האוניברסיטה העברית בירושלים
The Hebrew University of Jerusalem

# The Data treatment of complex dielectric behaviour

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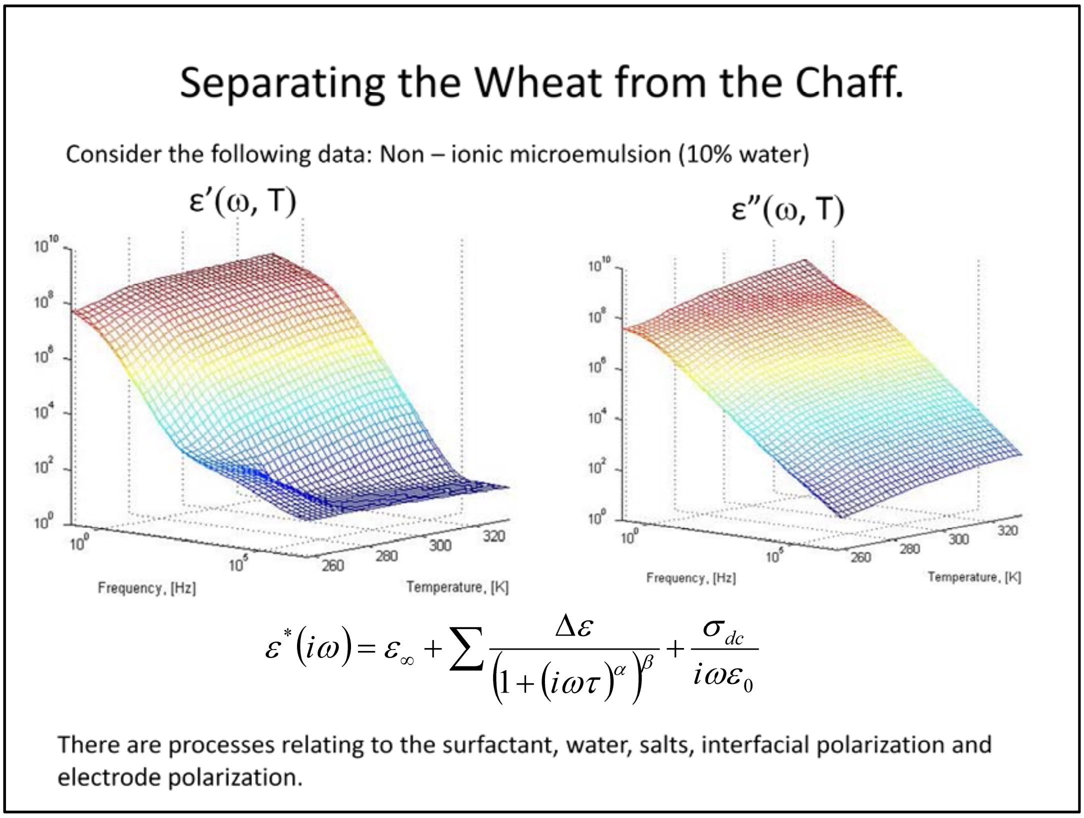
# The Problem

- Complex systems necessarily entail complex dielectric behaviour. How do we “mine” the nuggets from all the dirt??
- Most Fitting routines consider one variable, frequency, and a parameter set. Yet the energy landscape is governed by temperature. How do we fit over 2 variables and a parameter set?
- How do we deal with Electrode Polarization?



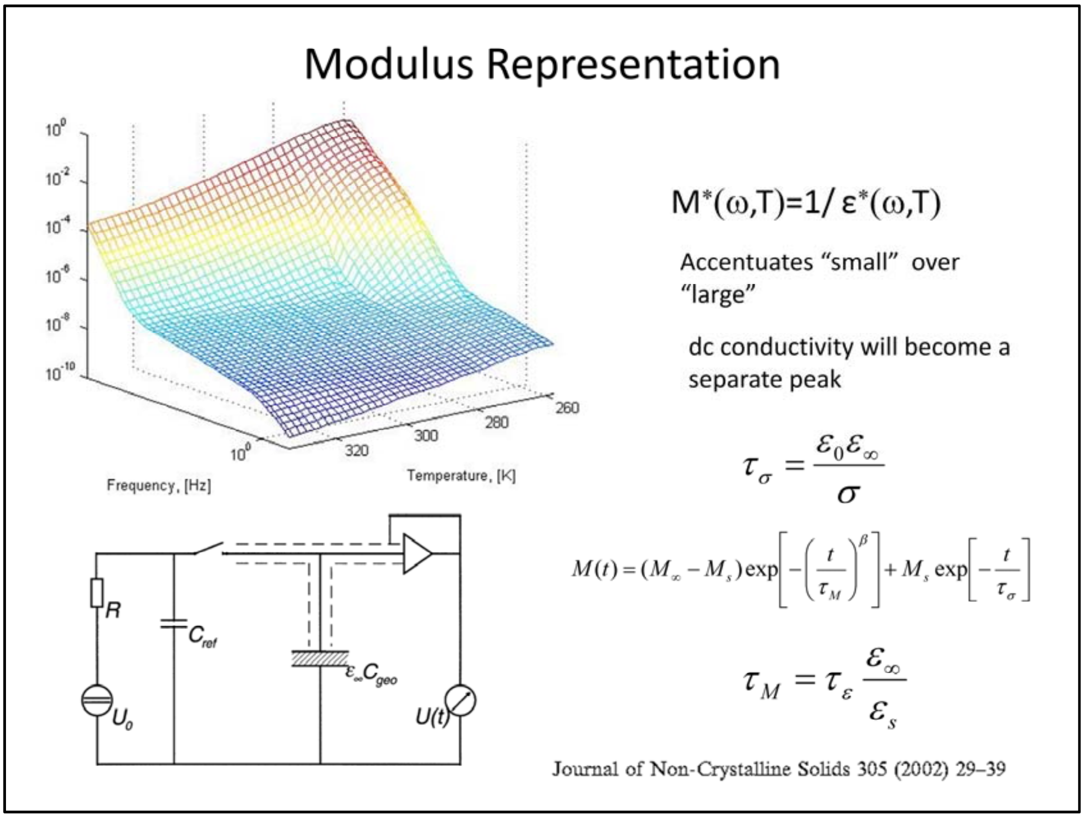
## Separating the Wheat from the Chaff.

Consider the following data: Non – ionic microemulsion (10% water)

$$\varepsilon^*(i\omega) = \varepsilon_\infty + \sum \frac{\Delta\varepsilon}{\left(1+(i\omega\tau)^\alpha\right)^\beta} + \frac{\sigma_{dc}}{i\omega\varepsilon_0}$$

There are processes relating to the surfactant, water, salts, interfacial polarization and electrode polarization.

In the slide one can see a number of features, sometimes more easily in ε' than in ε". Each feature represents the relaxation of a dielectric process-dipole orientation, interfacial polarization charge transport, etc. Our goal is to study the temperature dependence (or other thermodynamic variable dependence, e.g. Pressure) of each individually. To this end we will carry out a fitting using phenomenological functions such as Havilak-Negami and its derivatives, the Cole-Cole function ($0<\alpha<1$, $\beta=1$) or Cole-Davidson ($0<\beta<1$, $\alpha=1$) or Debye ($\alpha=1$, $\beta=1$). While the debate as to the meaning of the structural parameters, α and β, is still an open debate we can gain a lot of information from the temperature behavior of the relaxation time, τ.



## Modulus Representation

$$M^*(\omega,T)=1/\,\varepsilon^*(\omega,T)$$

Accentuates “small” over “large”

dc conductivity will become a separate peak

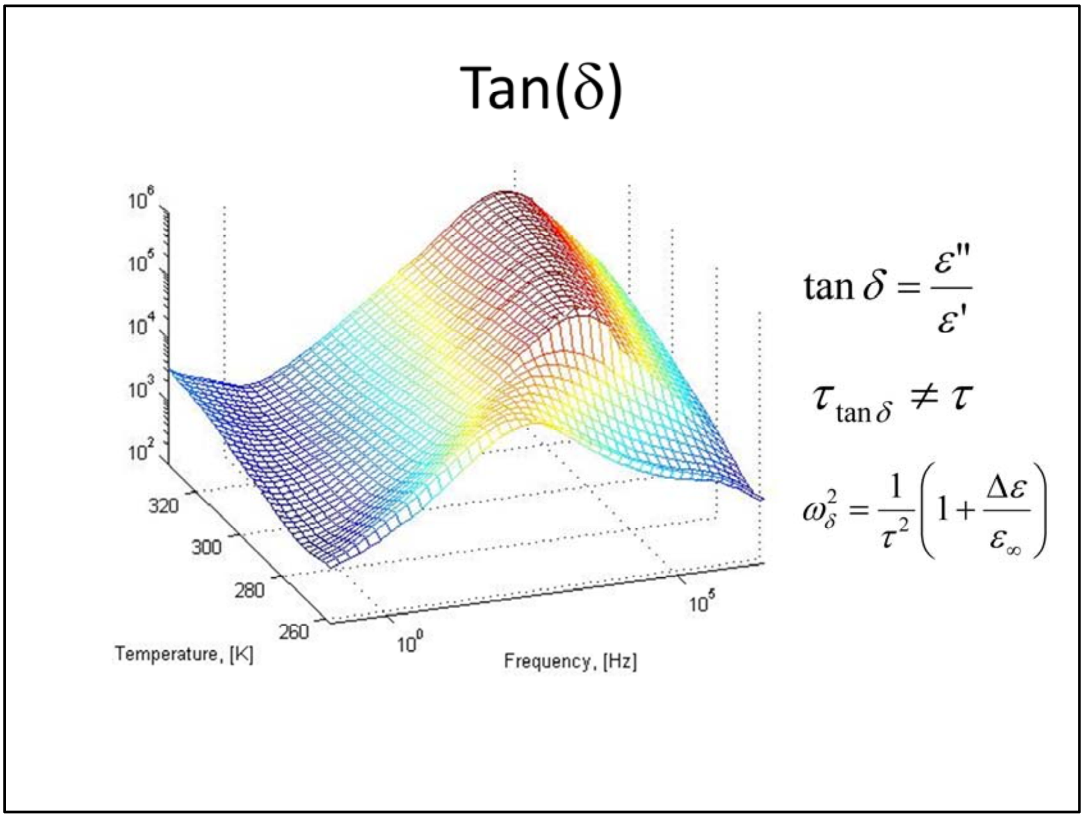
$$\tau_\sigma = \frac{\varepsilon_0 \varepsilon_\infty}{\sigma}$$

$$M(t) = (M_\infty - M_s)\exp\left[-\left(\frac{t}{\tau_M}\right)^\beta\right] + M_s \exp\left[-\frac{t}{\tau_\sigma}\right]$$

$$\tau_M = \tau_\varepsilon \frac{\varepsilon_\infty}{\varepsilon_s}$$

Journal of Non-Crystalline Solids 305 (2002) 29–39

However, there are more than one way to view the data. We could choose a Modulus representation, as defined in the slide. This has a tendency to emphasize the weaker processes over the stronger process. Importantly dc conductivity in Modulus representation becomes a peak with its relaxation time defined by the Maxwell time of the system (defined in the slide as $\tau_\sigma$). The Modulus of the sample can also be measured directly (see the paper in the slide). By placing a fixed current over the sample and measuring the resulting change in the field. This is simply done by charging the sample and then opening the switch (current is constant at zero.) A detailed description is available in the referred paper.



