Non-linear Effects in Physics of Dielectrics

DIELECTRIC TUTORIAL

Madrid, Spain
6 September 2010

High-Field Dielectric Response:

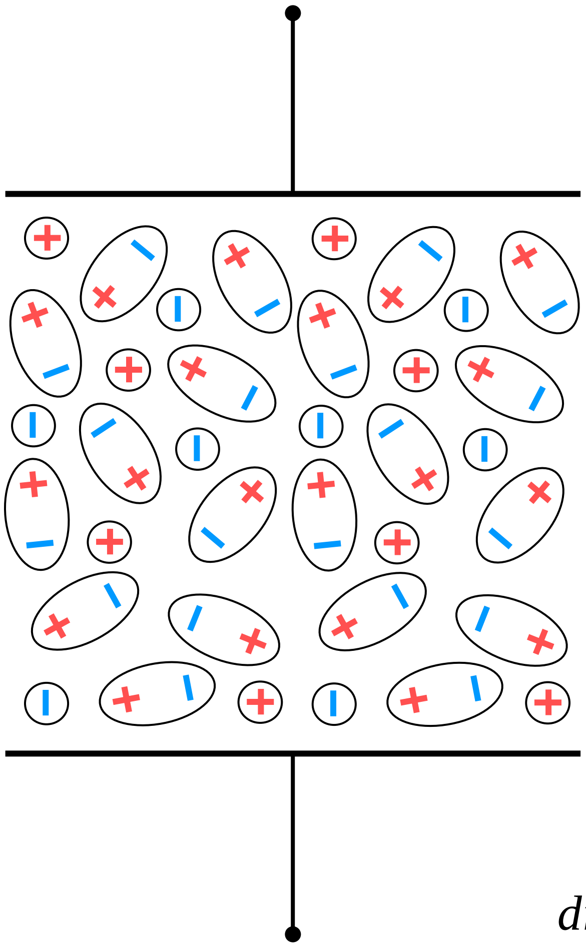
- ► Coulombic stress
- ► Langevin effect
- ► Energy absorption
- ► Time-resolved technique
- ► Reverse isothermal calorimetry

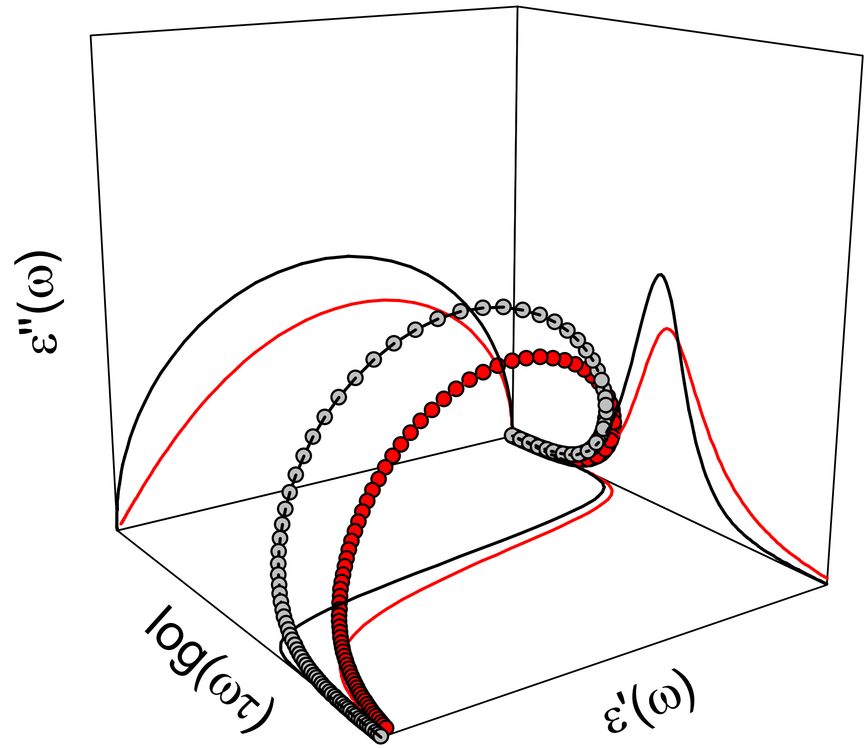
Ranko Richert

Arizona State University

dielectric relaxation technique

$$\mathbf{D} = \boldsymbol{\varepsilon} \ \boldsymbol{\varepsilon}_0 \ \mathbf{E}$$

