Dielectric spectroscopy of complex systems in Time and Frequency Domains: Problems and solutions


Dr. A. Puzenko


Dr. Ya.Ryabov


Mr. I. Beilin


Mr. L. Livshitz

Yuri Feldman

Department of Applied Physics,

The Hebrew University of Jerusalem,

Israel


Dr. Y. Hayashi

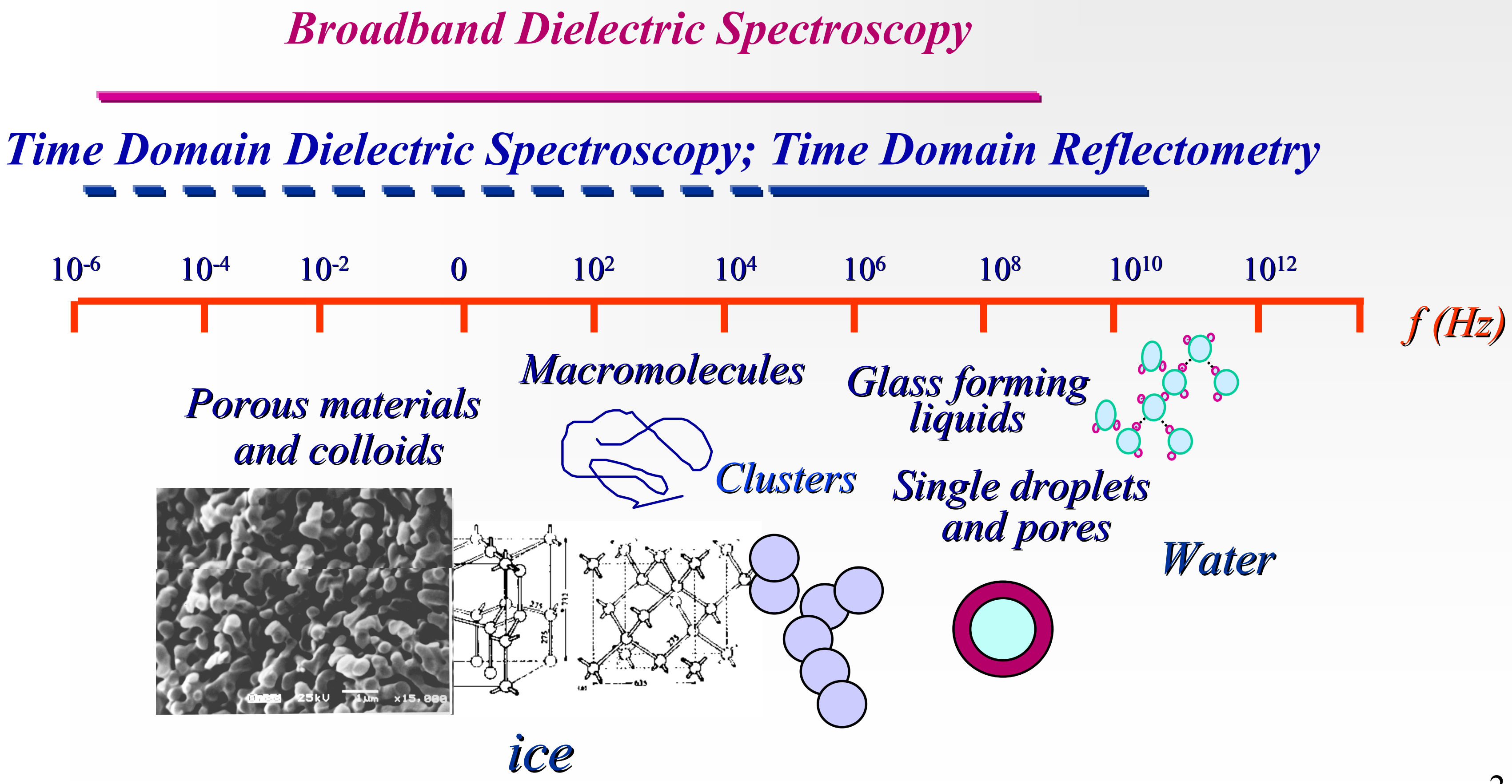

Dr. A. Gutina


Mrs.E. Axelrod


Mr. P. Ben Ishai

Dielectric response on mesoscale

Dielectric spectroscopy is sensitive to relaxation processes in an extremely wide range of characteristic times (10^{5} - 10^{-12} s)



Broadband Dielectric Spectroscopy

Time Domain Dielectric Spectroscopy; Time Domain Reflectometry

10^{-6} 10^{-4} 10^{-2} 0 10^{2} 10^{4} 10^{6} 10^{8} 10^{10} 10^{12} *f (Hz)*

Porous materials and colloids

Macromolecules

Glass forming liquids

Clusters

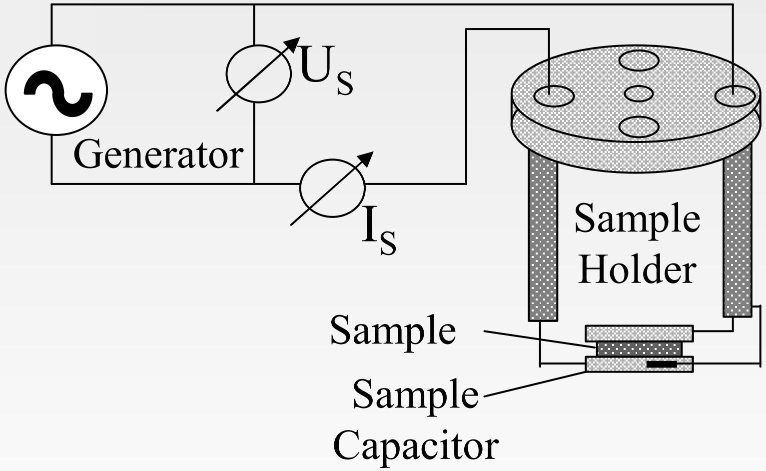
Single droplets and pores

Water

ice

Measurement Setup

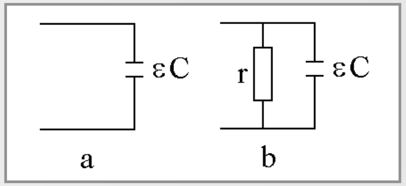
Broad-Band Dielectric Spectrometer BDS 80 **(NOVOCONTROL) in the frequency range 10 μHz – 1.8 GHz with automatic temperature control by QUATRO Cryosystem (temperature range -150 ^{0}C - +400 ^{0}C)**

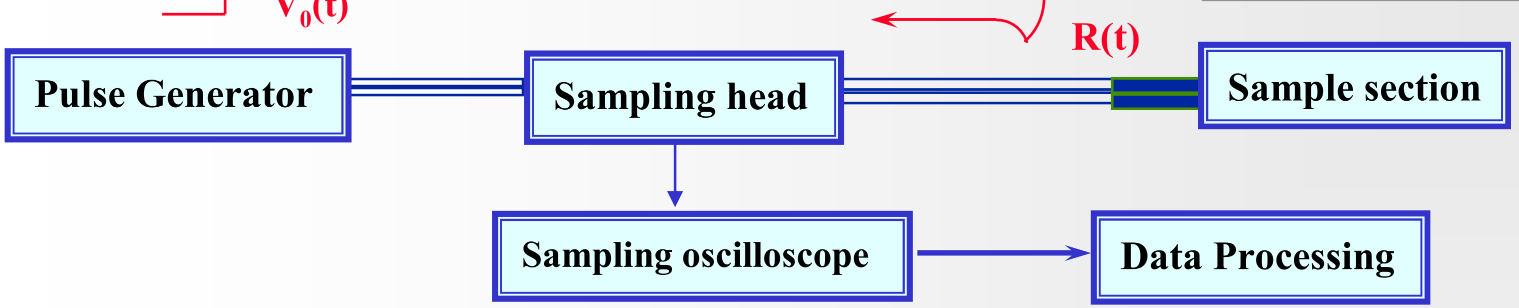


$$Z^*(\omega) = Z'(\omega) + iZ''(\omega) = U_s(\omega)/I_s(\omega)$$

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = -i/2\pi f Z(f) C_0$$

Time domain dielectric spectroscopy





Pulse Generator

Sampling head

Sample section

Sampling oscilloscope

Data Processing

$$V(t)=V_0(t)+R(t)$$

$$I(t)=\frac{1}{Z_0}[V_0(t)-R(t)],$$

lumped capacitance approximation in time domain:

$$Q(t)=C_0\left[\varepsilon_\infty V(t)+\int_0^t \dot{\Phi}(t-t')V(t')dt'\right]$$

Spectrum

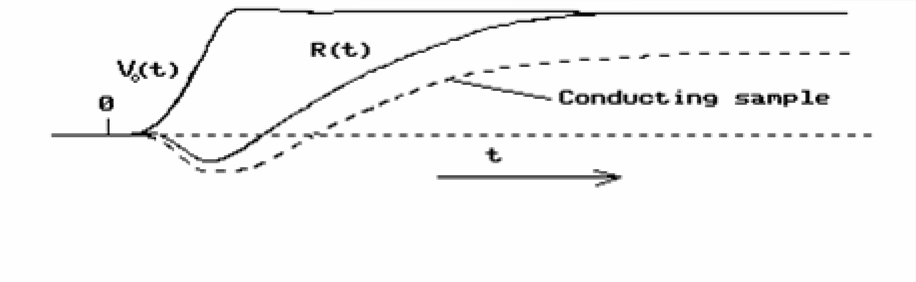
Dipole Correlation Function

100KHz – 18 GHz

Yu. Feldman,et al., (1996)
Rev. Sci. Instrum. 67, 3208.

$$\varepsilon^*(\omega)=\varepsilon_\infty+\frac{1}{Z_0C_0}\cdot\frac{L[Q(t)]}{L[V(t)]}$$

$$\frac{\varepsilon_s-\Phi(t)}{\varepsilon_s-\varepsilon_\infty}\approx\Gamma(t)=\frac{<\bar{M}(0)\bar{M}(t)>}{<\bar{M}(0)\bar{M}(0)>}$$



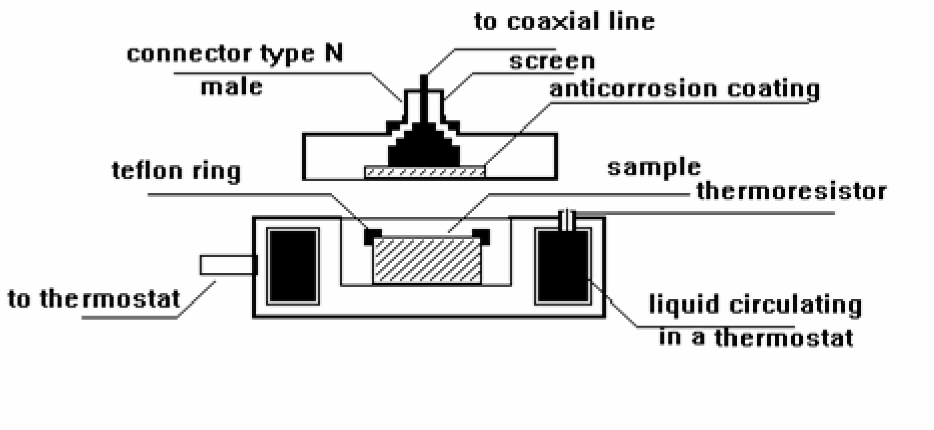
$$r = \lim_{t\to\infty}\frac{V(t)}{I(t)} = Z_0\lim_{t\to\infty}\frac{V_0(t)+R(t)}{V_0(t)-R(t)}$$

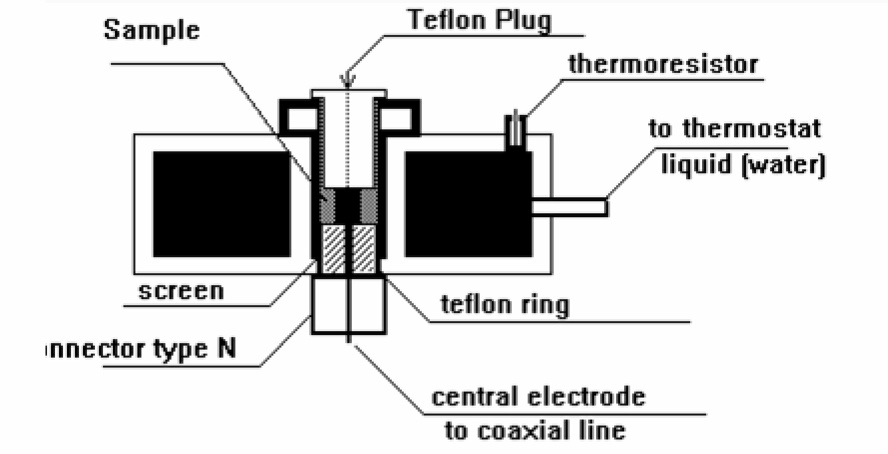
$$I_R(t) = \frac{V(t)}{r} = \frac{V_0(t)+R(t)}{Z_0}\lim_{t\to\infty}\frac{V_0(t)-R(t)}{V_0(t)+R(t)}$$

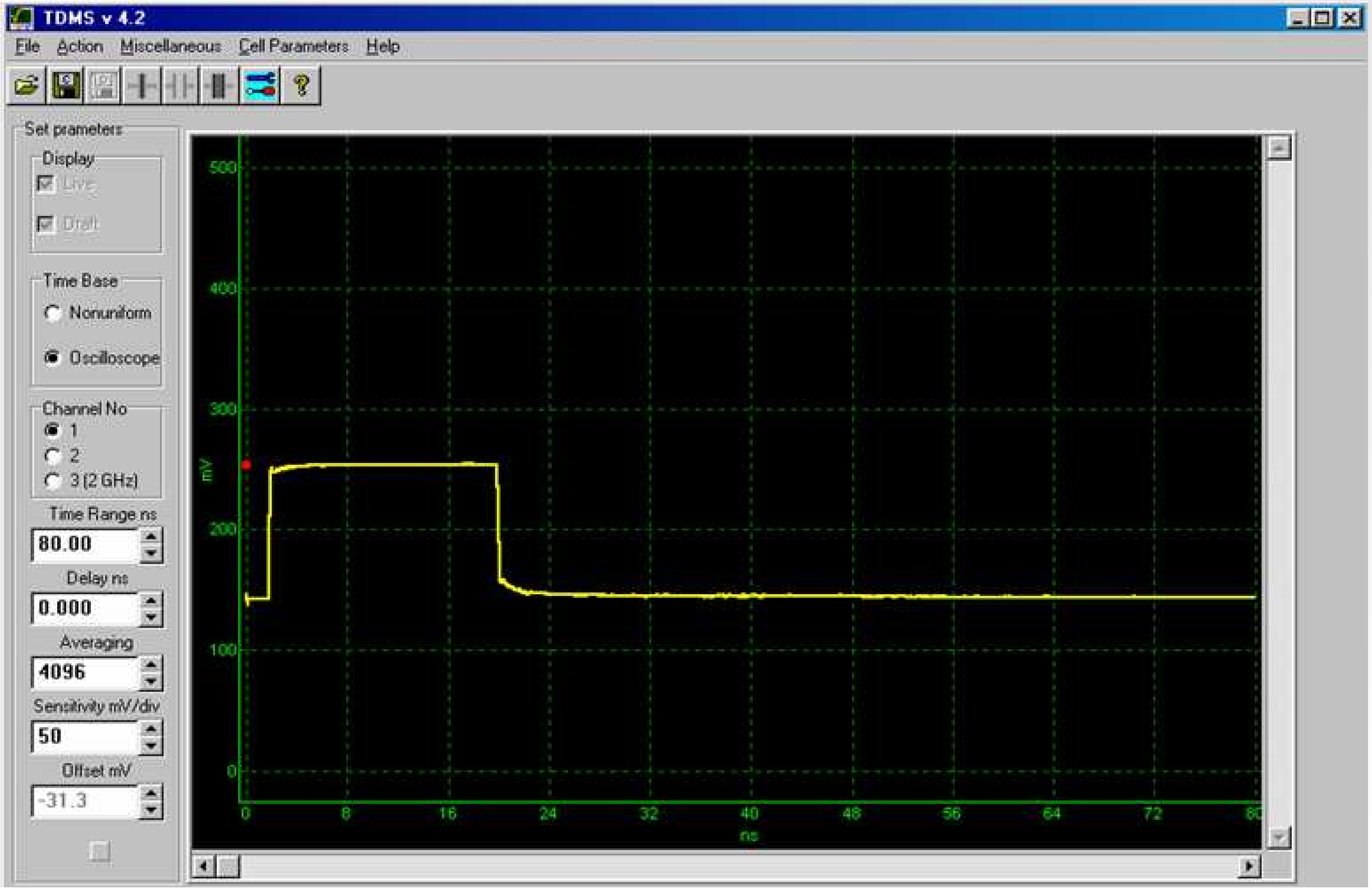
$$I_D(t) = \frac{1}{Z_0}\left\{\left[V_0(t)-R(t)\right]-\left[V_0(t)+R(t)\right]\lim_{t\to\infty}\frac{V_0(t)-R(t)}{V_0(t)+R(t)}\right\}$$

$$\sigma = \frac{\varepsilon_0}{Z_0C_0}\lim_{t\to\infty}\frac{V_0(t)-R(t)}{V_0(t)+R(t)}$$

$$Q(t) = \int_0^t I_D(t')dt'$$







Set prameters

Display

☑ Live

☑ Draft

Time Base

○ Nonuniform

● Oscilloscope

Channel No

● 1

○ 2

○ 3 (2 GHz)

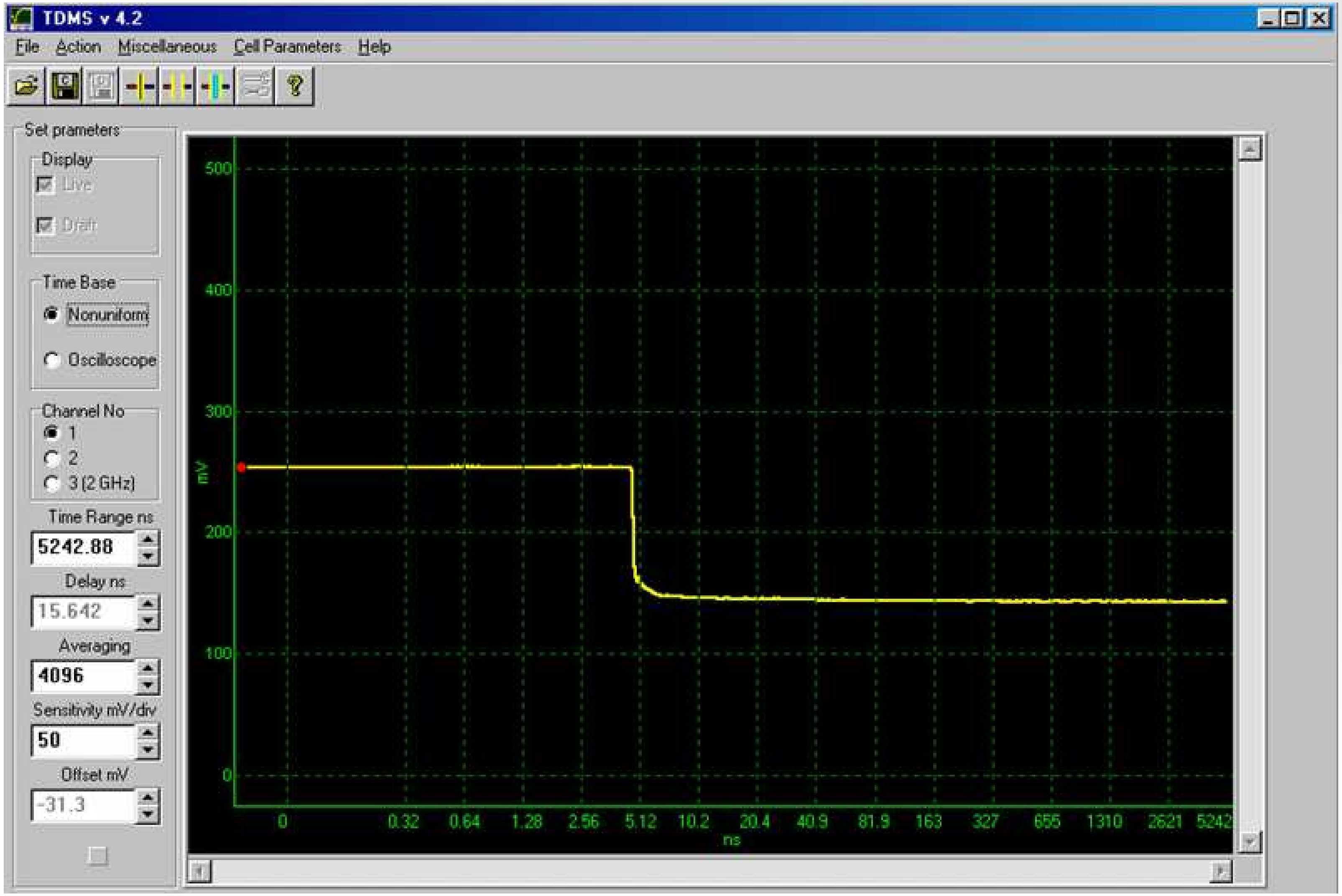
Time Range ns: 80.00

Delay ns: 0.000

Averaging: 4096

Sensitivity mV/div: 50

Offset mV: -31.3



Set prameters

Display
☑ Live
☑ Draw

Time Base
● Nonuniform
○ Oscilloscope

Channel No
● 1
○ 2
○ 3 (2 GHz)

