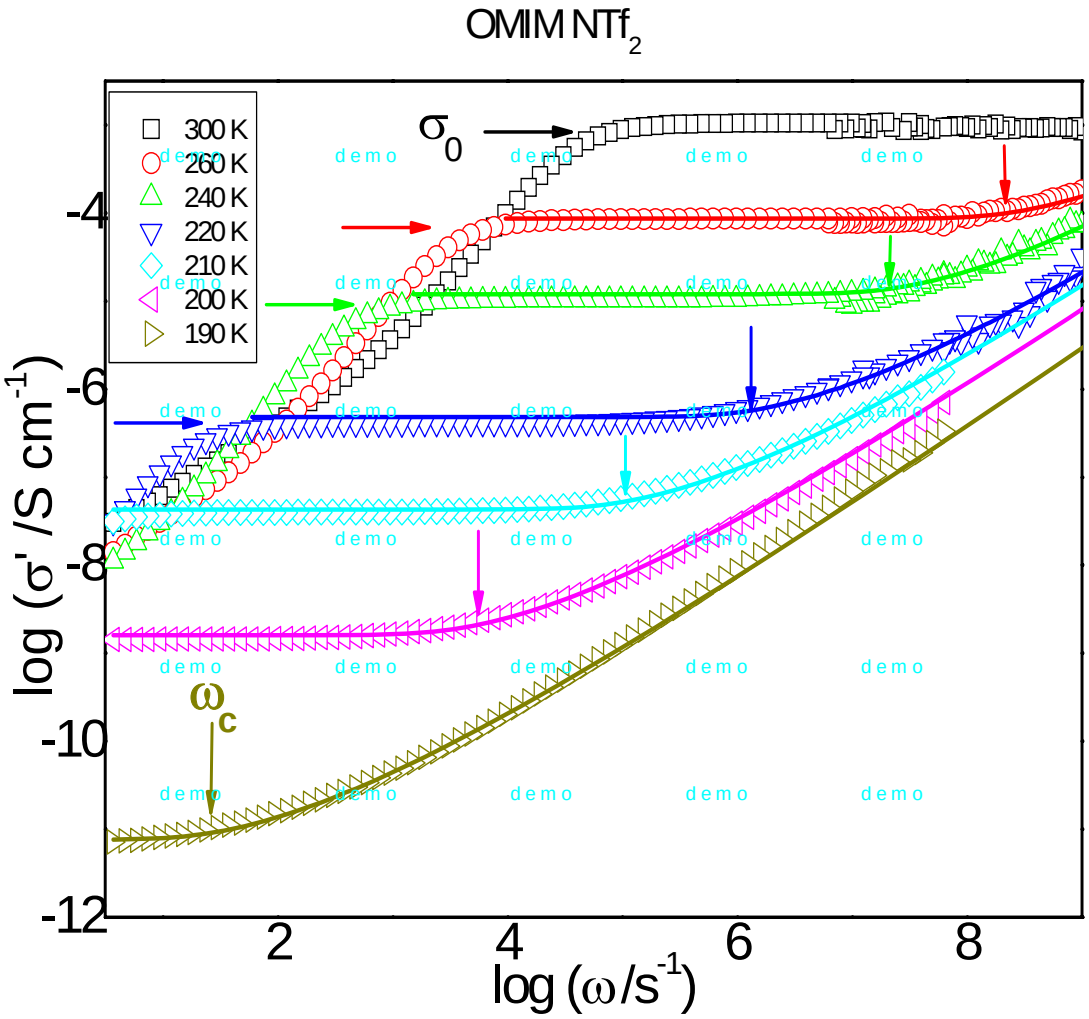
Random Barrier Model (Jeppe Dyre et al.)

- Hopping conduction in a spatially randomly varying energy landscape
- Analytic solution obtained within Continuous-Time-Random Walk (CTRW) approximation
- The largest energy barrier determines Dc conduction
- The complex conductivity is described by:

$$\sigma(\omega) = \sigma_0 \left(\frac{i\omega\tau_e}{\ln(1+i\omega\tau_e)} \right)$$

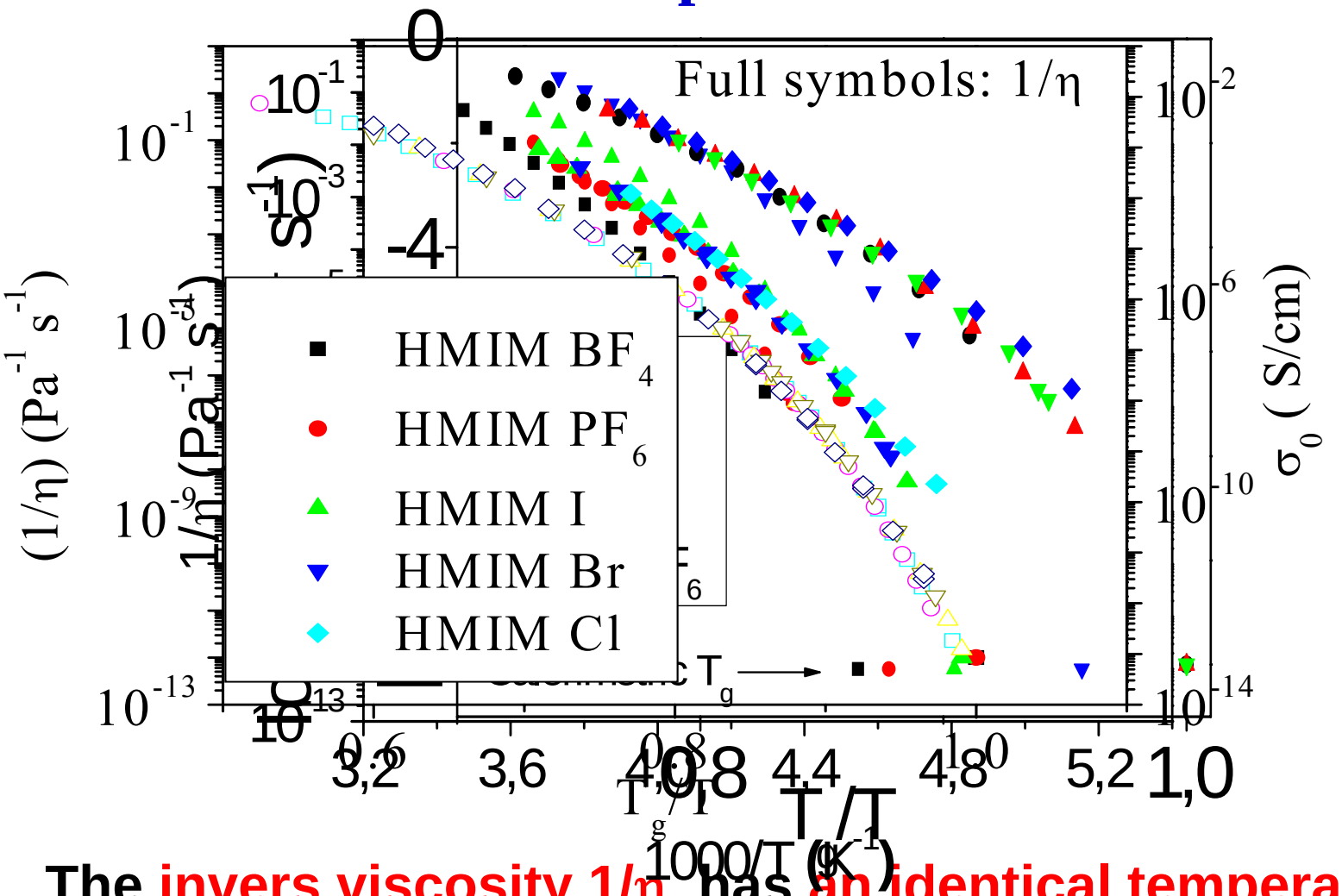
τ_e is the characteristic time related to the attempt frequency to overcome the largest barrier determining the Dc conductivity. „Hopping time“.

Random Barrier Model (RBM) used to fit the conductivity spectra of ionic liquid (MMIM Me2PO4)



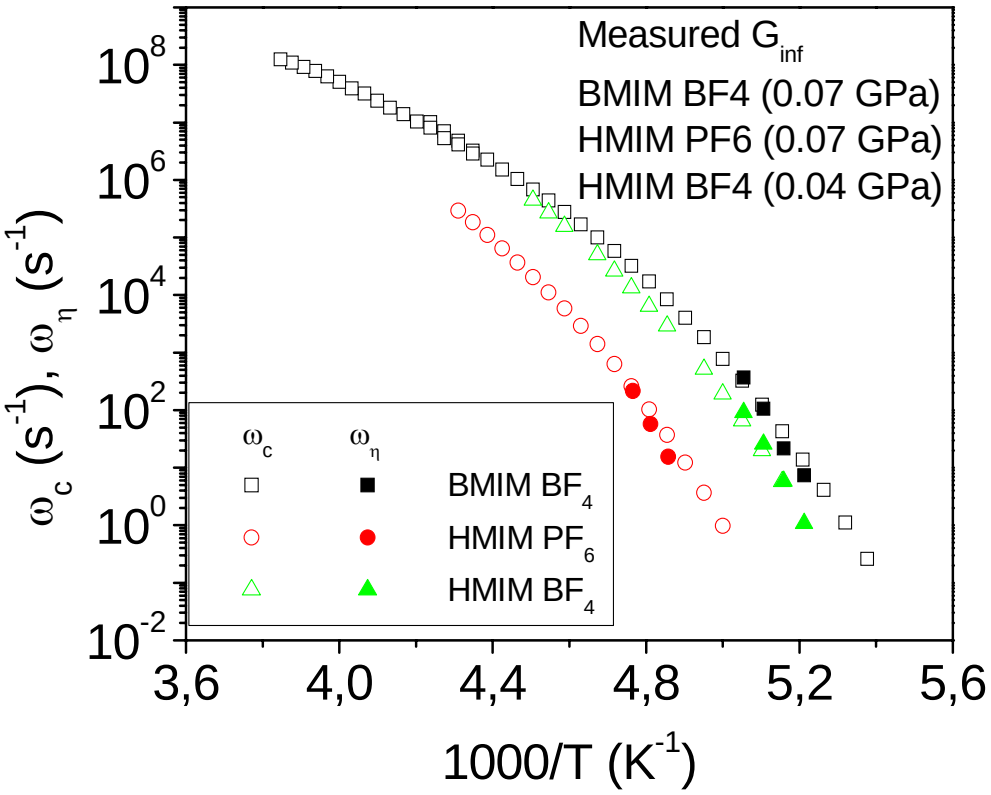
The RBM fits quantitatively the data; $\omega_c = 1/\tau_e$

Scaling of invers viscosity $1/\eta$ and conductivity s_0 with temperature



The invers viscosity $1/\eta$ has an identical temperature dependence as σ_0 and scales with T_g.

Correlation between translational and rotational diffusion



Stokes-Einstein, Einstein-Smoluchowski and Maxwell relations:

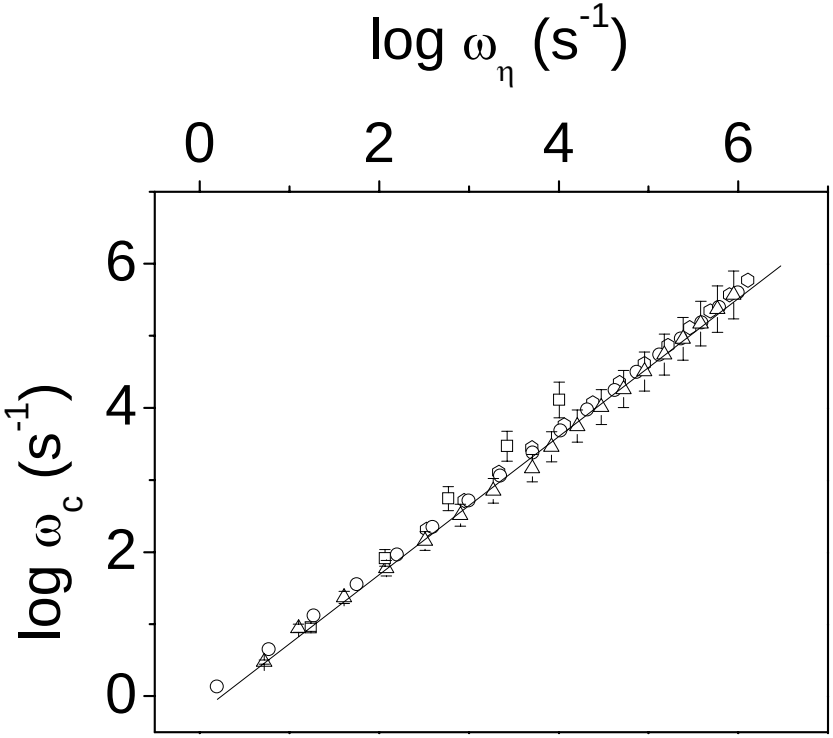
$$\omega_c = P\,\omega_\eta$$

$$P = \frac{kT}{2G_\infty \pi^2 G_\infty \lambda^2 a_s} \simeq 1$$

Typically: $G_\infty \cong 0.1$ GPa; $\lambda \cong .2$ nm; $a_s \cong .1$ nm;

J. R. Sangoro et al.(2009) Phys. Chem. Chem. Phys.

Correlation between translational and rotational diffusion



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J. R. Sangoro et al.Phys. Chem. Chem. Phys, DOI: 0.1039/b816106b,(2009) .