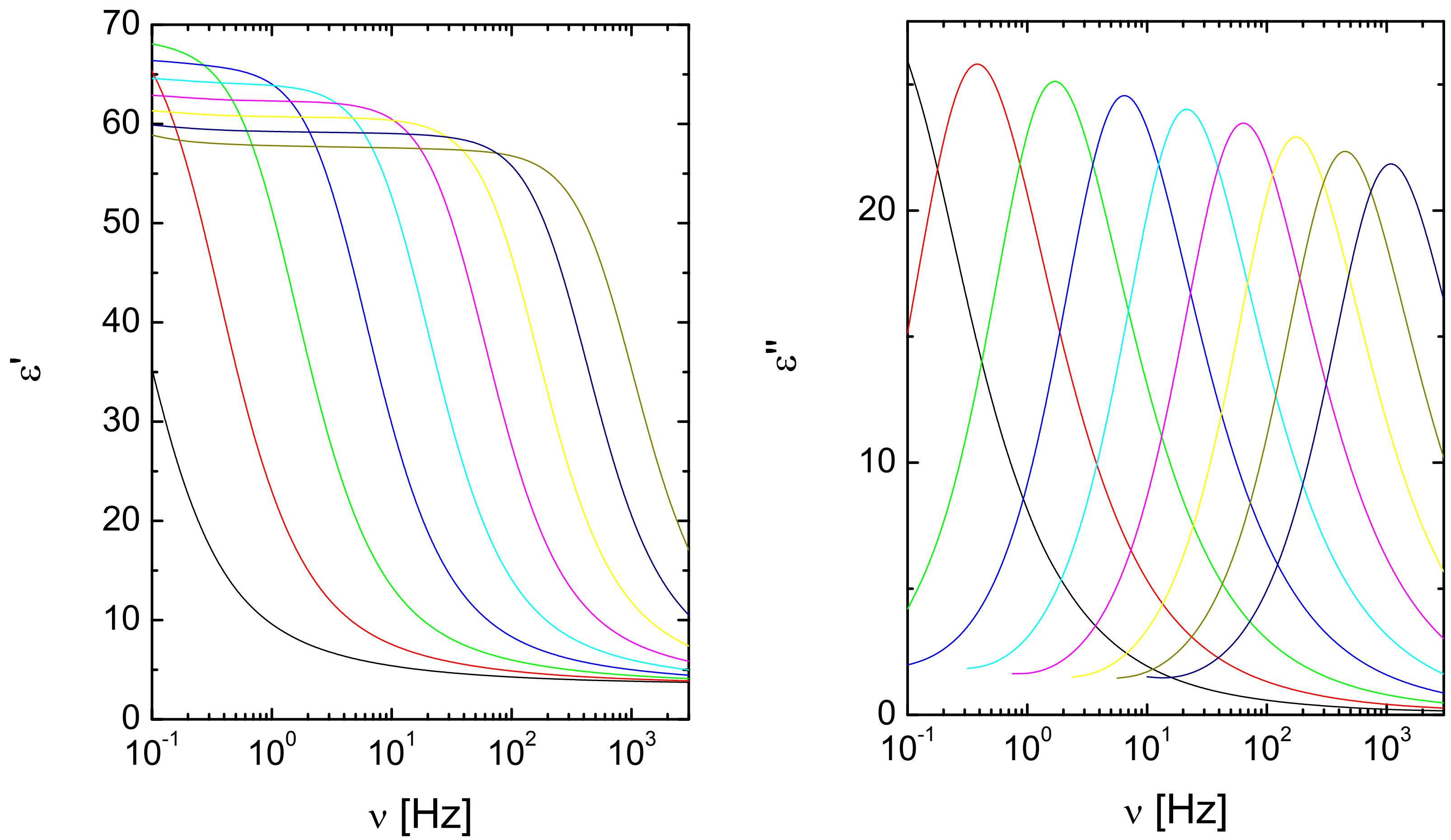




dielectric displacement $\mathbf{D} \equiv \frac{\mathbf{Q}}{\mathbf{A}} \propto \frac{\mathbf{V}}{\mathbf{d}} \equiv \mathbf{E}$ *electric field*