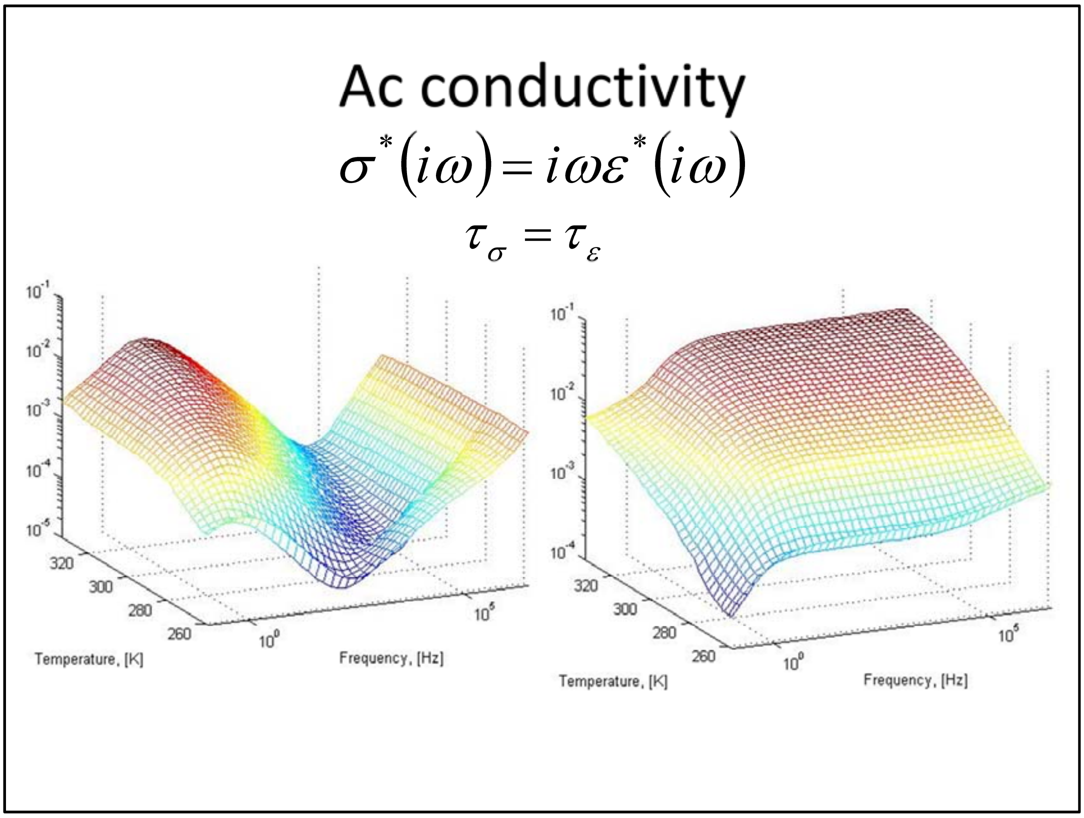
# Tan(δ)

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

$$\tau_{\tan\delta} \neq \tau$$

$$\omega_\delta^2 = \frac{1}{\tau^2}\left(1+\frac{\Delta\varepsilon}{\varepsilon_\infty}\right)$$

Tan delta is a convenient way to show the number of relaxation peaks in the data. While the temperature behaviour of the peaks is maintained they do not necessarily coincide with the dielectric peaks. For a pure Debye relaxation with no dc conductivity the peak in tan(δ) will occur at an angular frequency given by $\omega^2=(1/\tau^2)(1+\Delta\varepsilon/\varepsilon_\infty)$. If the entire frequency spectrum is visible then the correction term is usually negligible. However, we usually see only a portion of the window and in this case it may be significant and, worse still, have a different temperature dependence than the dielectric relaxation time. Beware when comparing relaxation times and energies of activation this way!!



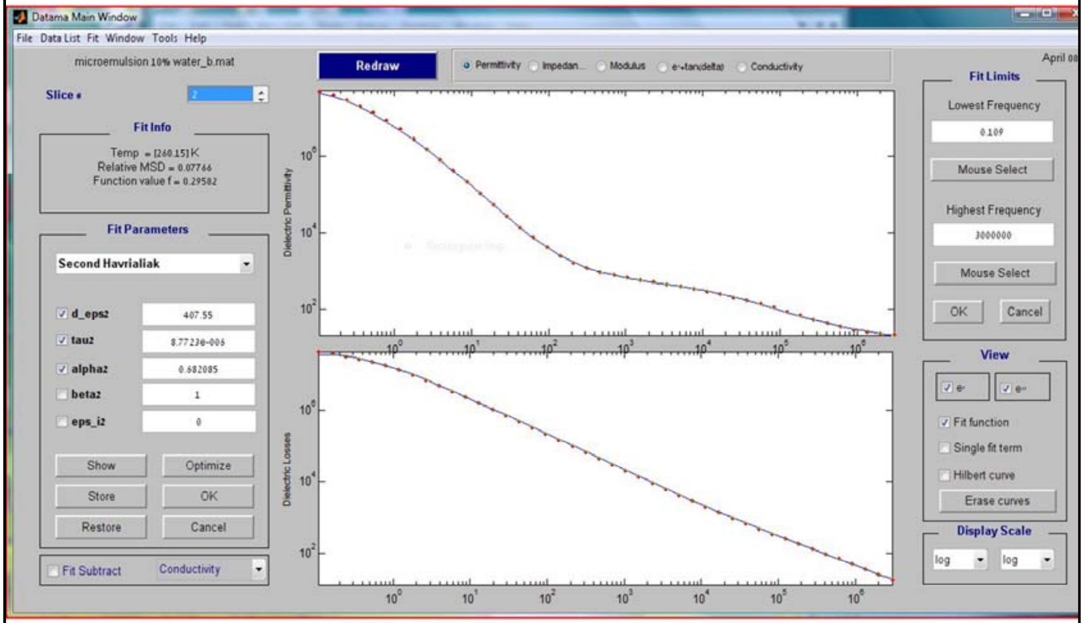
# Ac conductivity

$$\sigma^*(i\omega) = i\omega\varepsilon^*(i\omega)$$

$$\tau_\sigma = \tau_\varepsilon$$

When an understanding of dc conductivity is required it is sometimes more sensible to view data in terms of the ac conductivity. The low frequency plateau of the real component is all that is required to establish its value. Unlike the example of tanδ in the previous slide the relaxation times of a Debye process in permittivity and in ac conductivity do coincide. All of the previous slides were based on the same data. While it is not always possible to compare energies of activation between the different representations, one can note the same critical points in each. For instance a phase transition at a particular temperature will be maintained in the representations used.

# Datama Face Plate


Datama Main Window

microemulsion 10% water_b.mat

Slice # 2

Fit Info

Temp = [260.15] K
Relative MSD = 0.07766
Function value f = 0.29582

Fit Parameters: Second Havrialiak

☑ d_eps2 407.55
☑ tau2 8.77230-005
☑ alpha2 0.682085
☐ beta2 1
☐ eps_i2 0

☐ Fit Subtract: Conductivity

● Permittivity ○ Impedan... ○ Modulus ○ e-tan(delta) ○ Conductivity

Fit Limits

Lowest Frequency: 0.109

Highest Frequency: 3000000

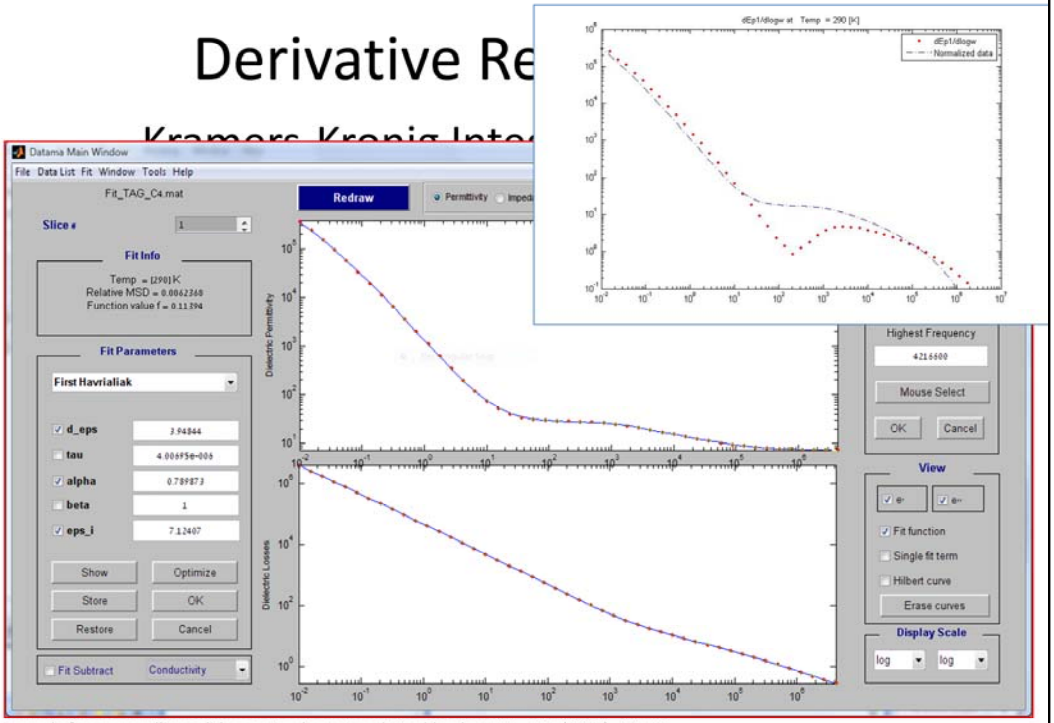
View: ☑ e' ☑ e'' ☑ Fit function ☐ Single fit term ☐ Hilbert curve

Display Scale: log log

Datama is an in house program based on Matlab and capable of fitting complex dielectric data. The built in functions are Havrilak – Negami , johnscher and dc conductivity. It also implements Recaps in order to fit electrode polarization tails. More of this in later slides. It is described in the article: “**Dielectric spectroscopy data treatment: I. Frequency Domain**” N. Axelrod, E. Axelrod, A. Gutina, A. Puzenko, P. Ben Ishai and Yu. Feldman, Meas. Sci. Technol. **15** (2004) 755-764.

# Derivative Re

Kramers Kronig Inte



Fit_TAG_C4.mat

Slice # 1

Fit Info
Temp = [290] K
Relative MSD = 0.0062368
Function value f = 0.11394

Fit Parameters
First Havrialiak
☑ d_eps 3.94844
☐ tau 4.00695e-006
☑ alpha 0.789873
☐ beta 1
☑ eps_i 7.12407

☐ Fit Subtract Conductivity

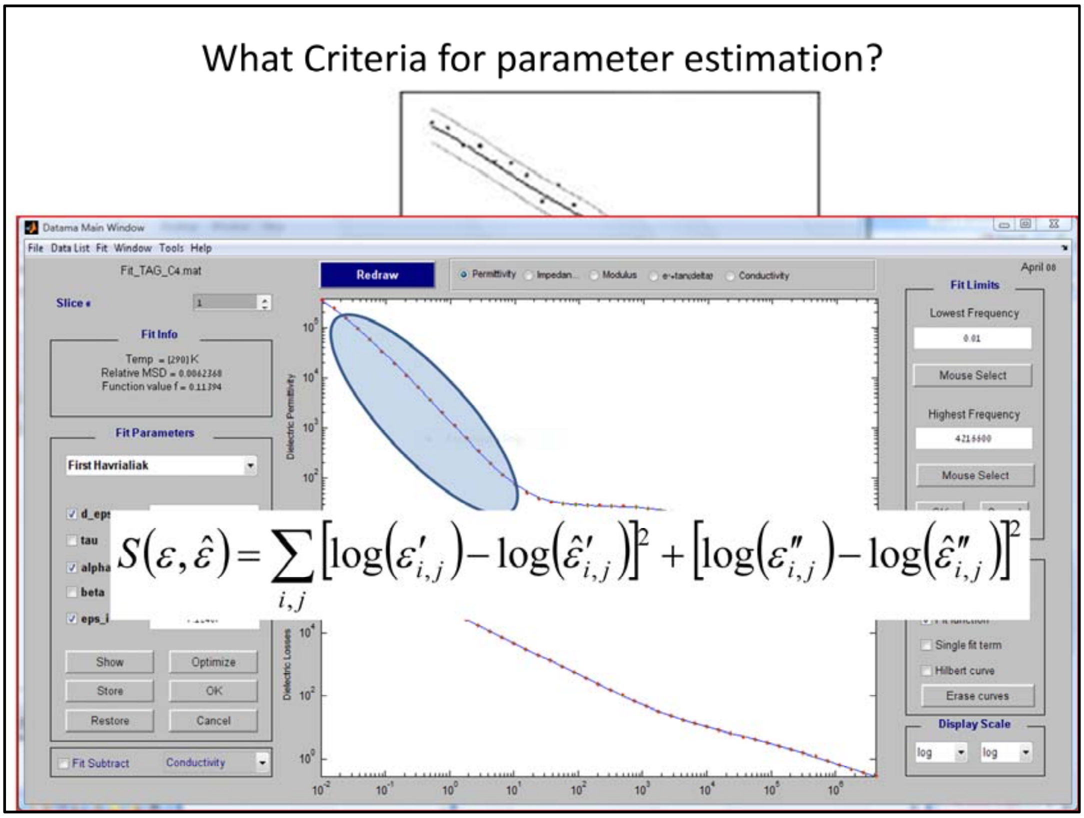
Highest Frequency 4216600

☑ Fit function
☐ Single fit term
☐ Hilbert curve

Display Scale log log

Journal of non-crystalline solids, van Turnhout J. and Wuebbenhorst M., **305** (2002), 40 -49

When first viewing data a useful technique to evaluate the number of processes is to consider the derivatives. This and a few other good tips can be found in the article: Journal of non-crystalline solids, van Turnhout J. and Wuebbenhorst M., **305** (2002), 40 -49



## What Criteria for parameter estimation?

$$S(\varepsilon,\hat{\varepsilon})=\sum_{i,j}\left[\log\left(\varepsilon'_{i,j}\right)-\log\left(\hat{\varepsilon}'_{i,j}\right)\right]^2+\left[\log\left(\varepsilon''_{i,j}\right)-\log\left(\hat{\varepsilon}''_{i,j}\right)\right]^2$$