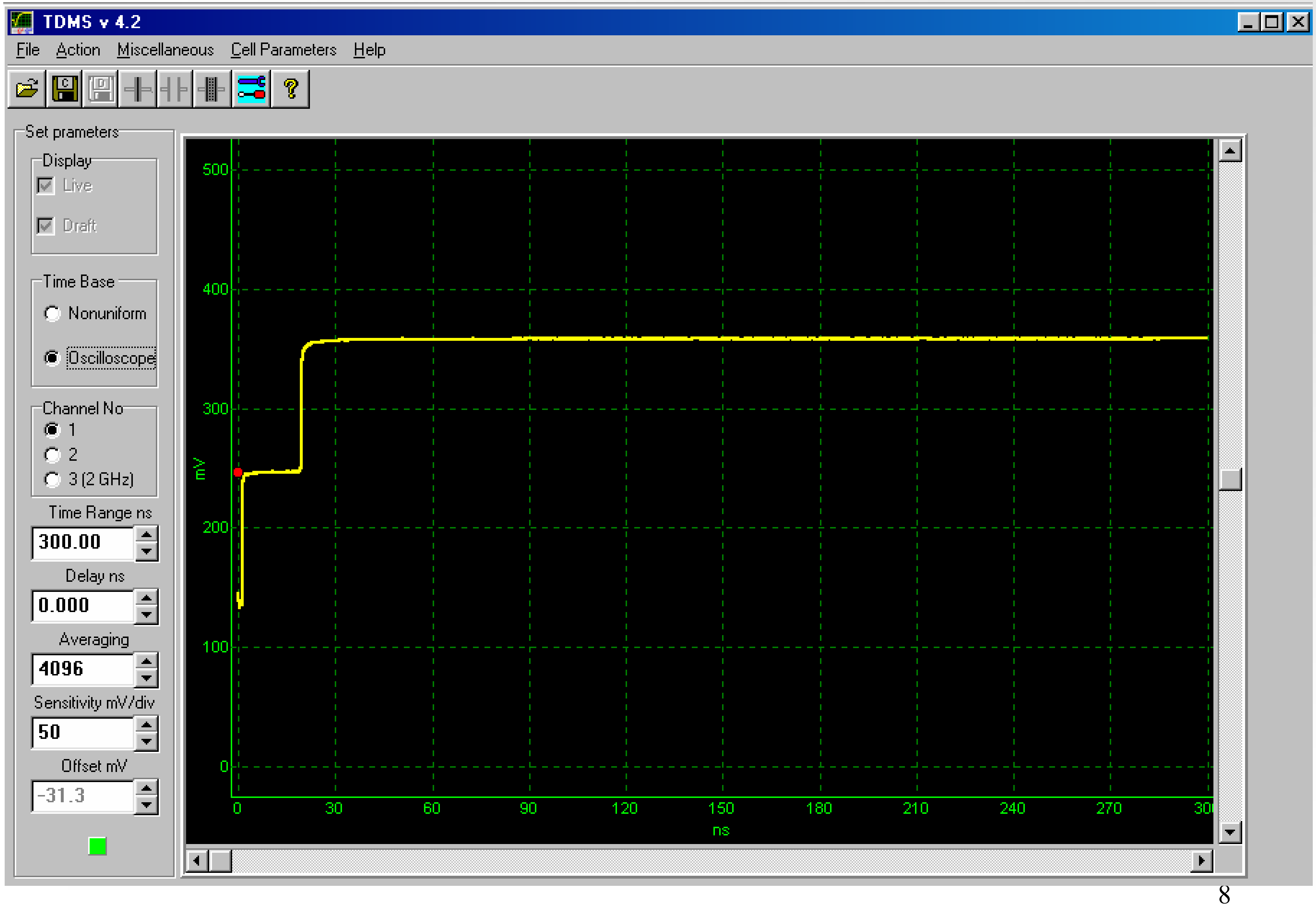
Time Range ns: 5242.88

Delay ns: 15.642

Averaging: 4096

Sensitivity mV/div: 50

Offset mV: -31.3



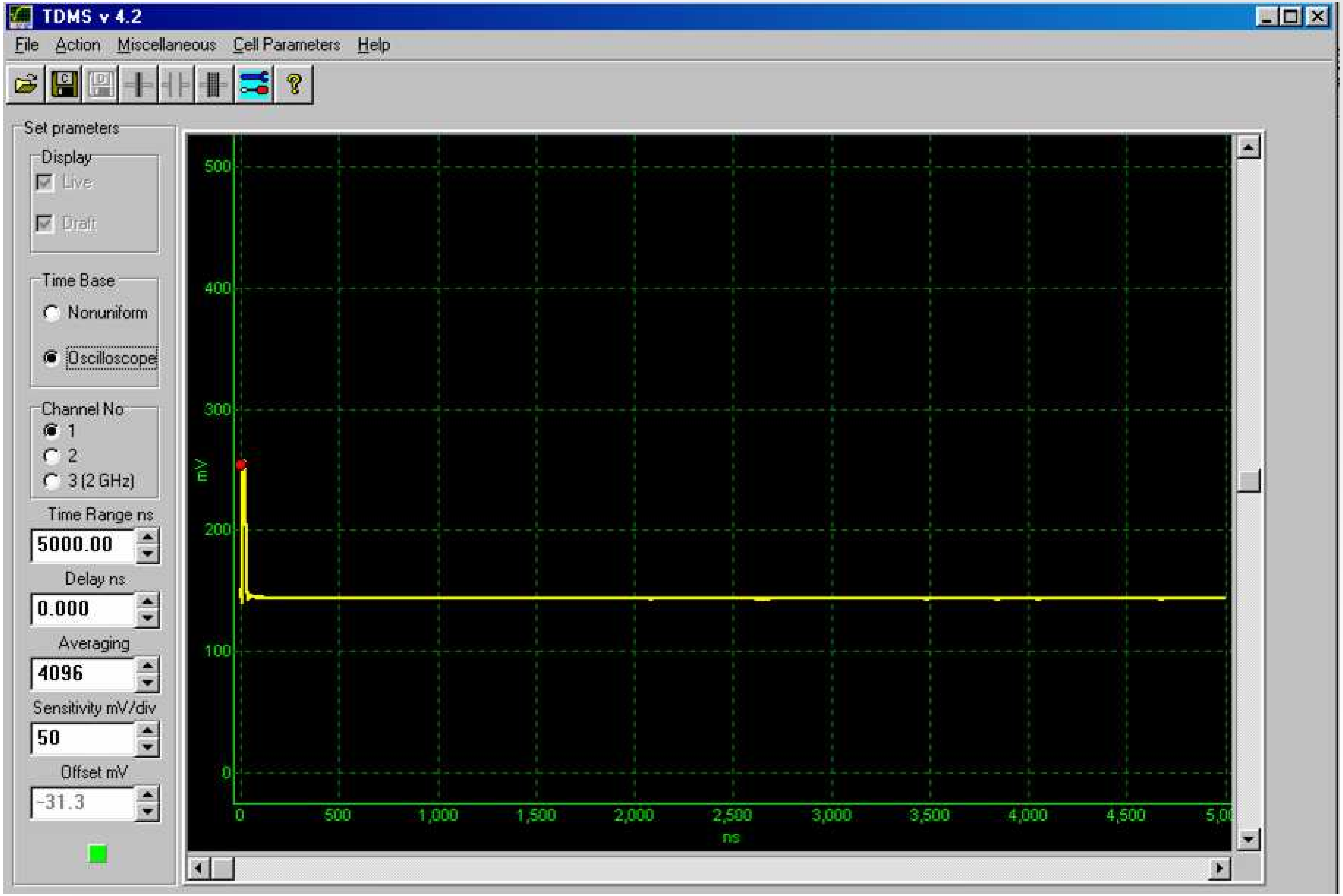
Set prameters

Display
☑ Live
☑ Draft

Time Base
○ Nonuniform
● Oscilloscope

Channel No
● 1
○ 2
○ 3 (2 GHz)

Time Range ns: 300.00
Delay ns: 0.000
Averaging: 4096
Sensitivity mV/div: 50
Offset mV: -31.3



Set prameters

Display
☑ Live
☑ Draft

Time Base
○ Nonuniform
● Oscilloscope

Channel No
● 1
○ 2
○ 3 (2 GHz)

Time Range ns: 5000.00

Delay ns: 0.000

Averaging: 4096

Sensitivity mV/div: 50

Offset mV: -31.3

TDS Problems

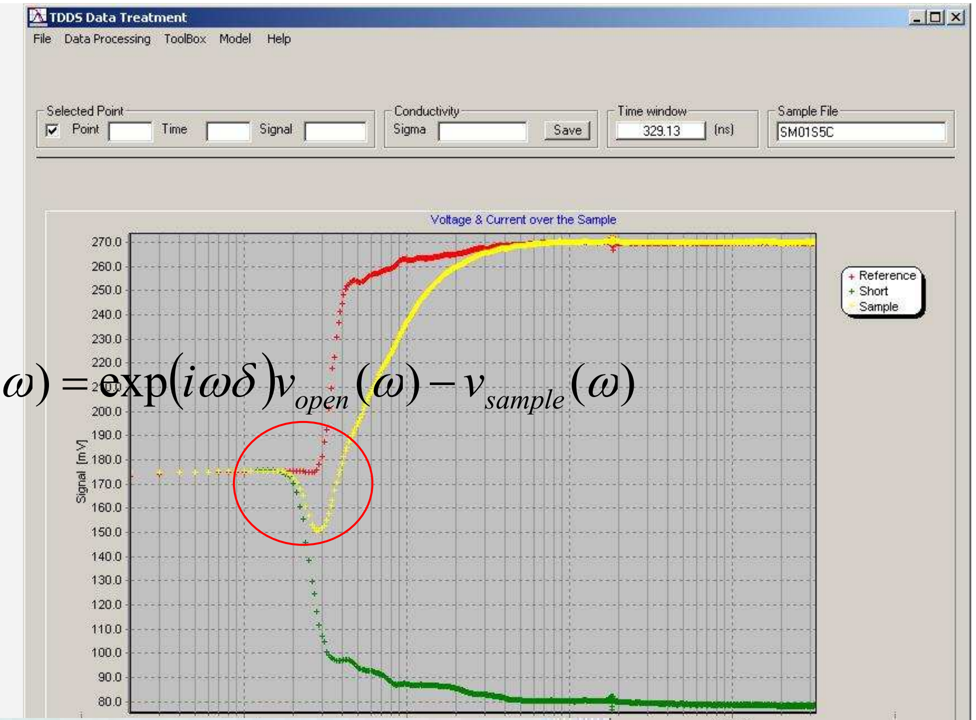
Mismatch of signals in time

$$I(t) \propto V_{open}(t+\delta) - V_{sample}(t) \longrightarrow i(\omega) = \exp(i\omega\delta)v_{open}(\omega) - v_{sample}(\omega)$$

Solution:

Time Shift in signal using the criteria

$$\left.\frac{dI}{dt}\right|_{t_{\max}} = 0 : \left.\frac{d^2V}{dt^2}\right|_{t_{\max}} = 0$$



Selected Point ☑ Point Time Signal

Conductivity Sigma

Time window 329.13 (ns)

Sample File SM01S5C

Iteration Step 1 ☑ No Iteration

Selected Point ☑ Point 1175 Freq 5.7421 Signal 0.1382376

Conductivity Sigma

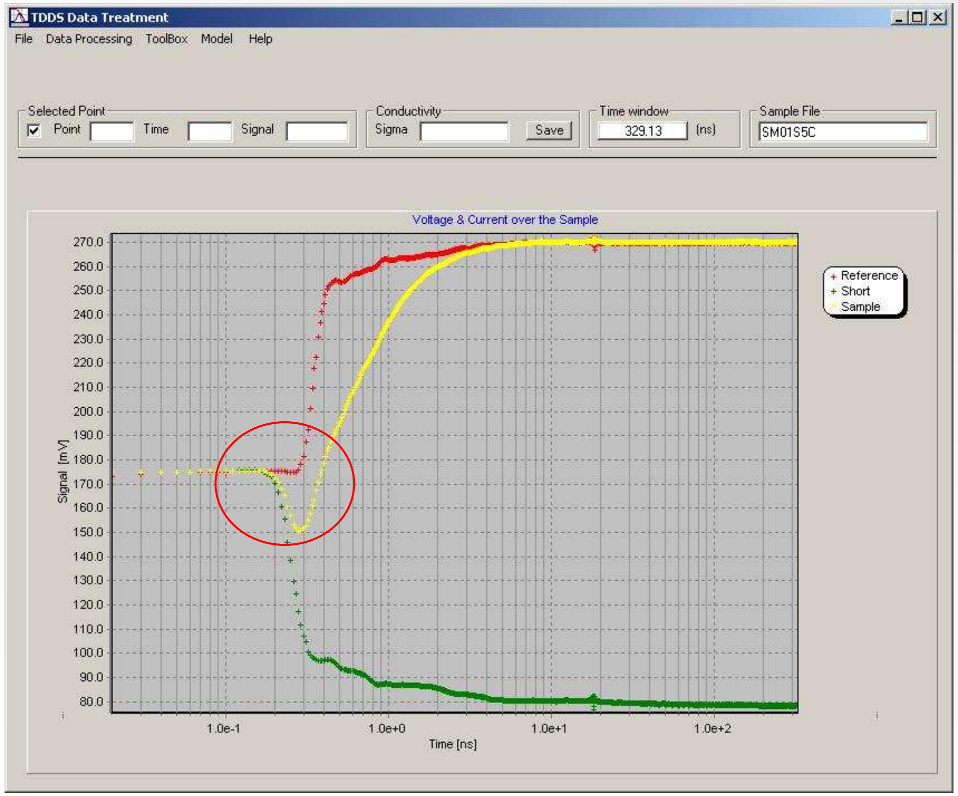
Time window 338.0397 (ns)

Sample File butanol2.ddf

TDS Problems

Mismatch of signals in time

$$I(t) \propto V_{open}(t+\delta) - V_{sample}(t) \longrightarrow i(\omega) = \exp(i\omega\delta) v_{open}(\omega) - v_{sample}(\omega)$$



Selected Point: ☑ Point Time Signal

Conductivity: Sigma

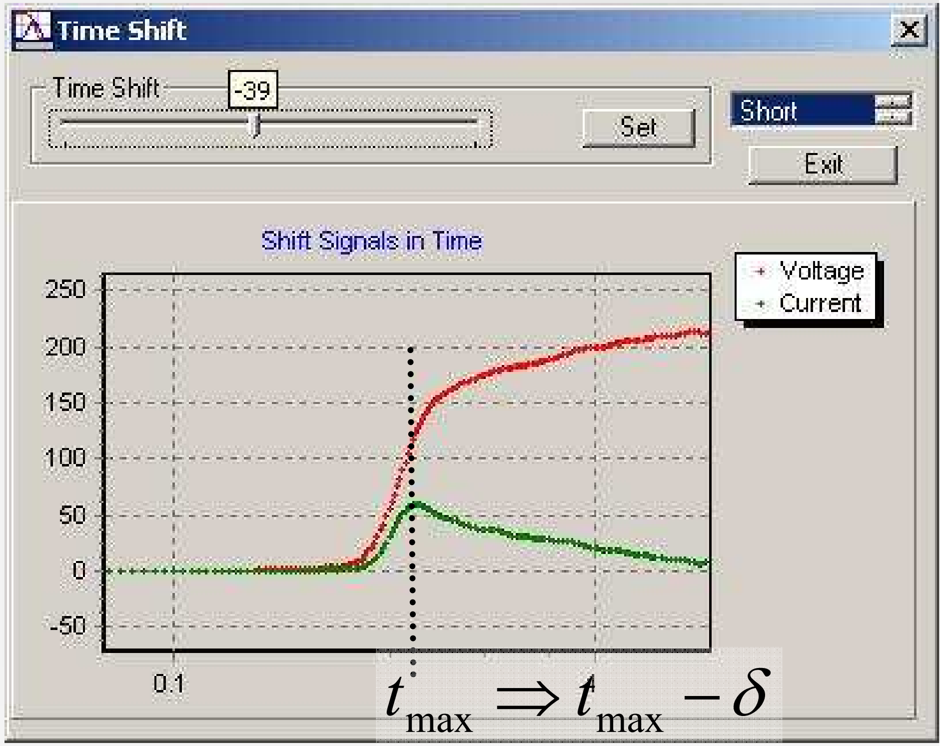
Time window: 329.13 (ns)

Sample File: SM01S5C

Solution:

Time Shift in signal using the criteria

$$\left.\frac{dI}{dt}\right|_{t_{\max}} = 0 : \left.\frac{d^2V}{dt^2}\right|_{t_{\max}} = 0$$



$$t_{\max} \Rightarrow t_{\max} - \delta$$

Iteration Step: 1

☑ No Iteration

Selected Point: ☑ Point 166 Freq 3.160 Signal 224.930

Conductivity: Sigma

Time window: 102.52 [ns]

Sample File: butanol2.ddf

TDS Problems

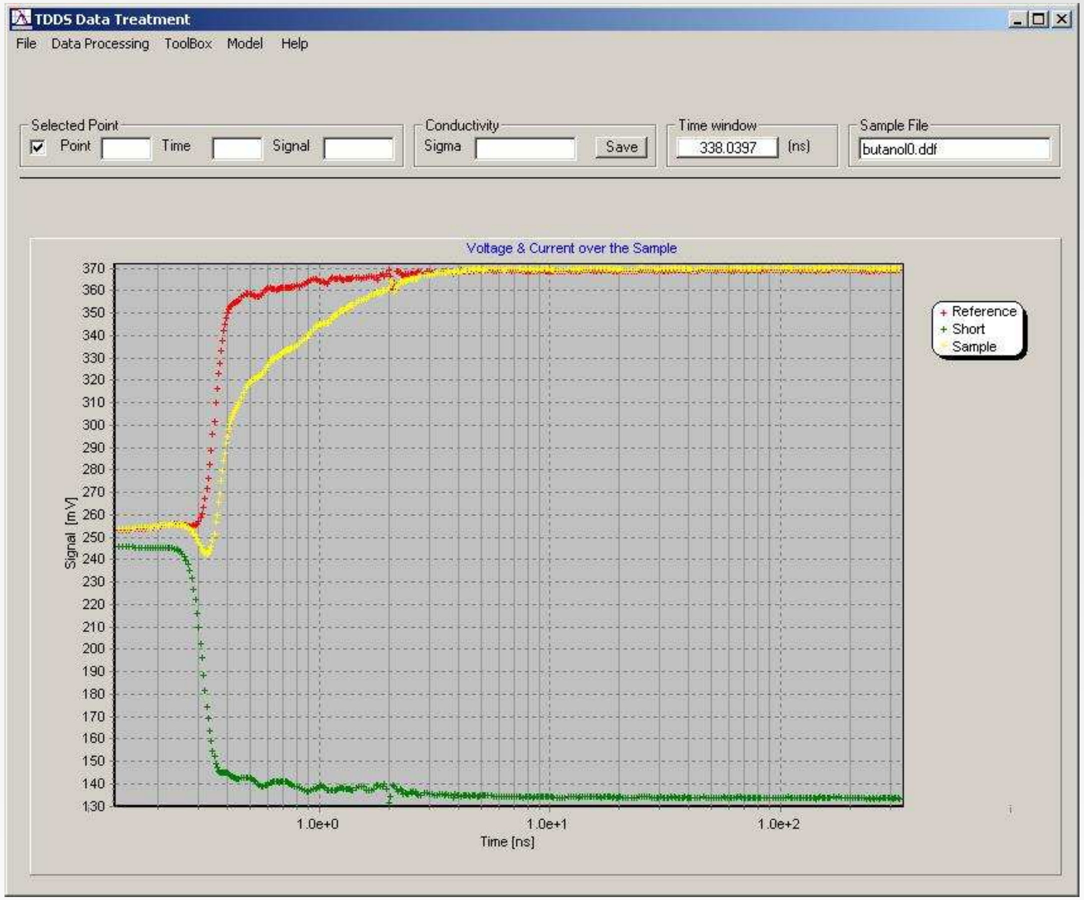
Vertical Shift in signal

$$V_{short}(t) \rightarrow V_{short}(t) + \Delta$$

False Conductivity

$$\sigma = \lim_{t\rightarrow\infty} \frac{I(t)}{V(t)} \propto \frac{V_{open}(t) - V_{sample}(t)}{V_{sample}(t) - V_{short}(t) - \Delta}$$

$$\approx \sigma_0 \left(1 + \frac{\Delta}{V_{sample}(t) - V_{short}(t)} \right)$$



Selected Point: ☑ Point Time Signal

Conductivity: Sigma

Time window: 338.0397 (ns)

Sample File: butanol0.ddf

TDS Problems

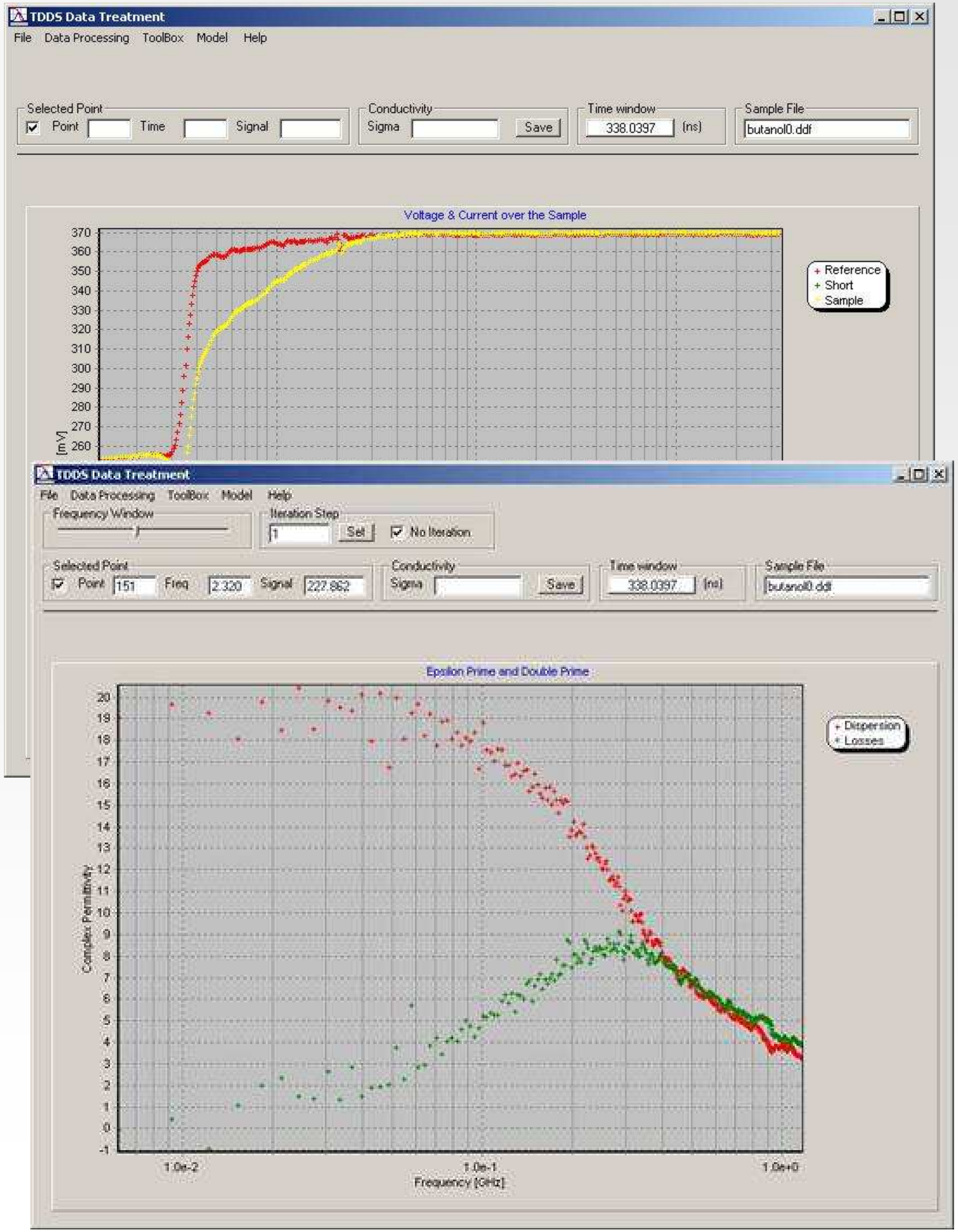
Vertical Shift in signal

$$V_{short}(t) \rightarrow V_{short}(t) + \Delta$$

False Conductivity

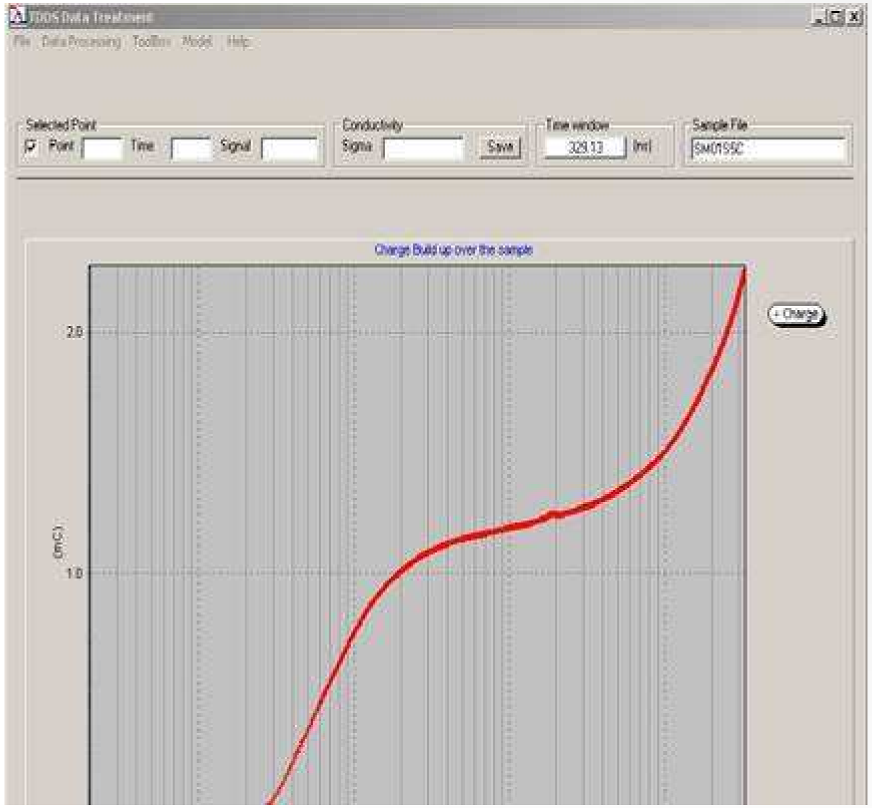
$$\sigma = \lim_{t\to\infty} \frac{I(t)}{V(t)} \propto \frac{V_{open}(t) - V_{sample}(t)}{V_{sample}(t) - V_{short}(t) - \Delta}$$
$$\approx \sigma_0 \left(1 + \frac{\Delta}{V_{sample}(t) - V_{short}(t)} \right)$$