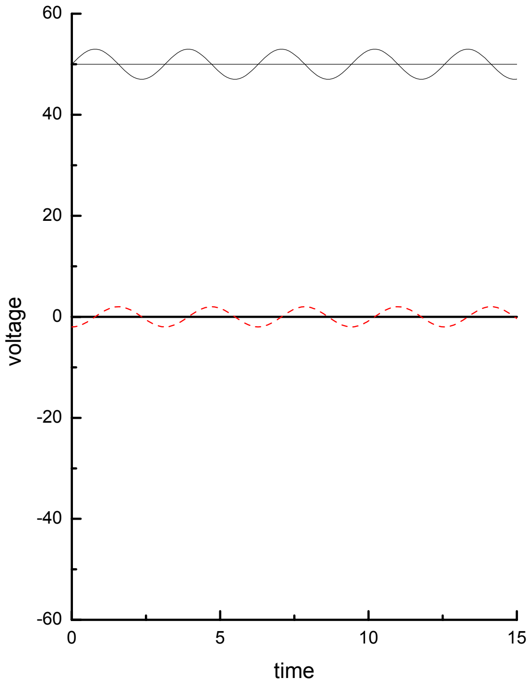
typical case near the glass transition

propylene glycol T = 174 - 198 K (3 K)



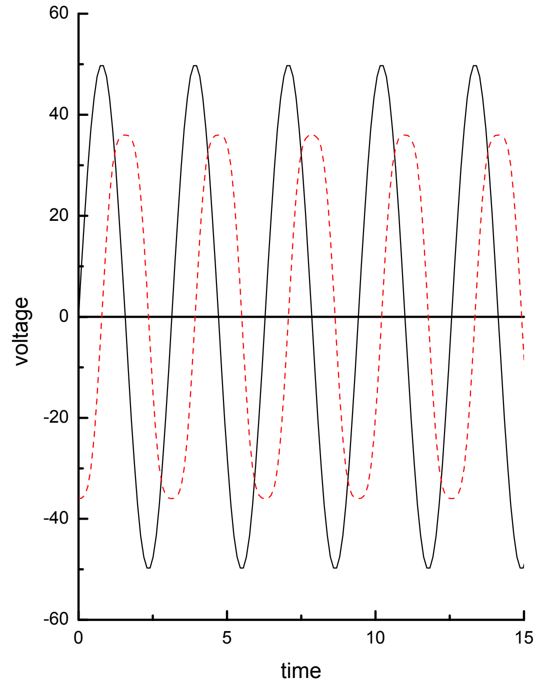
result usually independent of field amplitude

variety of high field techniques

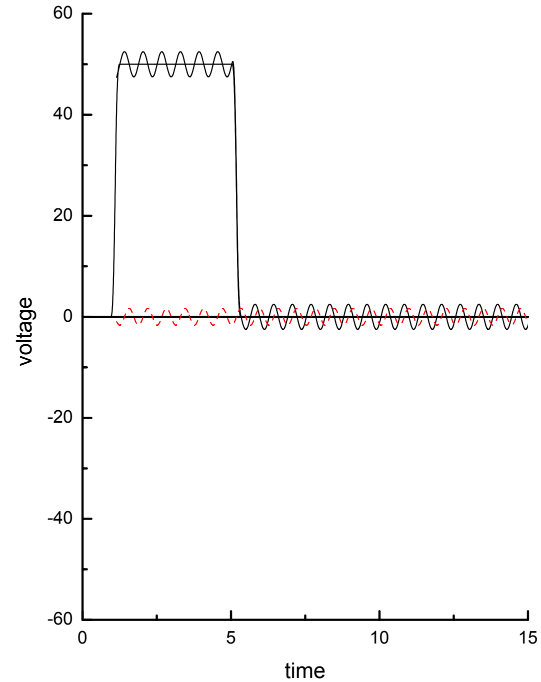


high DC field
low AC field
mainly 1ω

Heats via σ_{dc}



high AC field
no bias
$1\omega + 3\omega$



low AC field
on high pulse
NDE(t)

avoid heating

non-linear susceptibility

$$\frac{\mathbf{P}}{\varepsilon_0} = \underbrace{\chi^{electret}}_{\substack{=0 \\ \text{causality}}} + \chi\mathbf{E} + \underbrace{\chi^{(1)}E\mathbf{E}}_{\substack{=0 \\ \text{symmetry}}} + \chi^{(2)}E^2\mathbf{E} + \underbrace{\chi^{(3)}E^3\mathbf{E}}_{\substack{=0 \\ \text{symmetry}}} + \chi^{(4)}E^4\mathbf{E} + \ldots$$

$$\text{causality}: \ \mathbf{P}(0) = 0$$

$$\text{symmetry}: \ \mathbf{P}(\mathbf{E}) = -\mathbf{P}(-\mathbf{E})$$

$$\frac{\mathbf{P}}{\varepsilon_0 \mathbf{E}} = \chi + \chi^{(2)}E^2 + \chi^{(4)}E^4 + \ldots$$