Fit_TAG_C4.mat

Slice 1

Temp = [290] K
Relative MSD = 0.0062368
Function value f = 0.11394

First Havrialiak

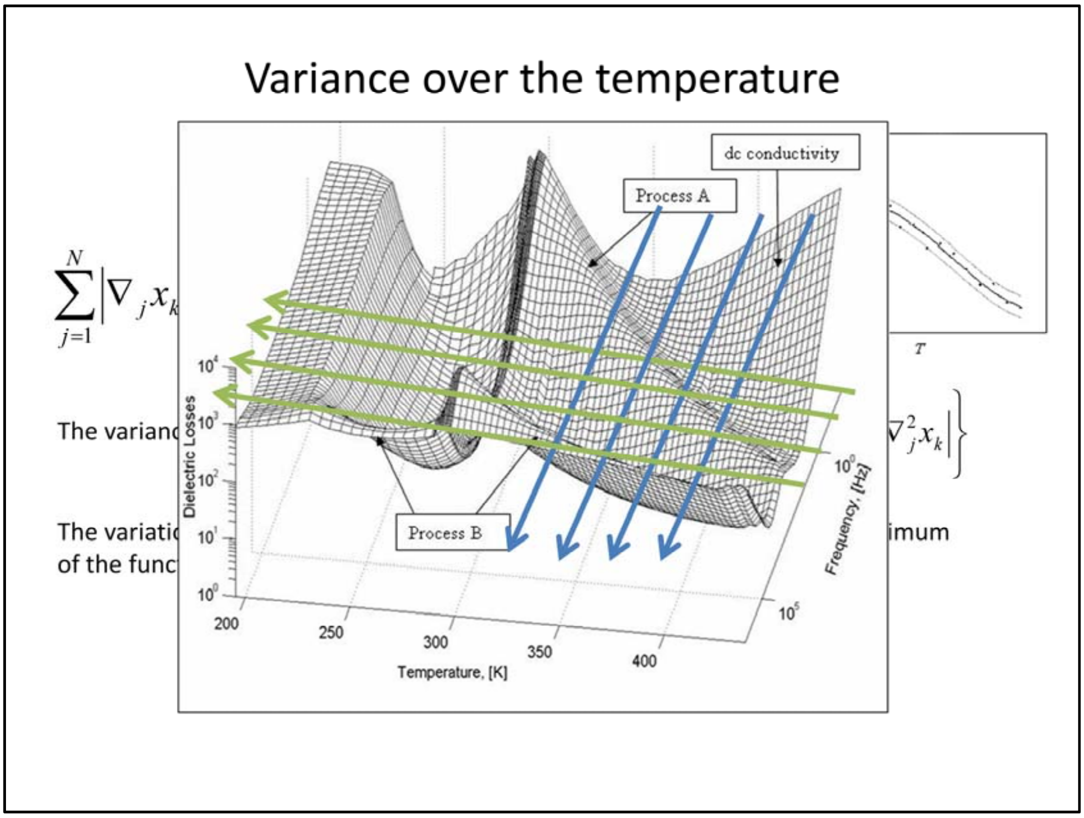
Lowest Frequency 0.01

Highest Frequency 4216600

A strong advantage of an in-house program is the measure by which a dielectric model is evaluated in regards to the experimental data. Because Broad band dielectric spectroscopy covers such a broad frequency range it can also cover in a single measurement an extraordinarily large range of different types of polarization. Some is these, such as interfacial or electrode polarization, maybe of many orders of magnitude stronger than interesting processes occurring at the higher frequencies. A regular linear measure for the Chi function will fail to fit such data. The disparity between dielectric strengths can be evened out by using a logarithmic measure, making fitting possible.

# Global Fitting

- Usually we refer only to frequency as a variable and fit accordingly. We end up with a set of fitting parameters which demonstrate a temperature dependence. In other words temperature is also a variable.
- A proper fit should include temperature as well.
- How can this be achieved?
- Post-fitted parameter smoothing can spoil the quality of the fit.



## Variance over the temperature

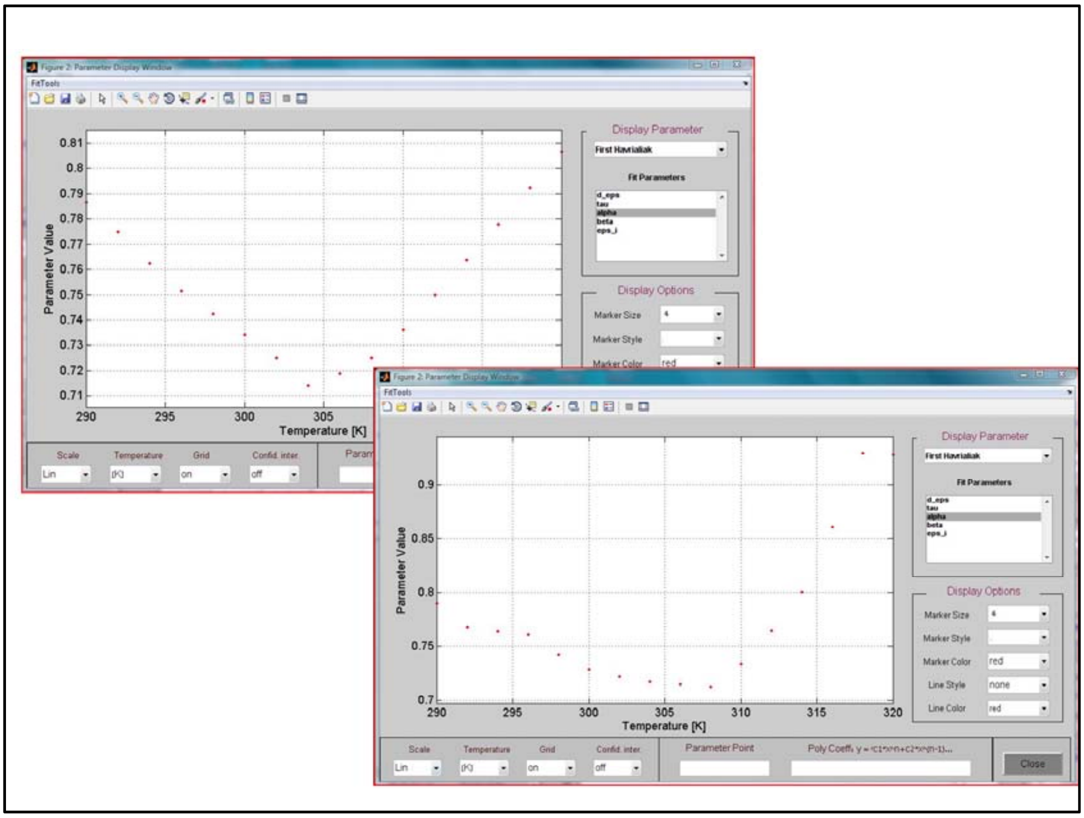
$\sum_{j=1}^{N} \left| \nabla_j x_k \right.$

The varianc

$\left. \nabla_j^2 x_k \right| \}$

The variati imum
of the func

A Global fit is achieved by taking the temperature, after an initial fit over every temperature slice, and using it to make a further variation of the parameters themselves (*α, ε∞, Δε, β*). To do so an additional penalty function is defined (L[x]) and the measure is then redefined. The initial set of parameters acts as the starting point for a further optimization. In this way a valid smoothing of the parameters in temperature is obtained. A more detailed description of this procedure is found in the article;
"**Dielectric spectroscopy data treatment: I. Frequency Domain**" N. Axelrod, E. Axelrod, A. Gutina, A. Puzenko, P. Ben Ishai and Yu. Feldman, Meas. Sci. Technol. **15** (2004) 755-764



Display Parameter: First Havriliak

Fit Parameters: alpha

Marker Size: 4

Marker Color: red

Line Style: none

Line Color: red

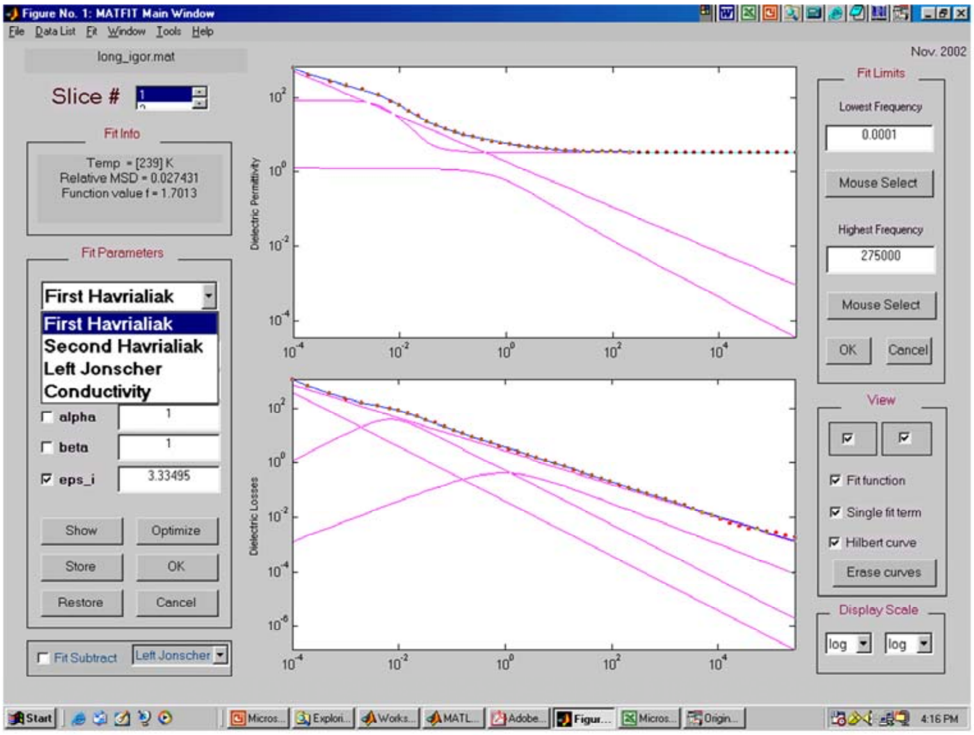
Scale: Lin

Temperature: (K)