Incorrect Amplitudes



Selected Point: ☑ Point Time Signal
Conductivity: Sigma
Time window: 338.0397 (ns)
Sample File: butanol0.ddf

Iteration Step: 1
☑ No Iteration
Selected Point: ☑ Point 151 Freq 2.320 Signal 227.862
Conductivity: Sigma
Time window: 338.0397 (ns)
Sample File: butanol0.ddf

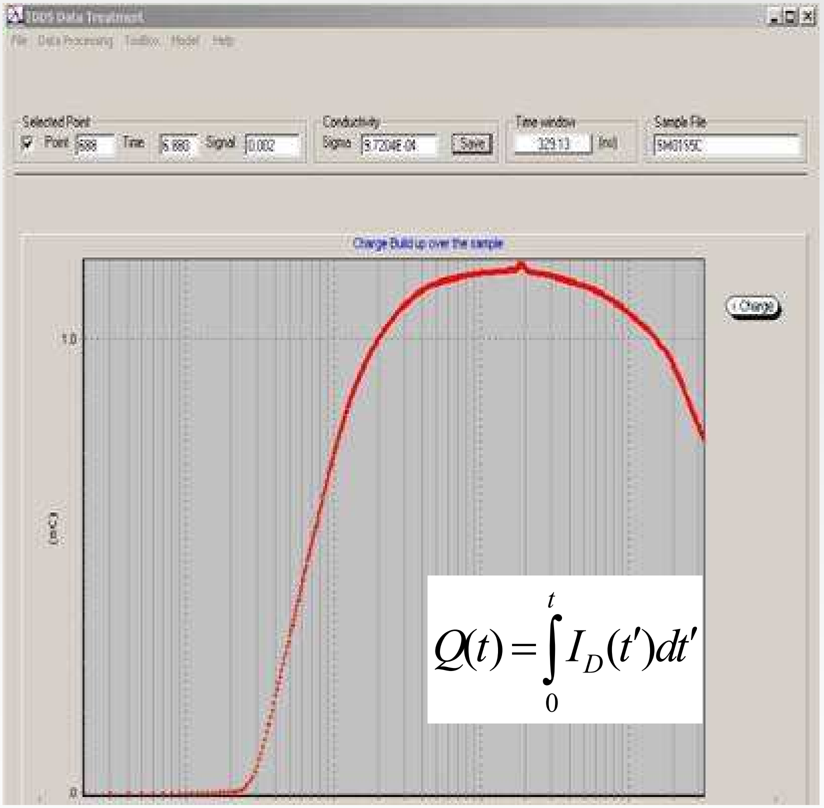


Selected Point: ☑ Point Time Signal

Conductivity: Sigma

Time window: 329.13 [ns]

Sample File: SM0155C



Selected Point: ☑ Point 688 Time 6.880 Signal 0.002

Conductivity: Sigma 9.7204E-04

Time window: 329.13 [ns]

Sample File: SM0195C

$$Q(t) = \int_0^t I_D(t')dt'$$

TDS Problems

Fourier Transforms – 2 main problems:

Truncation errors

Using derivatives - $i\omega F(f(t)) = F(\dot{f}(t))$ Or Samoloon Algorithm

Descrete data

Attenuation factor based on cubic spline with end point correction

$$\frac{1}{T} \le f \le \frac{1}{2\Delta} \qquad F\left[h(t)\right](f) = H_n \approx \Delta \sum_{k=0}^{N-1} h_k e^{-2\pi kn/N} + O(\Delta^2)$$

The frequencies of the FFT are, in essence, integral cycles on the interval. Therefore at high frequencies the summation can be smaller than the second order errors (previously ignored). A correction must be added.

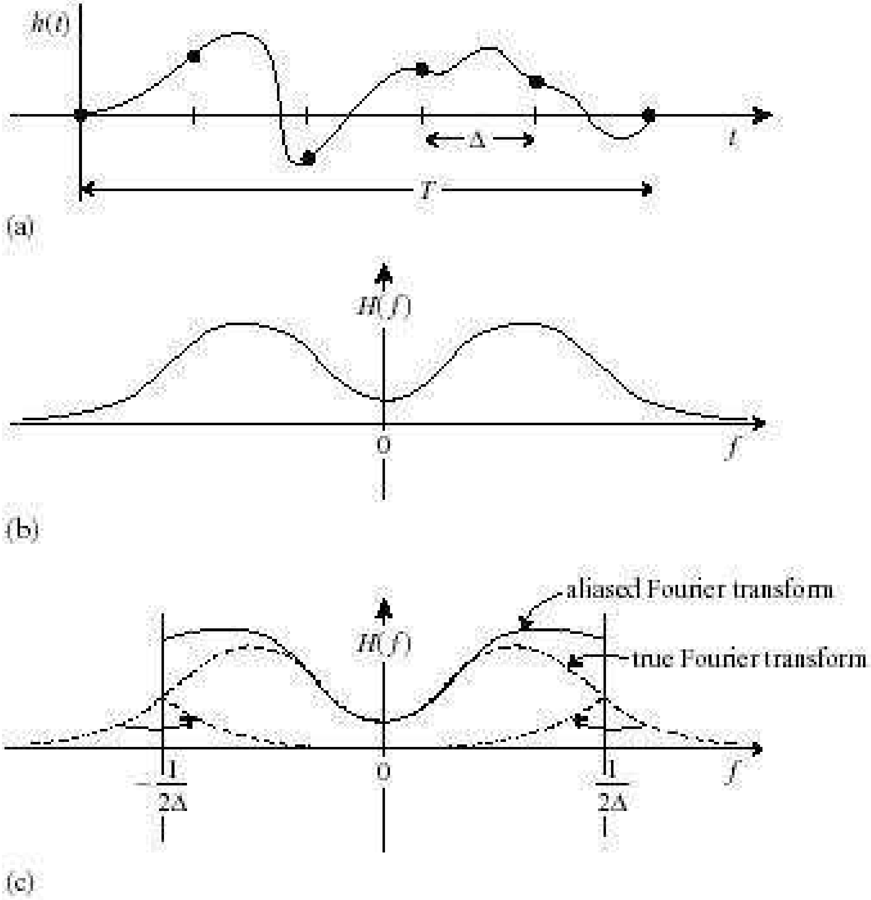
$$h(t) \approx \sum_{k=0}^{M} h_k \psi\left(\frac{t-t_k}{\Delta}\right) + \sum_{k=endpts} h_k \varphi_k\left(\frac{t-t_k}{\Delta}\right)$$

$$W(2\pi n/N) = \int_{-\infty}^{\infty} ds e^{i2\pi n/N} \psi(s)$$

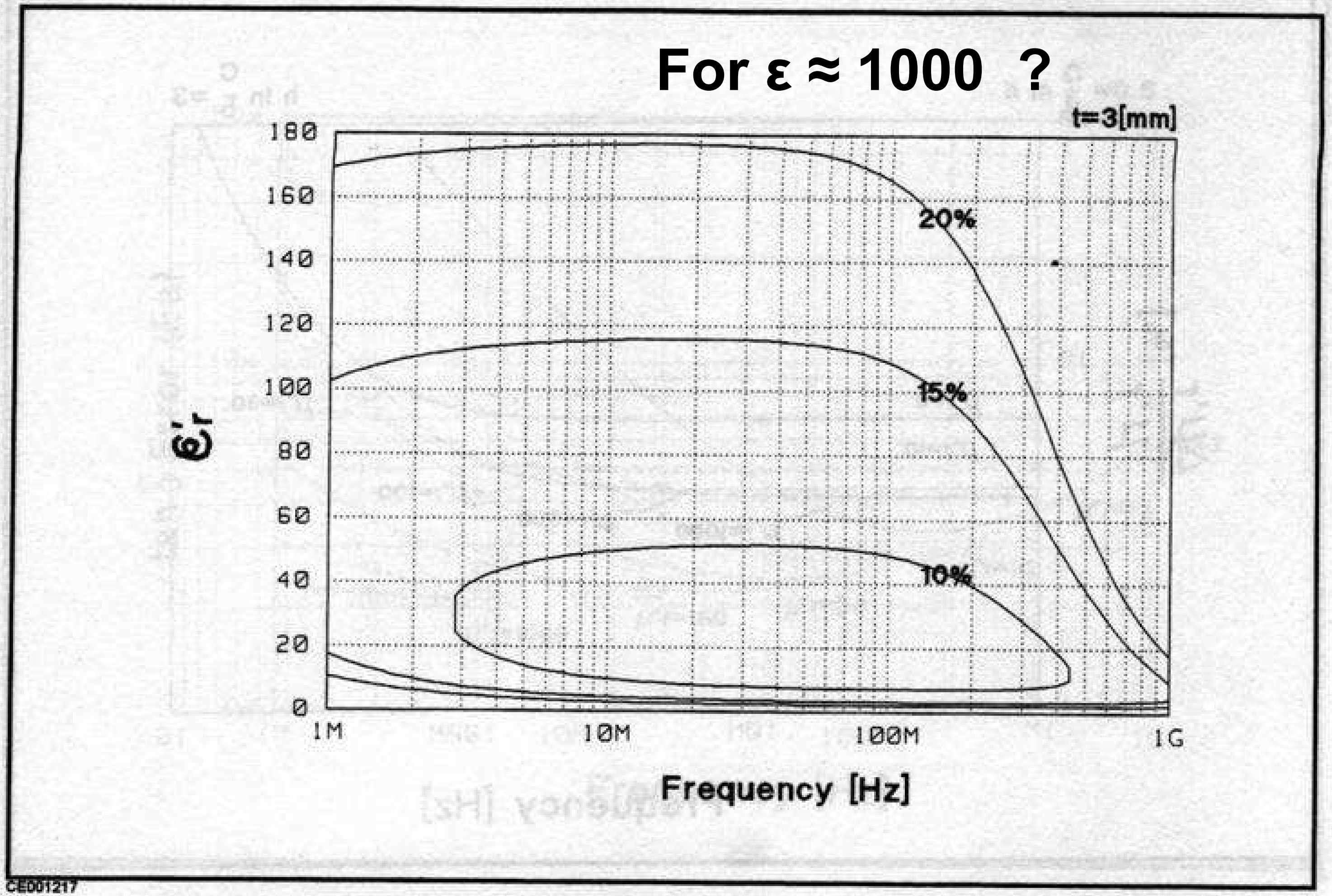
$$\alpha_k(2\pi n/N) = \int_{-\infty}^{\infty} ds e^{i2\pi n/N} \varphi_k(s-k)$$

$$\Downarrow$$

$$F[h(t)] = H_n \approx \Delta e^{i2\pi fa} \left(W\left(2\pi \, {}^{n}\!/_{N}\right) \sum_{k=0}^{M} h_k e^{ik\,2\pi\,{}^{n}\!/_{N}} + \sum_{k=endpts} h_k \alpha_k\left(2\pi \, {}^{n}\!/_{N}\right) \right)$$


h(t)
t
Δ
T
(a)
H(f)
0
f
(b)
aliased Fourier transform
true Fourier transform
H(f)
$-\frac{1}{2\Delta}$
0
$\frac{1}{2\Delta}$
f
(c)

Frequency Impedance Analyzers



For ε ≈ 1000 ?

Figure 12-24.
Typical Permittivity Measurement Accuracy (ε_r v.s. Frequency, @thickness = 3 mm)

Smith Chart

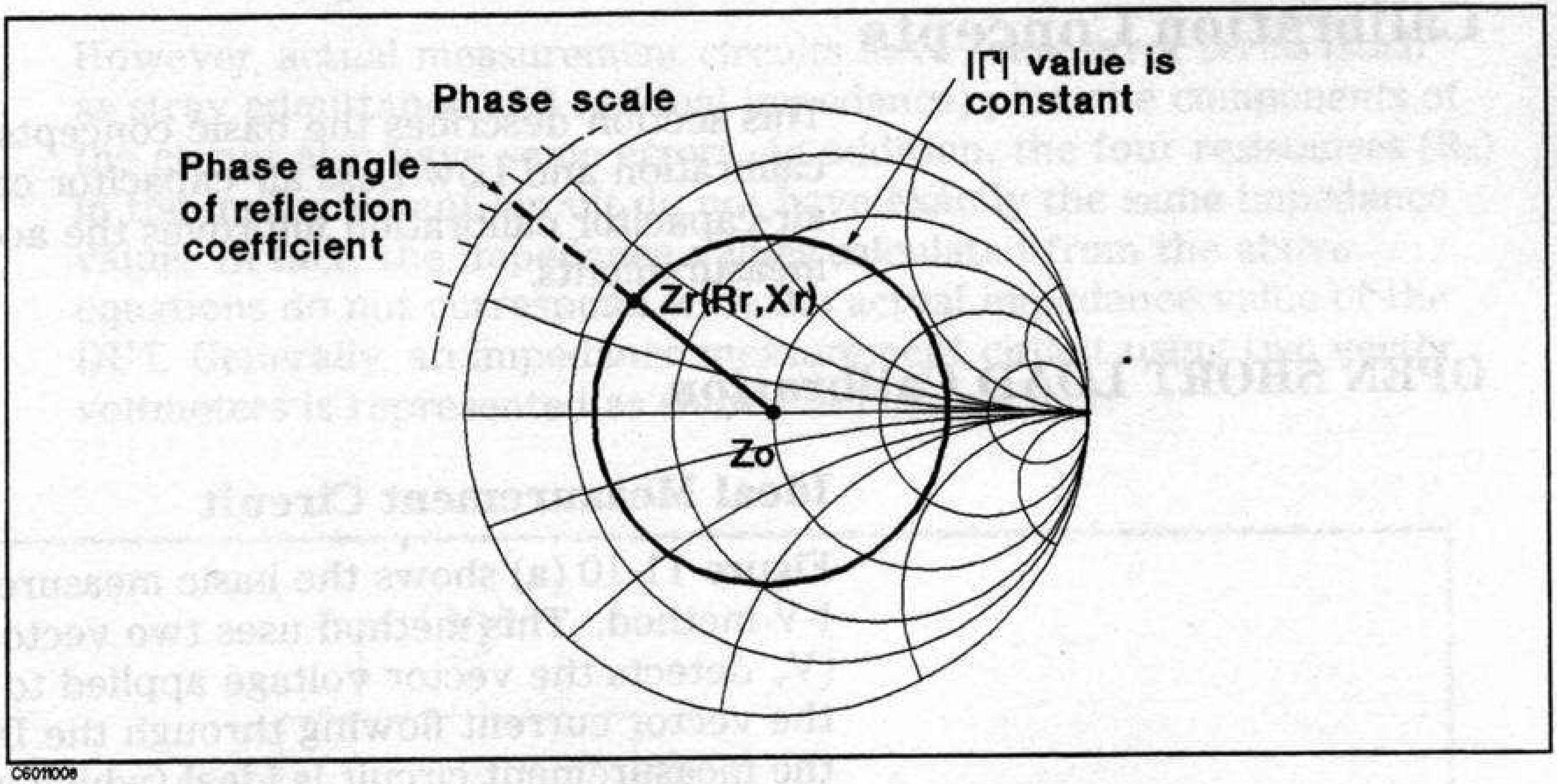
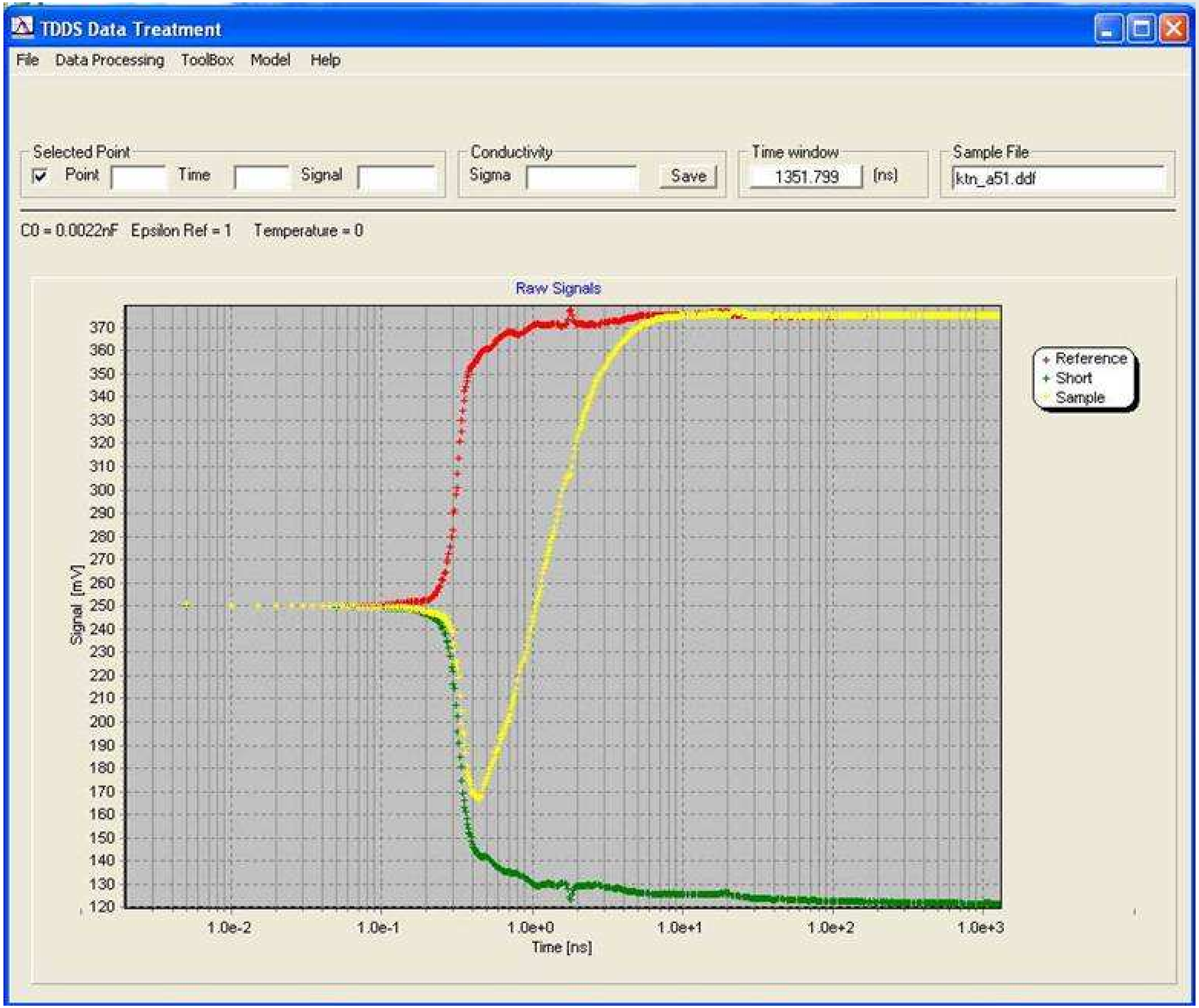


Figure 11-8. Impedance Read-out

TDDS

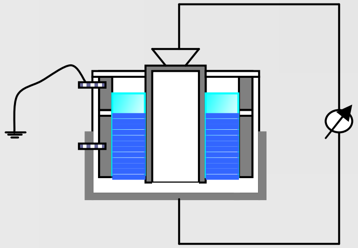


Time window: 1351.799 [ns]

Sample File: ktn_a51.ddf

C0 = 0.0022nF Epsilon Ref = 1 Temperature = 0

Sample Holders in BDS and TDS Measurements



Solids

Low Frequency (<10^7 Hz)

Liquids

Small angle spattering

Contacts

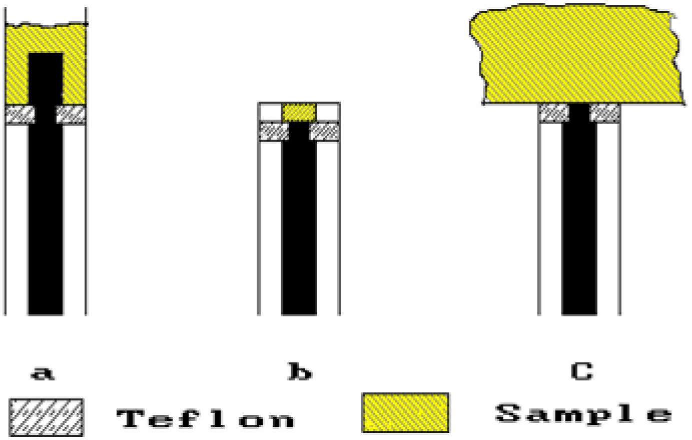
Polish electrodes

Electrode polarization

P, V conditions

Slide electrodes, open ended coaxial or mesh electrodes

High Frequency (>10^8 Hz)



$$R \le \frac{0.24\lambda}{2\pi\sqrt{\varepsilon}}$$

$$\lambda > \pi\sqrt{\varepsilon(b+a)}$$

The 3 electrode sample cell

How to account for leakage from a samples cell during an extended measurement?