$$\varepsilon_s\left(E^2\right) = \varepsilon_s(0) \times \left[1 - \lambda E^2\right]$$

$$\lambda = -\Delta \ln(\varepsilon_s)/E^2$$

Piekara factor :

$$\Delta\varepsilon_s/E^2 = -\lambda\varepsilon_s$$

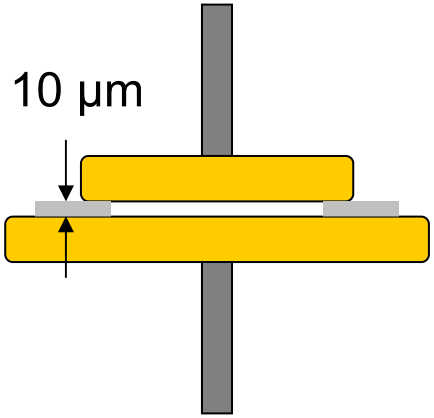
$$\text{superposition principle}: \ P(t) = \int_{-\infty}^{t} dP(\theta) = \chi\varepsilon_0 \int_{-\infty}^{t} E(\theta)\varphi(t-\theta)d\theta$$

M. S. Green, R. Kubo (1950's) : linear transport coefficients $L_{F_e=0}$ are related to auto - correlation function of the equilibrium fluctuations in the conjugate flux J

$$J = L_{F_e=0}F_e \qquad L_{F_e=0} = \frac{V}{kT}\int_0^\infty \left\langle J(0)J(t)\right\rangle_{F_e=0} dt$$

Coulombic stress

Coulombic stress exercise



top electrode 16 mm Ø
bottom electrode 30 mm Ø
ring outer: 20 mm Ø
ring inner: 14 mm Ø

glycerol at E_0 = 283 kV/cm

$$work\ \ Fd = energy\ \tfrac{1}{2}QV$$

$$F\partial d = \tfrac{1}{2}\partial(QV) = \underbrace{\tfrac{1}{2}Q\partial V}_{=0} + \tfrac{1}{2}V\partial Q =$$

$$\tfrac{1}{2}V\partial(CV) = \underbrace{\tfrac{1}{2}VC\partial V}_{=0} + \tfrac{1}{2}V^2\partial C = \tfrac{1}{2}V^2\varepsilon_0 A\partial d^{-1}$$

$$\Downarrow$$

$$F(t) = \frac{\varepsilon_s\varepsilon_0 A}{2}E^2(t) = \frac{\varepsilon_s\varepsilon_0 A}{4}E_0^2 \times [1-\cos(2\omega t)]$$

$$\Delta \ln\varepsilon = -\frac{\Delta d}{d} = +\frac{F_0}{aY} = \frac{\varepsilon_s\varepsilon_0 A}{4aY}E_0^2$$

$$a = 4.7\times10^{-5}\ \mathrm{m}^2\ (\text{Teflon ring, d} = 14\text{-}16\ \text{mm})$$

$$Y > 1\,\mathrm{GPa}\ (\text{Teflon only})$$

$$F_0 = 31\,\mathrm{N}$$

$$F_0/a = 0.67\,\mathrm{MPa}$$

$$\Delta \ln\varepsilon = -\frac{\Delta d}{d} \le 6.7\times10^{-4}$$

dielectric saturation

expected non-linearity: dielectric saturation (aka Langevin effect)

$$\langle \cos\theta \rangle = \frac{\int_0^\pi \cos\theta \, e^{\mu E \cos\theta / kT} d\theta}{\int_0^\pi e^{\mu E \cos\theta / kT} d\theta} \quad \Rightarrow$$

$$\langle \cos\theta \rangle = \mathrm{cotanh}\left(\frac{\mu E}{kT}\right) - \left(\frac{\mu E}{kT}\right)^{-1}$$