Grid: on

Confid. inter.: off

# Typical Curve-Fitting for Crystalline Glycerol, ~$10^{-4}$ Hz



long_igor.mat

Nov. 2002

Slice # 1

Temp = [239] K
Relative MSD = 0.027431
Function value f = 1.7013

First Havrialiak

☐ alpha 1
☐ beta 1
☑ eps_i 3.33495

☐ Fit Subtract Left Jonscher

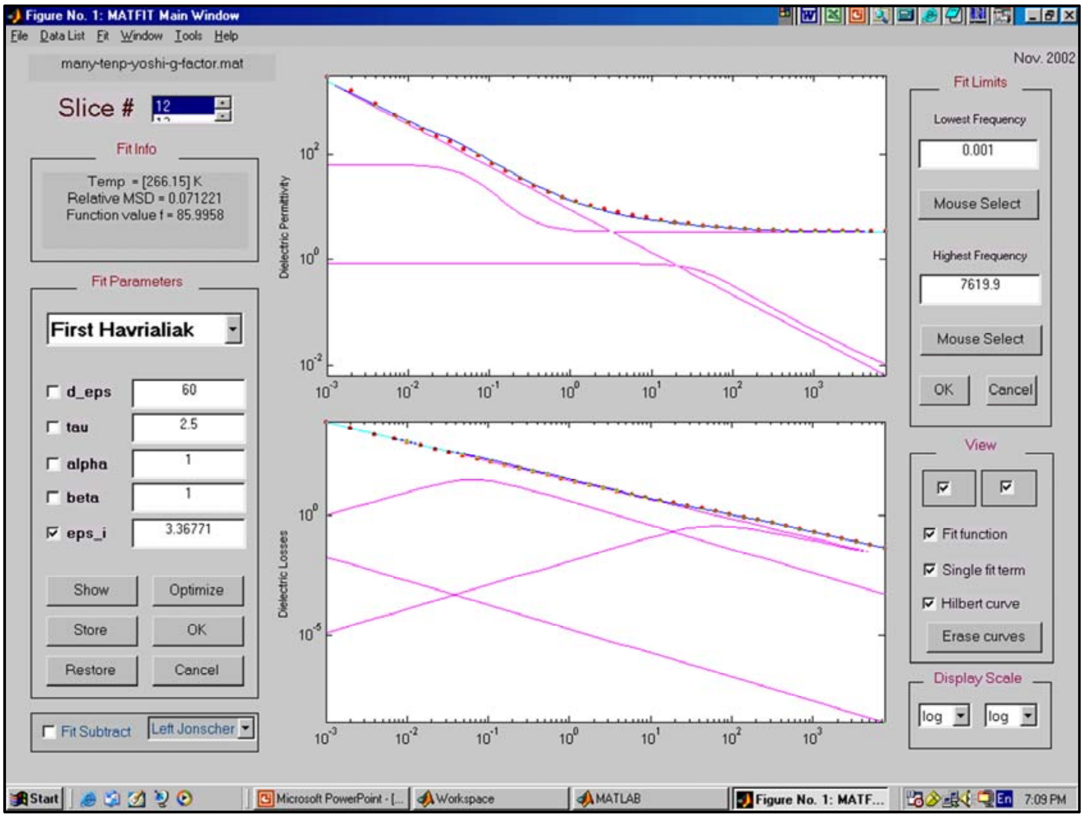
Lowest Frequency 0.0001

Highest Frequency 275000

☑ ☑

☑ Fit function
☑ Single fit term
☑ Hilbert curve

log log



many-tenp-yoshi-g-factor.mat

Nov. 2002

Slice # 12

Fit Info

Temp = [266.15] K
Relative MSD = 0.071221
Function value f = 85.9958

Fit Parameters

First Havrialiak

☐ d_eps 60
☐ tau 2.5
☐ alpha 1
☐ beta 1
☑ eps_i 3.36771

☐ Fit Subtract Left Jonscher

Fit Limits

Lowest Frequency 0.001

Highest Frequency 7619.9

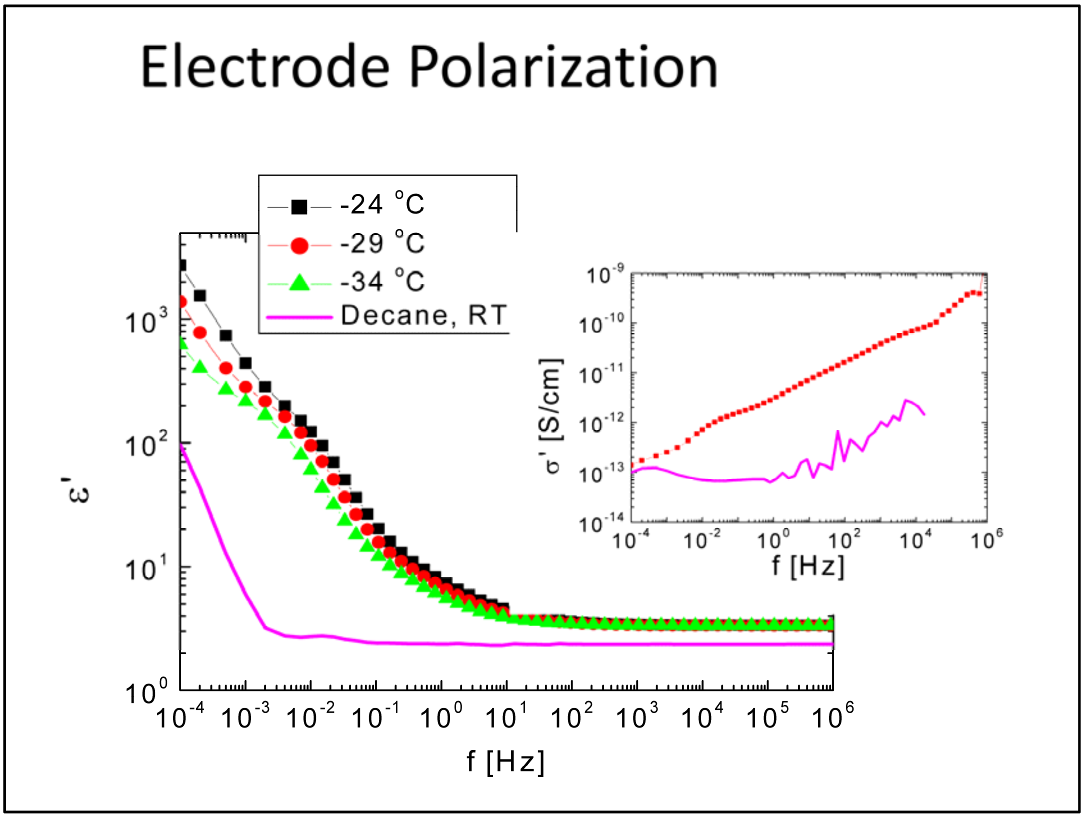
View

☑ ☑

☑ Fit function
☑ Single fit term
☑ Hilbert curve

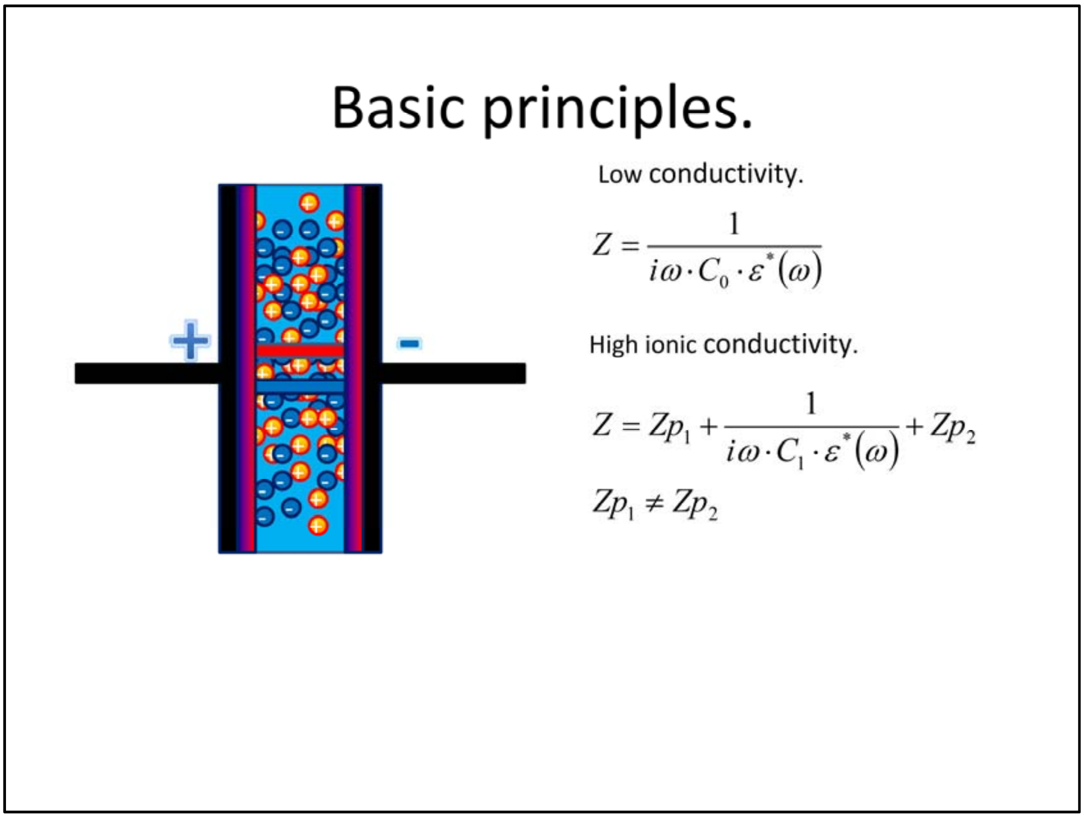
Display Scale

log log



# Electrode Polarization

Electrode polarization. For the electrochemical community contact potential is an important topic of research with strong implications for the catalyst and energy industries. For the Dielectrician it is a parasite that disrupts our ability to interpret dielectric data in the low frequencies. It occurs whenever there are free ions in the sample and affects mainly liquids. Even in something as non-polar as decane, there are enough pollutants to provide an electrode polarization effect. There are a number of articles and books describing the phenomena. A good place to start is: H. Ohshima, Electrical phenomena at interfaces, Marcel Dekker, Inc. Chapter #4, (1998).



## Basic principles.

Low conductivity.

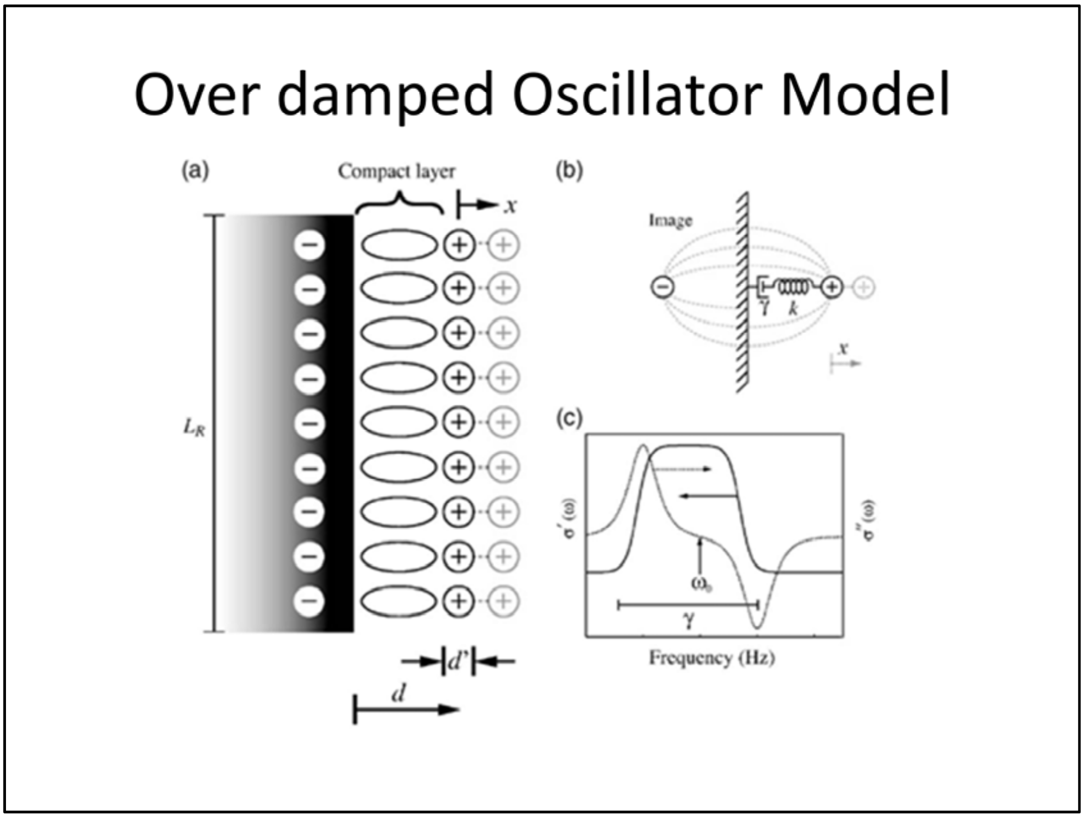
$$Z = \frac{1}{i\omega \cdot C_0 \cdot \varepsilon^*(\omega)}$$

High ionic conductivity.

$$Z = Zp_1 + \frac{1}{i\omega \cdot C_1 \cdot \varepsilon^*(\omega)} + Zp_2$$

$$Zp_1 \neq Zp_2$$

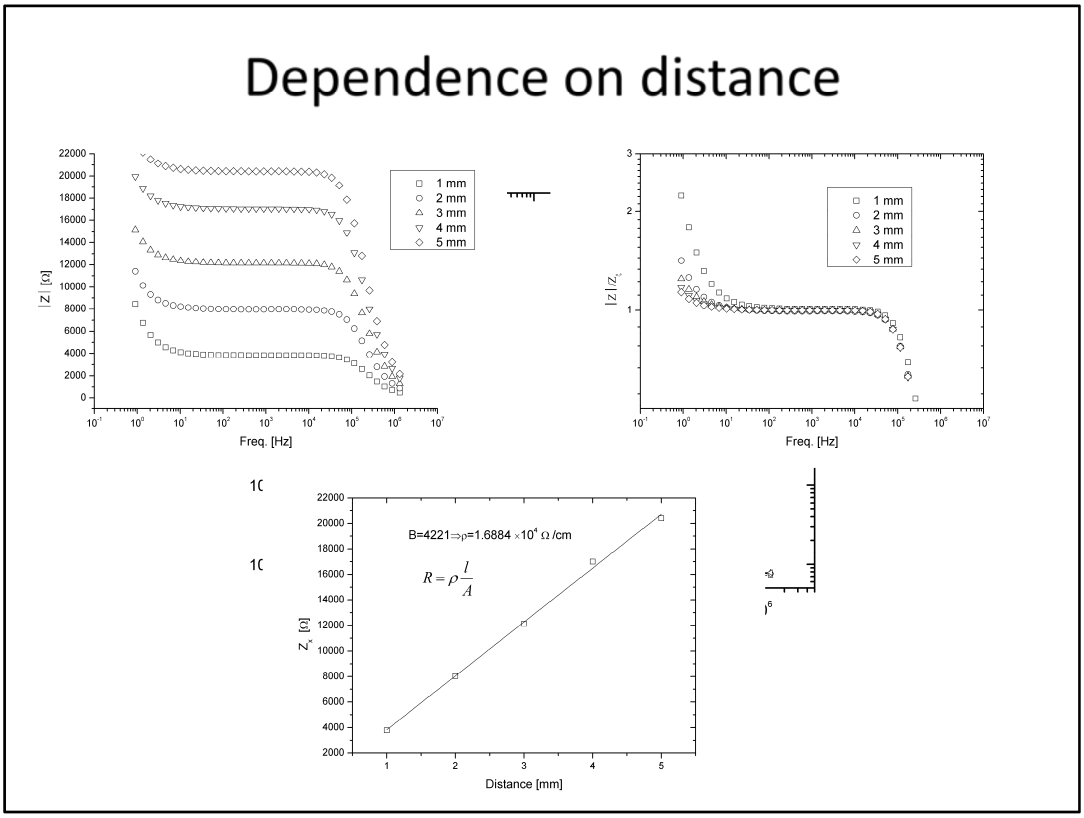
The basic model (*Helmholtz layer*, after the first description of the problem by Helmholtz , Helmholtz, H. *Pogg.Ann.* **LXXXIX**, 211 (1853), in 1853 ). A simplified description can be found at *http://en.wikipedia.org/wiki/Double_layer_(interfacial)*. In terms of impedances it can be considered as a serial impedance between the bulk and the electrode, that depends on a number of parameters and is stronger as the concentration of ions (or conductivity) is higher. The electrode polarization is not necessarily the same for each electrode and can depend on electrode polishing, metal and geometry.