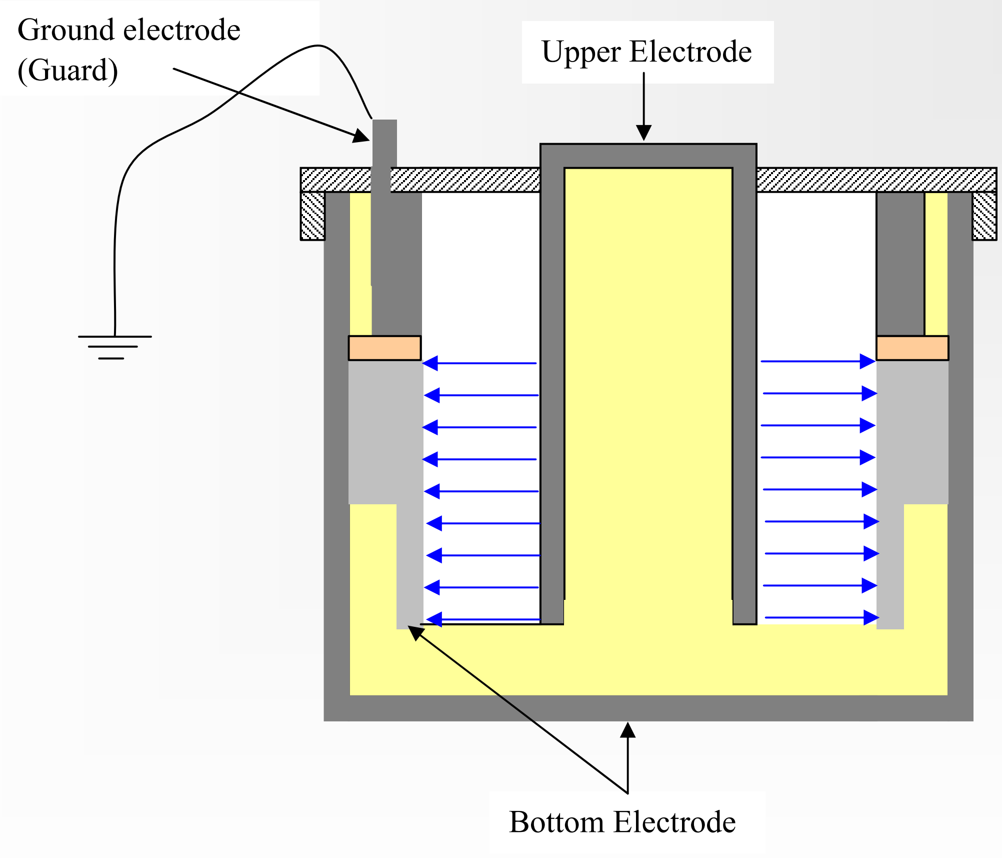
How to maintain a constant pressure during a wide temperature regime?

How to establish a fixed geometry for a liquid?

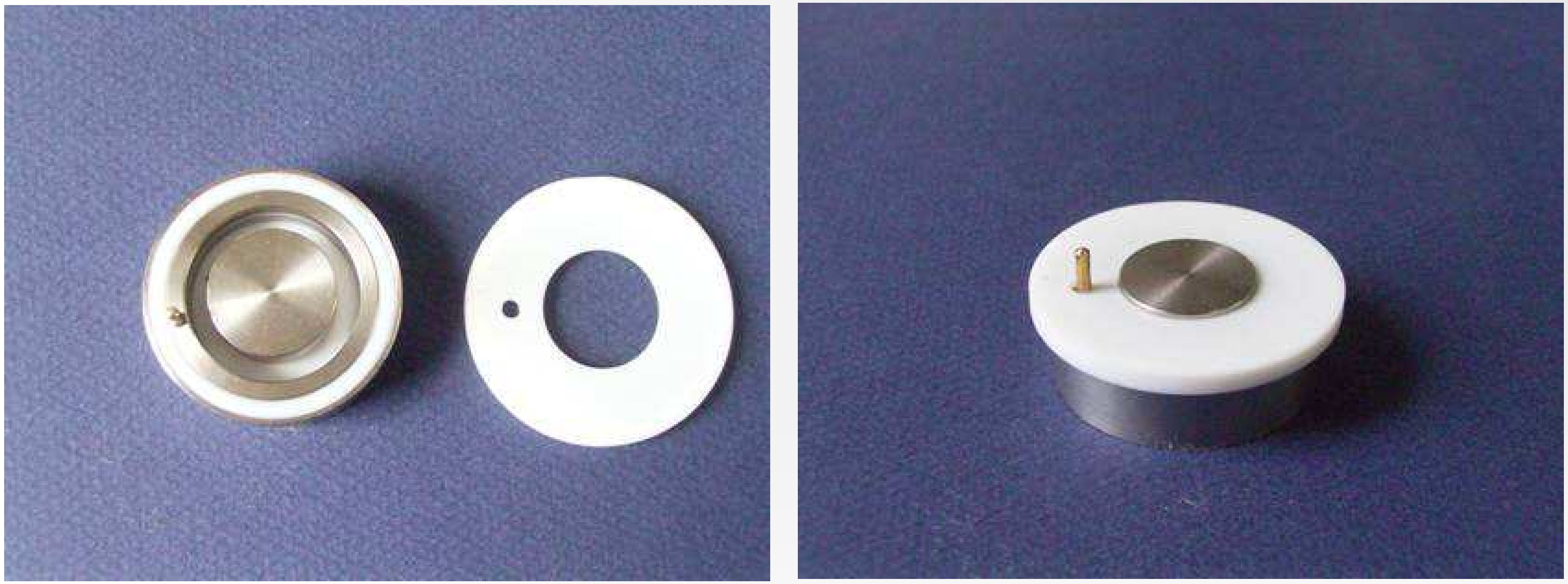
How to overcome expansion problems for liquids?

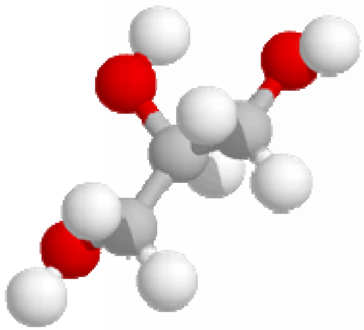
How to ensure that there will be no air pockets between electrode and sample?

$$C_0 = \frac{2\pi\varepsilon_0}{\ln\left(\frac{b}{a}\right)}$$

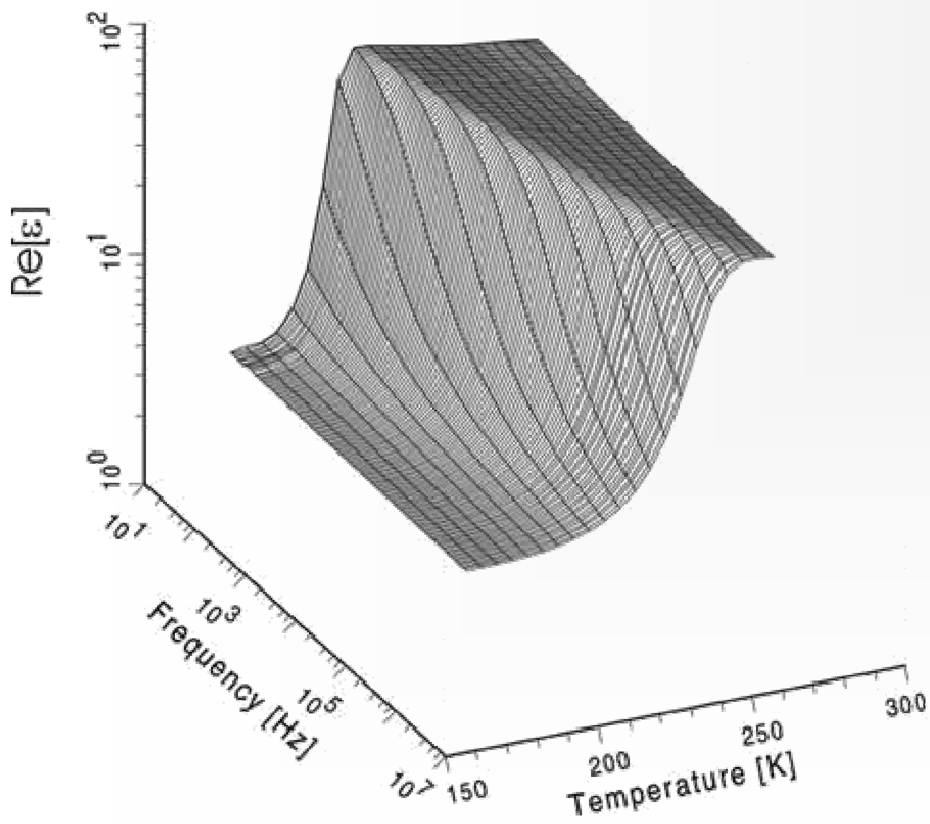


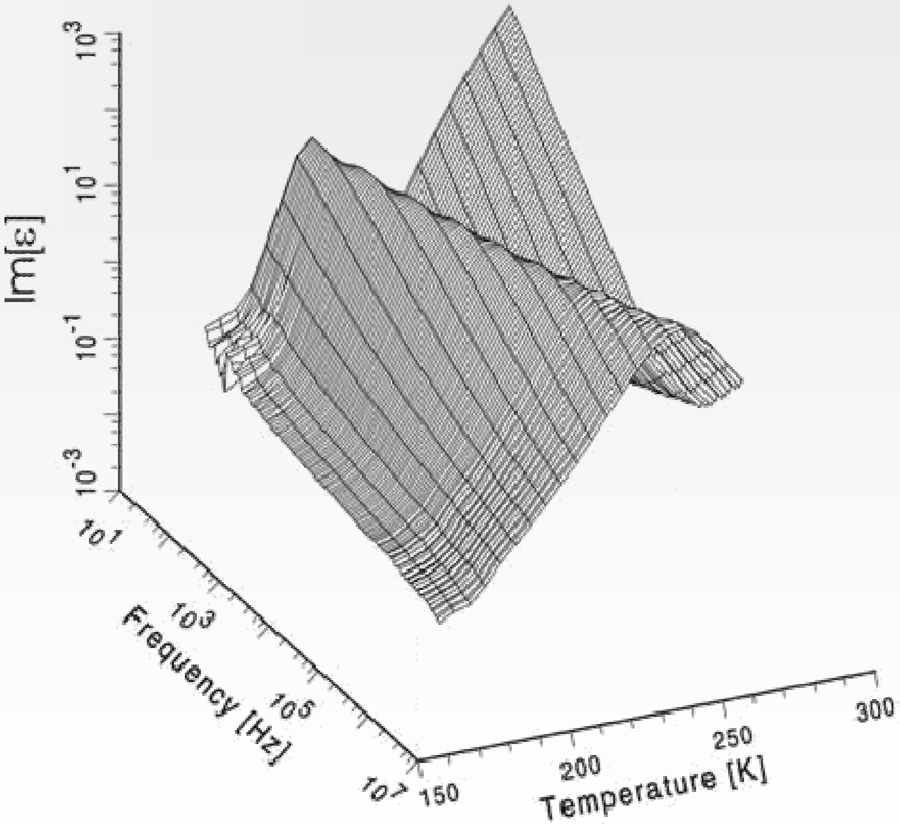
$$C_0 = \frac{2\pi\varepsilon_0}{\ln\left(\frac{b}{a}\right)}$$



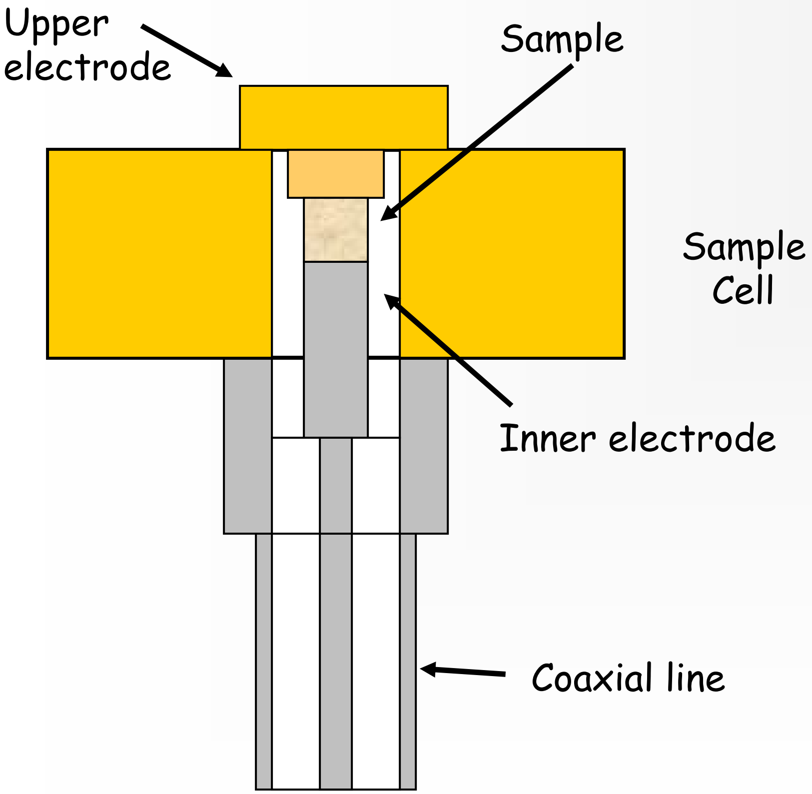


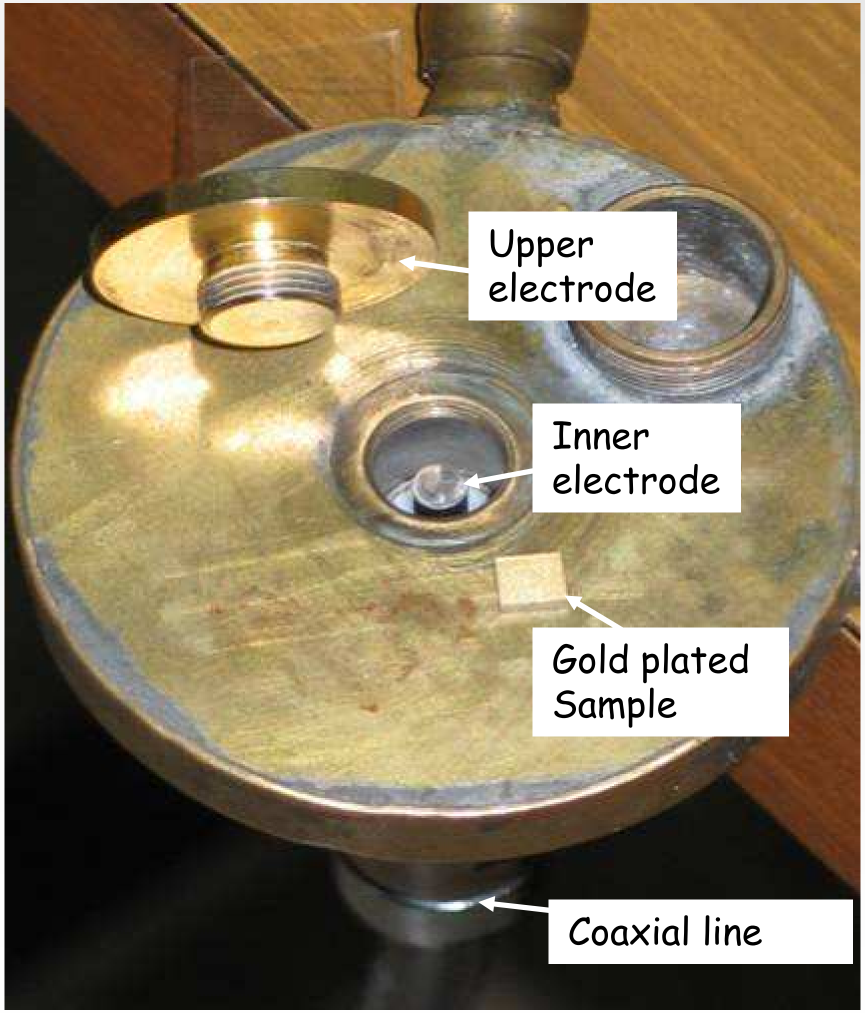
DS of Glycerol



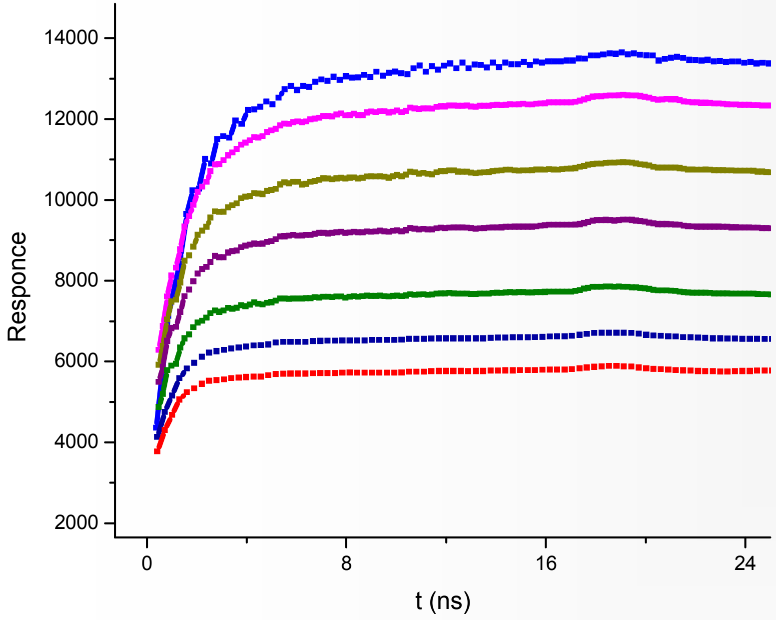


TDDS Sample Cell



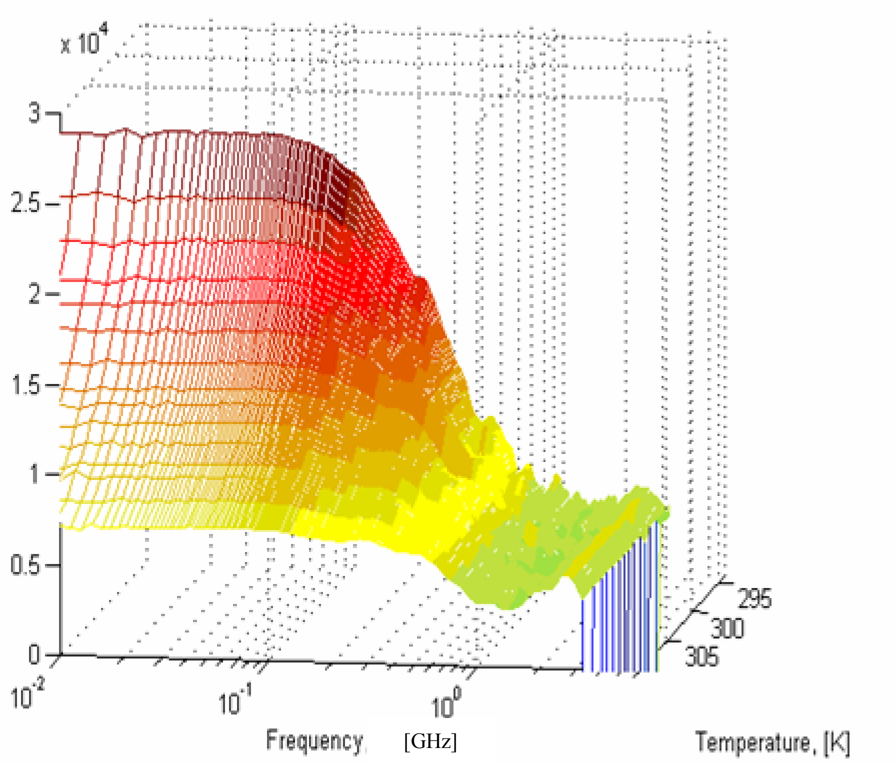


Typical Results



Time domain

Dielectric response function: $\Phi(t)$

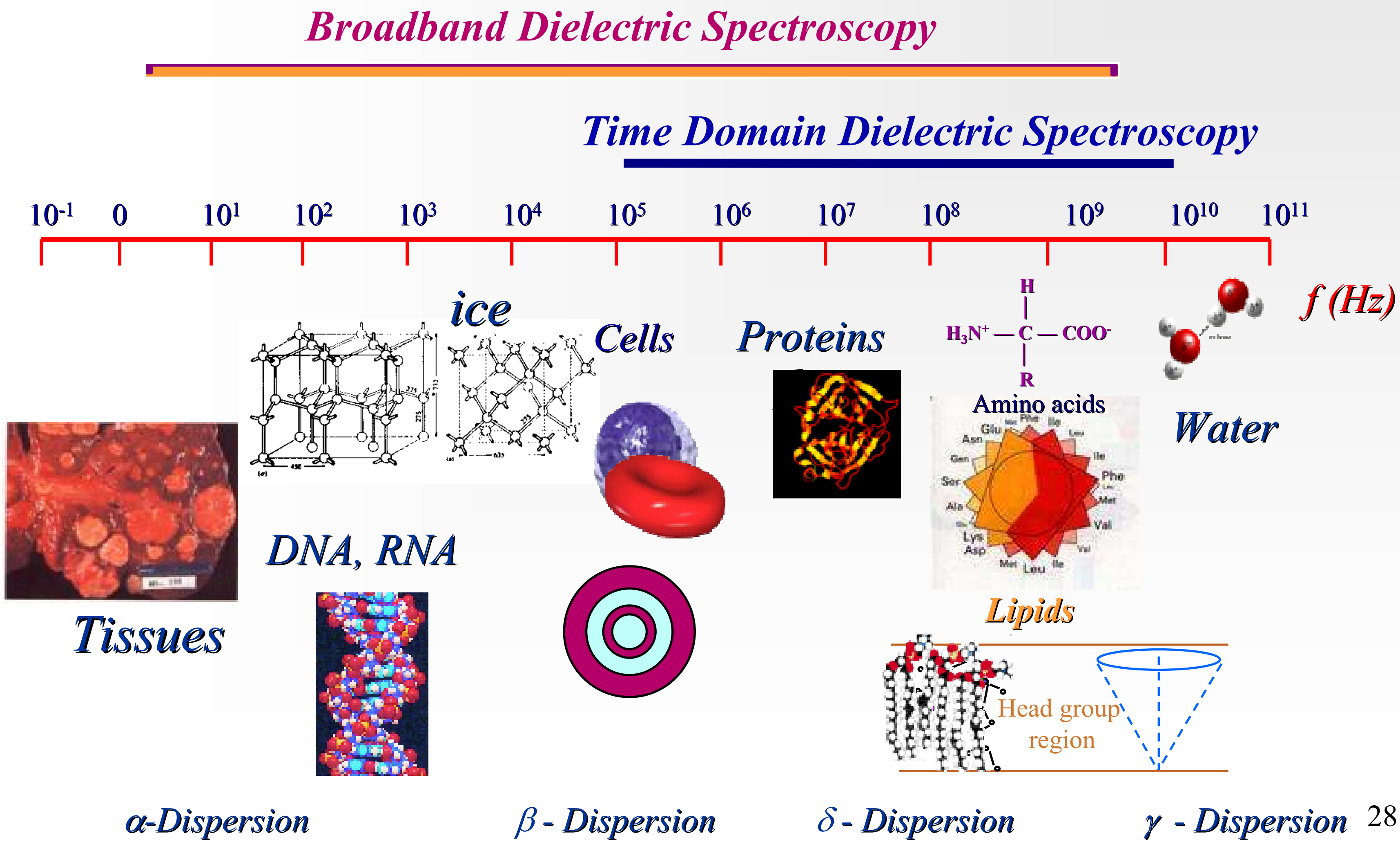


Frequency domain

Spectrum of dielectric permittivity: $\varepsilon'(\omega)$

Dielectric Response in Biological Systems

Dielectric spectroscopy is sensitive to relaxation processes in an extremely wide range of characteristic times (10^{5} - 10^{-11} s)