Prediction checked experimentally:

1.: $\omega_c = P\ \omega_\eta$

$$P = \frac{kT}{2G_\infty \pi^2 G_\infty \lambda^2 a_s} \simeq 1$$

ω_c: characteristic (diffusion) rate

ω_η: structural relaxation rate

G_∞: instantaneous shear modulus (~ 10^8 Pa for ILs),

a_s: Stokes' hydrodynamic radius ~λ,

k: Boltzmann constant,

λ: characteristic diffusion length ~ .2 nm

2. Prediction: $D(T) = \frac{\lambda^2}{2\tau_e(T)} \sim \omega_c$

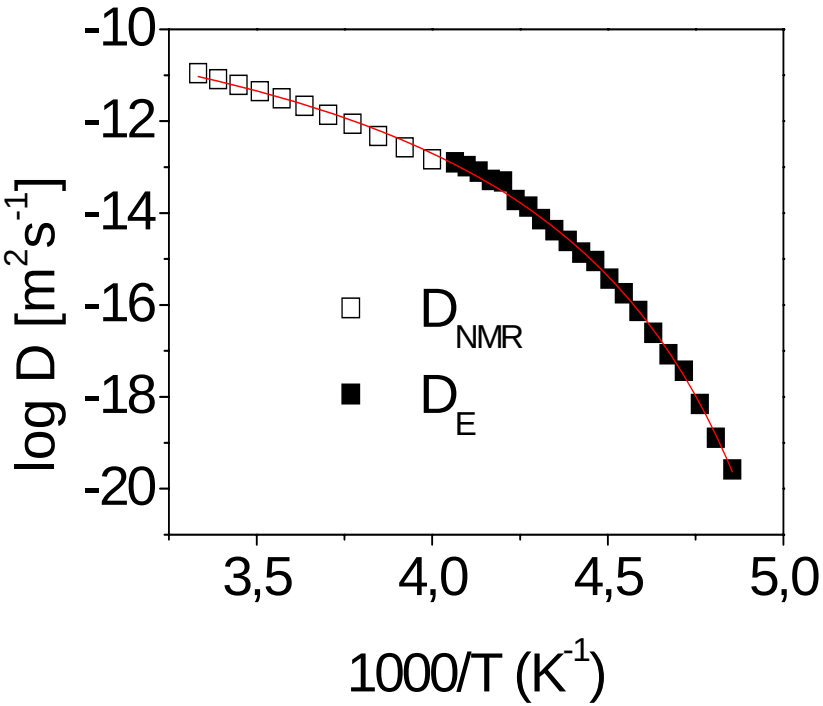
Pulsed-Field-Gradient NMR

Broadband Dielectric Spectroscopy (BDS)

Comparison with Pulsed-Field-Gradient NMR and determination of diffusion coefficients from dielectric spectra

Based on Einstein-Smoluchowski relation and using PFG NMR measurements of the diffusion coefficients enables one to determine the diffusion length λ :

$$D(T) = \frac{\lambda^2}{2\tau_e(T)} \sim \omega_c$$



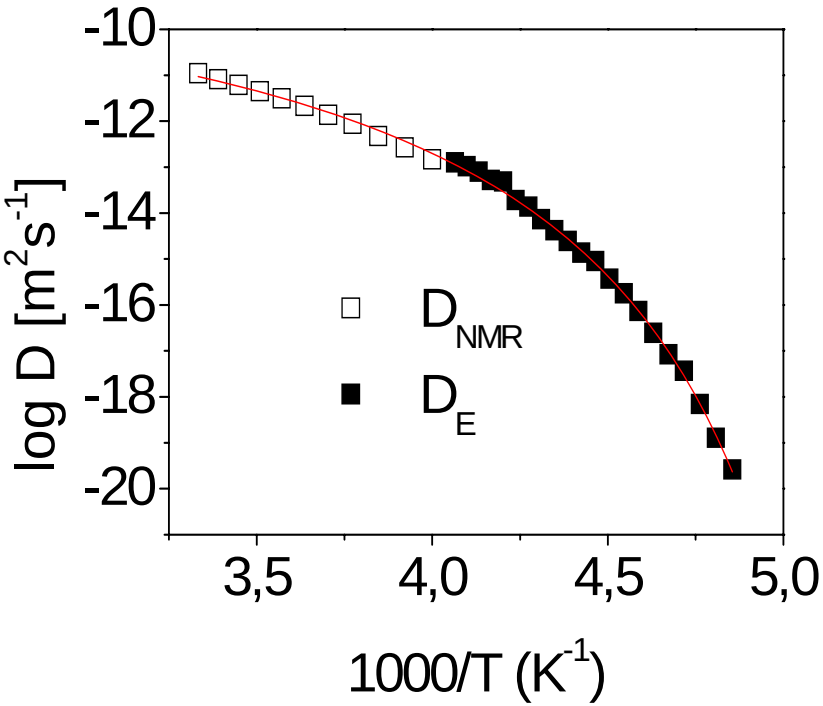
Quantitative agreement between PFG-NMR measurements and the dielectric determination of diffusion coefficients. Hence mass diffusion (PFG-NMR) equals charge transport (BDS)..

Comparison with Pulsed-Field-Gradient NMR and determination of diffusion coefficients from dielectric spectra

From Einstein-Smoluchowski and basic electrodynamic definitions it follows:

$$\sigma_0(T) = n(T)q\mu(T) = n(T)q\frac{qD(T)}{kT} = \frac{n(T)q^2}{kT}\frac{\lambda^2}{2\tau_e(T)} \sim \omega_c$$

(n(T):number-density of charge carriers; μ(T):mobility of charge carriers)

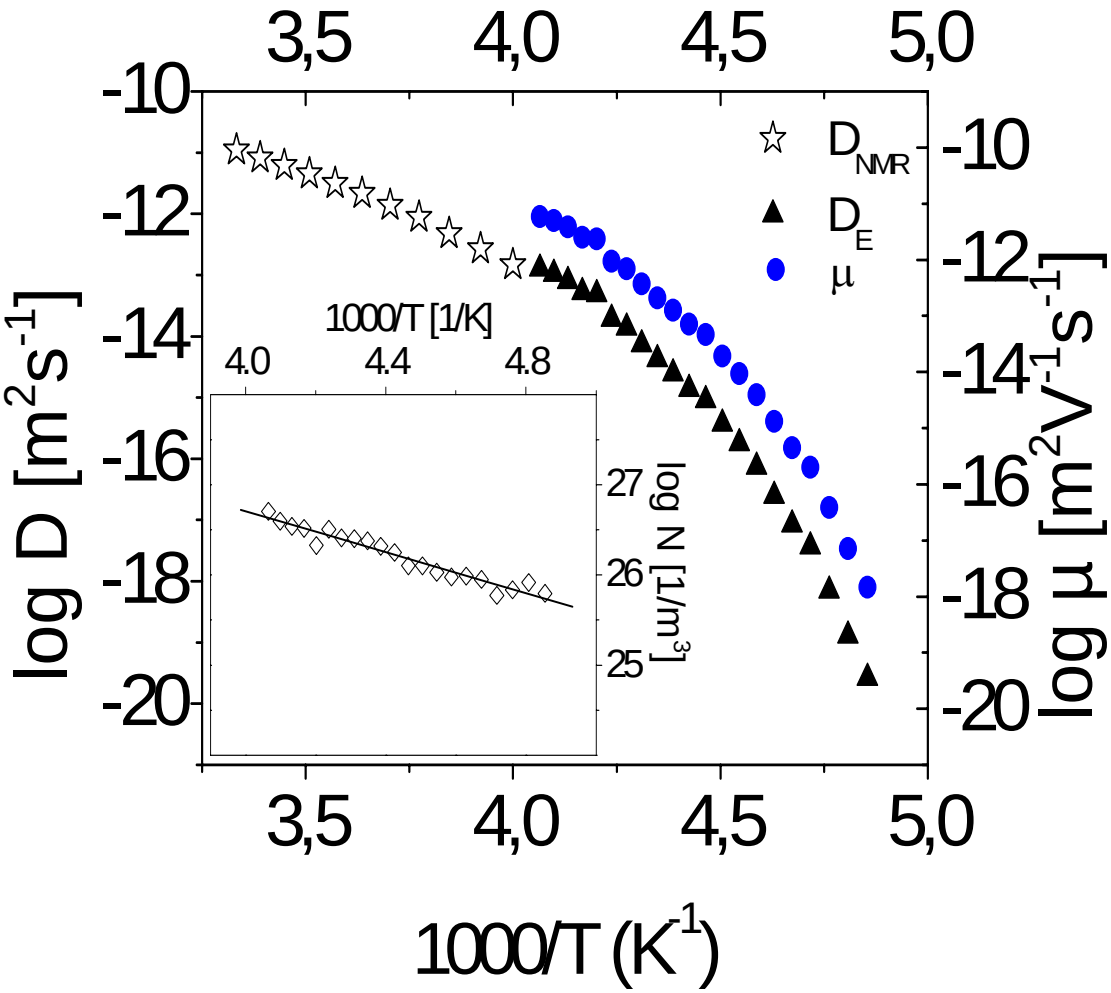


1. **The separation of n(T) and μ(T) from σ_0 (T) is readily possible.**

2. **The empirical BNN-relation is an immediate consequence.**

Separation of n(T) and μ(T) from σ_0 (T)

MMIM Me2PO4



1.: μ(T) shows a VFT temperature dependence

2.. n(T) shows Arrhenius-type temperature dependence

3.: the σ_0 (T) derives its dependence from μ(T)

J. Sangoro, *et al*., Phys. Rev. E 77, 051202 (2008)

Predictions checked experimentally:

2.: $D = \frac{\lambda^2 \omega_c}{2}$

ω_c: characteristic (diffusion) rate
λ: characteristic diffusion length ~ .2 nm
D : molecular diffusion coefficient
σ_0 : Dc conductivity

Applying the Einstein-Smoluchowski relation enables one to deduce the root mean square diffusion distance λ from the comparison between PFG-NMR and BDS measurements. A value of $\lambda \sim .2$ nm is obtained. Assuming λ to be temperature independent delivers from BDS measurements the molecular diffusion coefficient D. Furthermore the numberdensity n(T) and the mobility μ(T) can be separated and the BNN-relation is obtained.

3.: $\sigma_0 \sim \omega_c$ (Barton-Nishijima-Namikawa (BNN) relation)

Summary concerning Broadband Dielectric Spectroscopy (BDS) as applied to ionic charge transport

1.: The predictions based on the equations of Stokes-Einstein and Einstein-Smoluchowski are well fullfilled in the examined ion-conducting systems.

2.: Based on dielectric measurements the self-diffusion coefficient of the ionic charge carriers and their temperature dependence can be deduced.

3.: It is possible to separate the mobility $\mu(T)$ and the effective numberdensity n(T). The former has a VFT temperature-dependence, while the latter obeys an Arrehnius law.

4.: The Barton-Nishijima-Namikawa (BNN) relation turns out to be a trivial consequence of this approach.

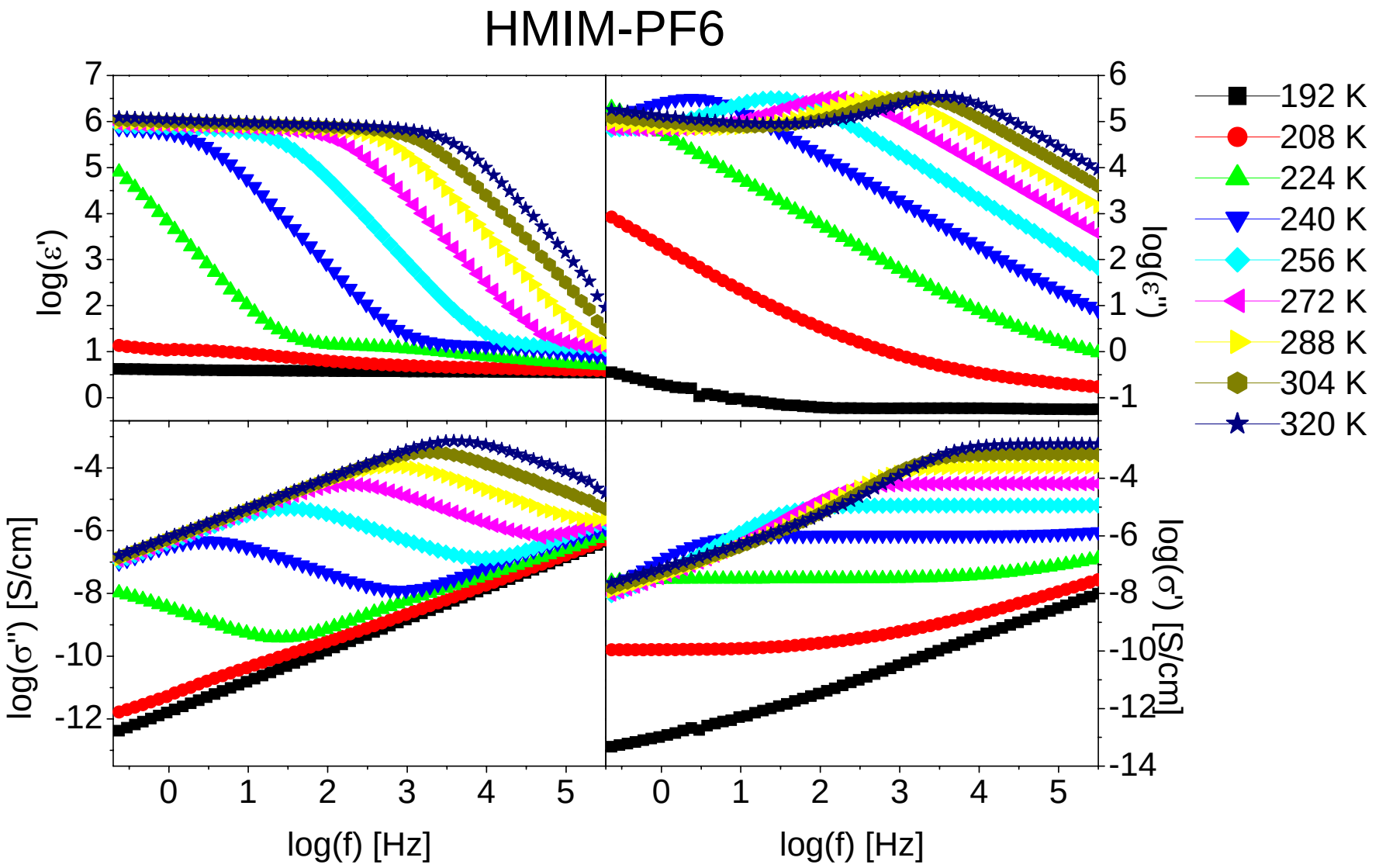
3. Electrode Polarisation (EP)

(polarisation of ionic charge carriers at a metal interface)

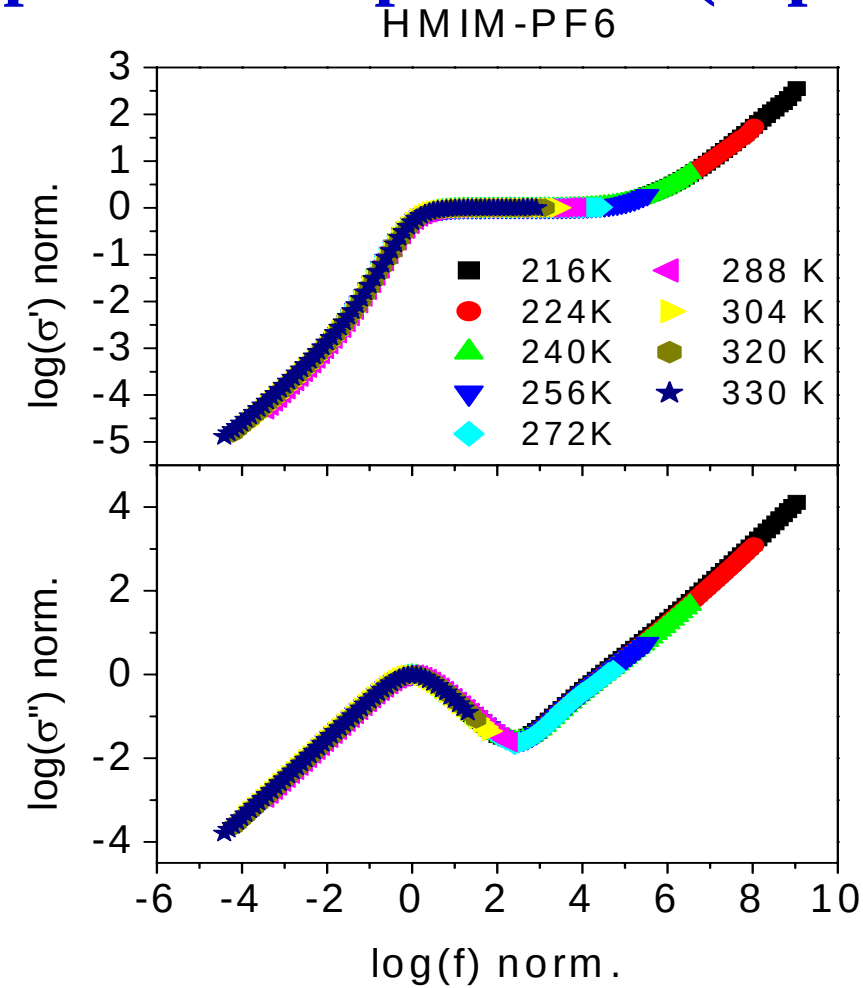
Questions to be adressed:

1. **What is the *signature* of electrode polarisation (EP) and how can it be analysed *quantitatively*?**
2. **What *quantitative* information can be deduced from fits of the EP?**
3. **What is the *quantitative* model to describe EP?**

Dielectric spectra of ionic liquids - temperature dependence (experiment)

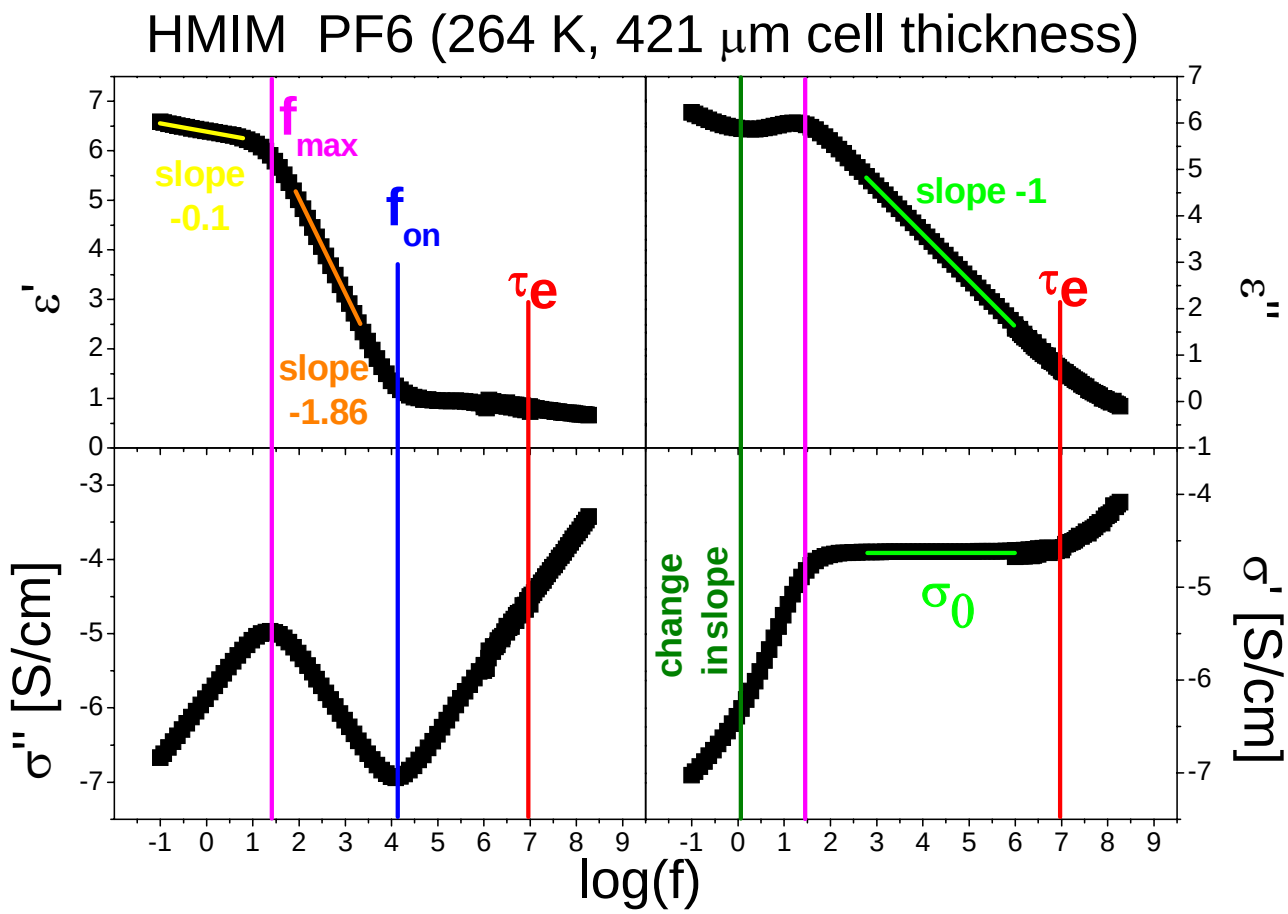


Dielectric spectra of ionic liquids - temperature dependence (experiment)



Charge transport and EP follow the identical temperature dependence over many orders of magnitude in time

The signature of electrode polarisation (EP)



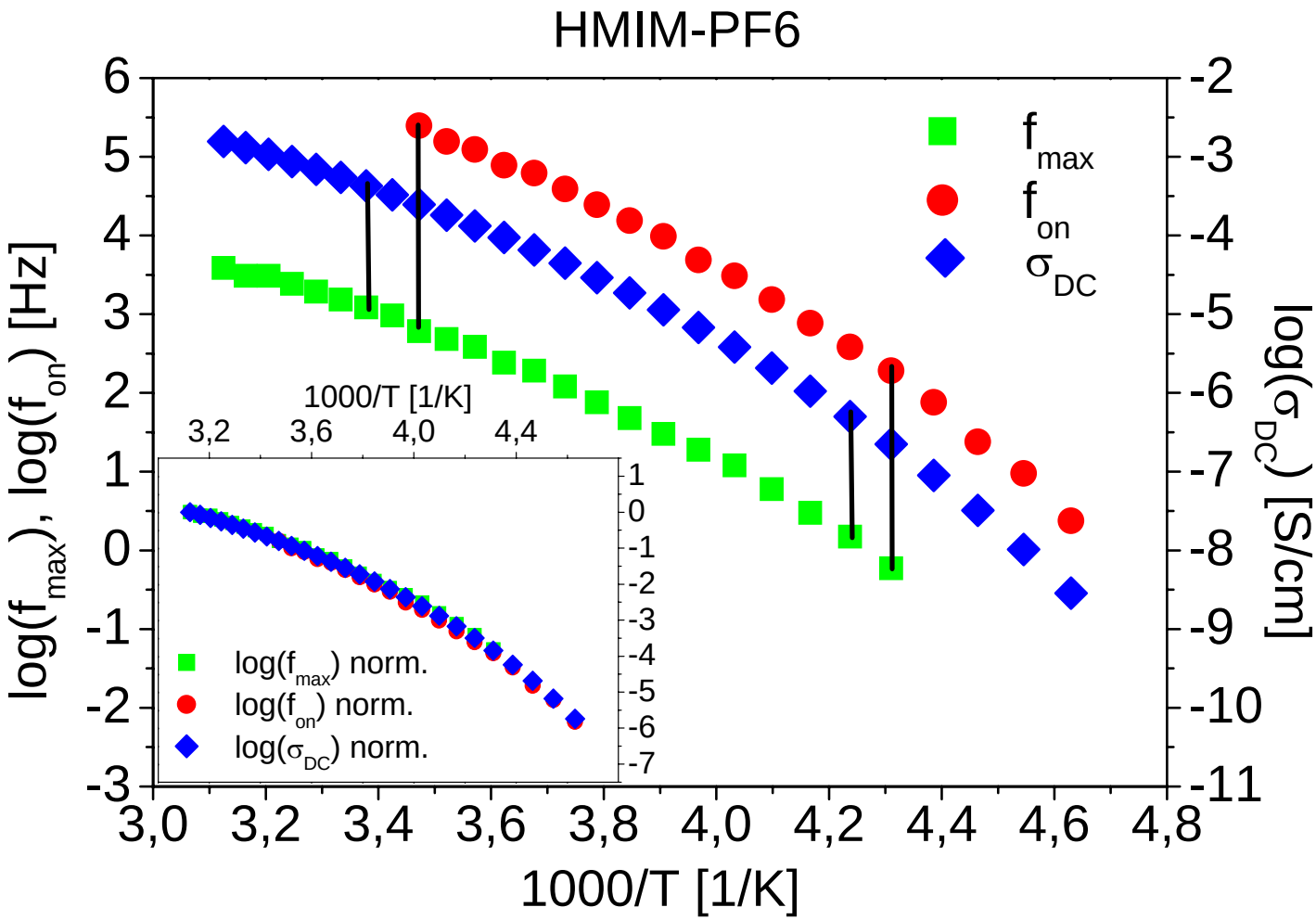
σ_0: DC conductivity

f_{on}: onset of electrode polarization

f_{max}: full development of EP

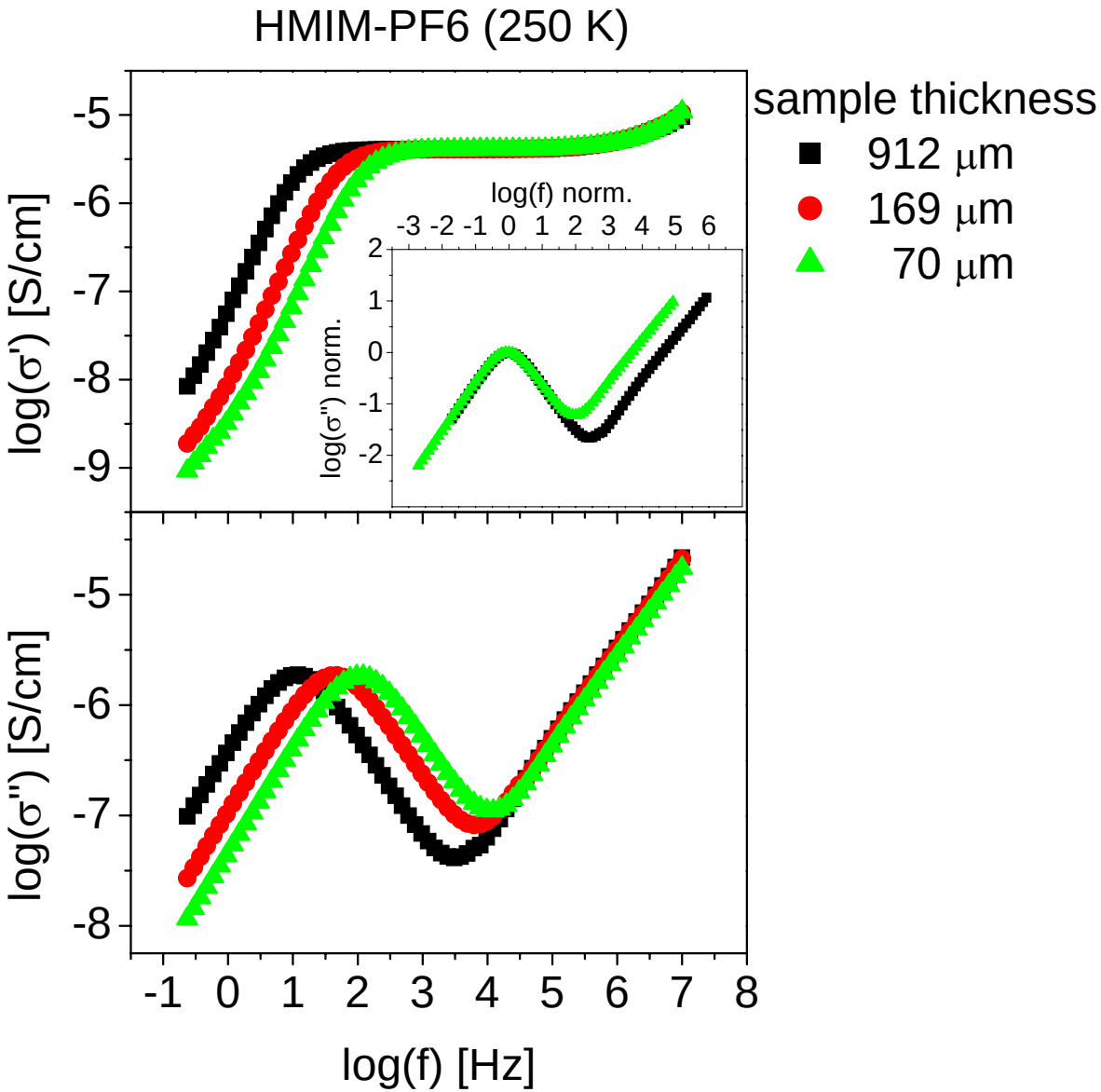
EP has a refined signature which shows up differently in $\varepsilon^*(\omega,T)$ and $\sigma^*(\omega,T)$

Dielectric spectra of ionic liquids - temperature dependence (experiment)