# Over damped Oscillator Model

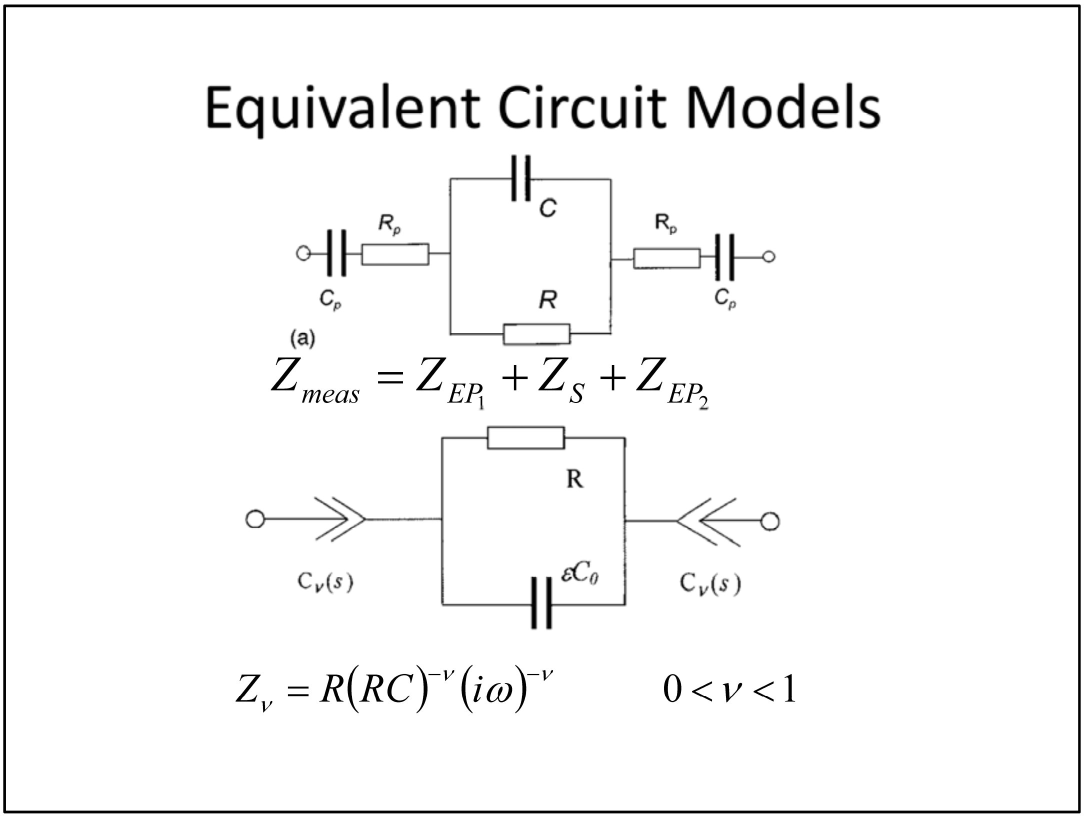
According to the characteristics of EP dispersion and its dependence on the ion's concentration, Miller et al [1] made an analogous behaviour to over-damped oscillators. In his model, the ions are oscillating near the interface, and the motion is over-damped with a dissipating force as a function of different mechanisms, such as Stoke’s drag force, which is a function of the fluid’s viscosity, and the dimension of ions. Other collision interactions will also dissipate energy in a similar fashion, and he attribute to include all of the possible factors that damped the oscillator. Miller et al. compared his model with well known constant phase element (CPE) approach and showed that theoretical descriptions of the fractal nature of the roughness of the electrode suggest that the power-law behavior of the CPE could be interpreted as the random walk of ions close to a rough surface described by Halsey-Leibig theory [2].

. Hugo Sanabria* and John H. Miller, J. PHYSICAL REVIEW E 74, 051505 (2006)
. T. C. Halsey and M. Leibig, Ann. Phys. _N.Y._ **219**, 109_1992_.



# Dependence on distance

Returning to a simplified phenomenological approach. The first graph is the dielectric permittivity for pure water. The electrodes were of polished titanium with a surface area of 400 mm$^2$ and a separation starting at 1 mm. Starting at 1 kHz one can observe the effects of electrode polarization with a strong growth in the permittivity as the frequency is lowered. When viewed in terms of the absolute impedance of the sample one can note a shifting of the impedance as the distance is increased. This is an obvious feature as we have simply increased the length of a resistor (at least in the higher frequencies) with a constant resistance (once again in the high frequencies). Applying Ohms law we can get a resistivity of 16884 × 10$^4$ Ohm or a conductivity of about 6×10$^{-5}$ Sm, which means that the water wasn't particularly clean! However we can use this to make a master plot and see how the distance effects the electrode polarization .

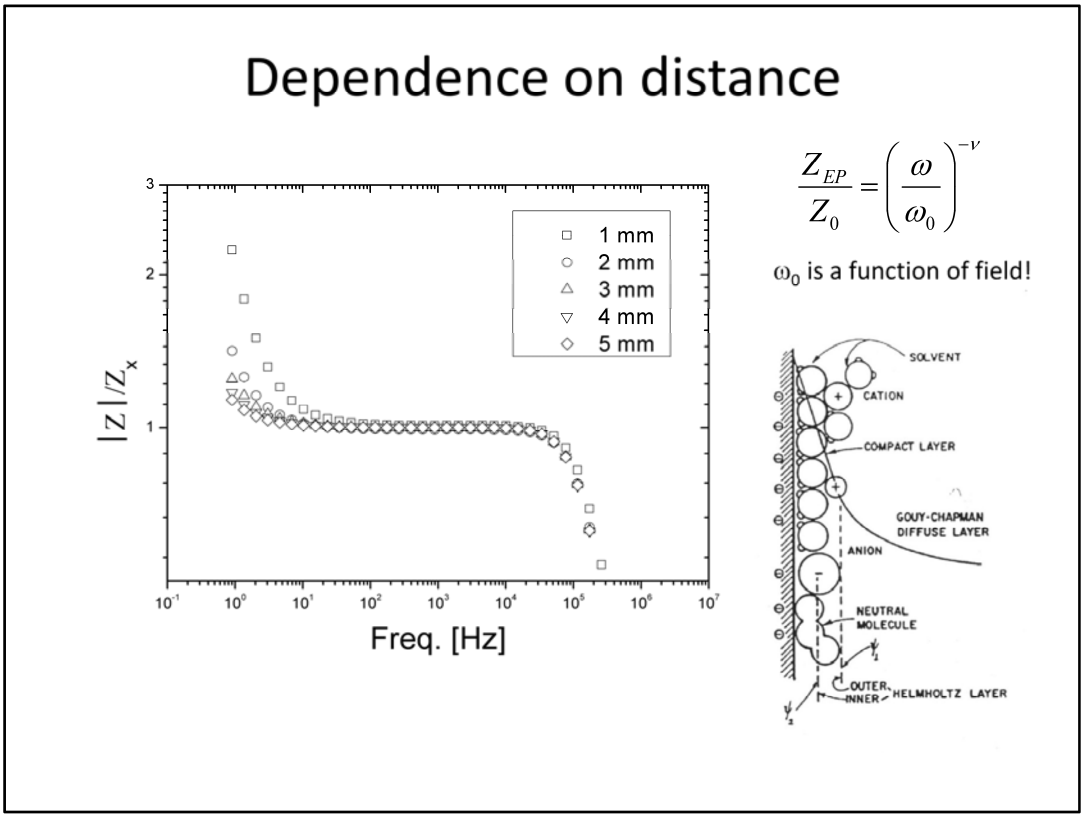


# Equivalent Circuit Models

$$Z_{meas} = Z_{EP_1} + Z_S + Z_{EP_2}$$

$$Z_\nu = R(RC)^{-\nu}(i\omega)^{-\nu} \qquad 0 < \nu < 1$$

One can model electrode polarization as a simple capacitor in series with the bulk capacitance. Consequently it will have a simple RC profile, depending on the dc conductivity of it. However, this is not an ideal model and a more sophisticated view is to model it as a recap. The impedance of a recap element, $Z_\nu$, is limited by the impedance of a capacitor for $\nu$=1 and by a resistor for $\nu$=0. The real impedance of electrode polarization is some where in between and demonstrates power law behaviour as a function of frequency.

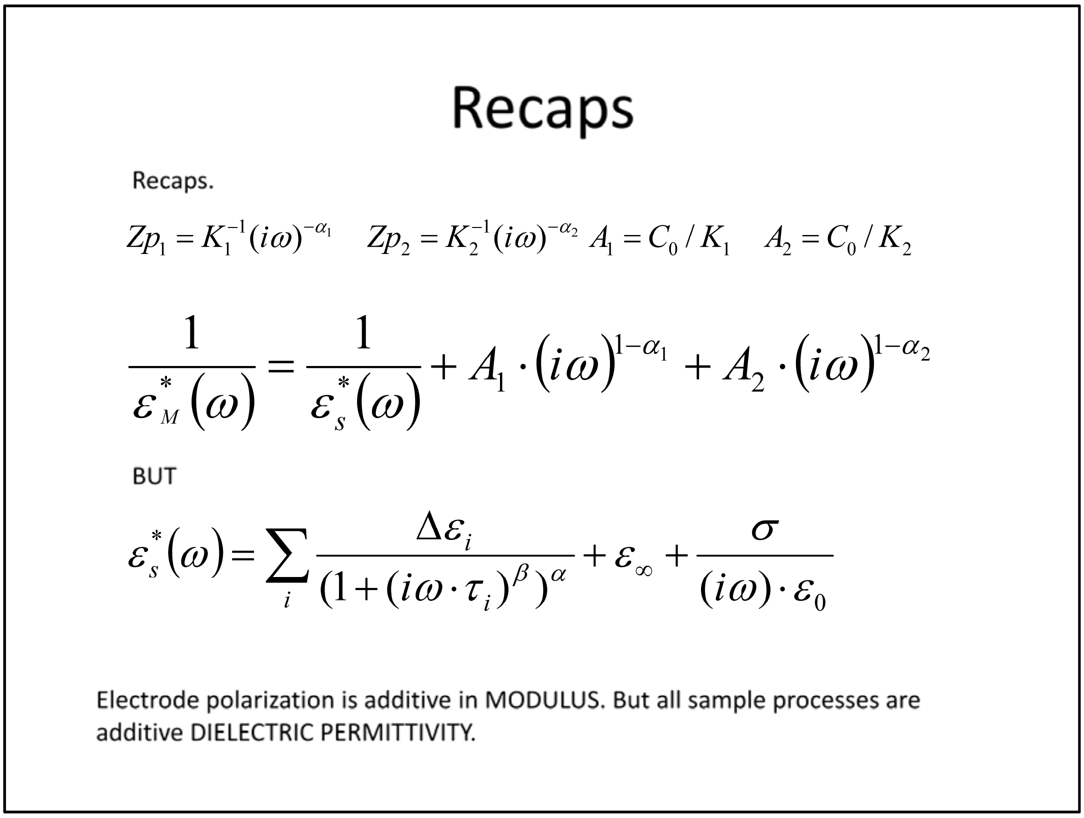


## Dependence on distance

$$\frac{Z_{EP}}{Z_0} = \left(\frac{\omega}{\omega_0}\right)^{-\nu}$$

$\omega_0$ is a function of field!

Returning to our master plot one can see that the electrode polarization is characterized by an onset frequency and shows a general power law expression in line with the Recap model of the previous slide. The onset frequency is a function of many parameters, such as temperature, bulk viscosity , pressure, and the distance between the electrodes. Seeing as the probing voltage was maintained constant between measurements and only the distance changed this is equivalent to a weaker field falling over the sample. The inner Helmholtz layer is not likely to be effected by this, but the outer Gouy – Chapman Diffuse Layer will be responsive to this. Schwan used this approach for cleaning the signal from the effects of electrode polarization by comparing the signal from two different distances. However the distances must be great enough so that the onset is no longer sensitive to the change in distance. For biological studies, such as cells in plasma, the sample size can be prohibitive.