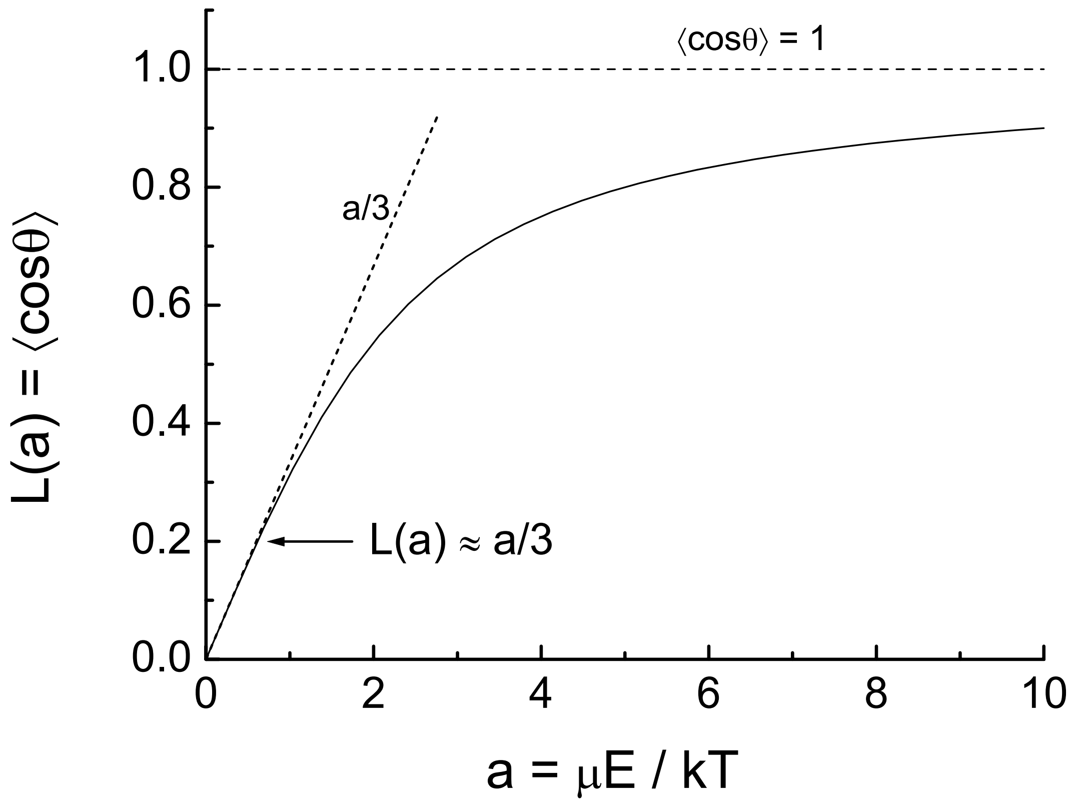
$$\langle \cos\theta \rangle = L\left(\frac{\mu E}{kT}\right) \quad \begin{pmatrix} \text{Langevin} \\ \text{function} \end{pmatrix}$$

with $a = \dfrac{\mu E}{kT}$

$$\langle \cos\theta \rangle = L(a) = \mathrm{cotanh}(a) - \frac{1}{a}$$

if $\mu E << kT$ or $a << 1$

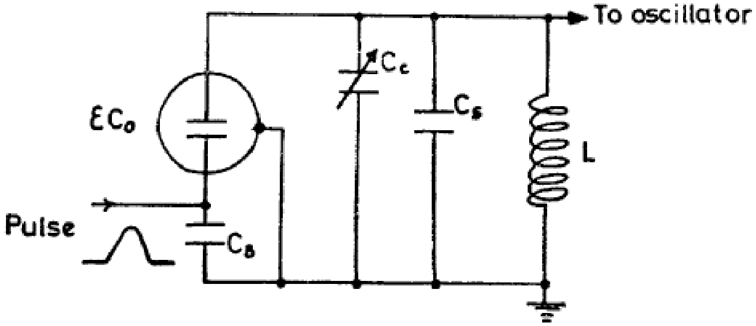
$$\langle \cos\theta \rangle \approx \frac{a}{3} = \frac{\mu E}{3kT}$$

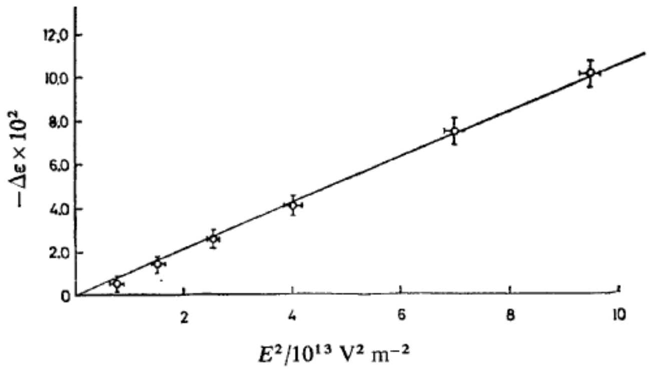


saturation in water at 293 K

Piekara $\Delta\varepsilon_s / E^2 = -\lambda\varepsilon_s$

vanVleck $$\frac{\Delta\varepsilon_s}{E^2} = \frac{\varepsilon_s(E^2) - \varepsilon_s(0)}{E^2} = -\frac{N\mu^4}{45\varepsilon_0 V(kT)^3} \times \frac{\varepsilon_s^4(\varepsilon_\infty + 2)^4}{(2\varepsilon_s + \varepsilon_\infty)^2(2\varepsilon_s^2 + \varepsilon_\infty^2)}$$