Broadband Dielectric Spectroscopy

Time Domain Dielectric Spectroscopy

10^{-1} 0 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7} 10^{8} 10^{9} 10^{10} 10^{11}

f (Hz)

ice

Cells

Proteins

$H_3N^+ - C(H)(R) - COO^-$

Amino acids

Water

Tissues

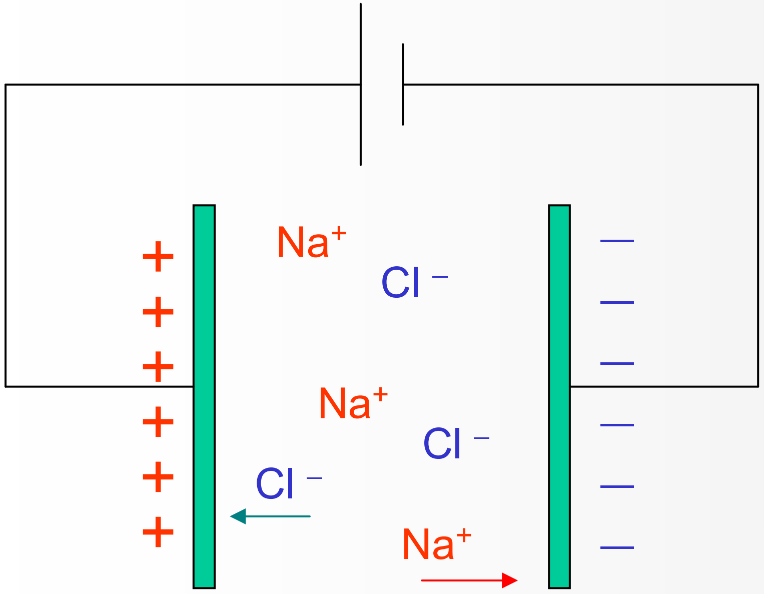
DNA, RNA

Lipids

Head group region

α-Dispersion *β - Dispersion* *δ - Dispersion* *γ - Dispersion*

dc conductivity

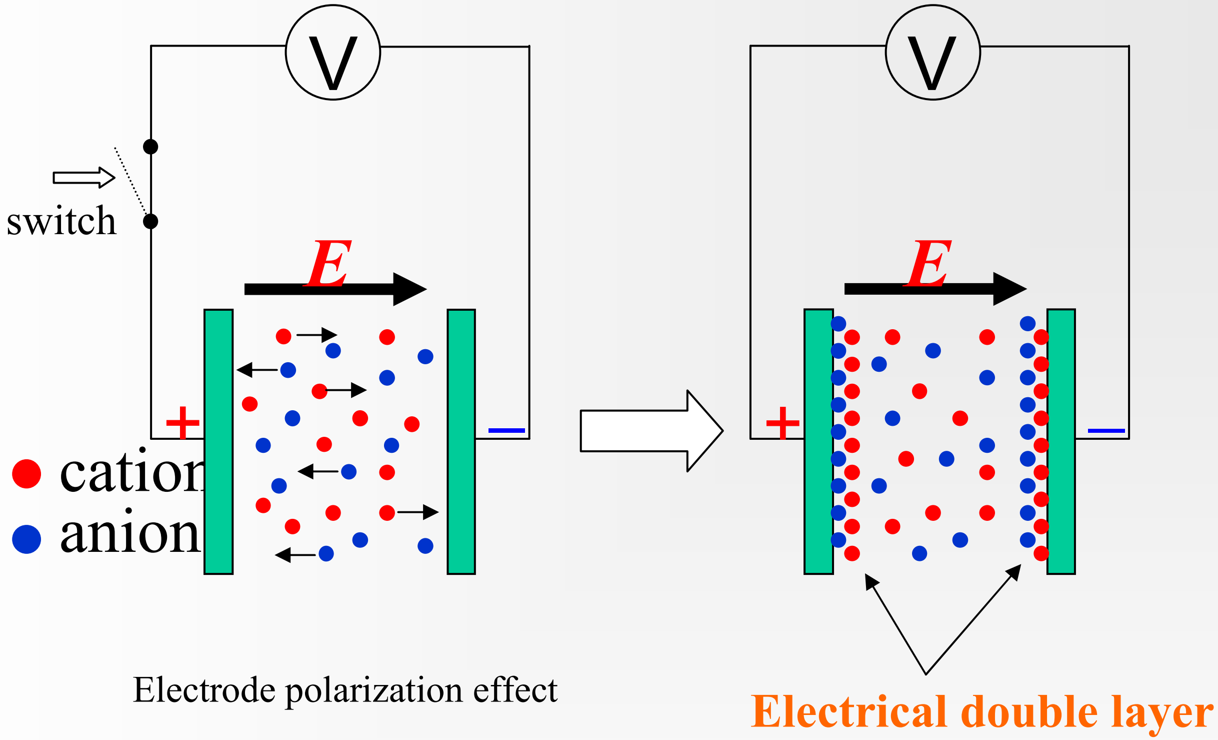


- In the cathode
  - $Na^+ + \text{electron} \rightarrow Na$
    - $2Na + H_2O \rightarrow 2Na^+ + 2OH^- + H_2$
- In the anode
  - $Cl^- - \text{electron} \rightarrow Cl$
    - $2Cl \rightarrow Cl_2$
    - $\text{Metal} + Cl \rightarrow MCl$ (e.g., $CuCl_2$)

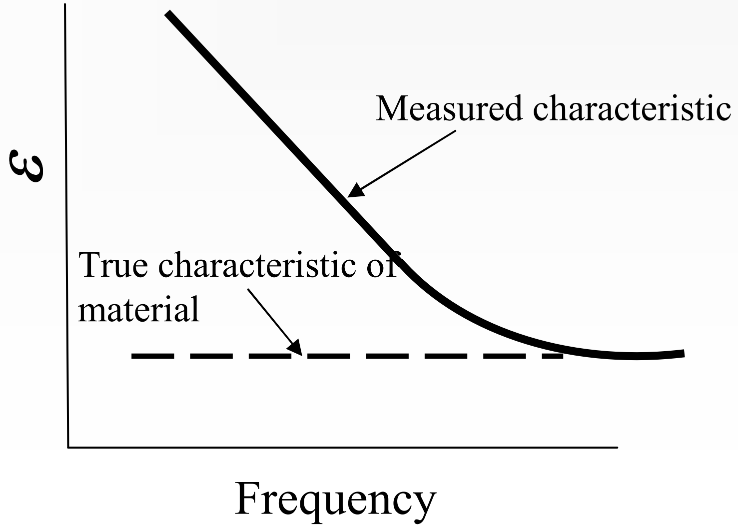
Problems are:

increase of **pH**, birth of **gases** and **corrosion** of the electrode. These are significant if current is not small.

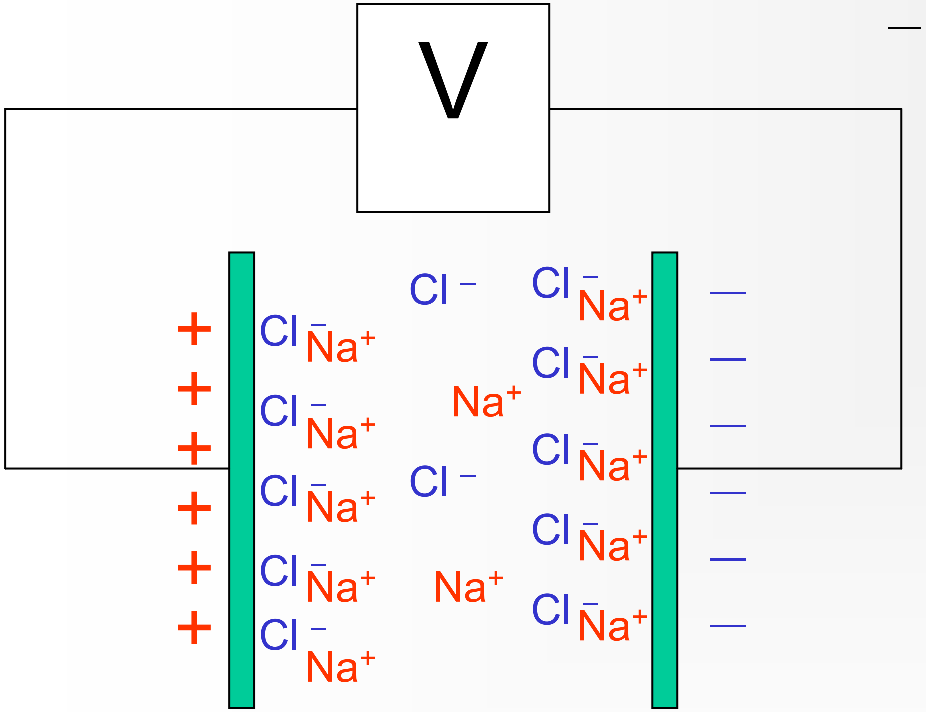
What is the electrode polarization?



Electrode polarization effect



Electrode Polarization

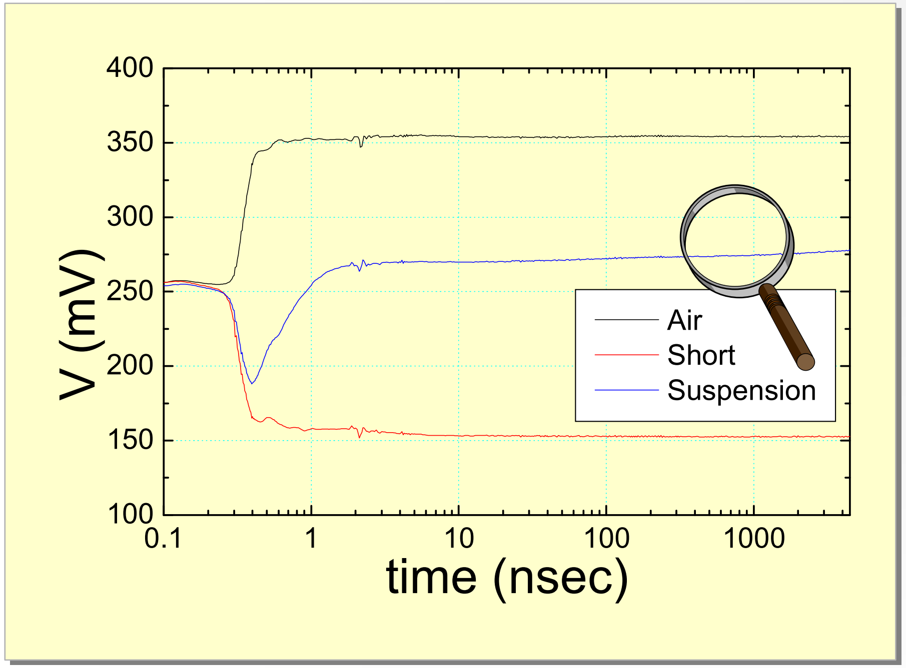


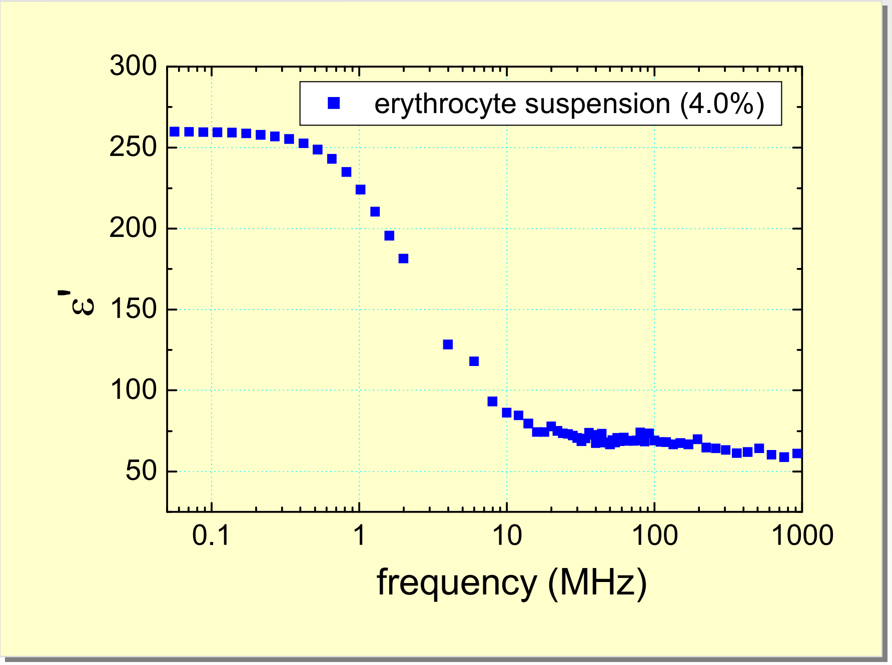
Electric double layer

- **List of possibilities of the corrections**
  - Substitution method
  - Single exponent method (F3)
  - Fractal method (F2)
  - Blocking electrode
  - Electromagnetic induction method
  - Combination of plate-capacitance and fractal method
  - Change of the distance (*d*) of plate-capacitance
  - Others?

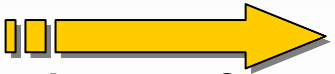
Data treatment from time domain to frequency domain

E.g., human erythrocyte suspension



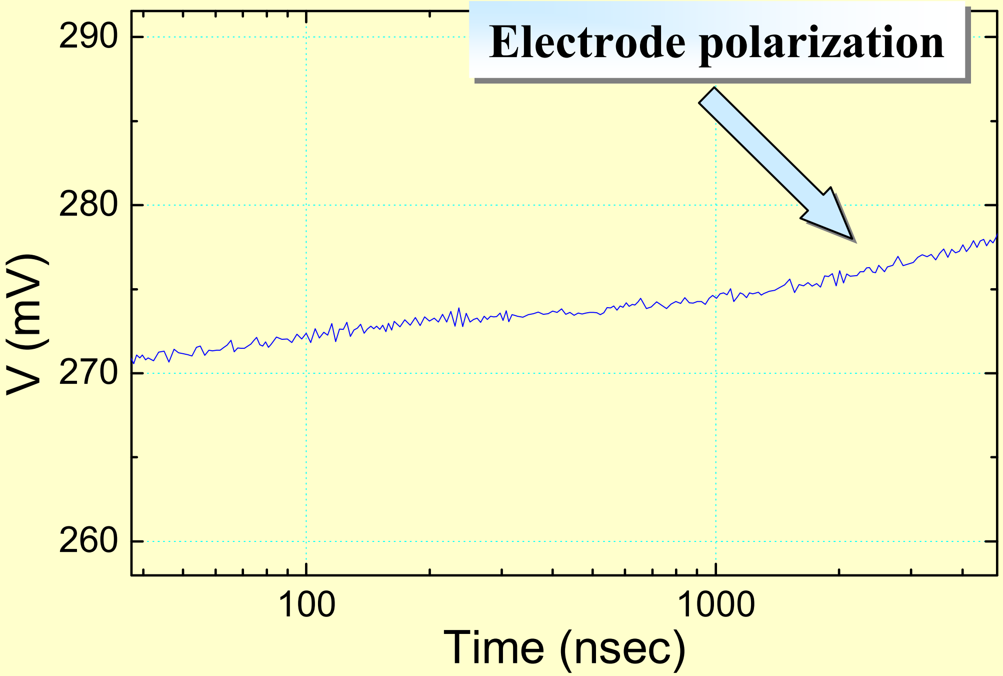


Signals in time domain



Fourier transform

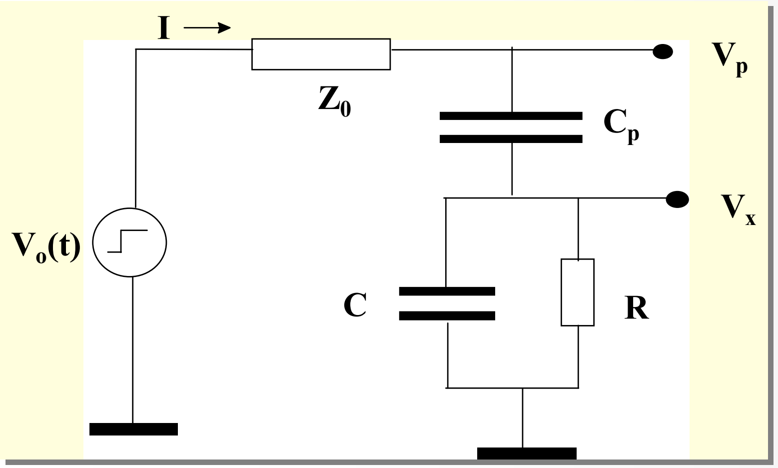
Dielectric spectrum in frequency domain

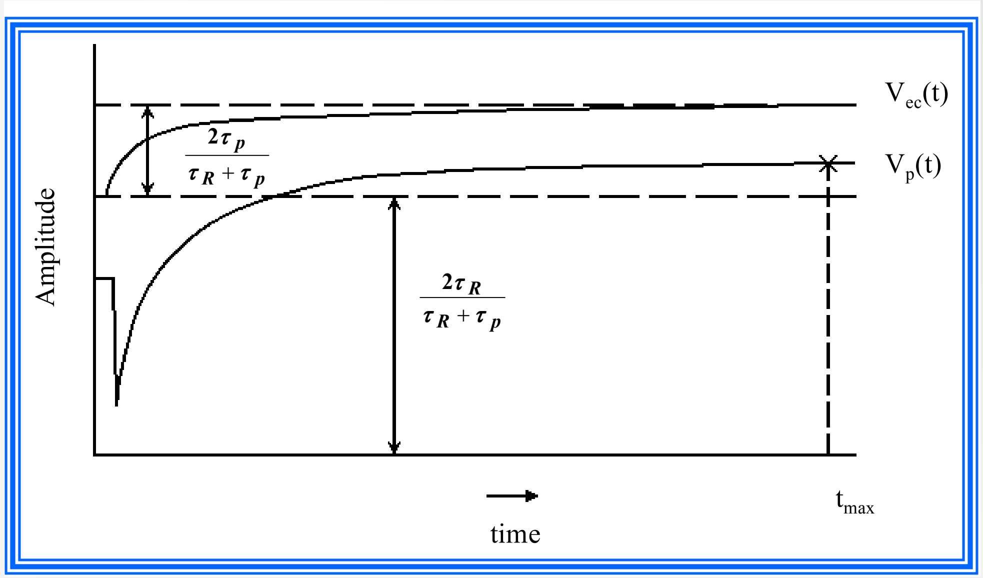


Electrode polarization

Single exponent method

for low conductive sample





$$V_p(t) = \underset{C_p\to\infty}{V_x(t)} + V_{ec}(t)$$

$$I(s) = V_0(s)\frac{(s\tau_0+1)sC_p}{(s\tau_0+1)(s\tau_p+1)+s\tau_R}$$

$$V_p(s) = V_0(s)\frac{s(\tau_R+\tau_0)+1}{(s\tau_0+1)(s\tau_p+1)+s\tau_R}$$

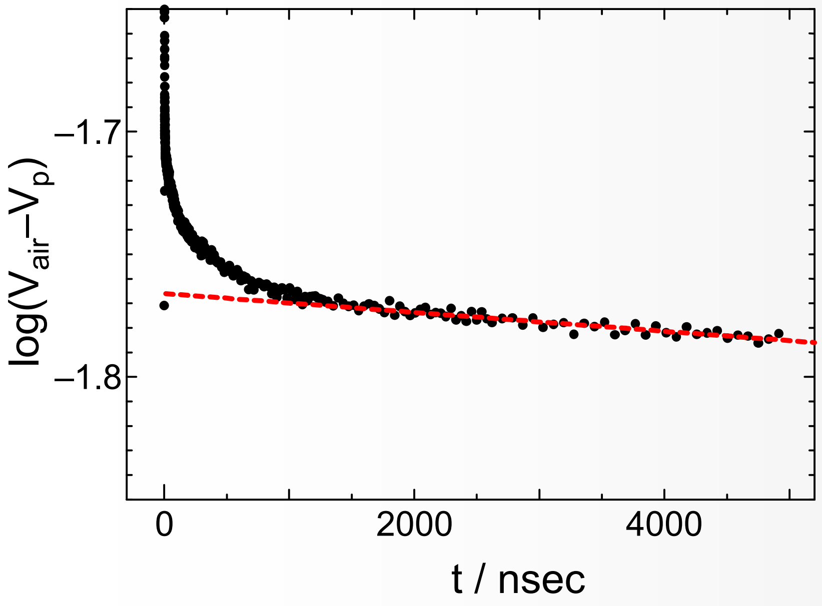
$\tau_p=Z_0C_p$, $\tau_R=RC_p$, $\tau_p=RC$, $s=j\omega$

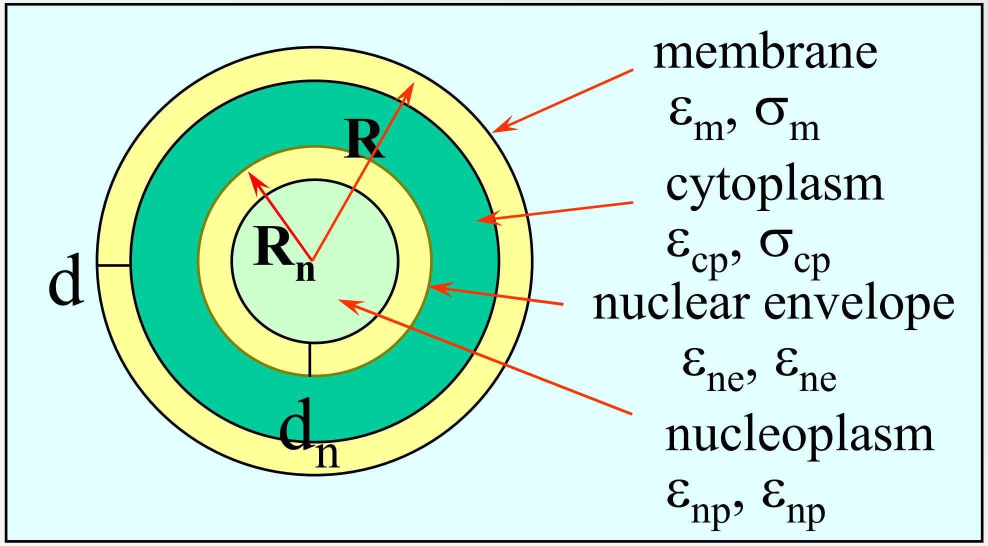
Electrode polarization correction function

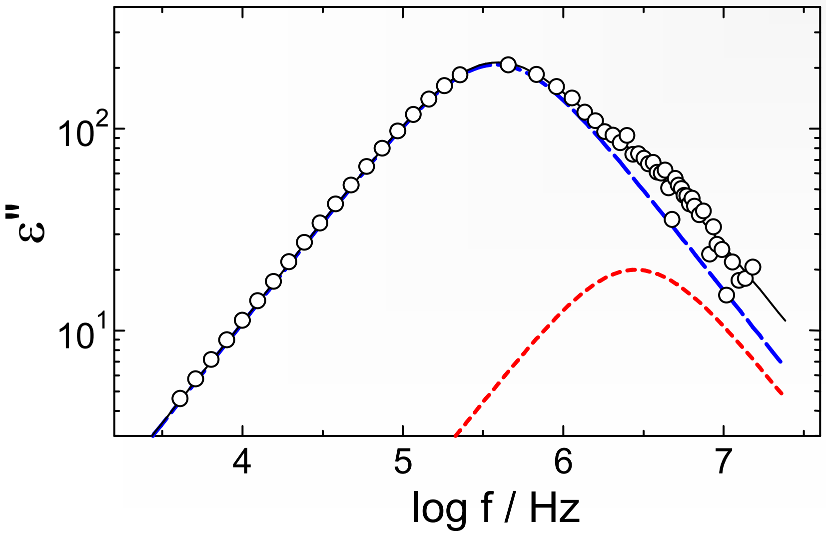
$$V_{ec}(t) = \frac{\tau_p}{\tau_R+\tau_p}\left(1-e^{-t/\tau_2}\right),$$