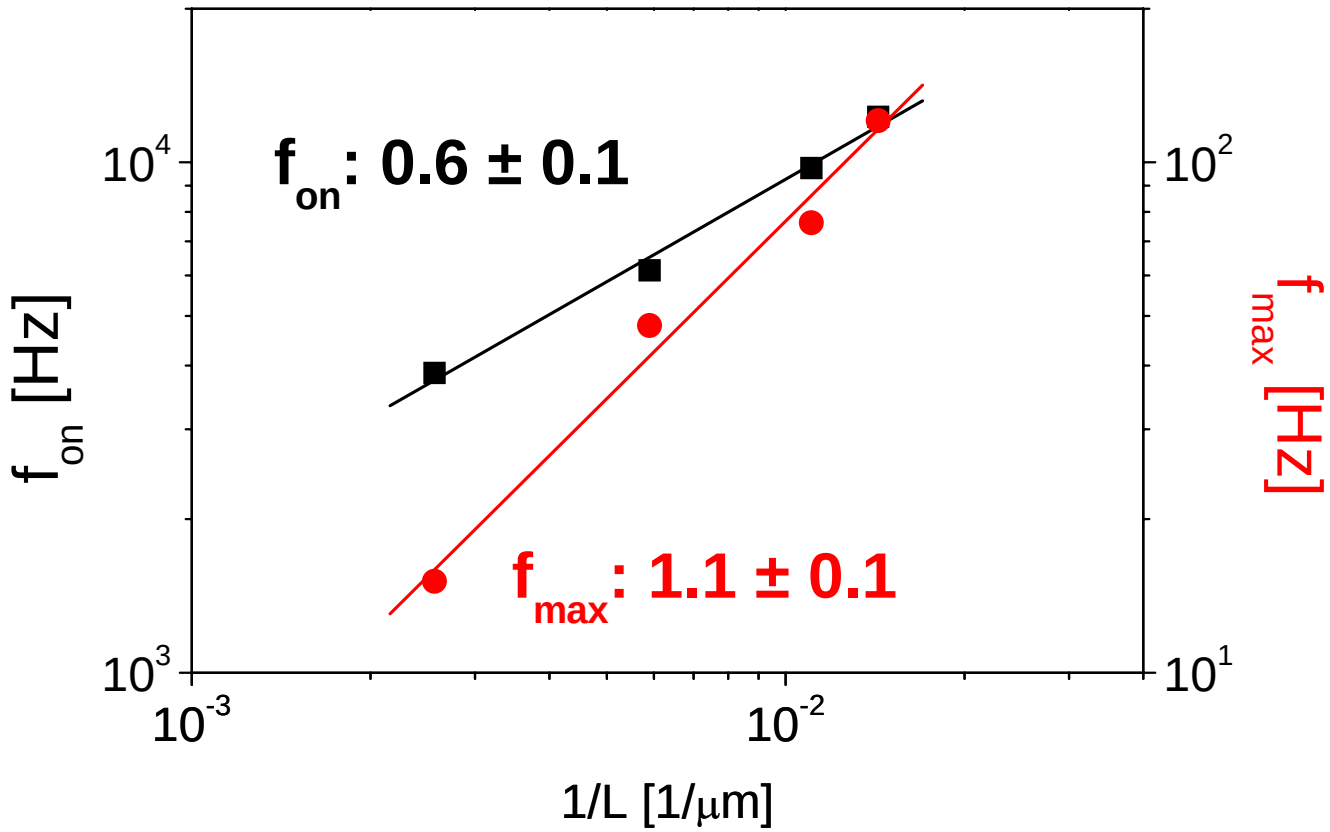


f_{max}, f_{on} and s_{DC} scale similarly with temperature

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

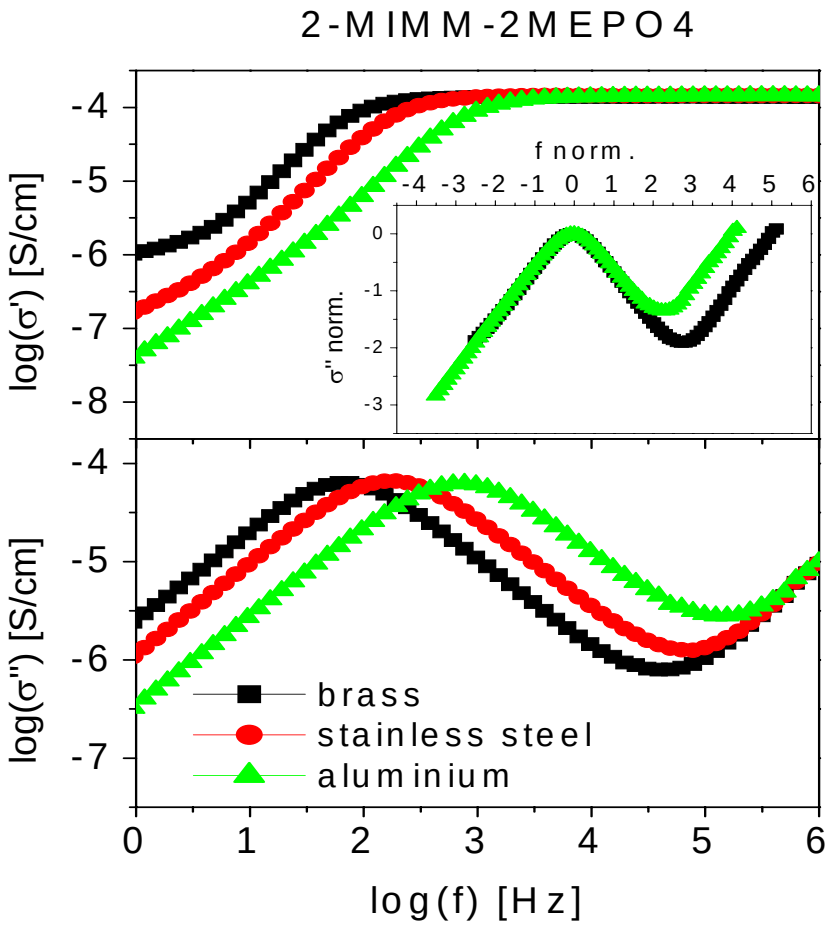


Dielectric spectra of ionic liquids- dependence on the length of the sample cell (experiment) -



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

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



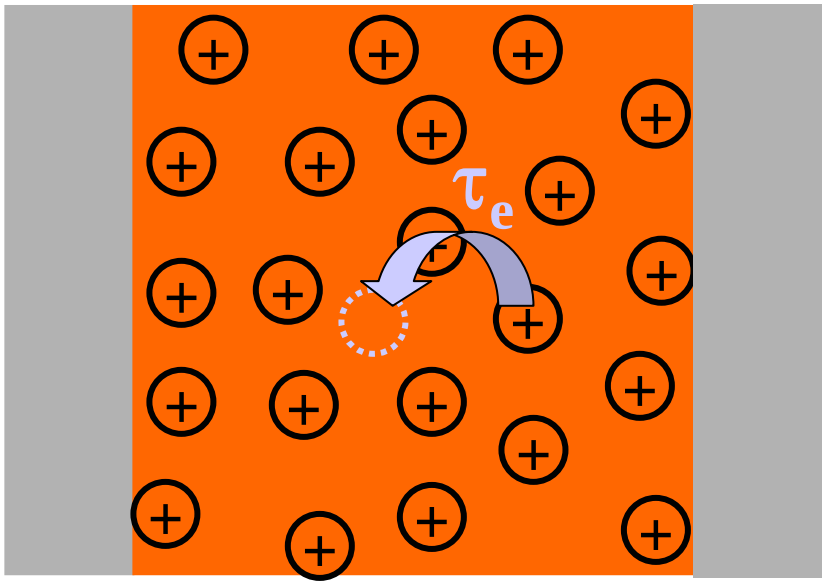
Pronounced effect of electrode material !

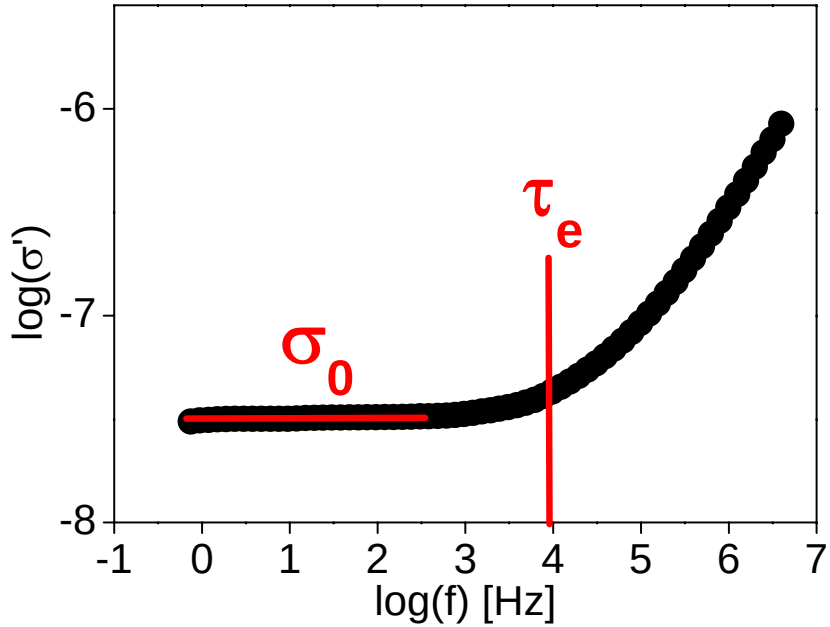
Experimental features of EP in ILs:

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



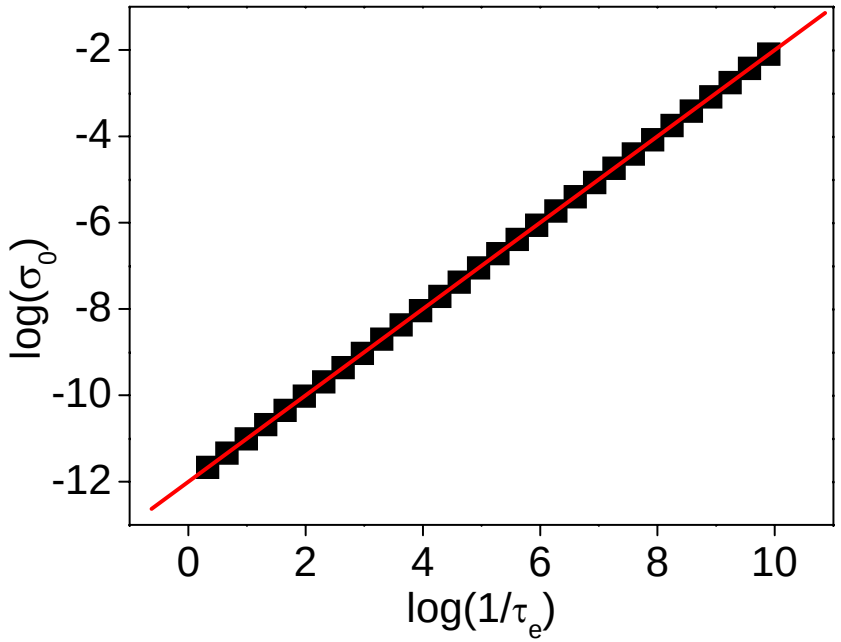


1. hoping time in bulk:

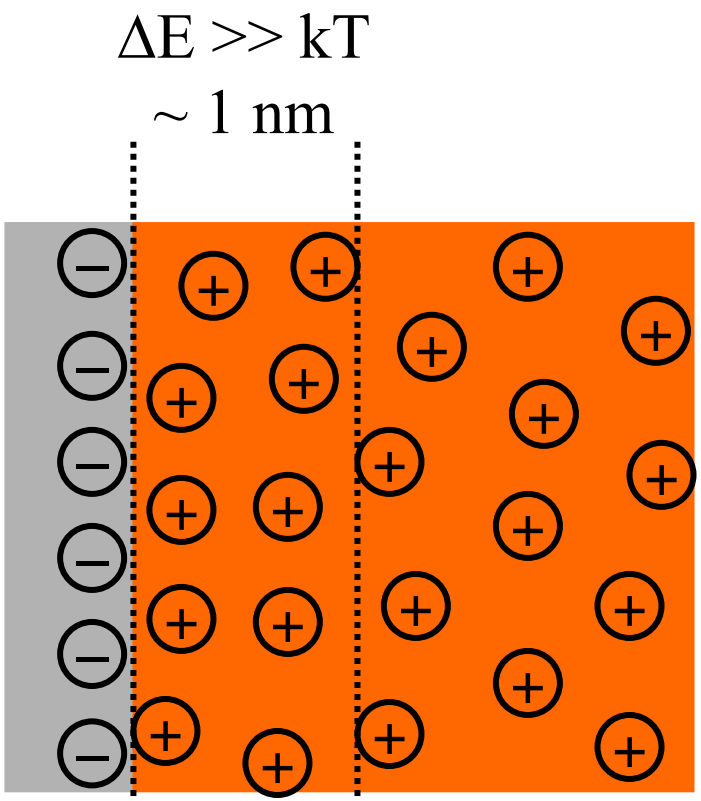
$$\tau_e = \tau_0 \exp\left(\frac{E}{kT}\right)$$

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:

$$E_i \cong E_b + \Delta E$$

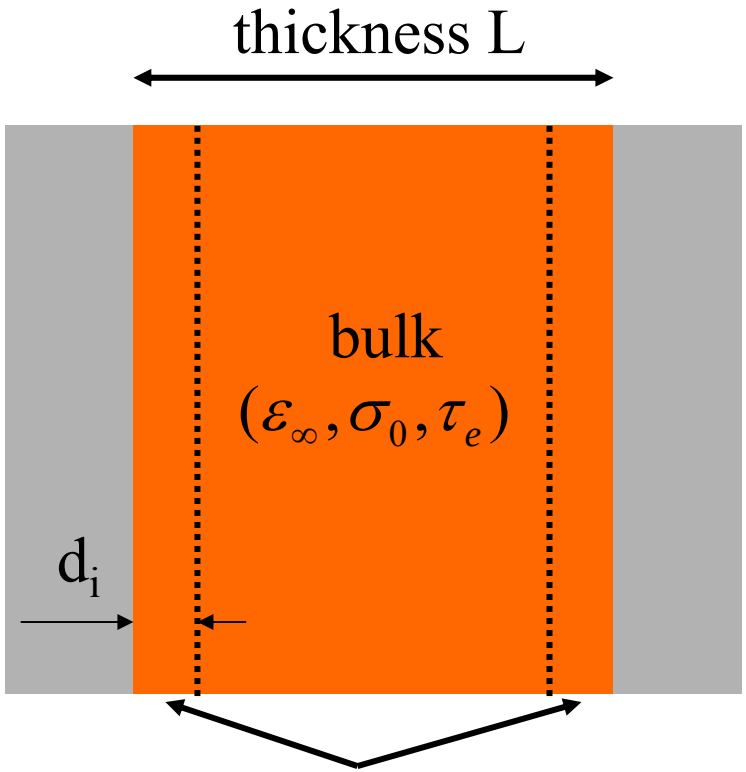
$$\frac{\tau_e(\text{interface})}{\tau_e(\text{bulk})} \approx \exp\left(\frac{\Delta E}{kT}\right) >> 1$$

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

this implies:

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

Microscopic model of sample cell



$$\frac{L}{\varepsilon^*_{meas}} = \frac{2d_i}{\varepsilon^*_i} + \frac{L-2d_i}{\varepsilon^*_b}$$

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

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

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

Electrode polarization

$$\frac{L}{\varepsilon^*_{meas}} = \frac{2d_i}{\varepsilon^*_i} + \frac{L-2d_i}{\varepsilon^*_b}$$

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

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

where: $x = \dfrac{L-2d_i}{2d_i}$ $y = \dfrac{(\varepsilon'_b)^2 + (\varepsilon''_b)^2}{(\varepsilon'_i)^2 + (\varepsilon''_i)^2}$

with

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

EP - consequences of the model

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

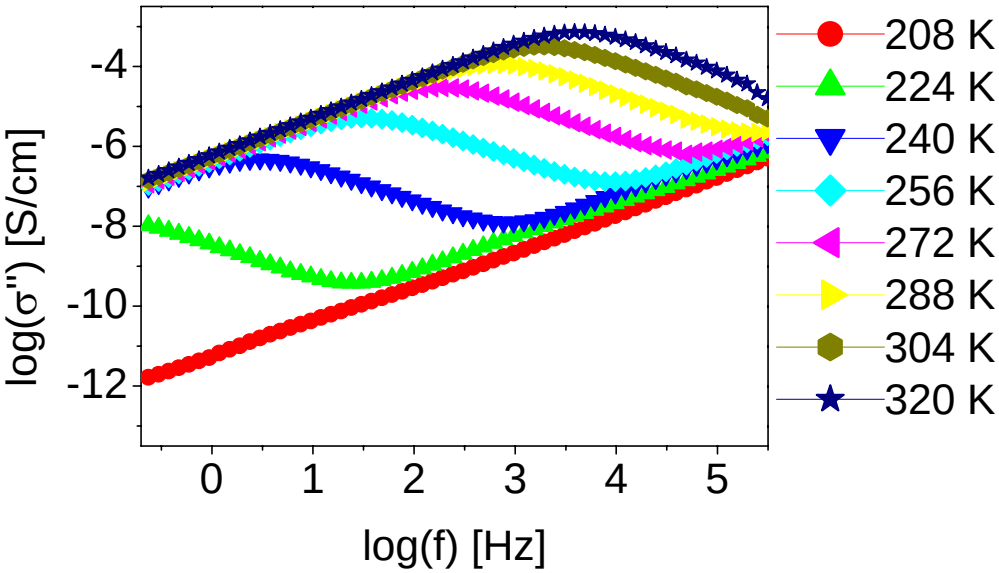
$$f_{max}\cong\frac{\sigma_0}{\varepsilon_0}\frac{1}{2\pi\varepsilon'_i}\frac{2d_i}{L}$$

Consequences:

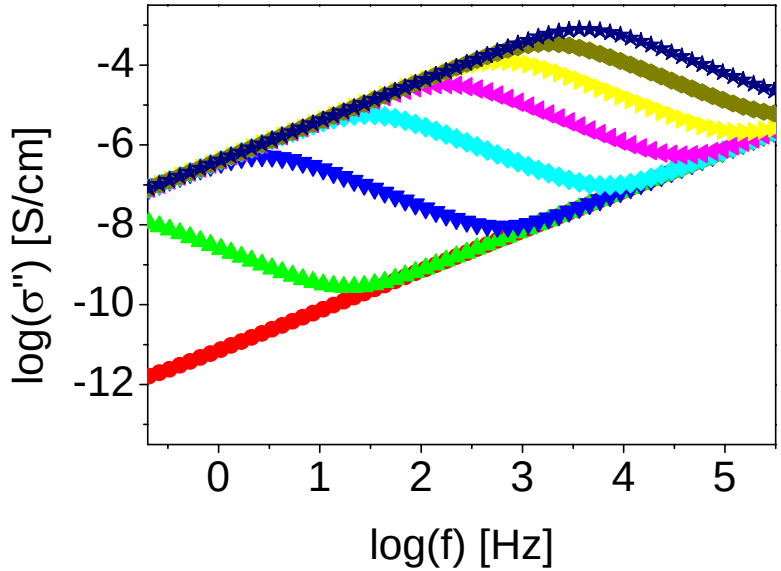
1. $f_{on}\sim f_{max}\sim\sigma_0$
2. $f_{on}\sim\frac{1}{\sqrt{L}}$, while $f_{max}\sim\frac{1}{L}$
3. $f_{on}\sim\sqrt{d_i}$, while $f_{max}\sim d_i$
4. $f=f_{max}$ solution for both $\frac{d\left(\sigma''_{meas}\right)}{d\omega}=0$ and $\frac{d\left(\varepsilon''_{meas}\right)}{d\omega}=0$
5. $\sigma_0=2\pi\varepsilon_0\varepsilon_S\frac{\left(f_{on}\right)^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

Comparison of experiment and calculations - dielectric spectra of ionic liquids

experiment

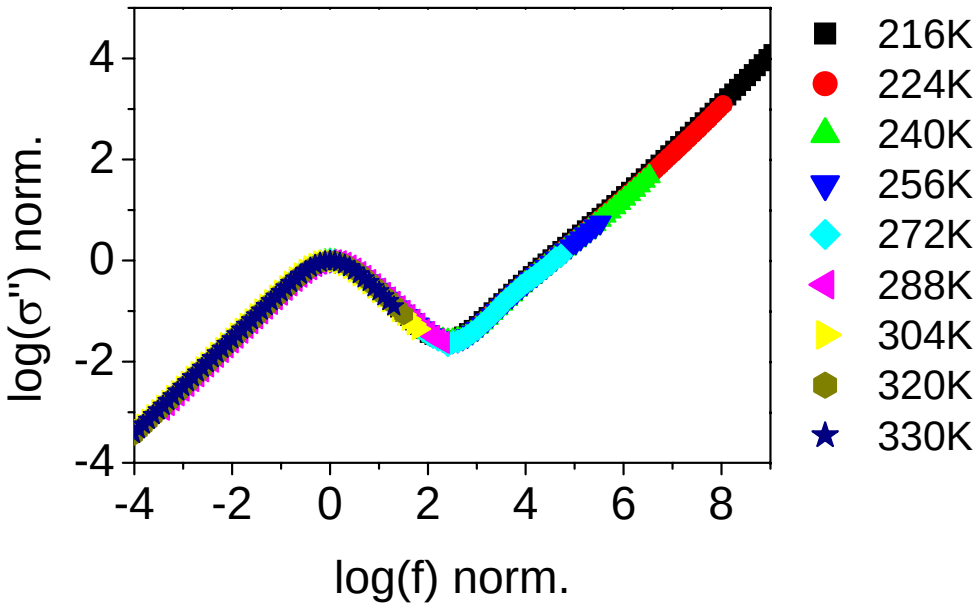


calculations

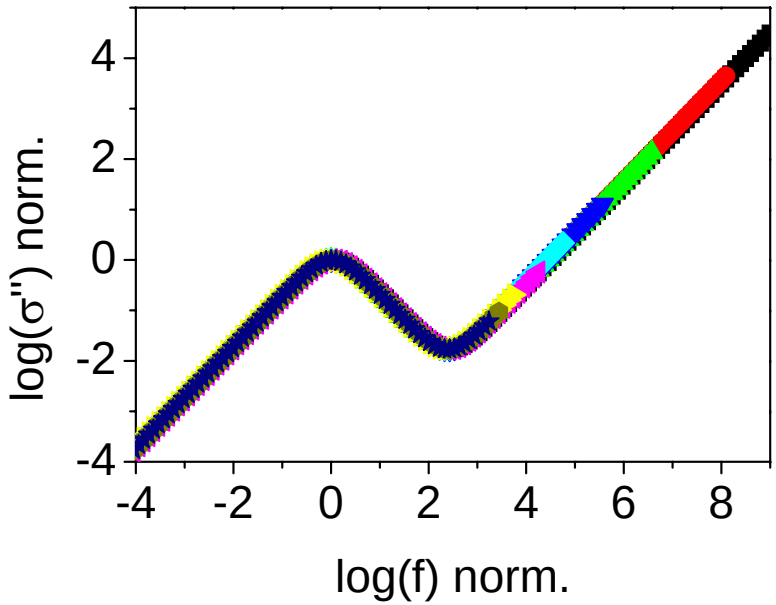


Comparison of experiment and calculations - dielectric spectra of ionic liquids

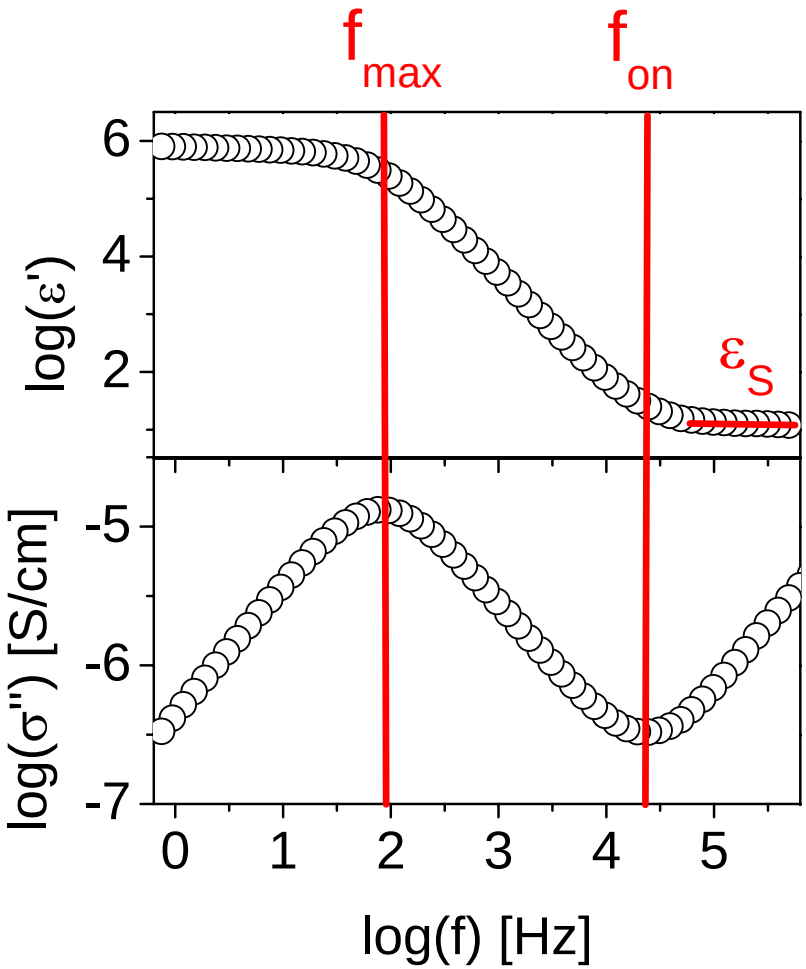
experiment



calculations



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



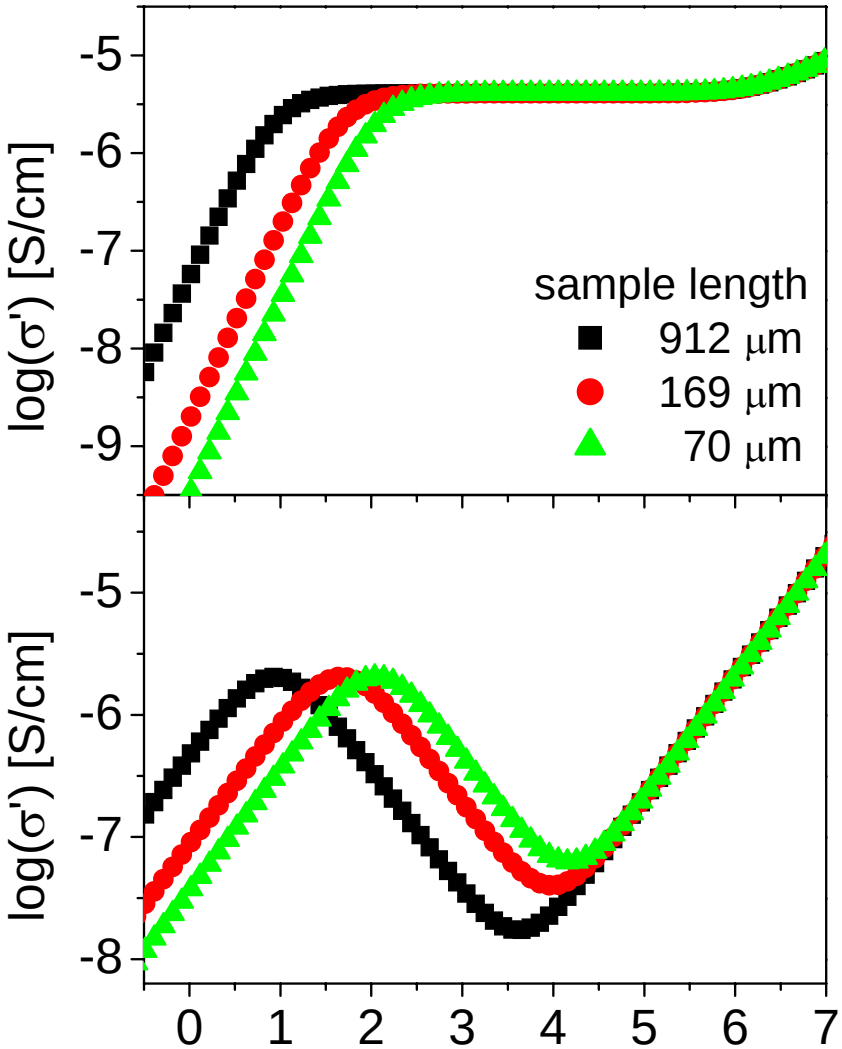
$$\sigma_0 = ?$$

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

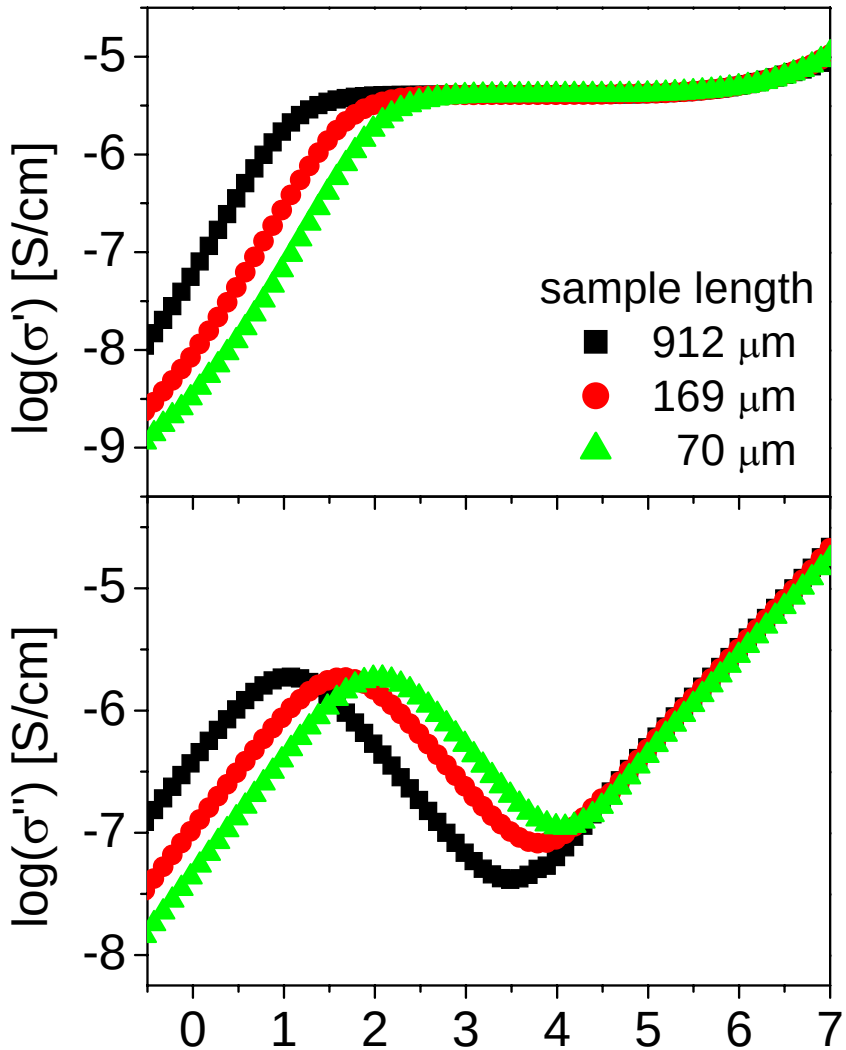
Serghei, A. et al. (2009) Phys. Rev. B, 80 184301.