# Recaps

Recaps.

$$Zp_1 = K_1^{-1}(i\omega)^{-\alpha_1} \quad Zp_2 = K_2^{-1}(i\omega)^{-\alpha_2} \; A_1 = C_0 / K_1 \quad A_2 = C_0 / K_2$$

$$\frac{1}{\varepsilon^*_M(\omega)} = \frac{1}{\varepsilon^*_s(\omega)} + A_1 \cdot (i\omega)^{1-\alpha_1} + A_2 \cdot (i\omega)^{1-\alpha_2}$$

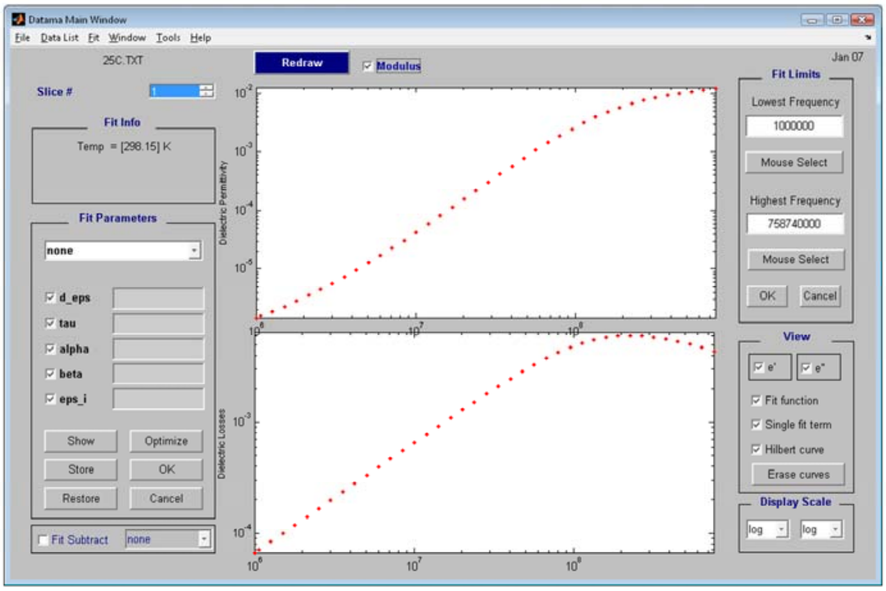
BUT

$$\varepsilon^*_s(\omega) = \sum_i \frac{\Delta\varepsilon_i}{(1+(i\omega\cdot\tau_i)^{\beta})^{\alpha}} + \varepsilon_\infty + \frac{\sigma}{(i\omega)\cdot\varepsilon_0}$$

Electrode polarization is additive in MODULUS. But all sample processes are additive DIELECTRIC PERMITTIVITY.

How can we use the recap model to “clean” our data from electrode polarization. In the Modulus representation electrode polarization is additive to the bulk response. However the bulk response itself can be considered as a sum of parallel capacitances and so is additive in the dielectric permittivity representation. As we usually record the data in terms of Epsilon it is normalized on the geometry of the cell. If we know the geometry then is it possible to work with impedance only.
Therefore if we study the Modulus first and look for power law behaviour at the low frequencies of our measurement window we can fit according the recap model and then subtract these processes from the real data and move back to Epsilon representation. An example of the procedure is presented in the next slides.

# Datama implementation.(ATP 5% example)



Datama Main Window

25C.TXT

Jan 07

Slice # 1

Fit Info

Temp = [298.15] K

Fit Parameters: none

☑ d_eps
☑ tau
☑ alpha
☑ beta
☑ eps_i

☐ Fit Subtract: none

☑ Modulus

Fit Limits

Lowest Frequency: 1000000

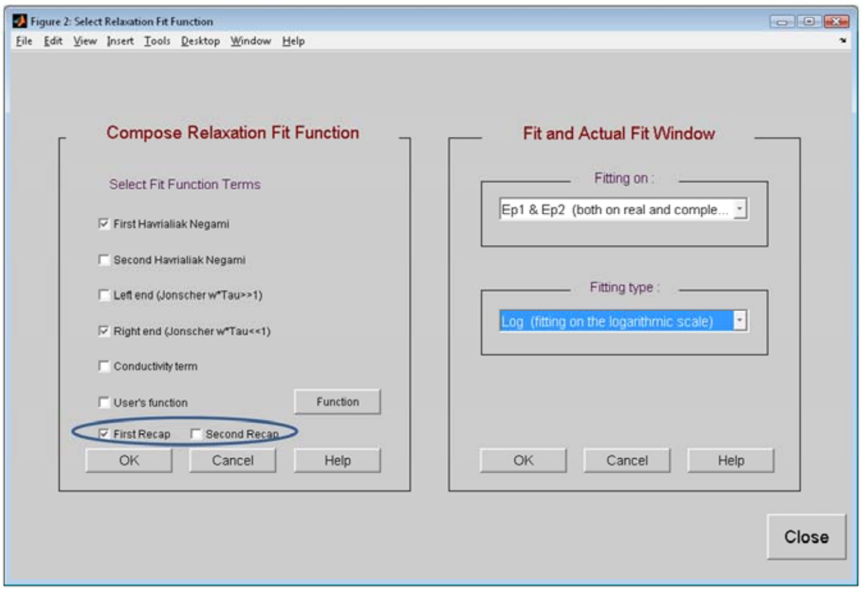
Highest Frequency: 758740000

View

☑ e'
☑ e"
☑ Fit function
☑ Single fit term
☑ Hilbert curve

Display Scale: log, log

# Datama implementation.(ATP 5% example)
# Extra functionality.



**Compose Relaxation Fit Function**

Select Fit Function Terms

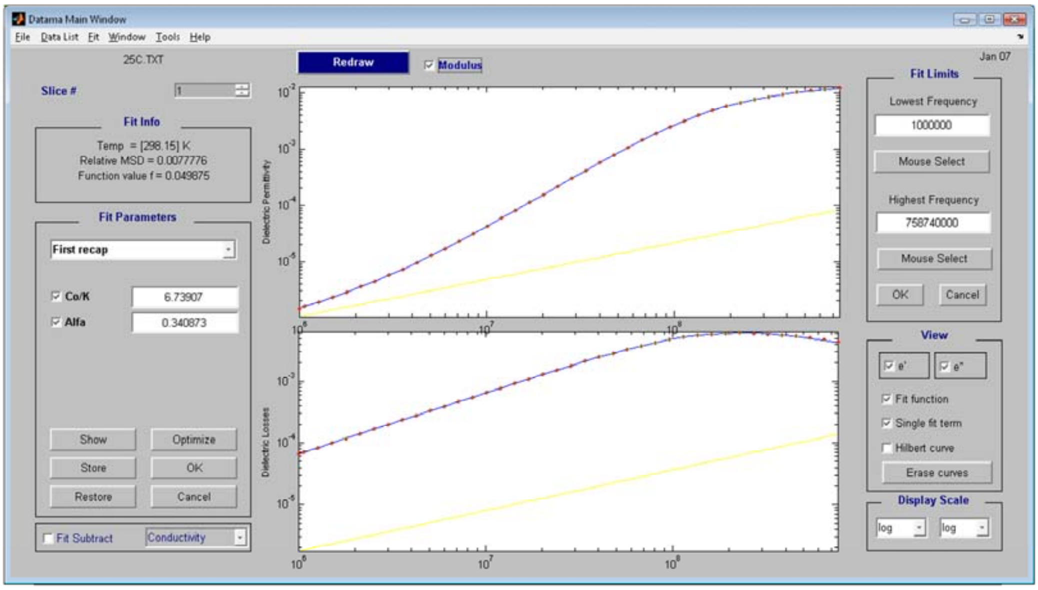
- ☑ First Havrialiak Negami
- ☐ Second Havrialiak Negami
- ☐ Left end (Jonscher w*Tau>>1)
- ☑ Right end (Jonscher w*Tau<<1)
- ☐ Conductivity term
- ☐ User's function
- ☑ First Recap ☐ Second Recap

**Fit and Actual Fit Window**

Fitting on : Ep1 & Ep2 (both on real and comple...

Fitting type : Log (fitting on the logarithmic scale)

# Dielectric permittivity and Modulus(ATP 5% example).



25C.TXT

Jan 07

☑ Modulus

Slice # 1

Temp = [298.15] K
Relative MSD = 0.0077776
Function value f = 0.049875

First recap

☑ Co/K 6.73907
☑ Alfa 0.340873

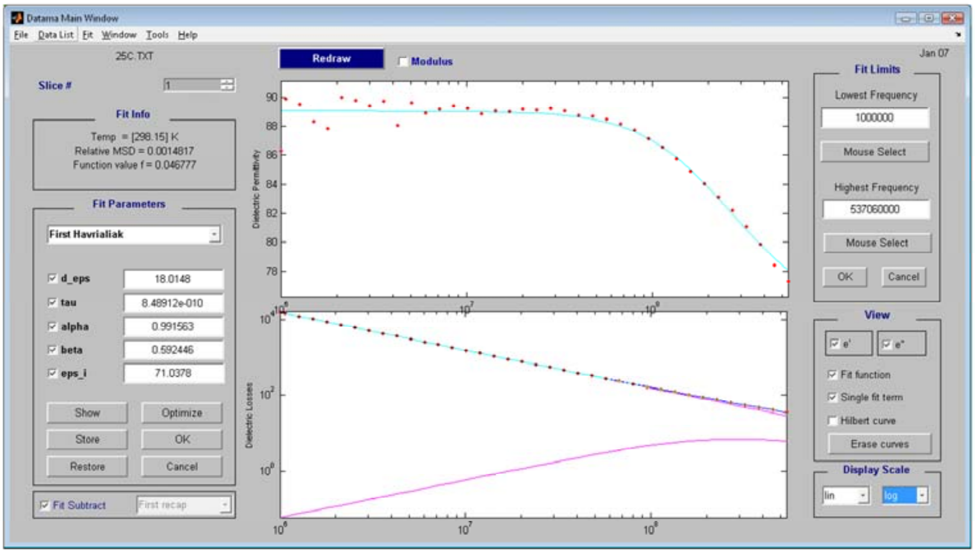
☐ Fit Subtract Conductivity

Lowest Frequency 1000000
Highest Frequency 758740000

☑ e' ☑ e"
☑ Fit function
☑ Single fit term
☐ Hilbert curve

log log

# Subtracting electrode polarization.



25C.TXT

Jan 07

**Slice #** 1

**Fit Info**

Temp = [298.15] K
Relative MSD = 0.0014817
Function value f = 0.046777

**Fit Parameters**

First Havrialiak

☑ **d_eps** 18.0148
☑ **tau** 8.48912e-010
☑ **alpha** 0.991563
☑ **beta** 0.592446
☑ **eps_i** 71.0378

☑ Fit Subtract — First recap

**Fit Limits**

Lowest Frequency: 1000000

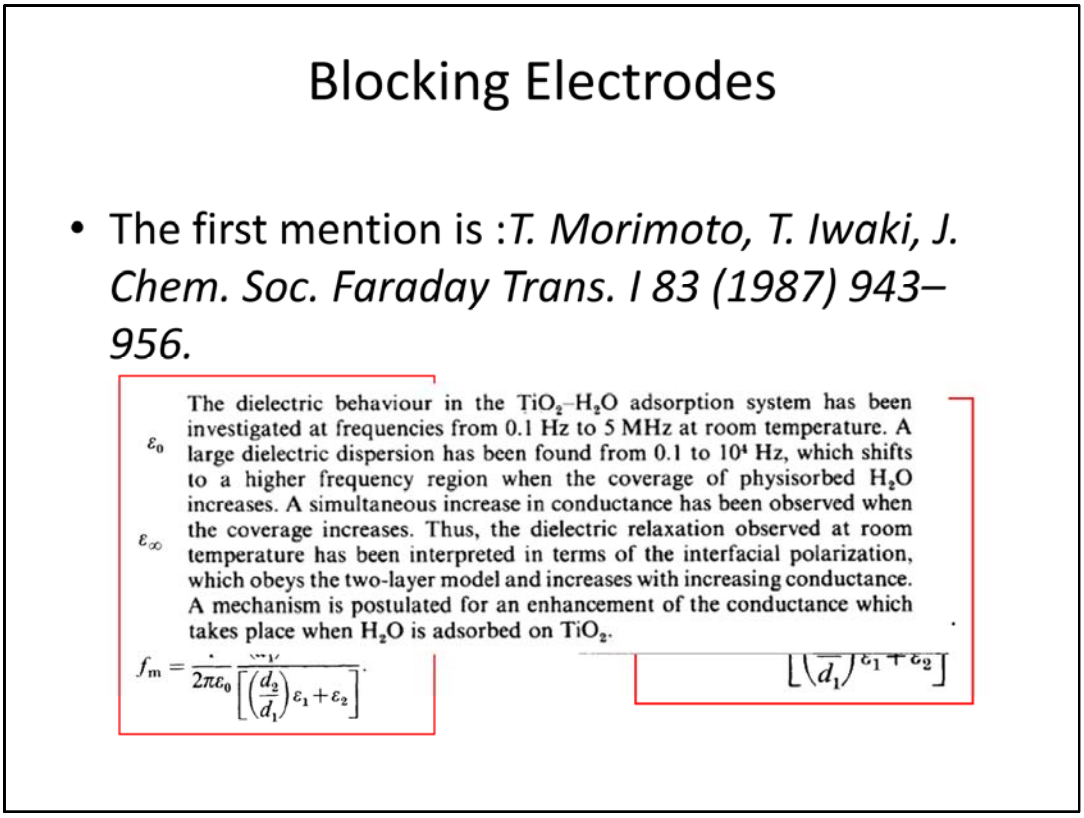
Highest Frequency: 537060000

**View**

☑ e' ☑ e"
☑ Fit function
☑ Single fit term
☐ Hilbert curve

**Display Scale**

lin — log



# Blocking Electrodes

- The first mention is :*T. Morimoto, T. Iwaki, J. Chem. Soc. Faraday Trans. I 83 (1987) 943–956.*