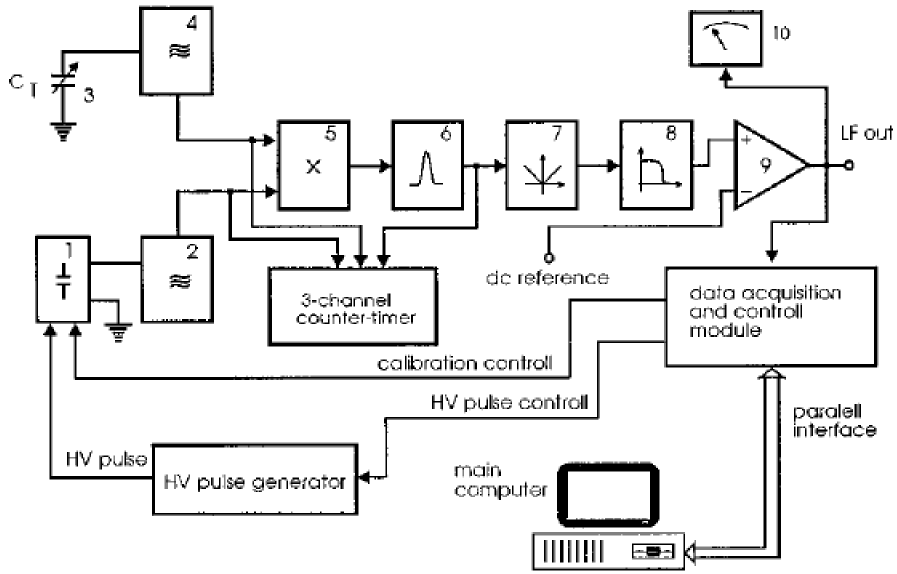




H. A. Kolodziej, G. Parry Jones, M. Davies, J. Chem. Soc. Faraday Trans. 2 71 (1975) 269

J. H. van Vleck, J. Chem. Phys. 5 (1937) 556
A. Piekara, Acta Phys. Polon. 18 (1959) 361

time resolved NDE experiments



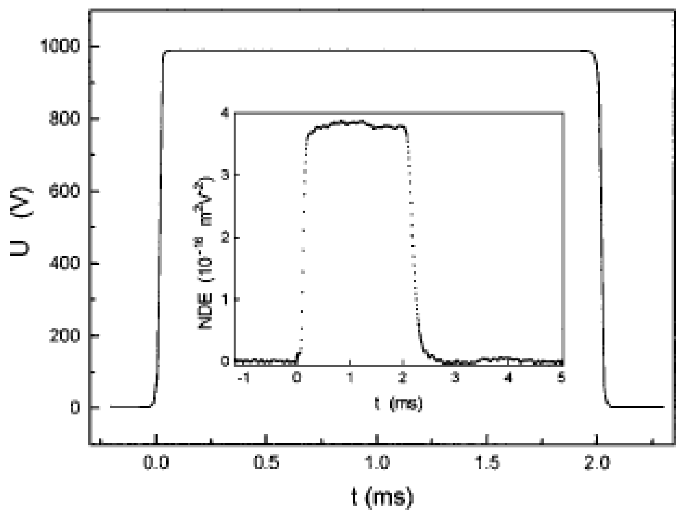
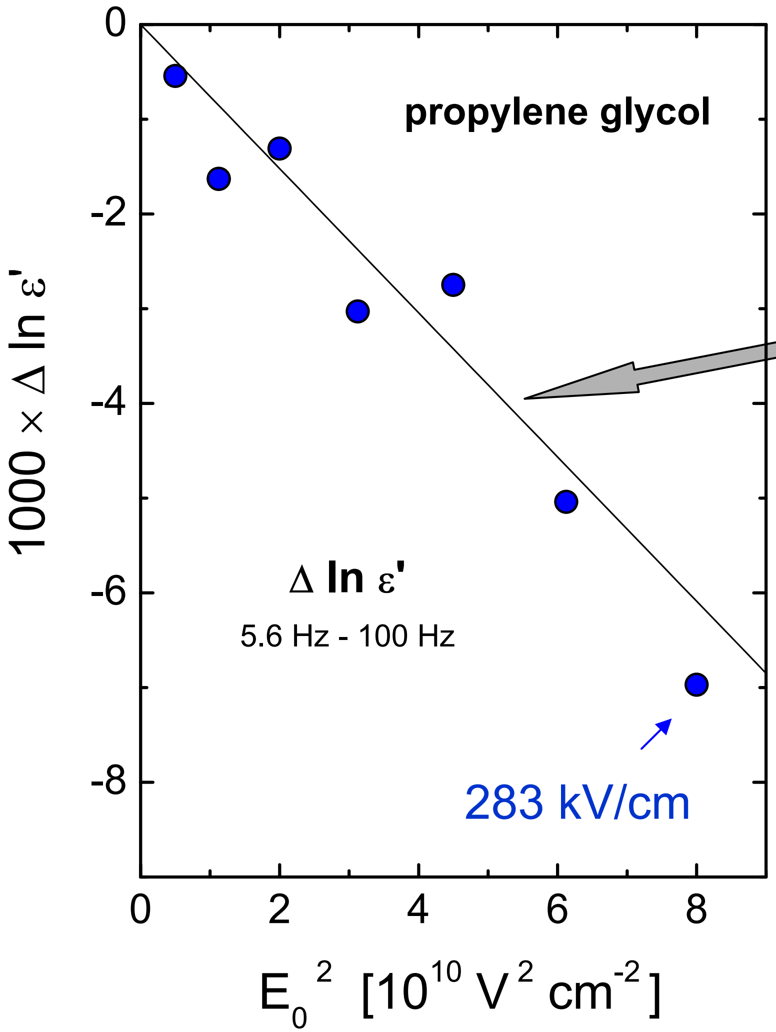