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

Calculations

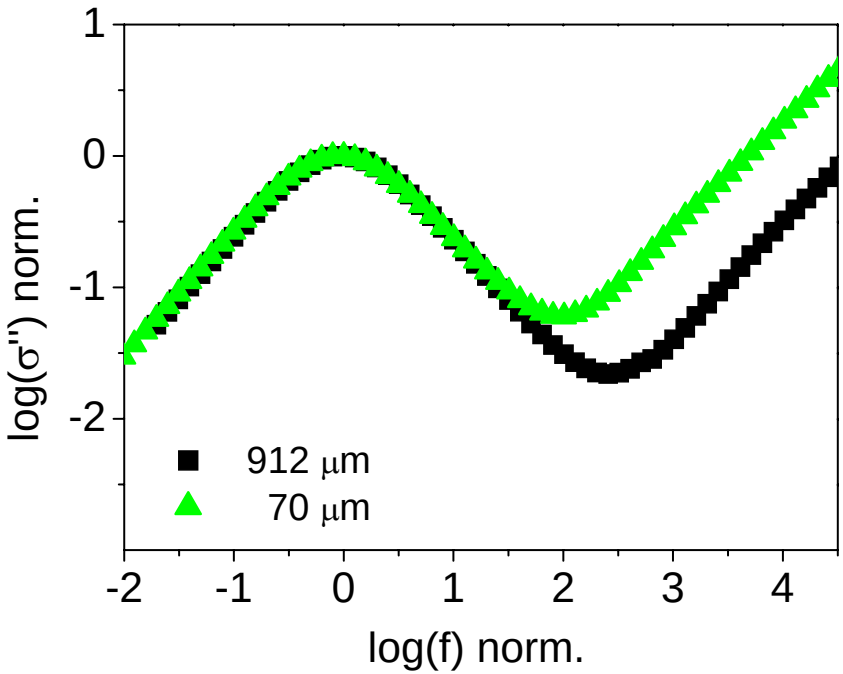


experiment

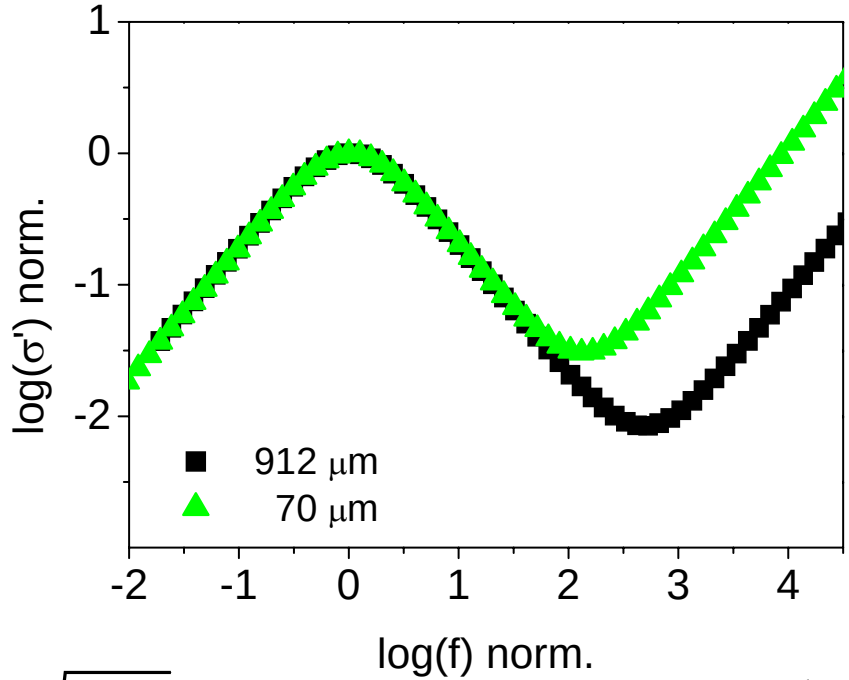


Dielectric spectra of ionic liquids
- length dependence, scaling -

experiment



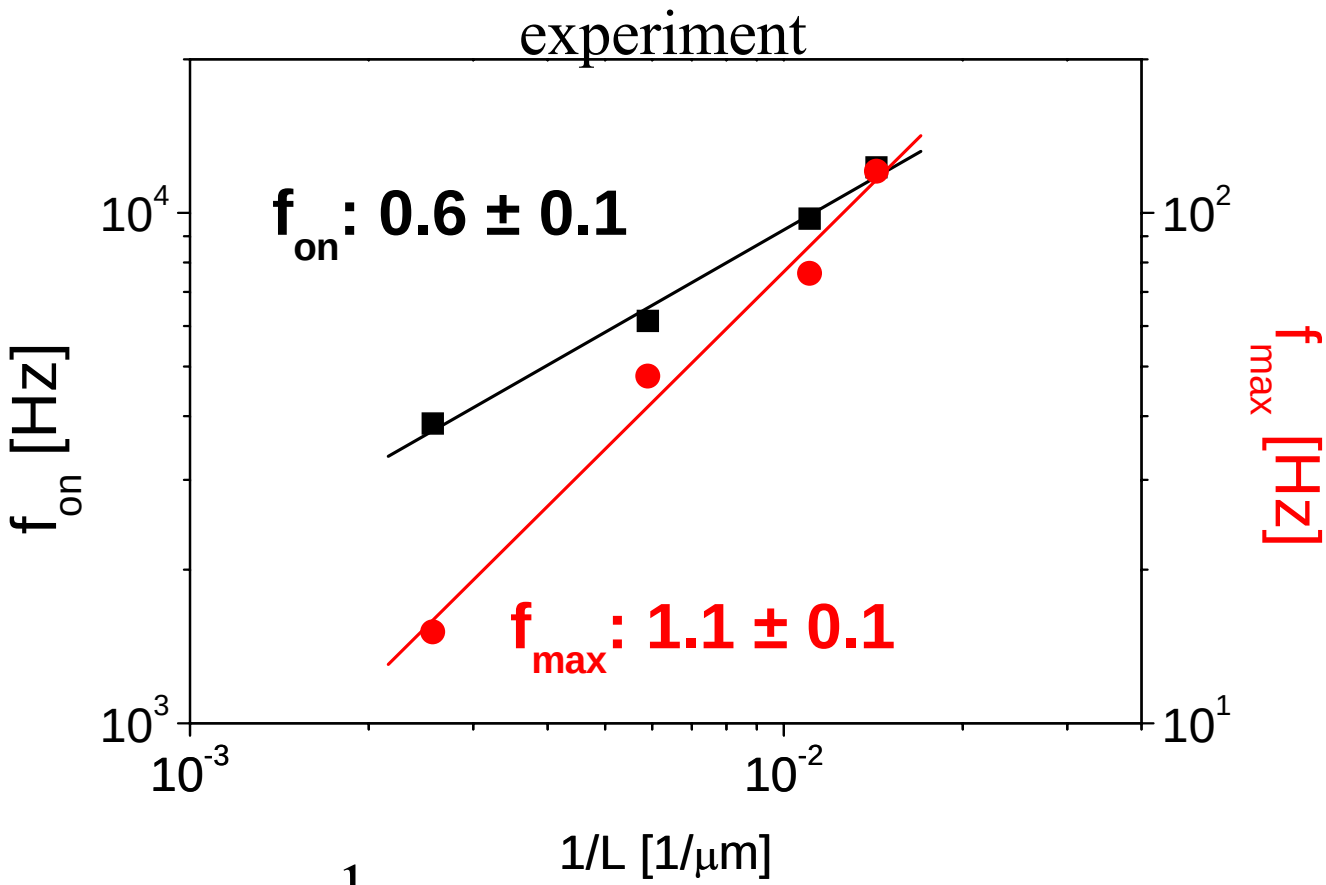
calculations



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

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

Dielectric spectra of ionic liquids - length dependence, scaling



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

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

Summary 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.

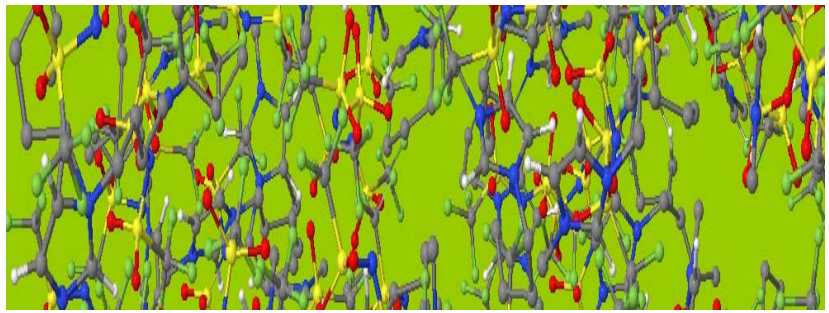
Publications

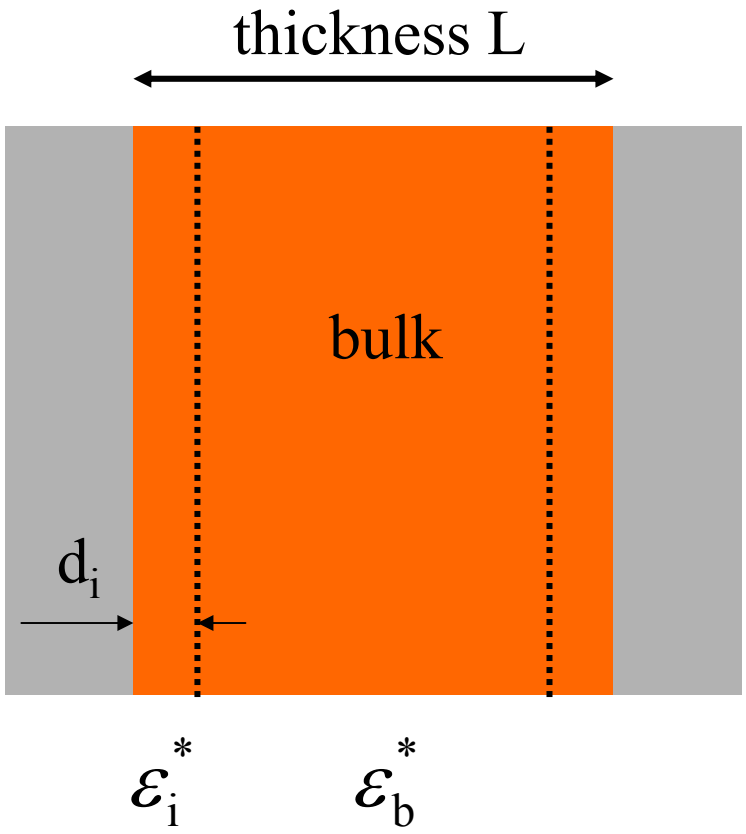
1. Sangoro, J.R., Serghei, A., Naumov, S., Galvosas, P., Kärger, J., Wespe, C., Bordusa, F., and Kremer,F. (2008)Charge transport and mass transport in imidazolium-based ionic liquids. Phys. Rev. E, 051202
2. Sangoro, J.R., Iacob, C., Serghei, A., Naumov, S., Galvosas, P., Kärger, J., Wespe, C., Bordusa, F., Stoppa, A., Hunger, J., Buchner, R., and Kremer, F. (2008) Electrical conductivity and translational diffusion in the 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid. J. Chem. Phys., 128 (21) 214509
3. Iacob, C., Sangoro, J. R., Serghei, A., Korth, Y., Naumov, S., Friedrich, C., Kärger, J. and Kremer, F. (2008) Charge transport and glassy dynamics in imidazole-based liquids. J. Chem. Phys., 129 (23) 234511
4. Sangoro, J. R., Iacob, C., Serghei, A., Friedrich, C., and Kremer, F. (2009) Universal scaling of charge transport in glass-forming ionic liquids. Phys. Chem. Chem. Phys., 11 (5) 913
5. Sangoro, J. R., Turky, G., Abdel-Rehim, M., Naumov, S., Ghoneim, A., Kärger, J., and Kremer, F. (2009) Charge transport and dipolar relaxations in hyperbranched polyamide amines. Macromolecules, 42(5) 1648-1651
6. Min, Y., Akbulut, M., Sangoro, J. R., Kremer, F., Prud'homme, R. K., Israelachvili, J. (2009) Measurement of forces across room temperature ionic liquids between mica surfaces. J. Phys. Chem. C, 113 (37), pp. 16445 – 16449
7. Krause, C., Sangoro, J.R., Iacob, C. and Kremer, F. (2010) Charge transport and dipolar relaxations in imidazolium-based ionic liquids. J. Phys. Chem. B, 114, 382-386.
8. Serghei, A., Tress, M., Sangoro, J. R., and Kremer, F. (2009) Electrode polarization and charge transport at metal-electrolyte interfaces. Phys. Rev. B, 80 184301.
9. Sangoro, J.R., Kärger, J., and Kremer, F. (2009). Broadband Dielectric Spectroscopy as a tool to study diffusion coefficients in conducting glass-forming systems. Dielectric Newsletter, 24,5.
10. Turky, G., Sangoro, J. R., Abdel-Rehim, M., and Kremer, F. (2010). Secondary relaxations and electrical conductivity in hyperbranched polyester amides. J. Polym. Sci. B: Polym. Phys., doi: 10.1002/polb.21966
11. Iacob, C., Sangoro, J. R., Papadopoulos, P., Schubert, T., Naumov, S., Valluilin, R., Kärger, J. and Kremer, F. (2010). Charge transport and diffusion of ionic liquids in nanoporous silica membranes. Submitted to: Phys. Chem. Chem. Phys.
12. Sangoro, J.R., and Kremer, F. (2010). Dielectric properties of ionic liquids. Dielectric Briefs, submitted.
13. Zech, O. Hunger, J., Sangoro, J. R., Kremer, F. Kunz, W., and Buchner, R. (2010). Correlation between polarity parameters and dielectric properties of [Na][TOTO] – a sodium-based ionic liquid. Submitted to: Green Chemistry.
14. Kremer, F., Serghei, A., Sangoro, J. R., Tress, M., and Mapesa, E. U. (2010) Broadband dielectric spectroscopy in nano-(bio)-physics. IEEE Trans. CEIDP, in press.