$\varepsilon_0$

$\varepsilon_\infty$

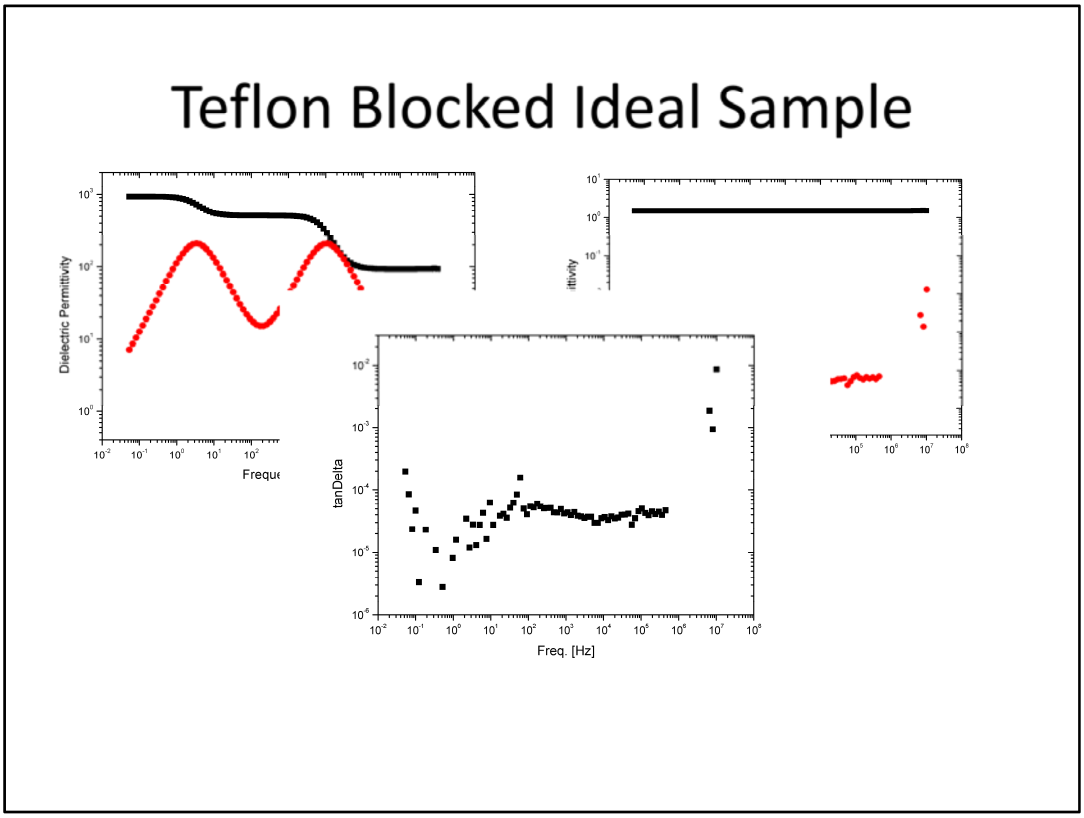
The dielectric behaviour in the $TiO_2$–$H_2O$ adsorption system has been investigated at frequencies from 0.1 Hz to 5 MHz at room temperature. A large dielectric dispersion has been found from 0.1 to $10^4$ Hz, which shifts to a higher frequency region when the coverage of physisorbed $H_2O$ increases. A simultaneous increase in conductance has been observed when the coverage increases. Thus, the dielectric relaxation observed at room temperature has been interpreted in terms of the interfacial polarization, which obeys the two-layer model and increases with increasing conductance. A mechanism is postulated for an enhancement of the conductance which takes place when $H_2O$ is adsorbed on $TiO_2$.

$$f_{\mathrm{m}} = \frac{}{2\pi\varepsilon_0}\frac{}{\left[\left(\frac{d_2}{d_1}\right)\varepsilon_1+\varepsilon_2\right]}.$$

$$\left[\left(\frac{}{d_1}\right)\varepsilon_1+\varepsilon_2\right]$$

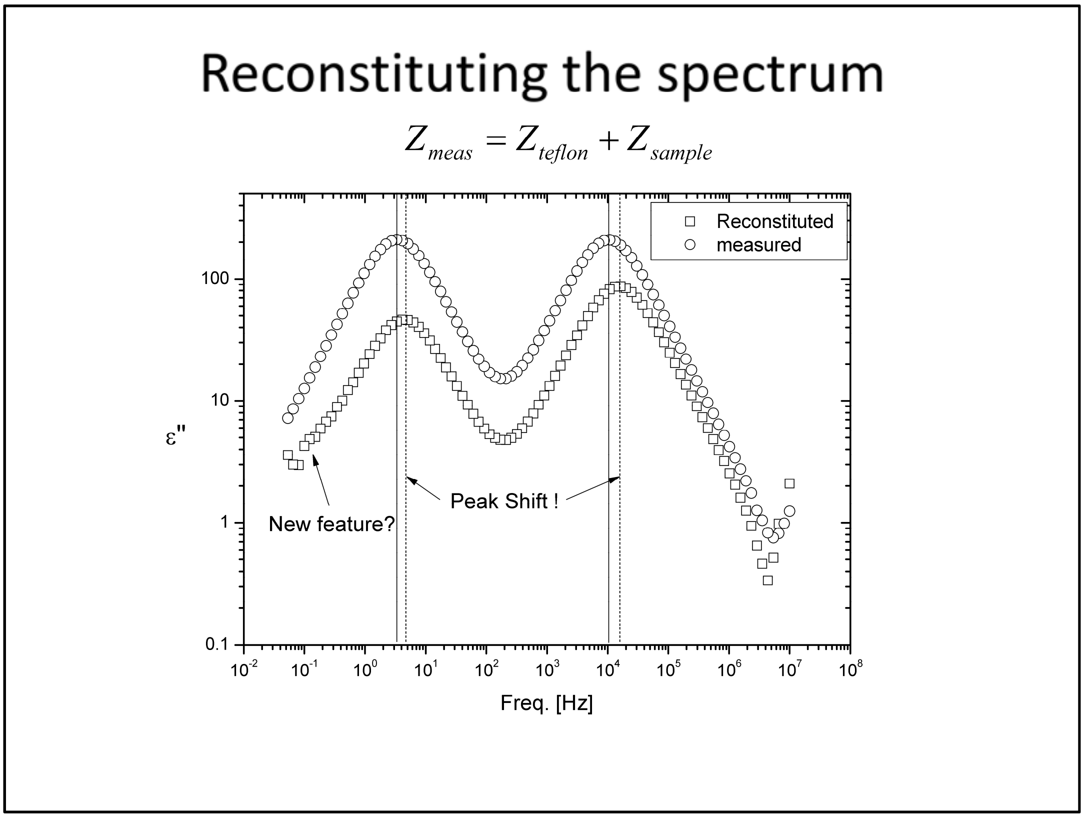
Blocking electrodes have been the subject of a number of publications recently, where the authors have succeeded in identifying hitherto unidentified processes in water and other significant systems. The claim is that by using a blocked electrode (usually done with Teflon) dc conductivity is removed, revealing these new processes. One of the earliest applications was by Morimoto et al. while investigating the dielectric behaviour of $TiO_2$-$H_2O$ complexes. They developed a two layer model to account for $TiO_2$ particles with absorbed $H_2O$ and bulk $H_2O$ in the second layer. Each layer has its own intrinsic permittivity and conductivity and thickness. If one electrode is blocked then the conductivity in the $TiO_2$ layer is virtually zero and the approximation in the slide is achieved. The frequency is of interfacial polarization between the layers. While the approximations only solve the static and high frequency limits and still contains 4 unknowns against 3 equations, it has not stopped a number of researchers implementing blocking electrodes.

It is a mistake to do so!



## Teflon Blocked Ideal Sample

The Novocontrol BDS 80 dielectric analyser system is one of the more popular systems in laboratory use. As a standard it comes with an artificial sample consisting of two ideal Debye processes with no conductivity (Left ). The upper electrode was blocked using a 50 micron sheet of teflon between the sample plate and the upper electrode of the active head. The graph on the right shows the measured permittivity of this new system and, as can be seen, tanδ is on the limit of measurement capability.



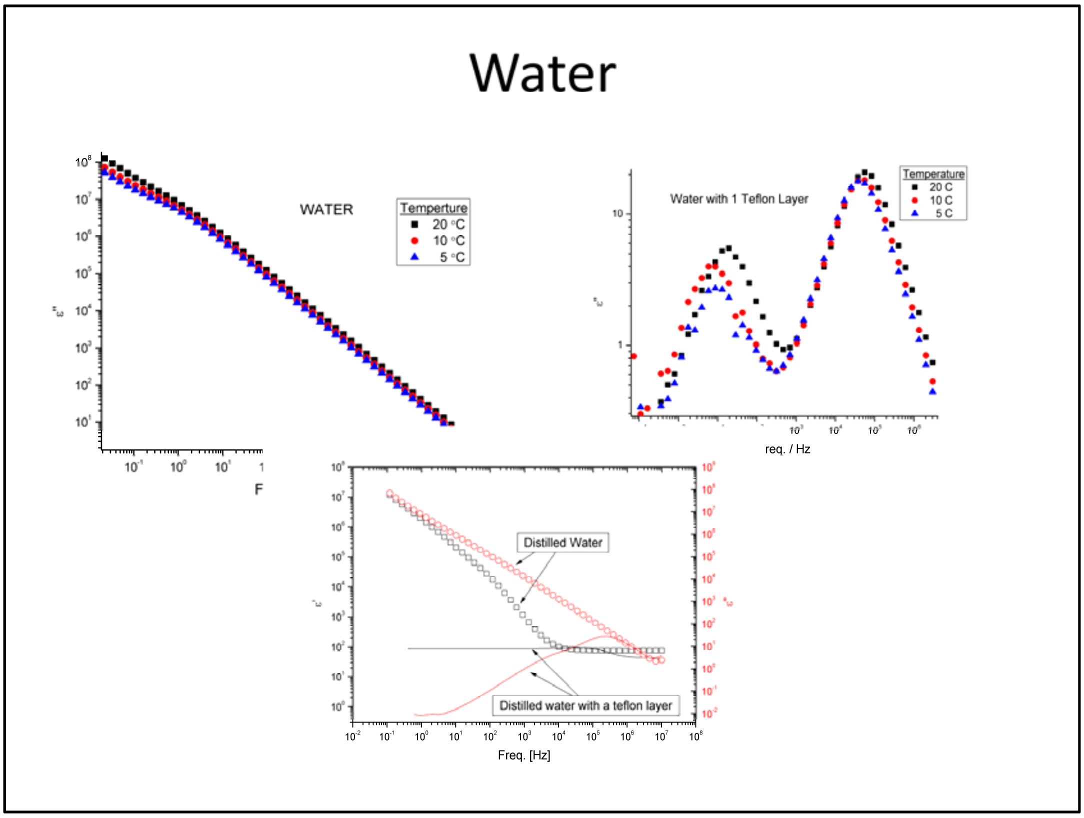
## Reconstituting the spectrum

$$Z_{meas} = Z_{teflon} + Z_{sample}$$

New feature?

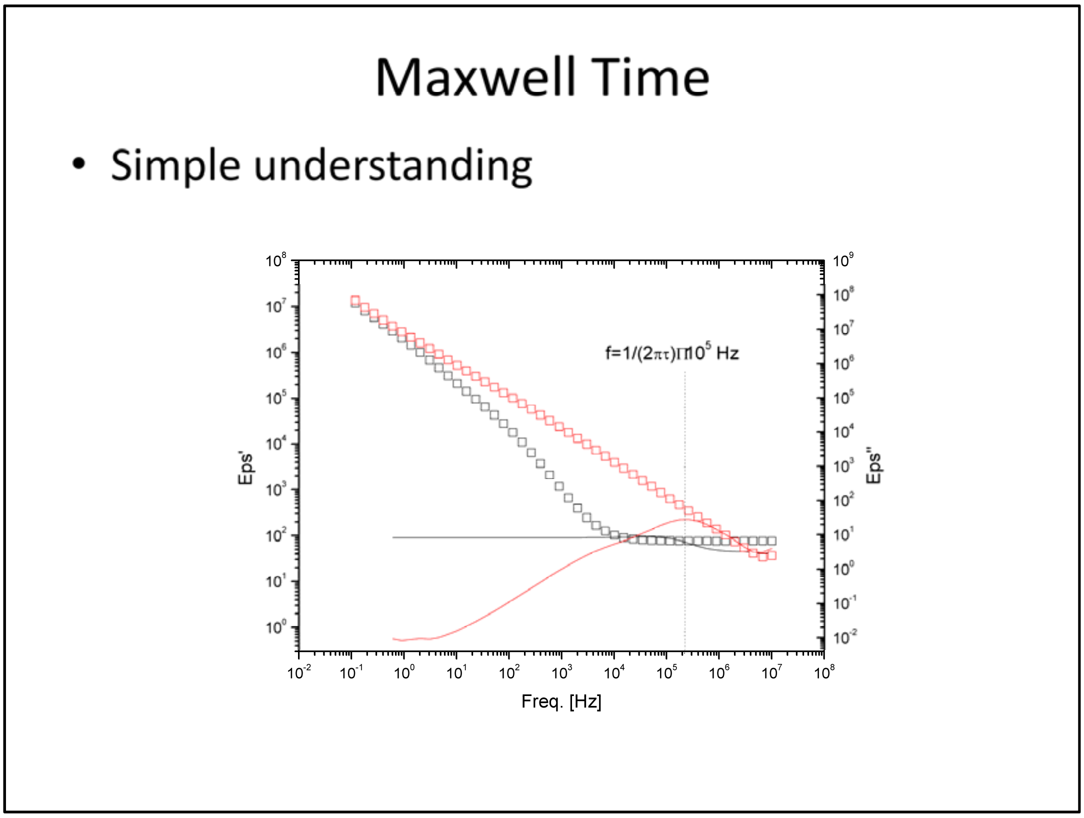
Peak Shift !