FIG. 1. The NDE measurement setup: 1—Measurement capacitor; 2—measurement generator ($G1$, freq. $f1+\Delta f$); 3,4—reference generator (G_2, freq. $f2$) with tuning capacitor; 5—mixer (freq. Δf); 6—bandpass filter; 7—rectifier; 8—low-pass filter; 9—amplifier; 10—indicator of the tuning of G_2 to $f_2=f_1+\Delta f$. The elements 2 and 4–10 are contained in one measurement unit.

M. Gorny, J. Ziolo, S. J. Rzoska, Rev. Sci. Instrum. 67 (1996) 4290

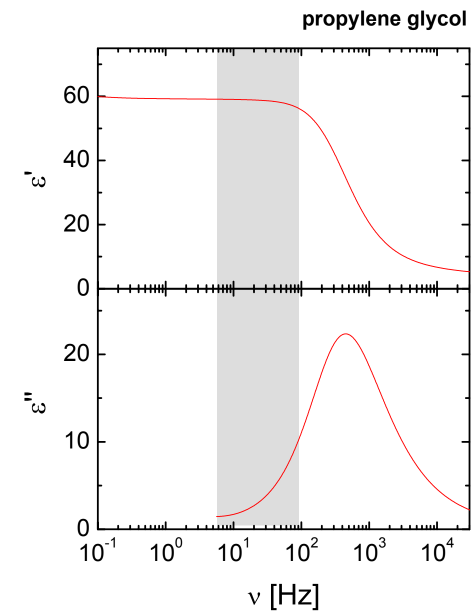
field effect (71 - 283 kV/cm) result for propylene glycol



$$\langle\cos\theta\rangle = \frac{\int_0^\pi \cos\theta\, e^{\mu E\cos\theta/kT}\,d\theta}{\int_0^\pi e^{\mu E\cos\theta/kT}\,d\theta} \approx \frac{\mu E}{3kT} \le 1$$

$$\frac{\Delta\varepsilon_s}{E^2} = -\frac{N\mu^4}{45\varepsilon_0 V(kT)^3}\times\frac{\varepsilon_s^4(\varepsilon_\infty+2)^4}{(2\varepsilon_s+\varepsilon_\infty)^2(2\varepsilon_s^2+\varepsilon_\infty^2)}$$