Thanks to

Ionic liquids

DFG SPP1191 priority program

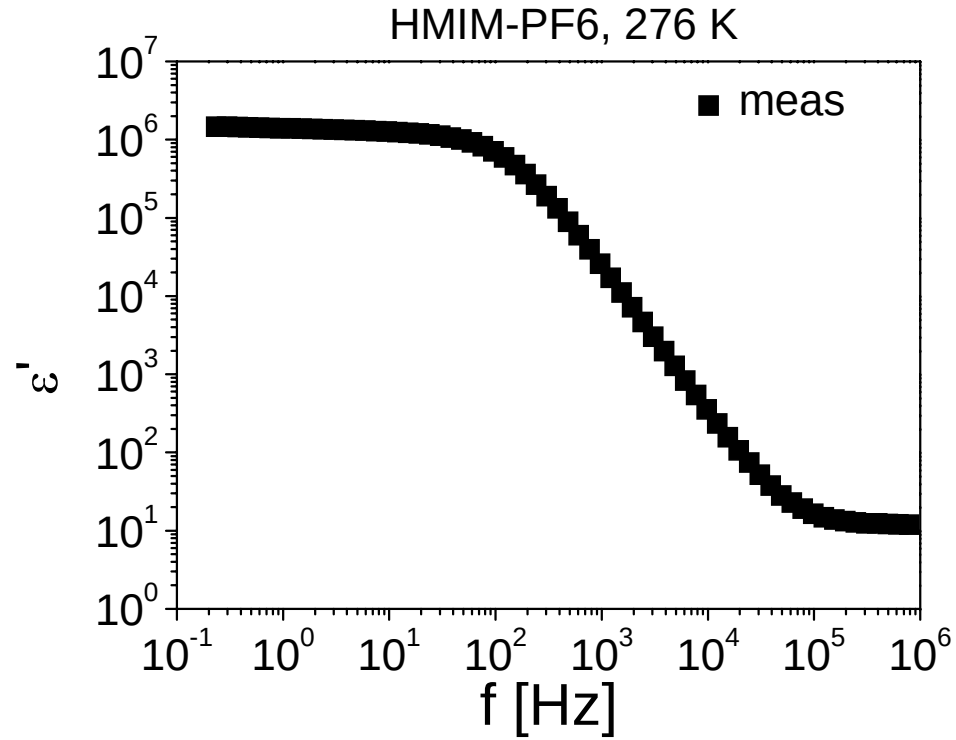


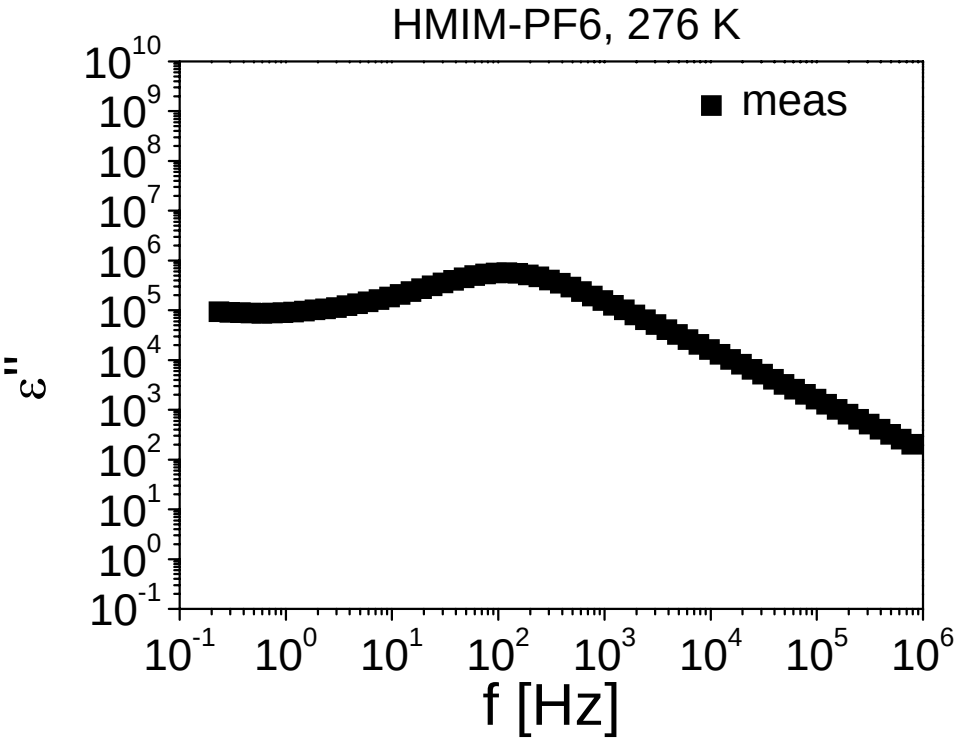


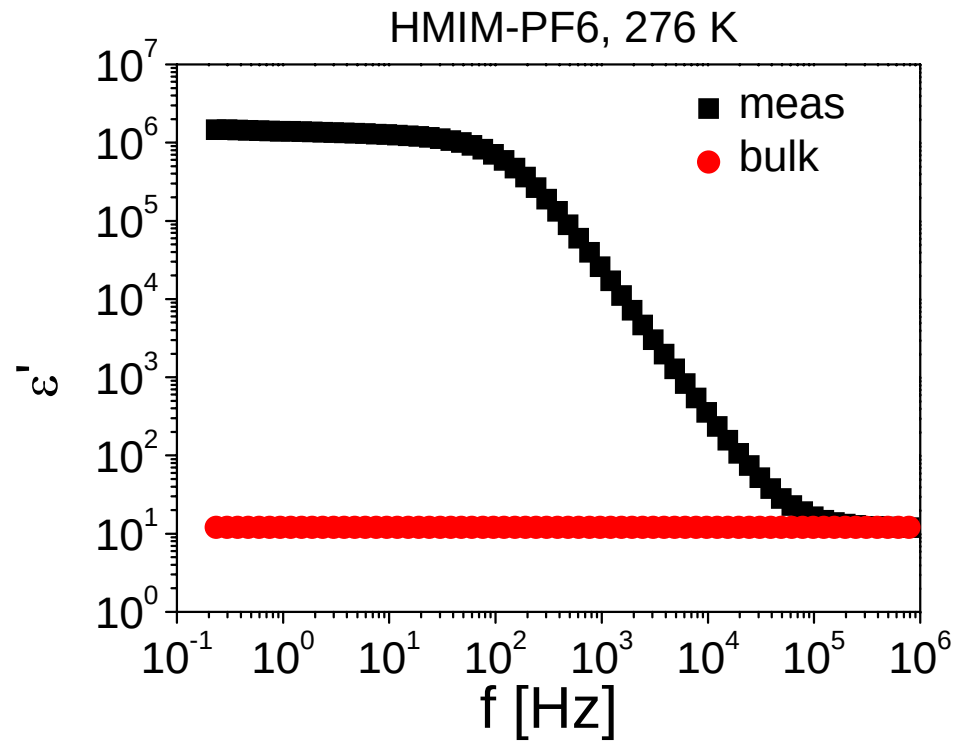
$$\frac{L}{\varepsilon^*_{meas}} = \frac{2d_i}{\varepsilon^*_i} + \frac{L\text{-}2d_i}{\varepsilon^*_b}$$

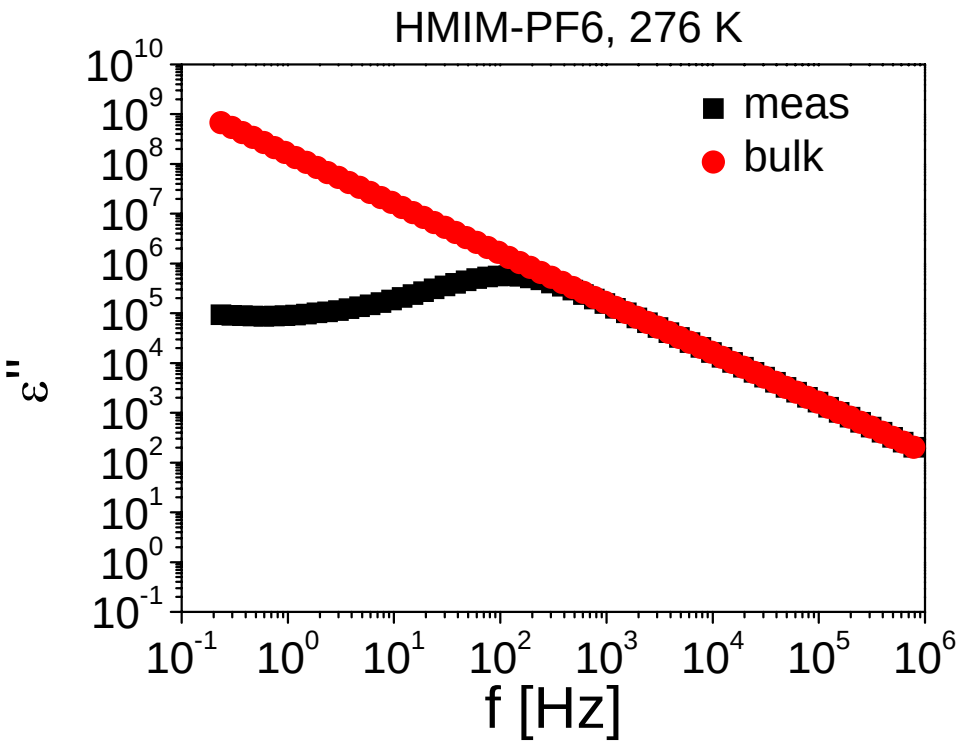
$$\varepsilon^*_i = \frac{\varepsilon^*_{meas}\varepsilon^*_b}{\varepsilon^*_b - \left(\frac{L}{2d_i} - 1\right)\varepsilon^*_{meas}}$$

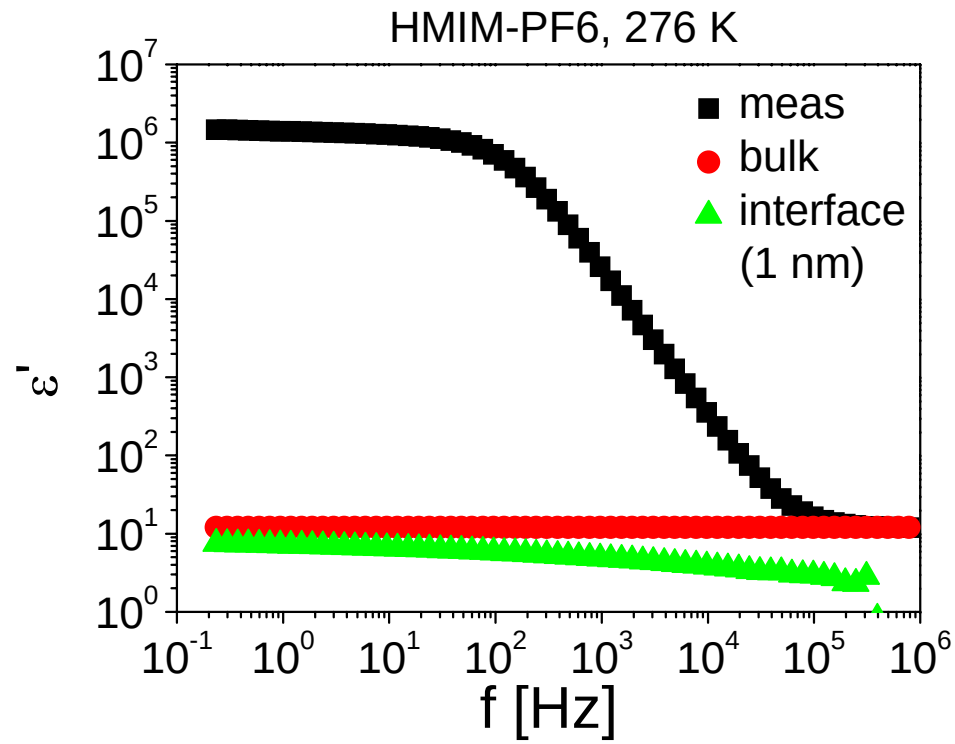
d_i is in the nanometric range

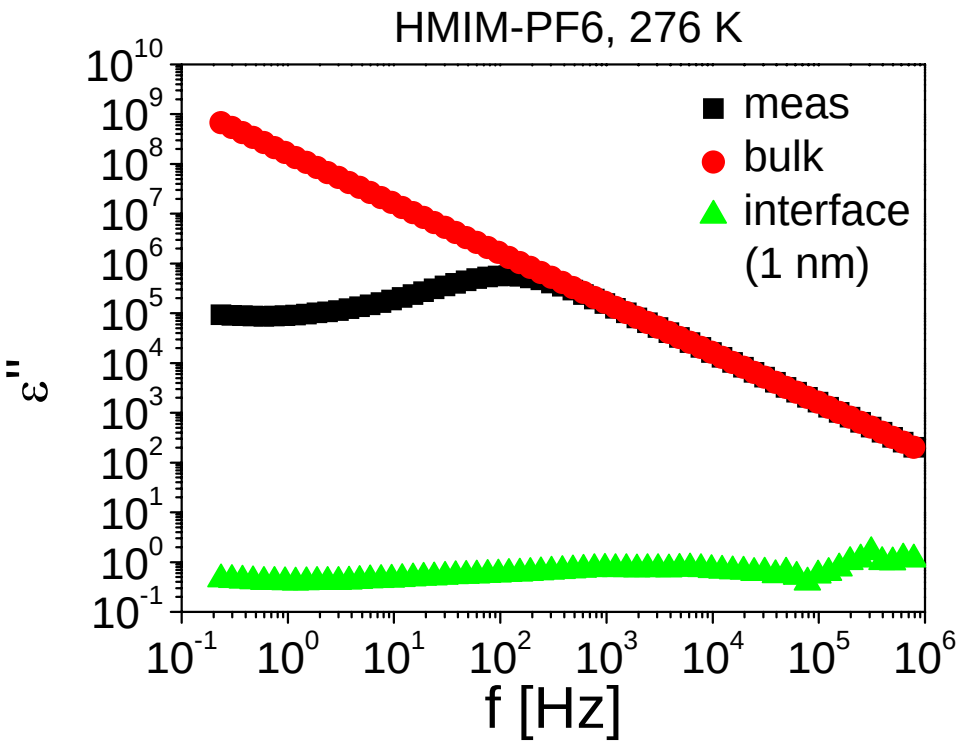

HMIM-PF6, 276 K
meas
ε'
f [Hz]


HMIM-PF6, 276 K
meas
ε''
f [Hz]

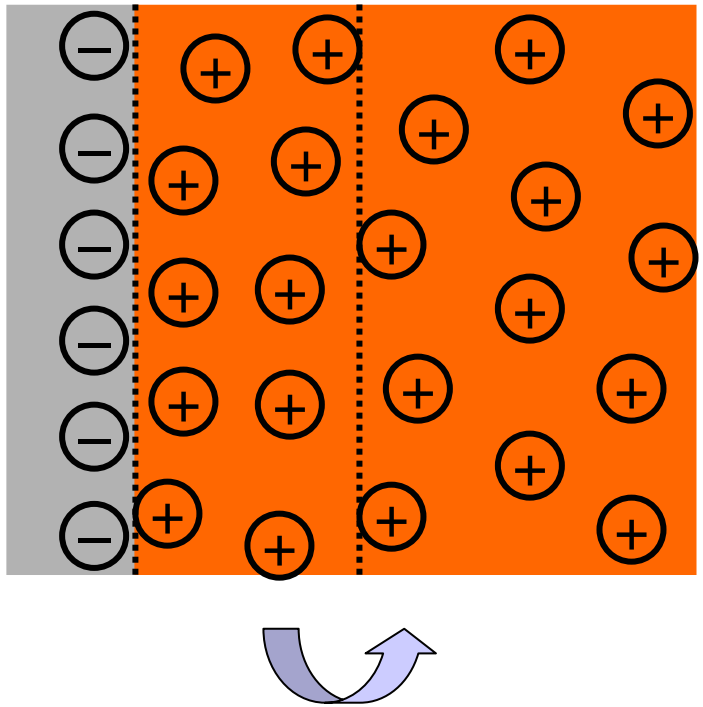

HMIM-PF6, 276 K
meas
bulk
ε'
f [Hz]


HMIM-PF6, 276 K
meas
bulk
ε''
f [Hz]


HMIM-PF6, 276 K
ε'
f [Hz]
meas
bulk
interface
(1 nm)