Using the simple expression for serial impedance and knowing the impedance of the teflon one can reconstitute the permittivity of the ideal sample.  As can be seen a number of unexpected artifacts appear, including a frequency shift in what should be immovable processes!



# Water

The situation is further complicated when the sample contains a dc conductivity component. The measurements in the slide are of triple distilled water in a plate capacitance with a 50 micron teflon between the sample and one electrode. Care was taken to make sure that there were no air pockets between the teflon and the metal and between the sample and teflon. The results are characterized by the appearance of two peaks hitherto hidden under the electrode polarization and conductivity in the sample. Or are they….. Electrode polarization has not disappeared. It is now along the interface of Teflon and water. It would be more correct to refer to it as an interfacial polarization because there is no electrochemical component to its behaviour , now that reduction and oxidization does not occur at the electrode water interface. However there yet another peak appearing in the high frequencies. This arises because of the presence of conductivity and is characterized by the Maxwell time.

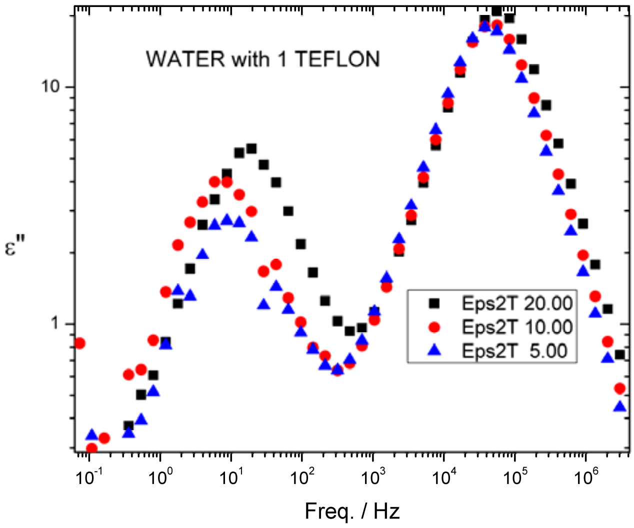


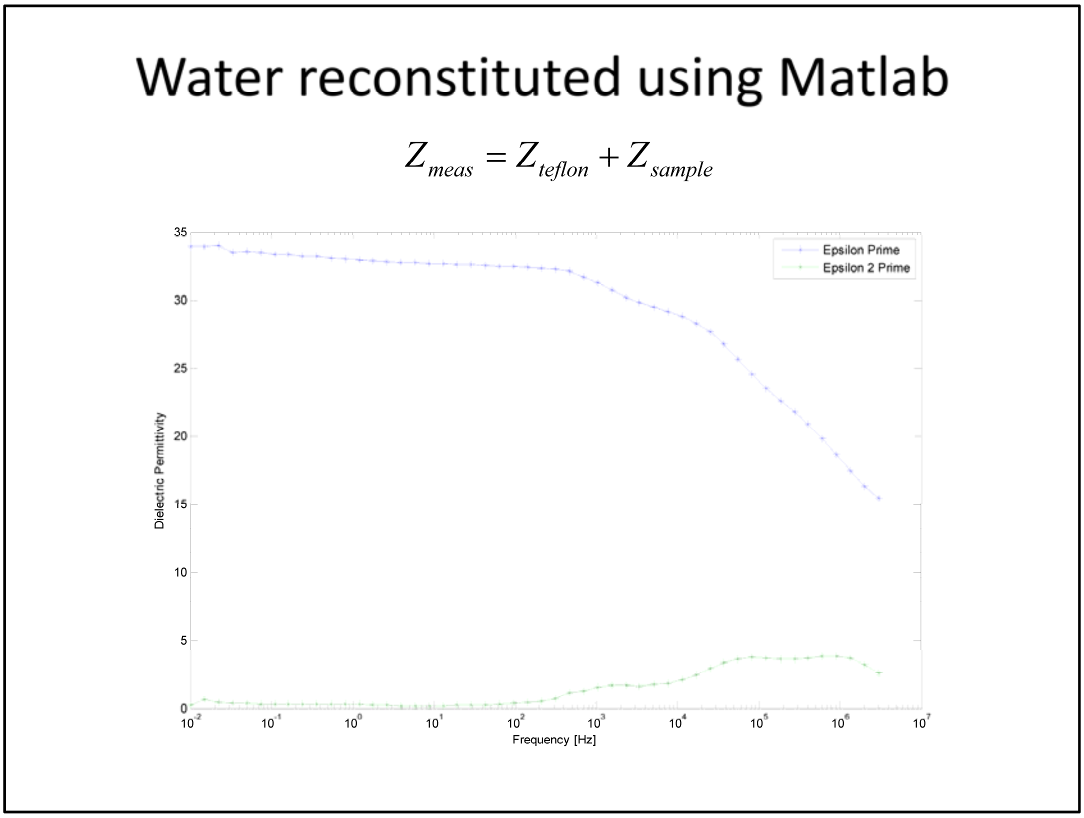
## Maxwell Time

- Simple understanding

The Maxwell time is an old concept in Dielectric Physics and can be conceptualized most simply by considering a volume in our dielectric medium. For simplicity we choose a box. One can ask the following question: “If our volume contains ions free to react to a dc voltage placed across opposing faces of our box, what would be their response time?” This is equivalent of calculating the RC of our segment. The final expression depends only of the dc conductivity and permittivity of the medium. As the blocking electrode has effectively cancelled a dc current through the sample the response now manifests itself as a peak in the dielectric response. In our example of water this the cause of the higher frequency process.

# Temperature based measurements

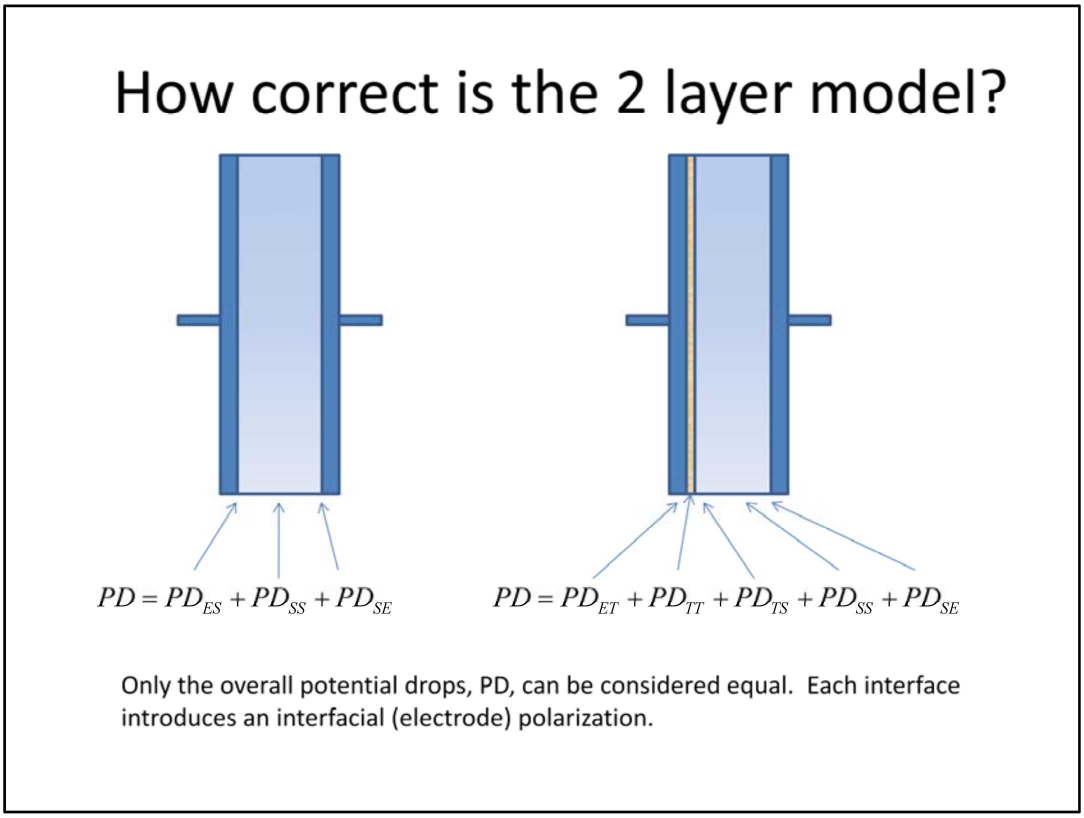




# Water reconstituted using Matlab

$$Z_{meas} = Z_{teflon} + Z_{sample}$$

Once again by taking the simple impedance model of serial impedances we could theoretically rebuild the dielectric picture of water. In the slide the measured impedance of the sample with blocking electrodes was used in conjunction with the impedance of our 50 micron teflon layer. As can be seen the desired permittivity is not obtained.



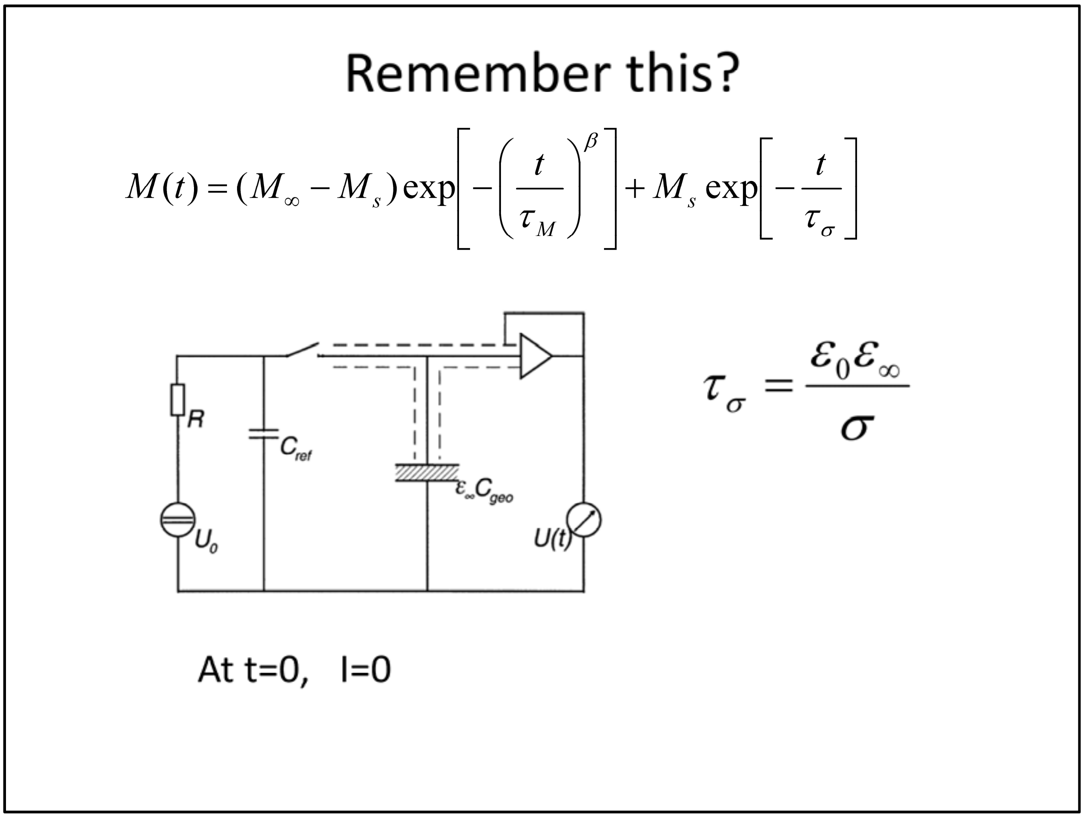
# How correct is the 2 layer model?

$$PD = PD_{ES} + PD_{SS} + PD_{SE}$$

$$PD = PD_{ET} + PD_{TT} + PD_{TS} + PD_{SS} + PD_{SE}$$

Only the overall potential drops, PD, can be considered equal. Each interface introduces an interfacial (electrode) polarization.

So one must ask how correct is the simple impedance model? Not very accurate. Once we have introduced the teflon layer we have also ingtroduced a number of interfacial polarizations of which we are unable to gauge. The Electrochemical community has long studied this problem and a good introduction can be found in the book “Modern Electrochemistry 2A – Fundamentals of Electrodics”, John Bockis, Kluwer Academic/Plenum Publishers 2002



## Remember this?

$$M(t) = (M_\infty - M_s)\exp\left[-\left(\frac{t}{\tau_M}\right)^\beta\right] + M_s \exp\left[-\frac{t}{\tau_\sigma}\right]$$

$$\tau_\sigma = \frac{\varepsilon_0 \varepsilon_\infty}{\sigma}$$

At t=0, I=0

In fact using a blocking electrode is reminiscent of the methodology used for making a direct measurement of the Modulus. The similarity arises because the current is zeroed, effectively changing the measurement to one of a changing displacement field in the presence of a constant current. So not surprisingly the dc conductivity is manifested as a separate peak.

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