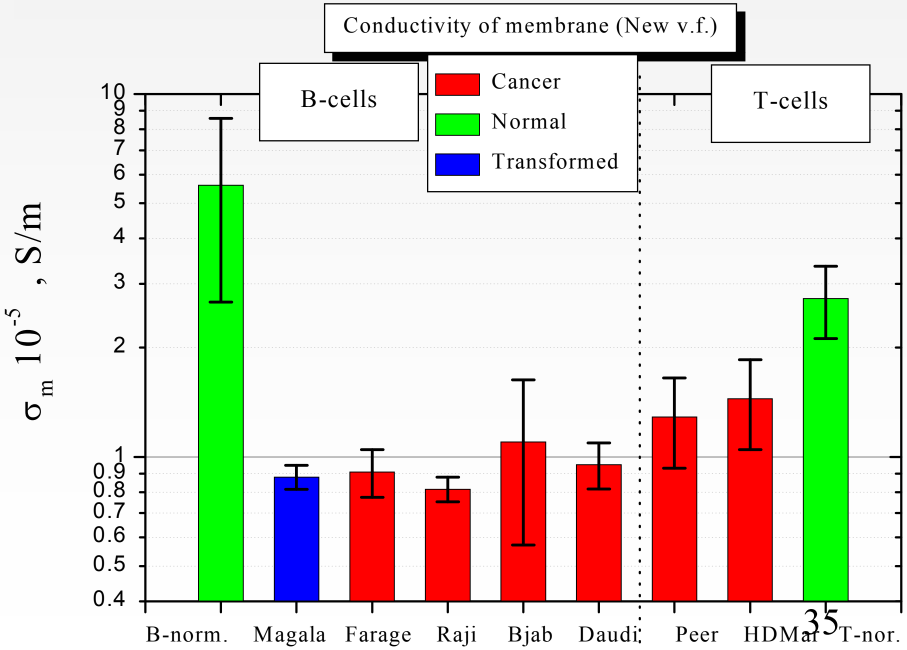
$$\text{where } \tau_2 = \frac{1-V_p(t_{\max})}{\dot{V}_p(t_{\max})}$$

Example B: Human lymphocyte suspension





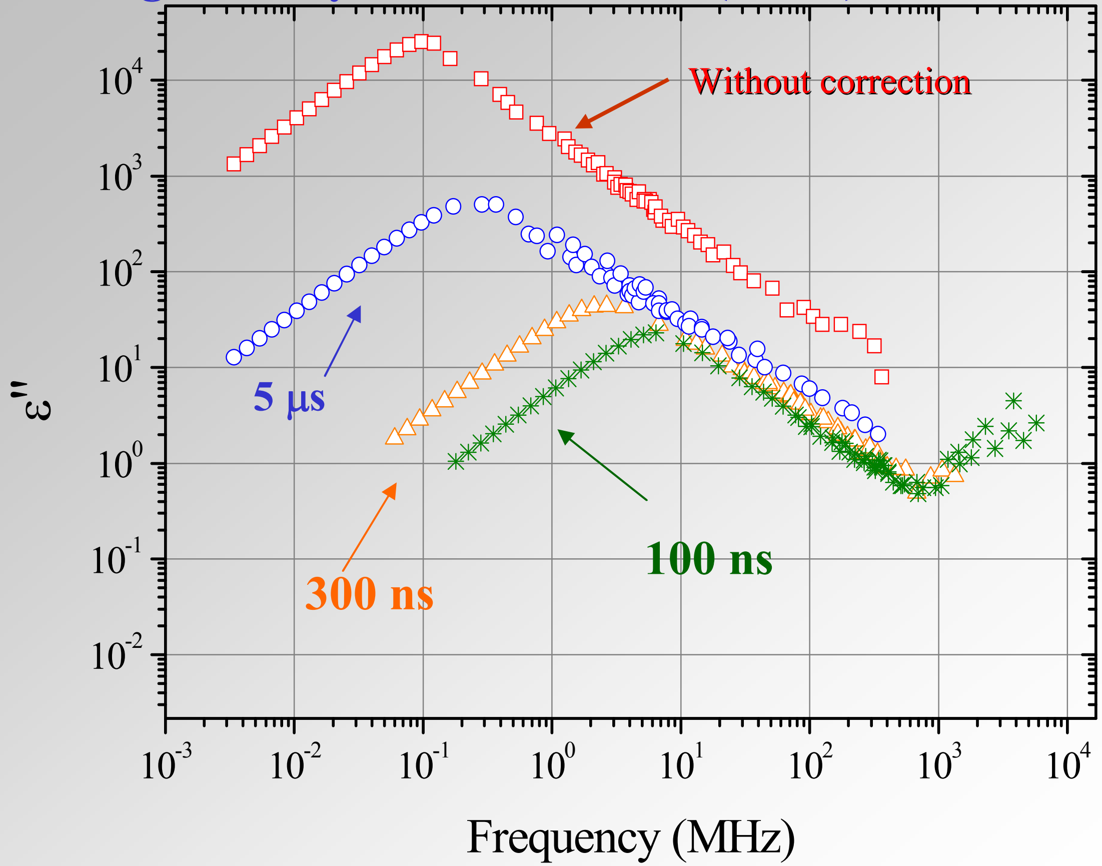




Single exponent method: *Limitation*

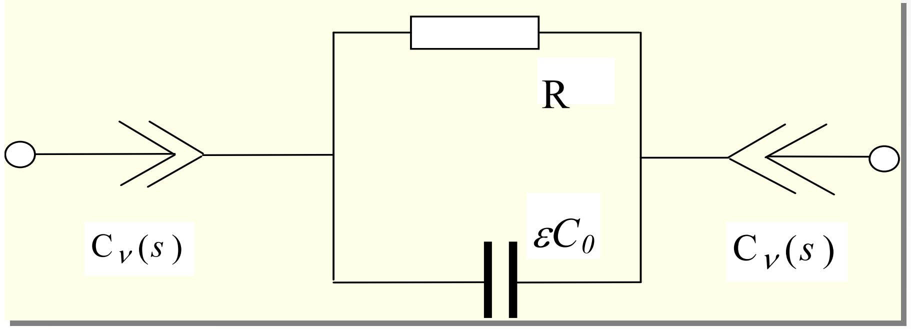
This behavior allows us to suggest the frequency (or time) self-similarity of the electrode polarization phenomenon, i.e. the fractal nature of this effect.

Strong electrolyte solution; NaCl (0.1 M) in water



Fractal approach *can be applied to high conductive sample*

Electrodes should be polished carefully because the electrode polarization depends on the fractal nature of the electrodes surfaces.



Equivalent circuits for a conductive sample with electrode polarization impedance described by recap C_ν

$$Z_0(j\omega) = A(\nu)(j\omega)^{-\nu}$$

In Frequency domain:

$$C_{\nu_i}(s) \equiv C_{\nu_i} \cdot s^{-\nu_i} = R_i (R_i C_i)^{-\nu_i} s^{-\nu_i}$$

$i=1,2;\ 0<\nu<1$

In Time domain:

$$V(t) \propto \frac{C_{\nu_1}}{\nu_1 \Gamma(\nu_1)} t^{\nu_1} + \frac{C_{\nu_2}}{\nu_2 \Gamma(\nu_2)} t^{\nu_2} + R\left[1 - \exp\left(-t/\tau_c\right)\right]$$

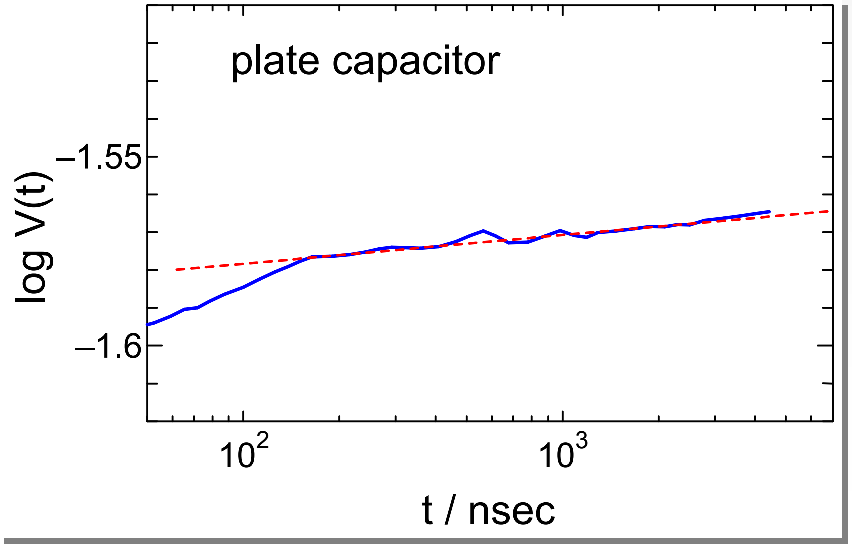
a) both electrodes of the sample holder have the same (or equivalent) electrode polarization ($\nu_1 = \nu_2$; $C_{\nu 1} = C_{\nu 2}$)

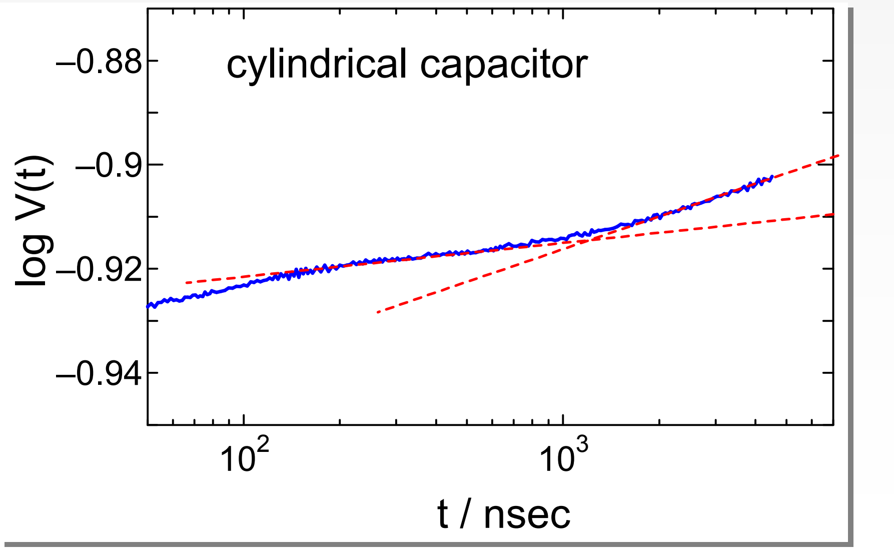
b) ($\nu_1 \neq \nu_2$; $C_{\nu 1} \neq C_{\nu 2}$)

$$V(t) = Bt^{\nu} + Rt/\tau_c \quad \text{for} \quad t/\tau_C \ll 1$$
$$V(t) = Bt^{\nu} + R \quad \text{for} \quad t/\tau_C \gg 1$$

$$V(t) = B_1 t^{\nu_1} + B_2 t^{\nu_2} + Rt/\tau_c \quad \text{for} \quad t/\tau_C \ll 1$$
$$V(t) = B_1 t^{\nu_1} + B_2 t^{\nu_2} + R \quad \text{for} \quad t/\tau_C \gg 1$$

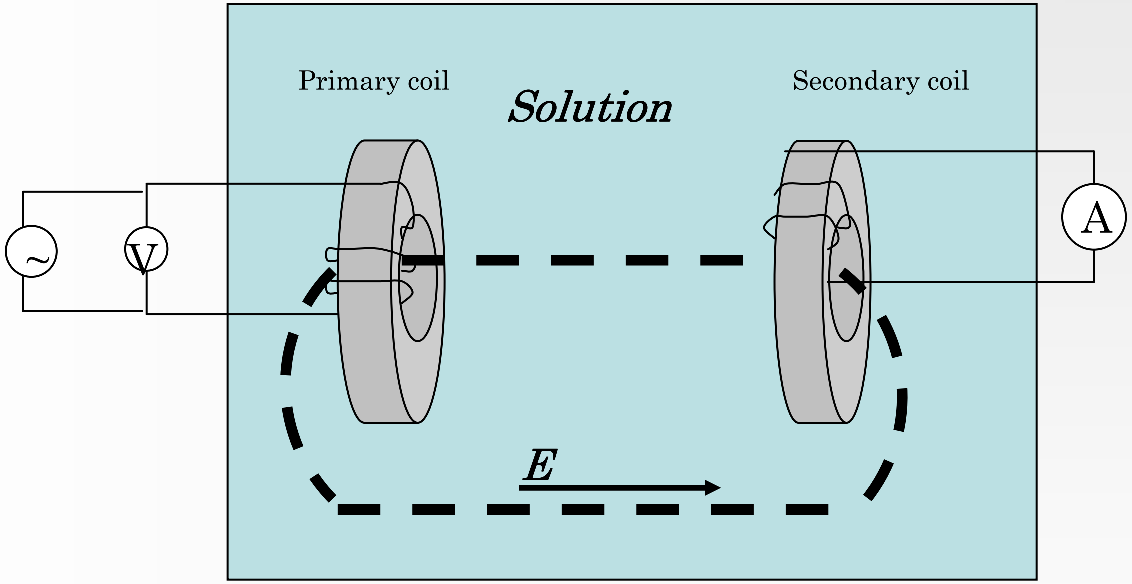
There is no dispersion of the conductive solution (sample) in the time window defined by τ_c ($> t_{min} = 1/\omega_{max}$)





Electromagnetic inductive method
- additional remark for near future -

The HP Sensor



There is no electrode polarization!

Problem is amount of sample (400 ml).

H. Wakamatsu, 1997. *Hewlett-Packard J.* **48,** 37.
K. Asami et al., 1999. *Biophys. J.* **76,** 3345.

Data Treatment

What function? *Fitting?* *dc conductivity correction?*

Frequency Domain →

$$\frac{\varepsilon^{*}(\omega)-\varepsilon_{\infty}}{\varepsilon_{s}-\varepsilon_{\infty}}=\hat{L}\left[-\frac{d}{dt}\phi(t)\right]$$

← *Time Domain*

Havriliak-Negami (HN)

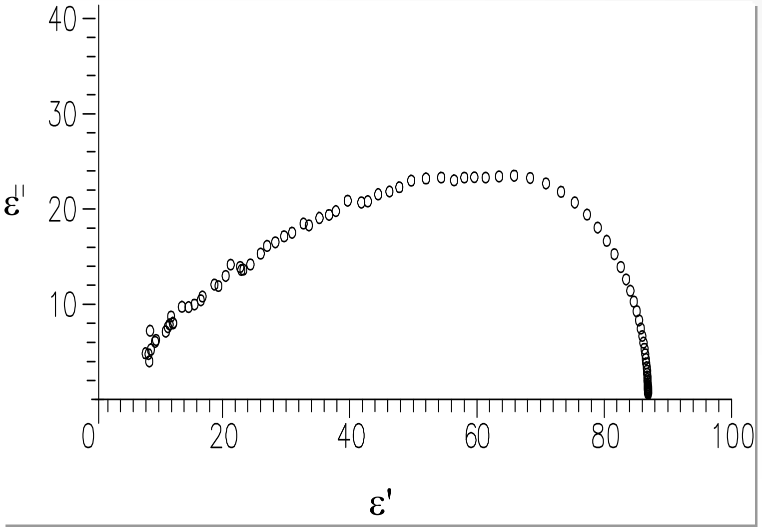
$$\varepsilon^{*}(\omega)=\varepsilon_{\infty}+\frac{\varepsilon_{s}-\varepsilon_{\infty}}{\left[1+(i\omega\tau_{m})^{\alpha}\right]^{\beta}}$$

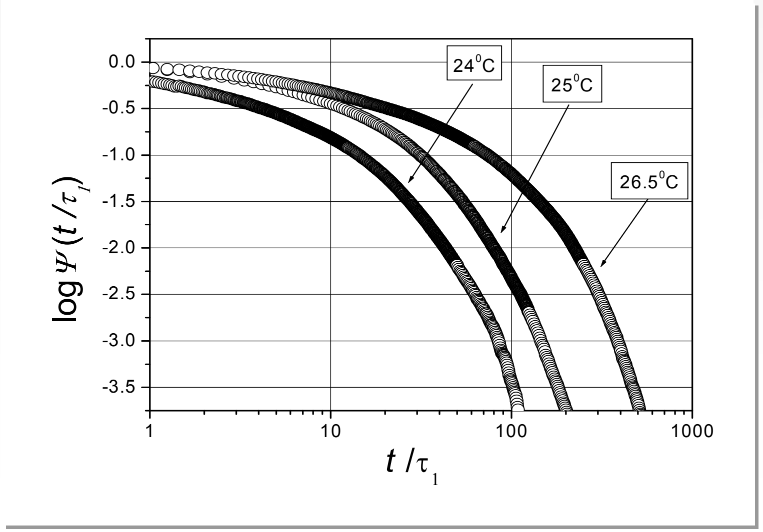
?

Power × stretched exponential

$$\phi(t)=A\left(\frac{t}{\tau_{1}}\right)^{-\mu}\exp\left\{-\left(\frac{t}{\tau_{m}}\right)^{\nu}\right\}$$

for $t/\tau_{1}>>1$





DS data treatment; problems of correct fitting

- **Simultaneous fit of both real and imaginary components of the complex dielectric permittivity data;**

- **Problems in selecting the proper fitting function, such as:**

  The limited frequency and temperature ranges of the experiment;

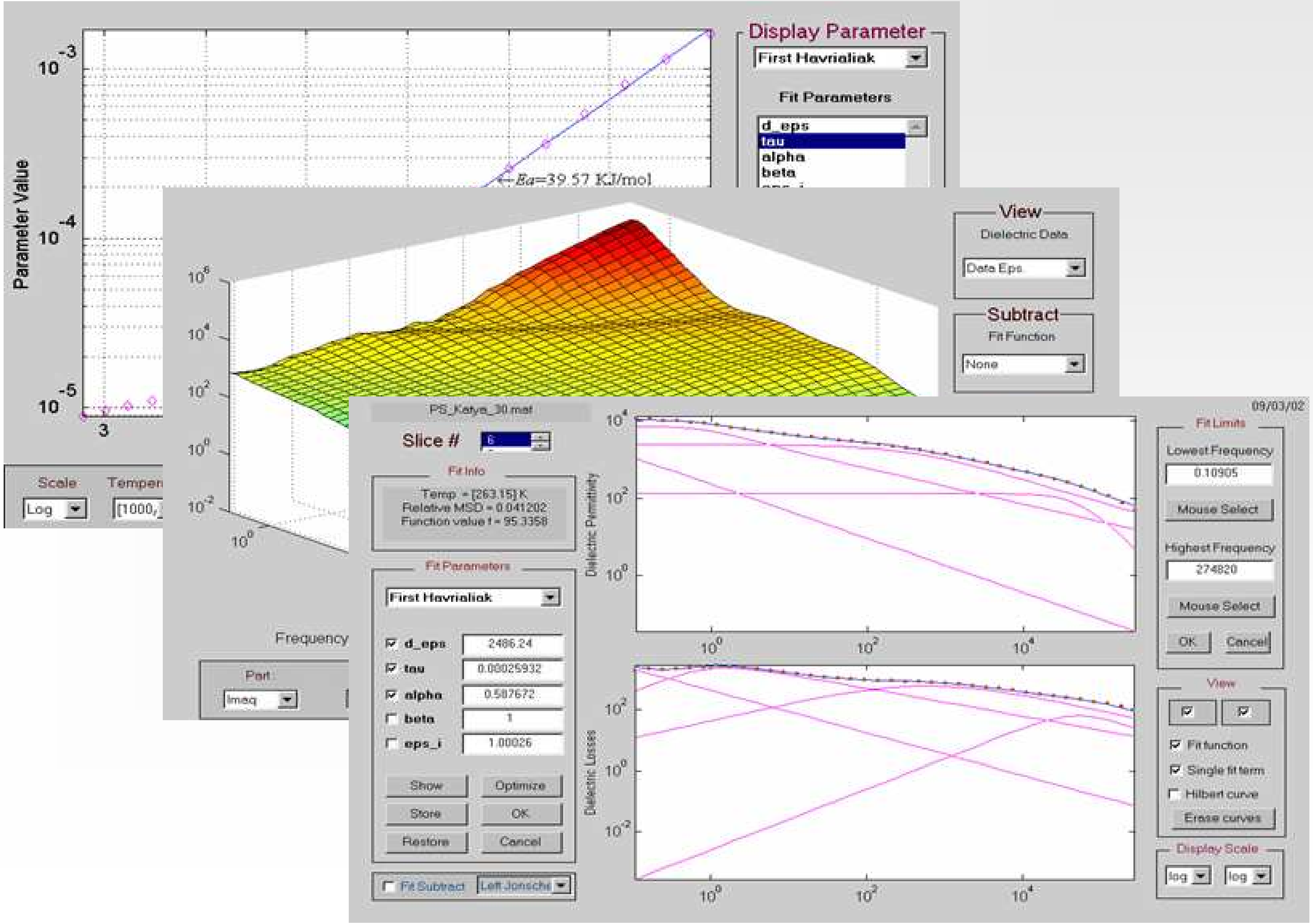
  Distortion influences of the sample holder;

  Overlapping of several physical processes with different amplitudes in the same frequency and temperature ranges.

- **Continuous parameter estimation;**

- **dc conductivity problems.**

New Fitting Software-”MatFit”



PS_Katya_30.mat

Slice # 6

Temp. = [263.15] K
Relative MSD = 0.041202
Function value f = 95.3358

Fit Parameters: First Havrialiak

☑ d_eps 2486.24
☑ tau 0.00025932
☑ alpha 0.587672
☐ beta 1
☐ eps_i 1.00026

☐ Fit Subtract: Left Jonscher

09/03/02

Lowest Frequency: 0.10905

Highest Frequency: 274820

☑ Fit function
☑ Single fit term
☐ Hilbert curve

Display Scale: log log

Display Parameter: First Havrialiak

Dielectric Data: Data Eps

Subtract Fit Function: None

Scale: Log

Part: Imag

Key features of the program

- Simultaneous fit of both real and imaginary components of the complex dielectric permittivity data;

- Linear and nonlinear fitting methods, from least squares and logarithmic to fitting procedures based on entropy norm;

- Global fit procedure on all selected temperature ranges for continuous parameter estimation;

- Hilbert Transform for computing dc conductivity.

Complex systems?

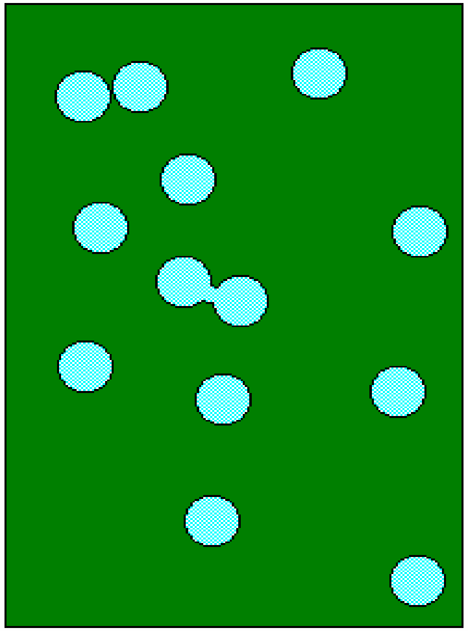
Complex systems involve in the appearance of a new "*mesoscopic*" length scale, intermediate between molecular and macroscopic.