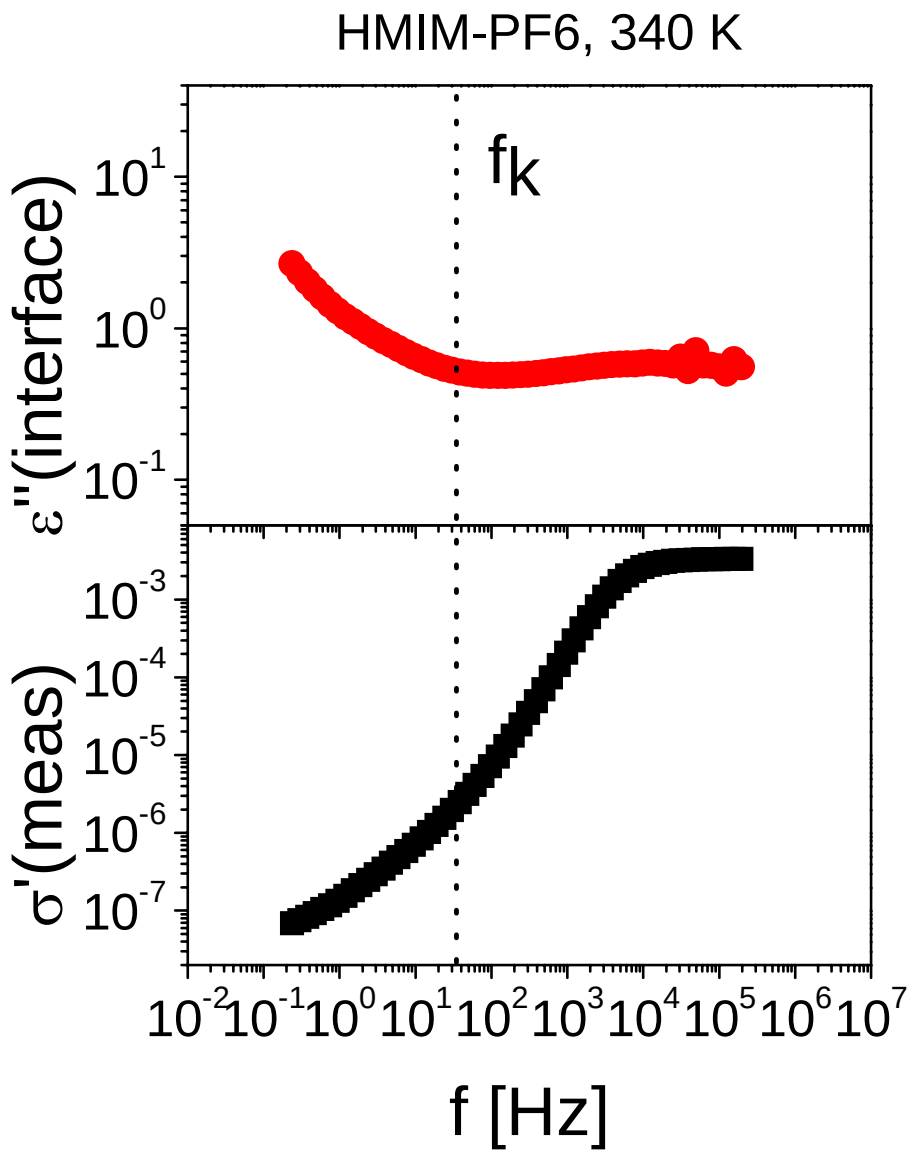

HMIM-PF6, 276 K
ε''
f [Hz]
meas
bulk
interface
(1 nm)

Charge transport at interfaces

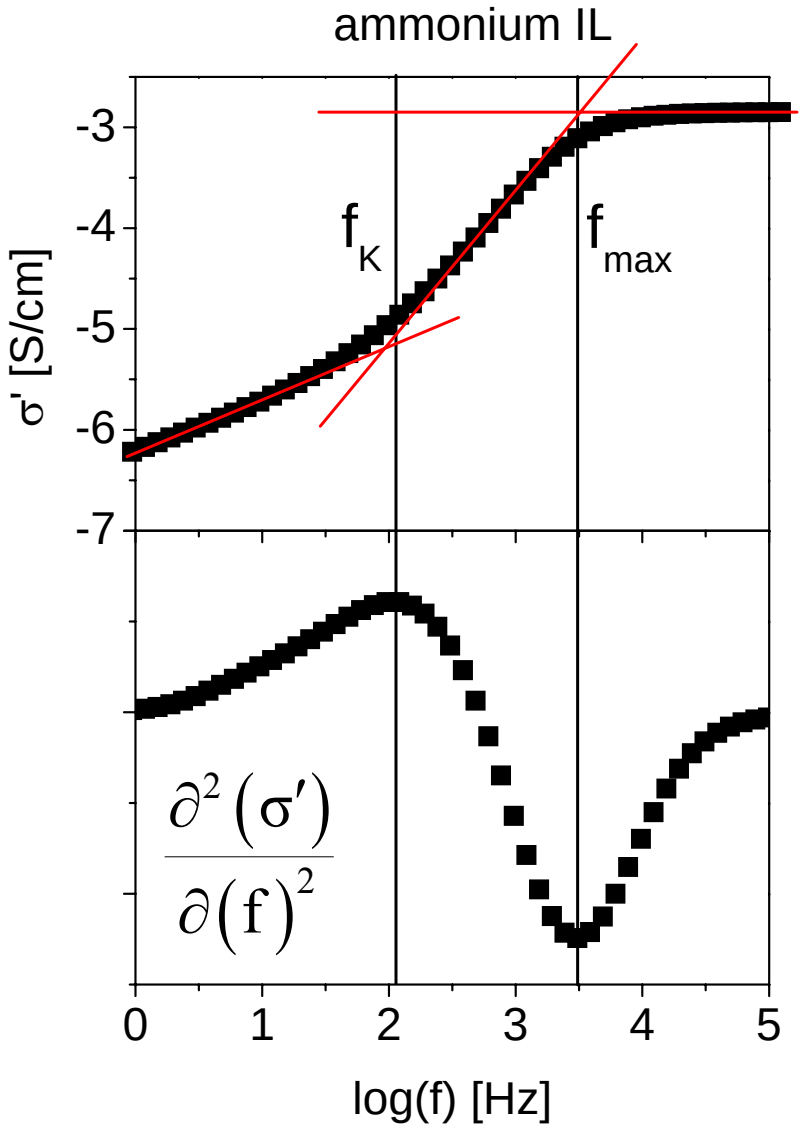


exchange process at rate $f_k(T)$

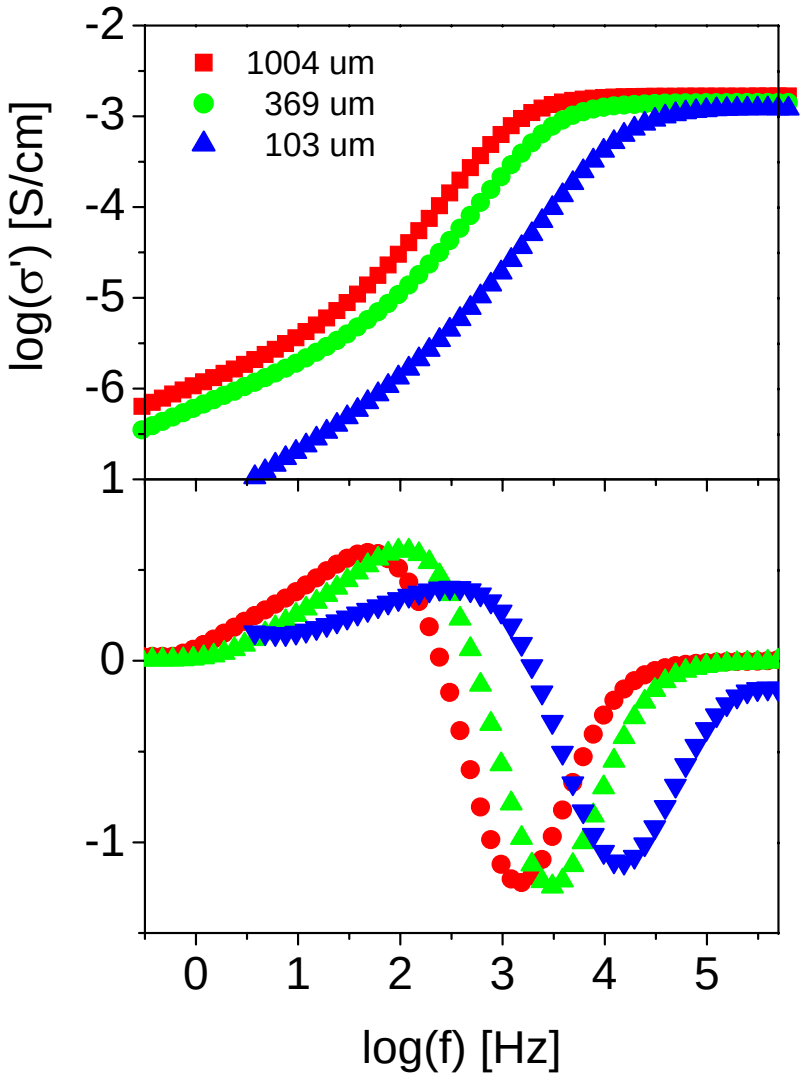
Charge transport at interfaces



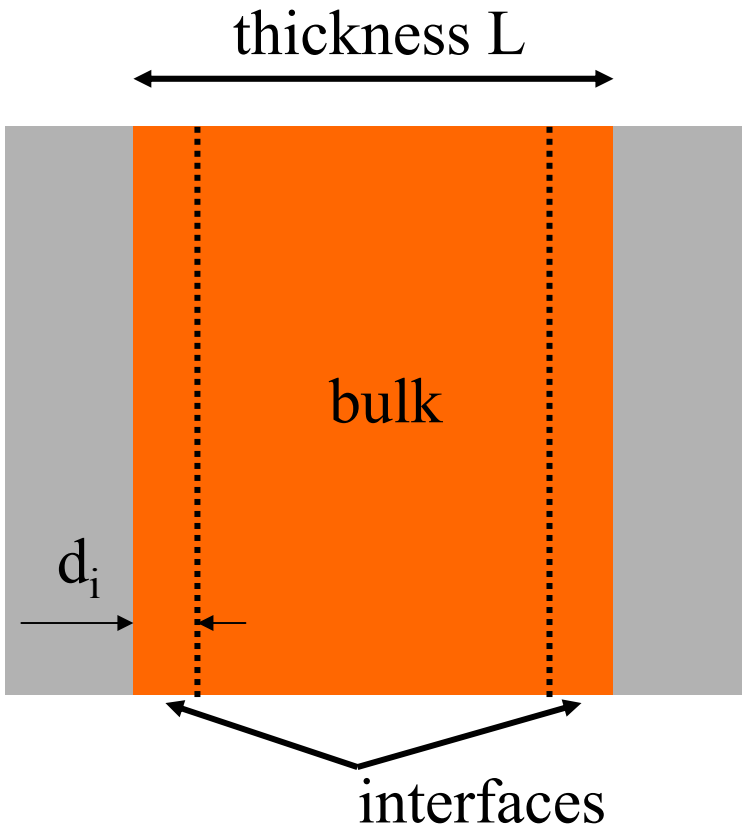
Charge transport at interfaces



Charge transport at interfaces



Dielectric function at the interface: first approach



Parameters of the problem:

Length L	measured
ε'_{meas}	measured
ε''_{meas}	measured
ε'_{bulk}	known
ε''_{bulk}	known
d_i	unknown
ε'_i	unknown
ε''_i	unknown

Dielectric function at the interface: first approach

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

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

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

Kramers-Kronig relation for $\varepsilon_i^*=\varepsilon_i^*(\omega, x)$

$$\varepsilon_i'(\omega,x)=\varepsilon_\infty+\frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon_i''(\omega,x)}{\omega^2-\omega_0^2}d\omega$$

$$\varepsilon_i''(\omega,x)=Y(\omega)X(x)$$

$$\varepsilon_i''(\omega,x)=\varepsilon_{bulk}''(\omega)X(x)$$

example: $\varepsilon_i''(\omega,x)=\varepsilon_{bulk}''(1-e^{-\lambda x})$

$$\varepsilon_i'(\omega,x)=\varepsilon_\infty+\frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon_i''(\omega,x)}{\omega^2-\omega_0^2}d\omega=\varepsilon_\infty+\frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon_{bulk}''(\omega)X(x)}{\omega^2-\omega_0^2}d\omega$$

$$=\varepsilon_\infty+X(x)\left(\frac{2}{\pi}\int_0^\infty \frac{\omega\varepsilon_{bulk}''(\omega)}{\omega^2-\omega_0^2}d\omega\right)$$

$$=\varepsilon_\infty+X(x)\left(\varepsilon_{bulk}'(\omega)-\varepsilon_\infty\right)$$

Dielectric function at the interface $\varepsilon_i^* = \varepsilon_i^*(\omega, x)$

$$\varepsilon_i'(\omega,x) = \varepsilon_\infty + X(x)\left(\varepsilon'_{bulk}(\omega) - \varepsilon_\infty\right)$$

$$\varepsilon_i''(\omega,x) = \varepsilon''_{bulk}(\omega) X(x)$$

$$X(x) = \frac{\varepsilon_i'(\omega,x) - \varepsilon_\infty}{\varepsilon'_{bulk}(\omega) - \varepsilon_\infty} = \frac{\varepsilon_i''(\omega,x)}{\varepsilon''_{bulk}(\omega)}$$

$$\boxed{\frac{\varepsilon_i''(\omega,x)}{\varepsilon''_{bulk}(\omega)} = \frac{\varepsilon_i'(\omega,x) - \varepsilon_\infty}{\varepsilon'_{bulk}(\omega) - \varepsilon_\infty}}$$

Dielectric function at the interface: first approach

$$\frac{L}{\varepsilon^{*}_{meas}} = \frac{2d_i}{\varepsilon^{*}_{i}} + \frac{L-2d_i}{\varepsilon^{*}_{bulk}}$$

$$\frac{\varepsilon''_i}{\varepsilon''_{bulk}} = \frac{\varepsilon'_i - \varepsilon_\infty}{\varepsilon'_{bulk} - \varepsilon_\infty}$$

Three equations with three unknown parameters:

d_i, ε'_i, ε''_i

Dielectric function at the interface: first approach

$$x=\frac{2d_i}{L},\quad Y=\frac{\left(\varepsilon'_{bulk}\right)^2+\left(\varepsilon''_{bulk}\right)^2}{\left(\varepsilon'_{meas}\right)^2+\left(\varepsilon''_{meas}\right)^2}=\frac{modb}{modm}$$

$$A=Y\varepsilon'_{meas}-(1-x)\varepsilon'_{bulk}$$

$$B=Y\varepsilon''_{meas}-(1-x)\varepsilon''_{bulk}$$

$$\varepsilon_\infty(A^2+B^2)=x\ modb\ (A-\varepsilon'_{bulk}B+\varepsilon_\infty B)$$

$$\alpha=\frac{\varepsilon'_{bulk}\varepsilon'_{meas}+\varepsilon''_{bulk}\varepsilon''_{meas}}{modb}$$

$$\beta=\varepsilon'_{meas}-\varepsilon'_{bulk}\varepsilon''_{meas}+\varepsilon_\infty\varepsilon''_{meas}$$

$$\gamma=\varepsilon'_{bulk}\varepsilon''_{bulk}-\varepsilon'_{bulk}-\varepsilon_\infty\varepsilon''_{bulk}$$

$$\varepsilon_\infty\left[Y+(1-x)2-2\alpha Y(1-x)\right]=x\left[\beta Y+\gamma(1-x)\right]$$

$$a=\varepsilon_\infty+\gamma$$

$$b=2\varepsilon_\infty-2\alpha Y\varepsilon_\infty+\beta Y+\gamma$$

$$c=\varepsilon_\infty Y+\varepsilon_\infty-2\alpha\varepsilon_\infty Y$$

$$a\,x^2-b\,x+c=0$$

$$x_{1,2}=\frac{b\pm\sqrt{b^2-4ac}}{2a}$$

$$d_i=x\frac{L}{2}$$

$$\varepsilon'_i=x\ modb\ \frac{Y\varepsilon'_{meas}-(1-x)\varepsilon'_{bulk}}{\left(Y\varepsilon'_{meas}-(1-x)\varepsilon'_{bulk}\right)^2+\left(Y\varepsilon''_{meas}-(1-x)\varepsilon''_{bulk}\right)^2}$$

$$\varepsilon''_i=x\ modb\ \frac{Y\varepsilon''_{meas}-(1-x)\varepsilon''_{bulk}}{\left(Y\varepsilon'_{meas}-(1-x)\varepsilon'_{bulk}\right)^2+\left(Y\varepsilon''_{meas}-(1-x)\varepsilon''_{bulk}\right)^2}$$