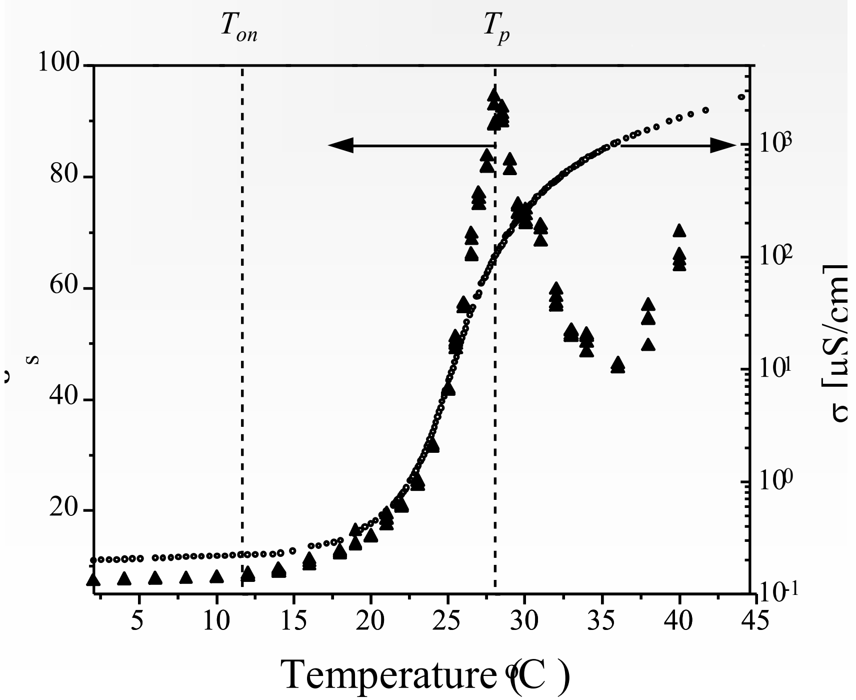
- ***Complex liquids (microemulsions, emulsions, etc.)***
- ***Porous materials (porous glasses, porous silicon, etc.)***
- ***Ferroelectrics***
- ***Glass forming liquids and polymers including composites***
- ***Biological systems (protein solutions, membranes and cell suspensions)***

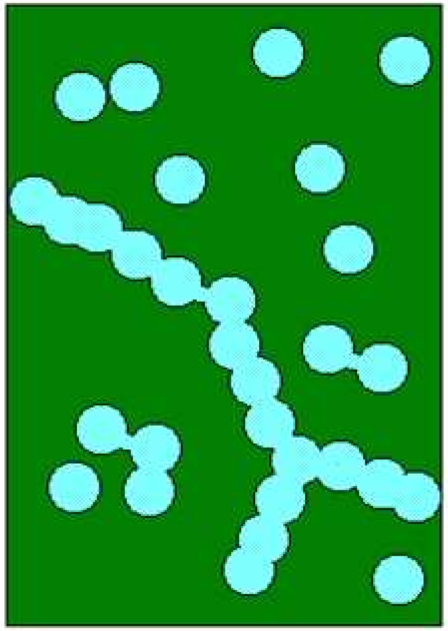
What is the percolation phenomenon?

Percolation: The transition associated with the formation of a continuous path spanning an arbitrarily large ("infinite") range.

The percolation cluster is a self-similar fractal.





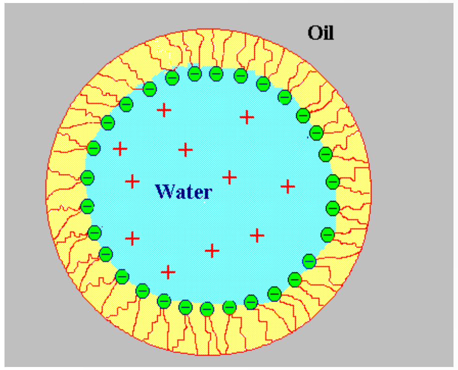


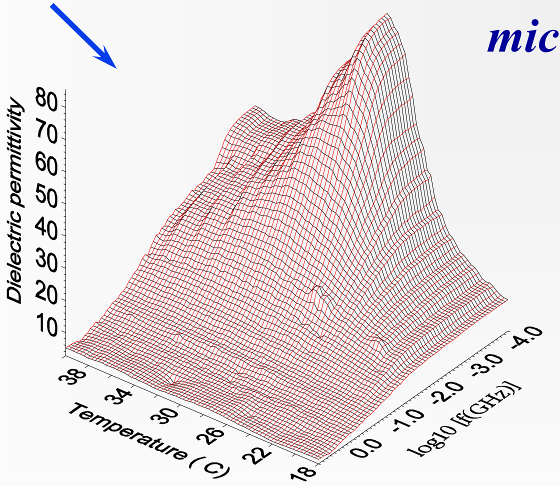
Dielectric response in microemulsions

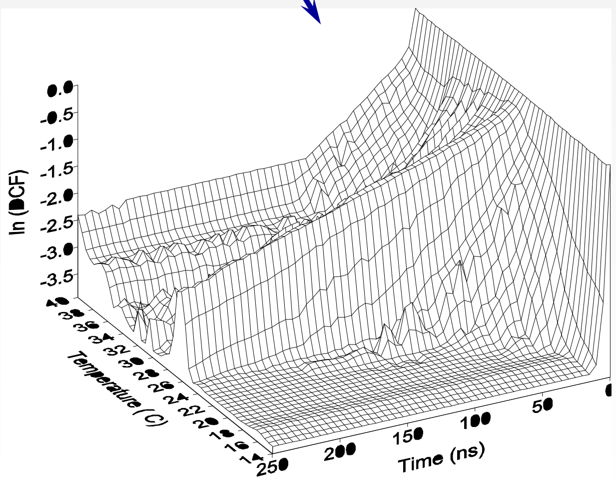
$$\psi(t) \approx \frac{\langle \overline{M}(0)\cdot\overline{M}(t)\rangle}{\langle \overline{M}(0)\cdot\overline{M}(0)\rangle},$$

Three dimensional plots of frequency and temperature dependence of the dielectric permittivity ε' for the AOT/water/decane microemulsion

Three-dimensional plots of the time and temperature dependence of the macroscopic Dipole Correlation Function for the AOT-water-decane microemulsion







AOT-water-decane microemulsion (17.5:21.3:61.2 vol%),
$W = 26.3$, $R_{wp} = 35.6$ Angstrom

(Yu.Feldman et. al., PRE. 1995,1996)

Dielectric response of the porous glass materials

Sample A

additional treatment in 0.5N KOH

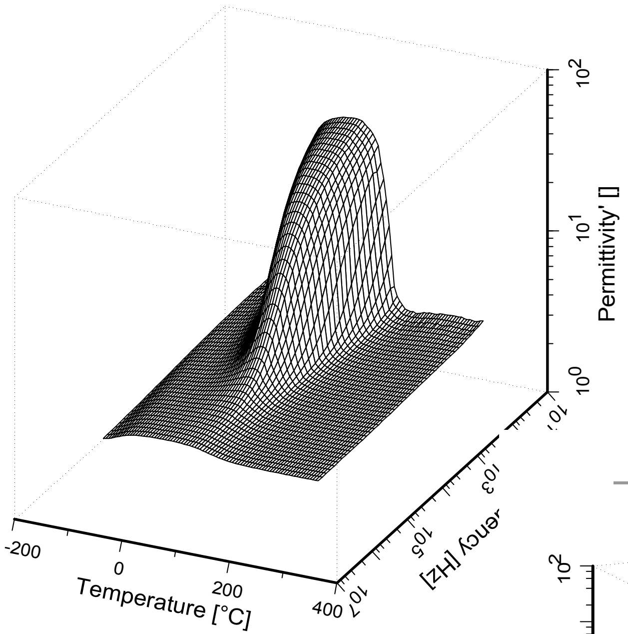
rinsing in deionized water

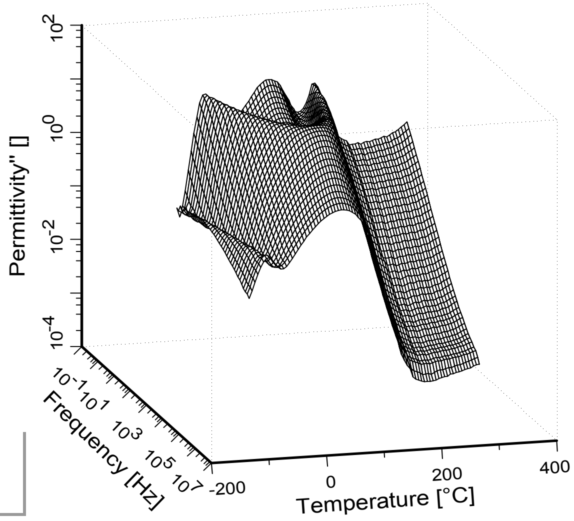
drying at 200^{0}C

Sample B

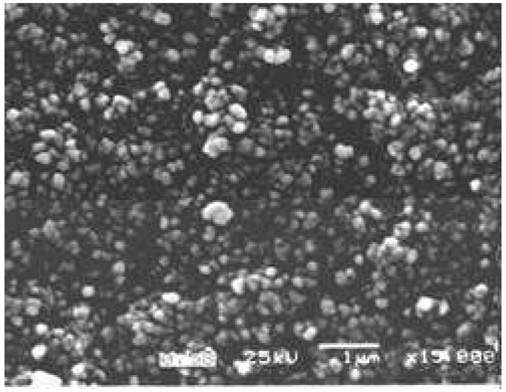
Sample D

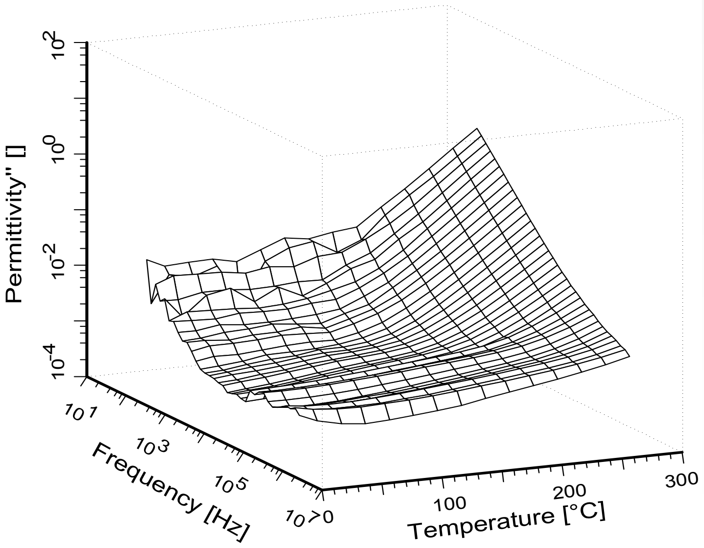
Sample C

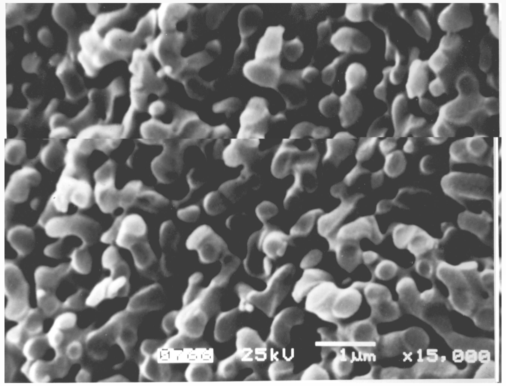




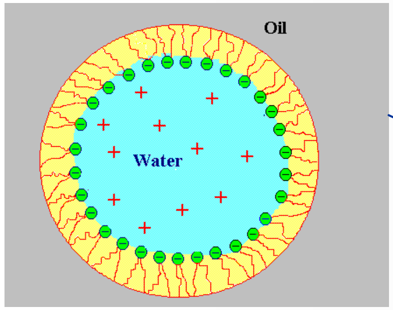
Sample C after heating



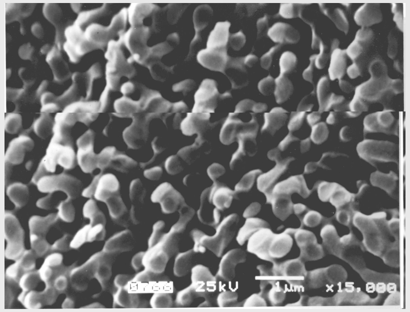




AOT-water-decane microemulsion

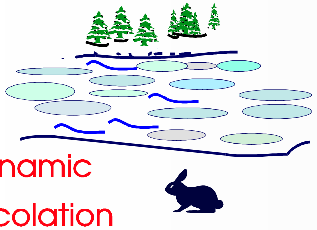


Porous borosilicate glass samples



$$\varepsilon^{*}(\omega)=\varepsilon_{\infty}+\Delta\varepsilon\hat{F}\left(-\frac{d}{dt}\Psi(t)\right)$$

$$\psi(t)\approx\frac{\langle\overline{M}(0)\cdot\overline{M}(t)\rangle}{\langle\overline{M}(0)\cdot\overline{M}(0)\rangle},$$



Dynamic Percolation

Static Percolation

$$\Psi(t) = A\,(t/\tau_1)^{-\mu}\ \exp[-(t/\tau_m)^{\nu}]$$

$$\alpha=\frac{1}{\nu}-1 \qquad \gamma=\frac{\mu}{\nu}+\frac{1}{2} \qquad S_m=\frac{1}{\alpha}\left(\frac{\tau}{\tau_1}\right)^{\frac{1}{\alpha}}\cdot(1+\alpha)^{-\frac{1+\alpha}{\alpha}}$$

$$\Psi(t) \sim \exp[-(t/\tau_m)^{\nu}]$$

Morphology parameters:

- *s_m : cut-off cluster size*
- *γ : polydispersity index*
- *η : cut-off rate index*

Dynamic parameters:

- *τ_1 : minimal time*
- *α : scaling parameter*

$$D_f = 3\nu,$$

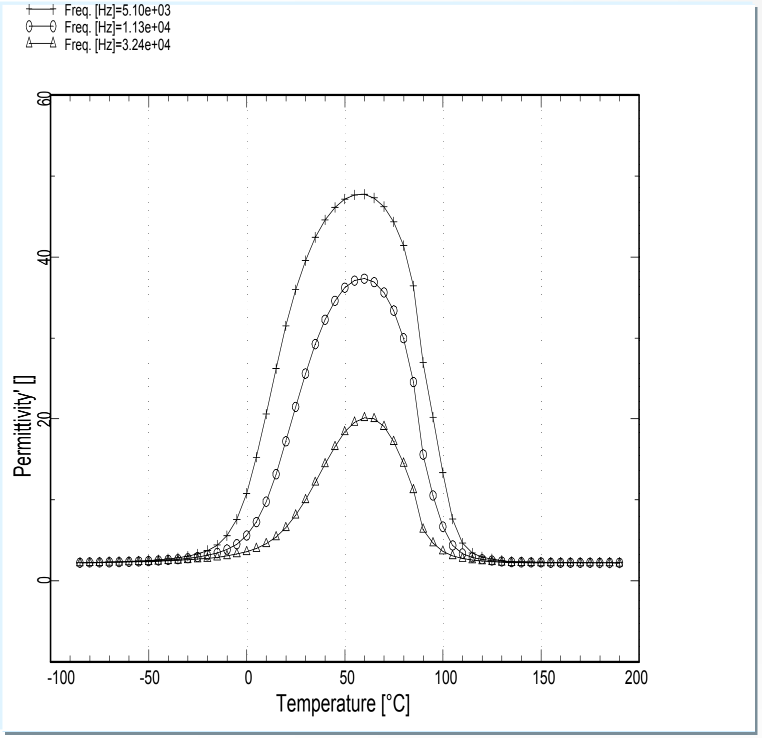
where D_f is a fractal dimension

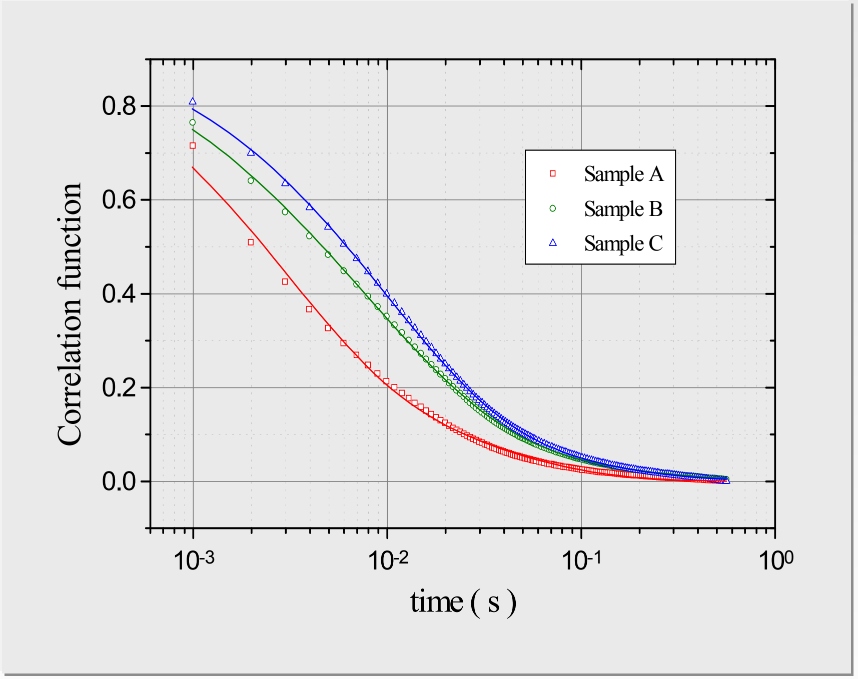
$$D_s=\frac{D_d}{1-D_d\dfrac{\lg\Theta}{\lg s_m}}$$

(Chem. Phys. (2002) V. 284 , 139-168)

Dielectric relaxation in percolation

***Percolation:** Transfer of electric excitation through the developed system of open pores*





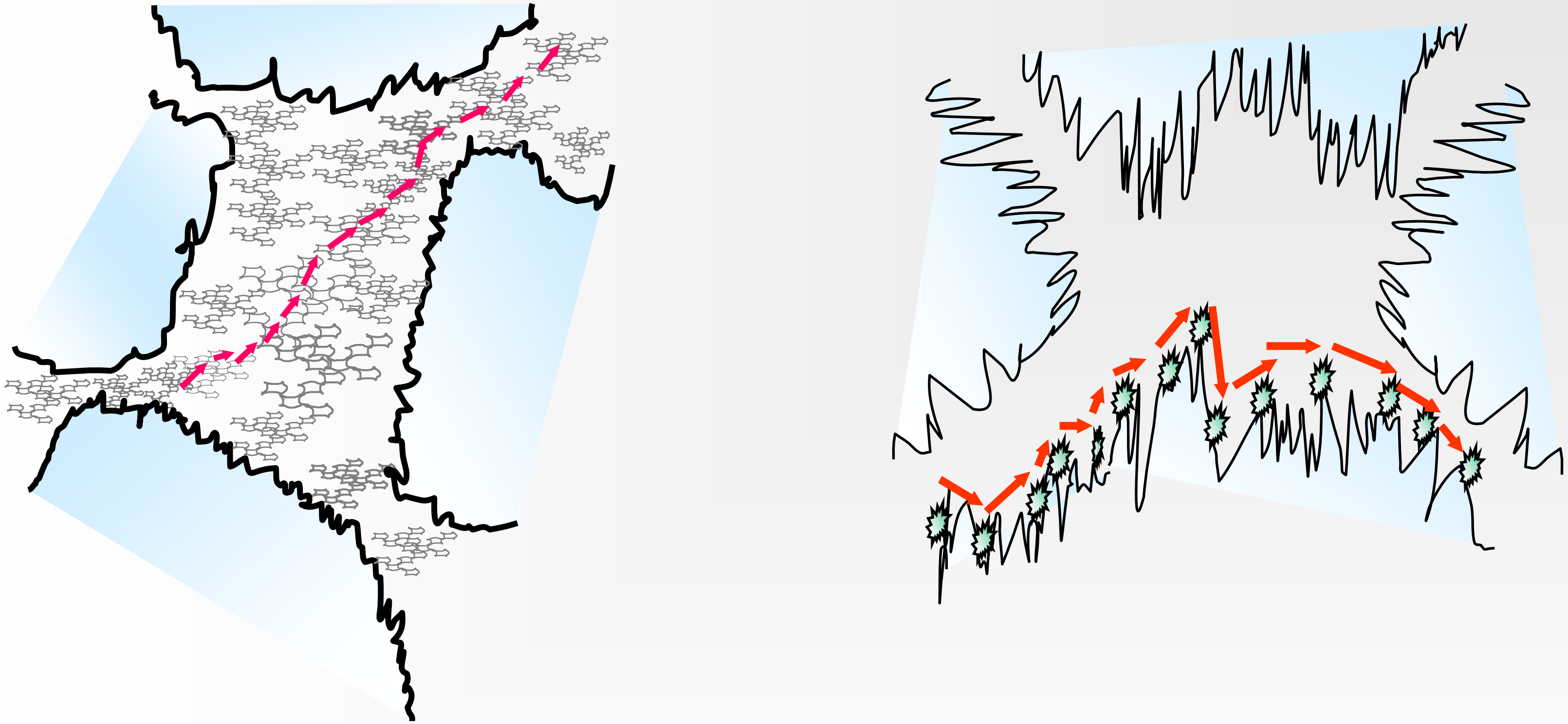
$$\Psi(t) \sim \exp\left[-\left(t/\tau_m\right)^{\nu}\right]$$

$$\varepsilon^{*}(\omega)=\varepsilon_{\infty}+\left(\varepsilon_{s}-\varepsilon_{\infty}\right)\hat{F}\left(-\frac{d}{dt}\Psi(t)\right)$$

$D_f = 3\nu$,

where D_f is a fractal dimension

The Fractal Dimension of Percolation Pass



Sample	**A**	**B**	**C**	**D**
Fractal dimension D_f	**0.99**	**1.89**	**1.31**	**2.5**

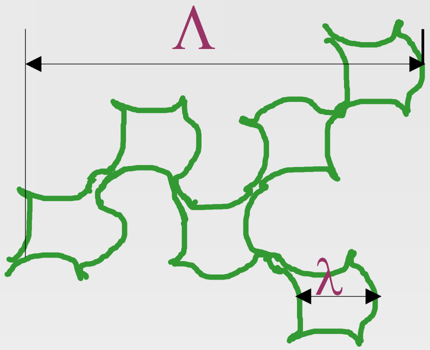
Porous medium in terms of regular and random fractals

$$\phi = \frac{V_p}{V}$$

ϕ : porosity of two phase solid-pore system

V_p : volume of the whole empty space

V : whole volume of the sample



$$\Phi = \int_{\mu}^{1} \phi(\xi, D) w(\xi) d\xi$$

$$\phi = \left(\frac{\lambda}{\Lambda}\right)^{d-D}$$

Λ , λ : upper and lower limits of self-similarity

D : regular fractal dimension of the system

$\mu = \lambda / \Lambda$

ξ : scale parameter $\xi \in [\mu, 1]$

$$w(\xi) = A \xi^{\alpha} \exp\left(-a \xi^{\beta}\right)$$

w : size distribution function

α, β, A: empirical parameters

Porosity Determination

(A.Puzenko,et al., Phys. Rev. (B), 60, 14348, 1999)

$$\mu = \lambda / \Lambda$$

$$1+\alpha > 0, |\alpha| << 1$$
$$d = 3, \qquad \mu << 1$$

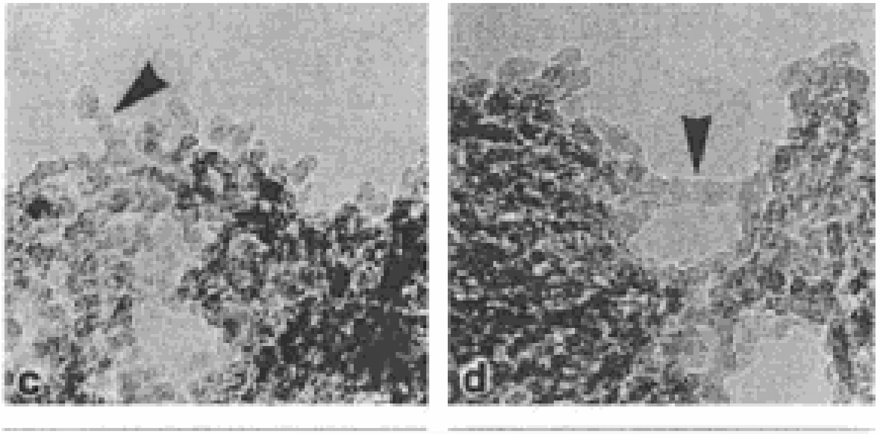
$$\phi \approx \frac{1+\alpha}{1+\alpha+d-D}\cdot\frac{1-\mu^{1+\alpha+d-D}}{1-\mu^{1+\alpha}},$$

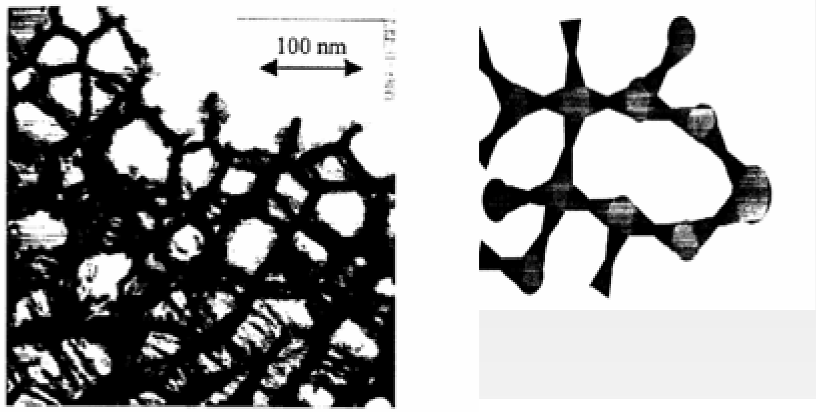
when $a << 1$, $\mu << 1$

$$\phi \approx \frac{1}{4-D}$$

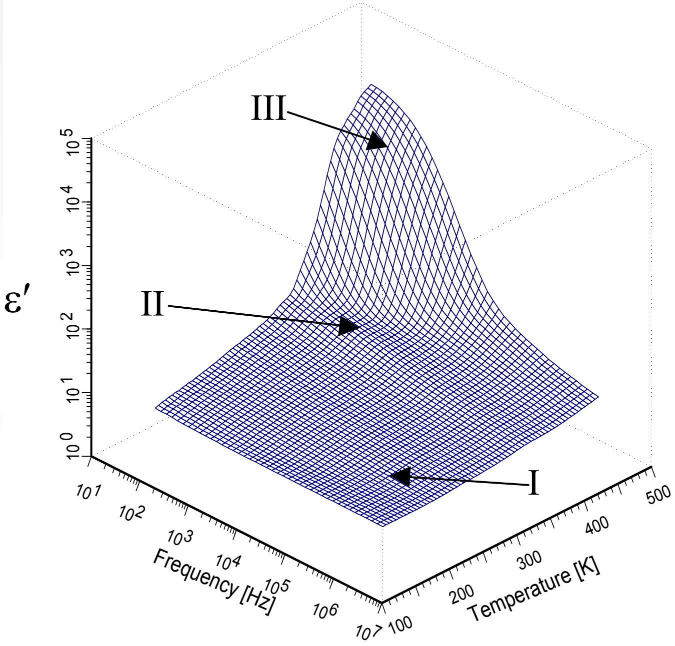
Sample	***Fractal dimension*** D_f	***Porosity*** ϕ ***(%)*** *(obtained from relative mass decrement measurements)*	***Porosity*** ϕ ***(%)*** *(obtained from dielectric measurements)*
A	**0.99**	**38**	**33**
B	**1.89**	**48**	**47**
C	**1.31**	**38**	**37**
D	**2.5**	**50**	**68**

PS HR-TEM micrographs and dielectric response





- *Disordered network of crystallites and pores*
- *Fractal structure*
- *Preserve the crystalline nature*



E. Axelrod, et al., JNCS. (2002)

PS Mid-T process II (300-400 K)

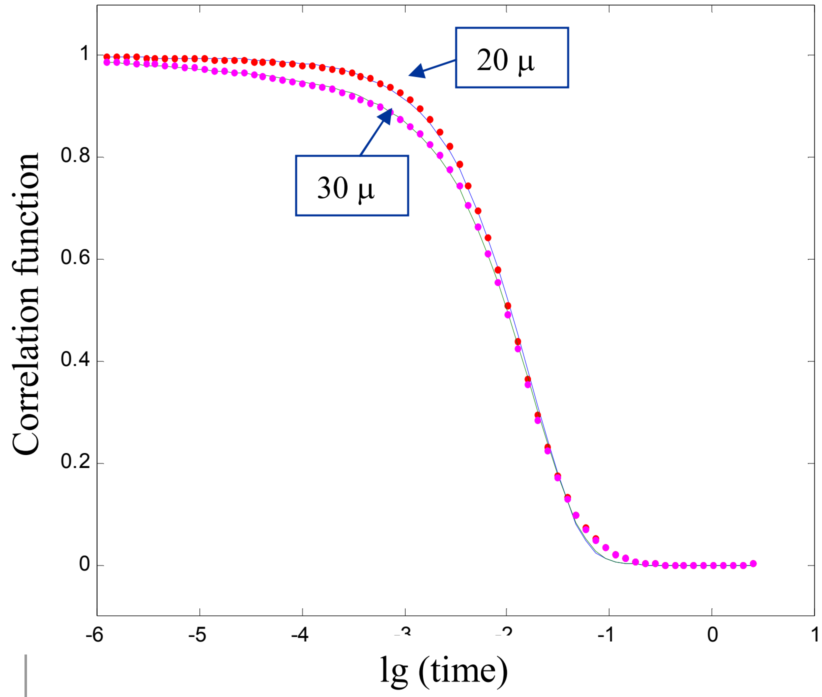
Porosity Determination

$$\Psi(t/\tau) \sim e^{-(t/\tau)^{\nu}}$$

Dielectric response at the percolation

D_f is the fractal dimension of the pore channel lengths

$$D_f = 3\nu$$



Sample	Stretching parameter ν	Fractal dimension D_f	Porosity ϕ (%) (obtained from dielectric measurements)
20 μ	0.88±0.02	2.64±0.06	74±1
30 μ	0.87±0.02	2.61±0.06	72±1

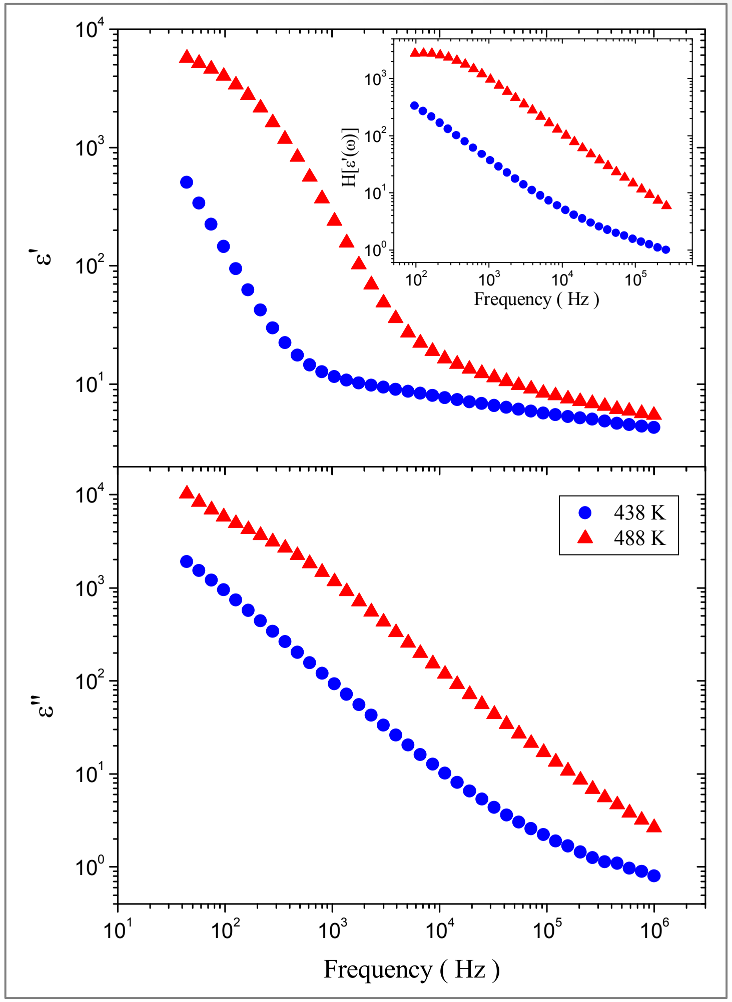
$$\phi = \frac{1}{4-D_f}\,\frac{1-\mu^{4-D_f}}{1-\mu} \approx \frac{1}{4-D_f}$$

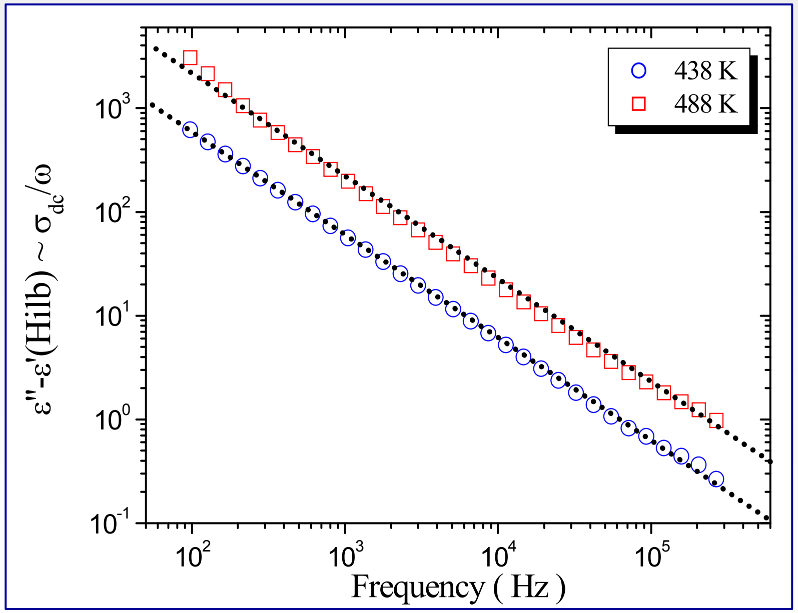
Hopping conductivity in a percolating model

DC conductivity

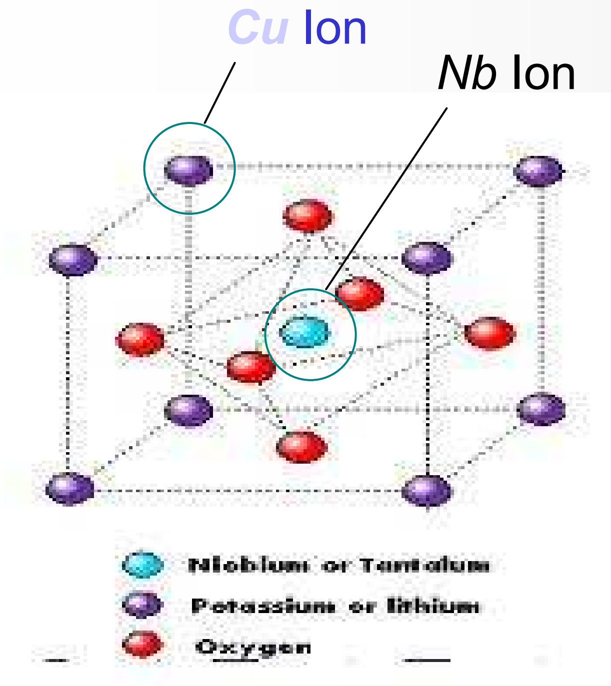
> 100 °C

Hilbert transform - **we applied the Kramers-Kronig relations to the real part of the dielectric function, and subtracted this term from the imaginary part of the measured dielectric data.**





KTN Crystals



$$K_1 Ta_{0.65} Nb_{0.35} O_3 : Cu$$

Perovskite Structure ABO_3

Cu doped at 2% by weight – 1:1000 unit cell volumes

Questions

- What does Cu do to the dielectric relaxation?
- Does Cu interact with Nb ?
- What effects do the differing ionic radii of Cu and K cause ?

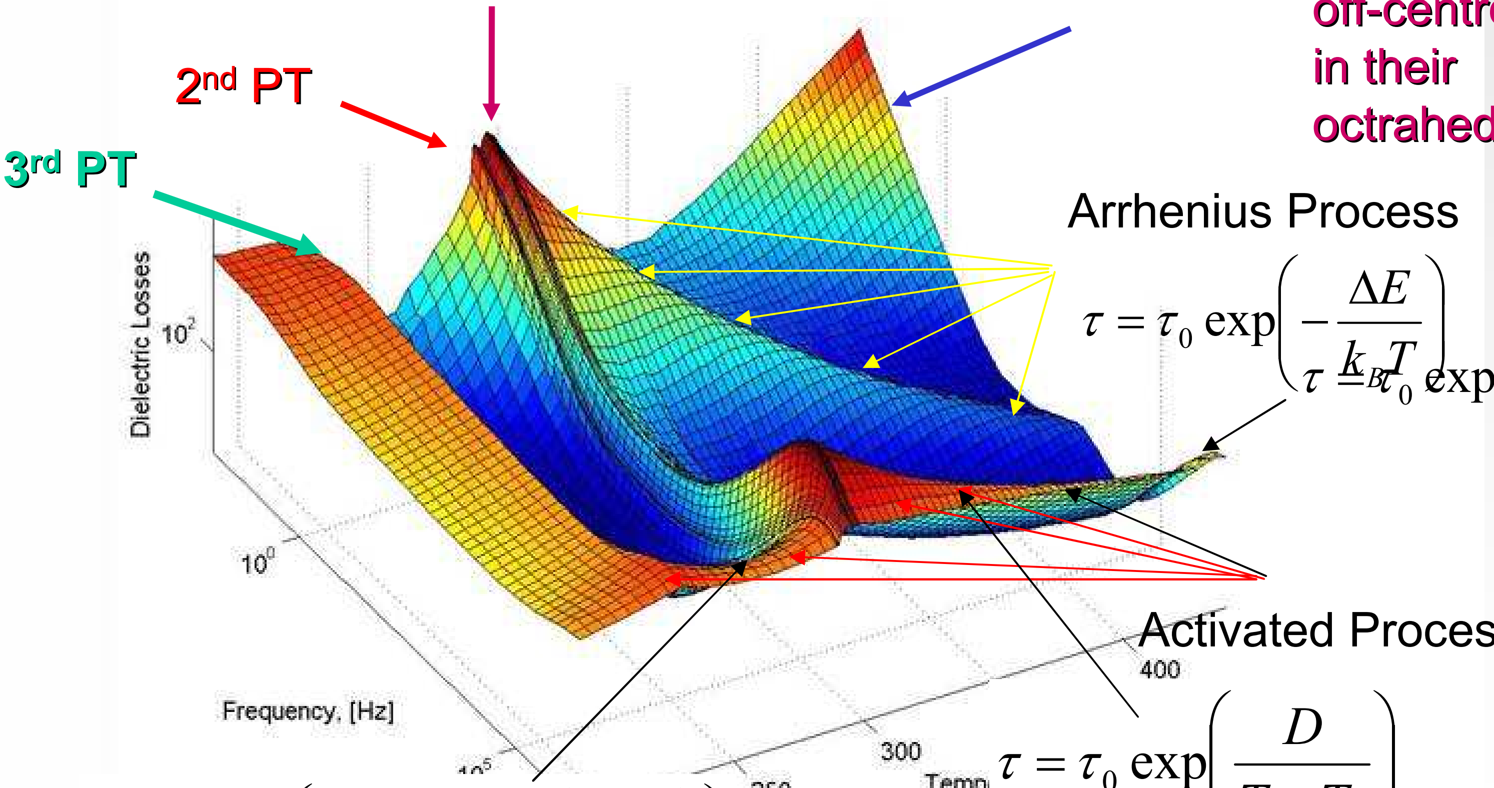
$$\varepsilon_s = \frac{C}{(T - T_0)}$$

High temperature → Low temperature

cubic → tetragonal → othorthorhombic → rombohedralic

Crystal 120 KTN – Dielectric Losses through the Ferroelectric phase transition

has been linked to dynamic relaxation of the off-centre Nb ions in their octrahedral site.



Ferroelectric PT

DC Conductivity

2nd PT

3rd PT

Arrhenius Process

$$\tau = \tau_0 \exp\left(-\frac{\Delta E}{k_B T}\right)$$

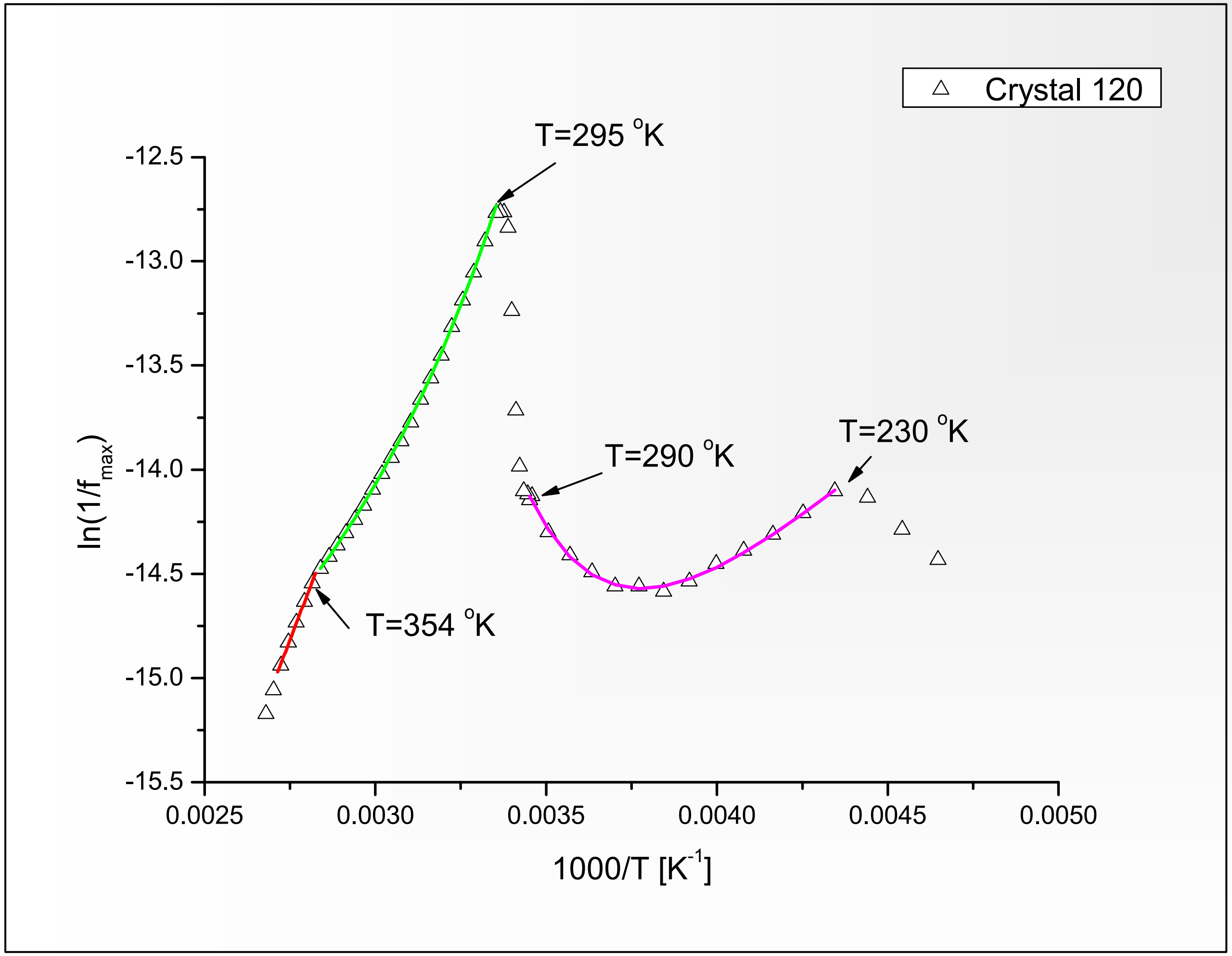
$$\tau = \tau_0 \exp\left(-\frac{\Delta E}{k_B T}\right)$$

Activated Process

$$\tau = \tau_0 \exp\left(\frac{D}{T - T_k}\right)$$

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT} + C \exp\left(-\frac{E_d}{kT}\right)\right)$$

Maximum Peak Frequency



Paraelectric Phase

$$T_x = 354\ {}^{o}K$$

$$T_k = 228\ {}^{o}K$$

$$\Delta\mu = 0.02\ eV$$

$$z^* \approx 3$$

$$\Delta E = 0.37\, eV$$

Ferroelectric Phase

$$E_a = 0.12\, eV$$

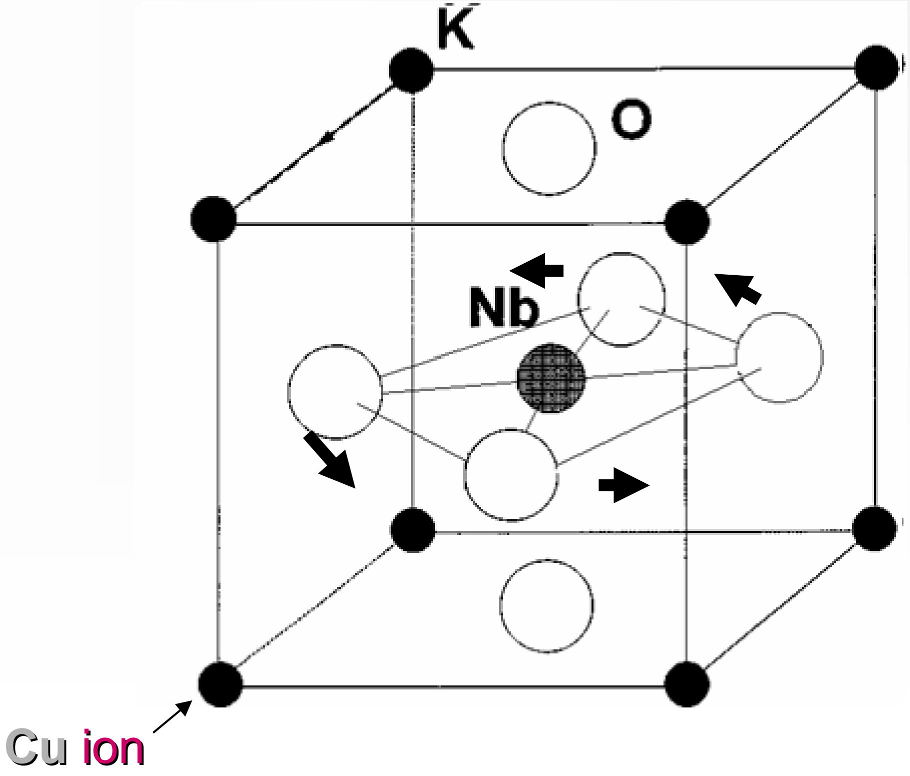
$$E_d = 0.32\, eV$$

$$C = \frac{1}{\eta} = 5.5 \times 10^5$$

Where η is the maximum defect concentration

Free Volume Model

- Ferroelectric Phase – Structural Shift constrains Cu relaxation
- Cu ions perturbate the Lattice structure
- Some of these “Defects” provide the space needed for the Oxygen Octahedra to “tilt”.
- Alternatively the Defects allow the migration of Oxygen Vacancies



K^+	1.37 pm
O^{-2}	1.40 pm
Cu^{+2}	0.73 pm
Cu^{+1}	0.77 pm