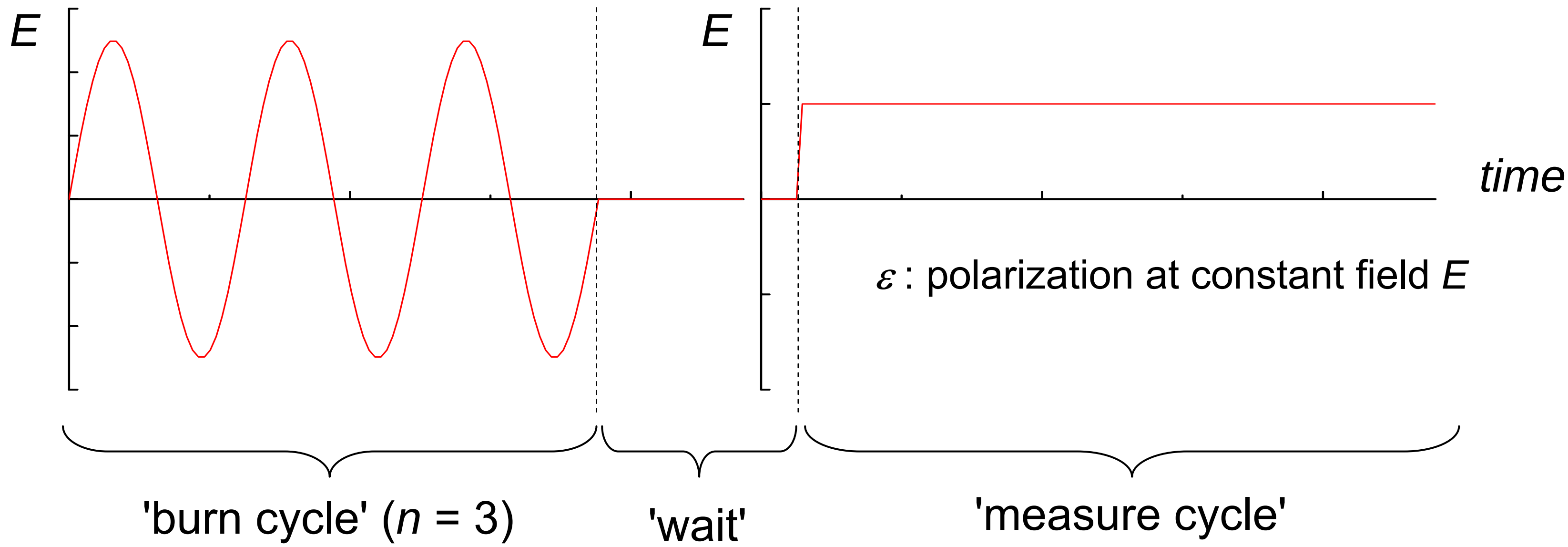
(van Vleck)



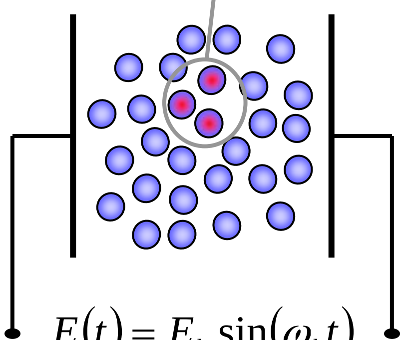
S. Weinstein, R. Richert, Phys. Rev. B 75 (2007) 064302
S. Weinstein, R. Richert, J. Phys.: Condens. Matter 19 (2007) 205128

energy absorption

dielectric hole-burning technique: summary

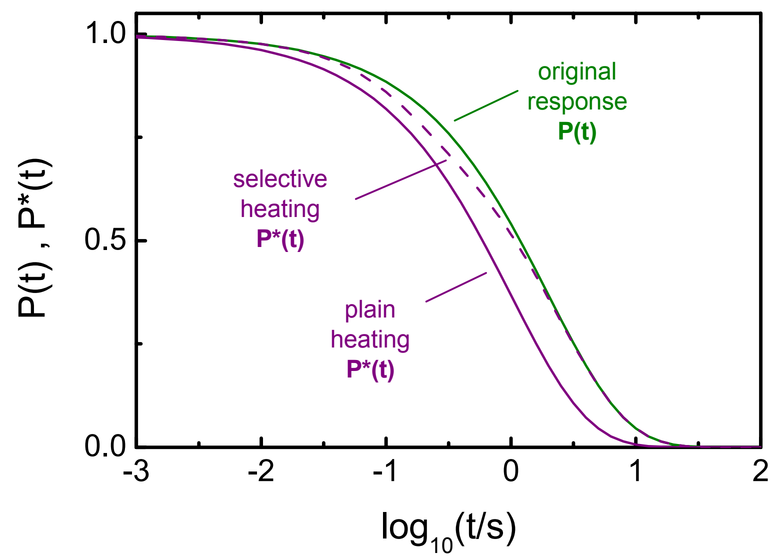


$$\tau_1 \approx \tau_2 \approx \tau_3 \approx 1/\omega_b$$



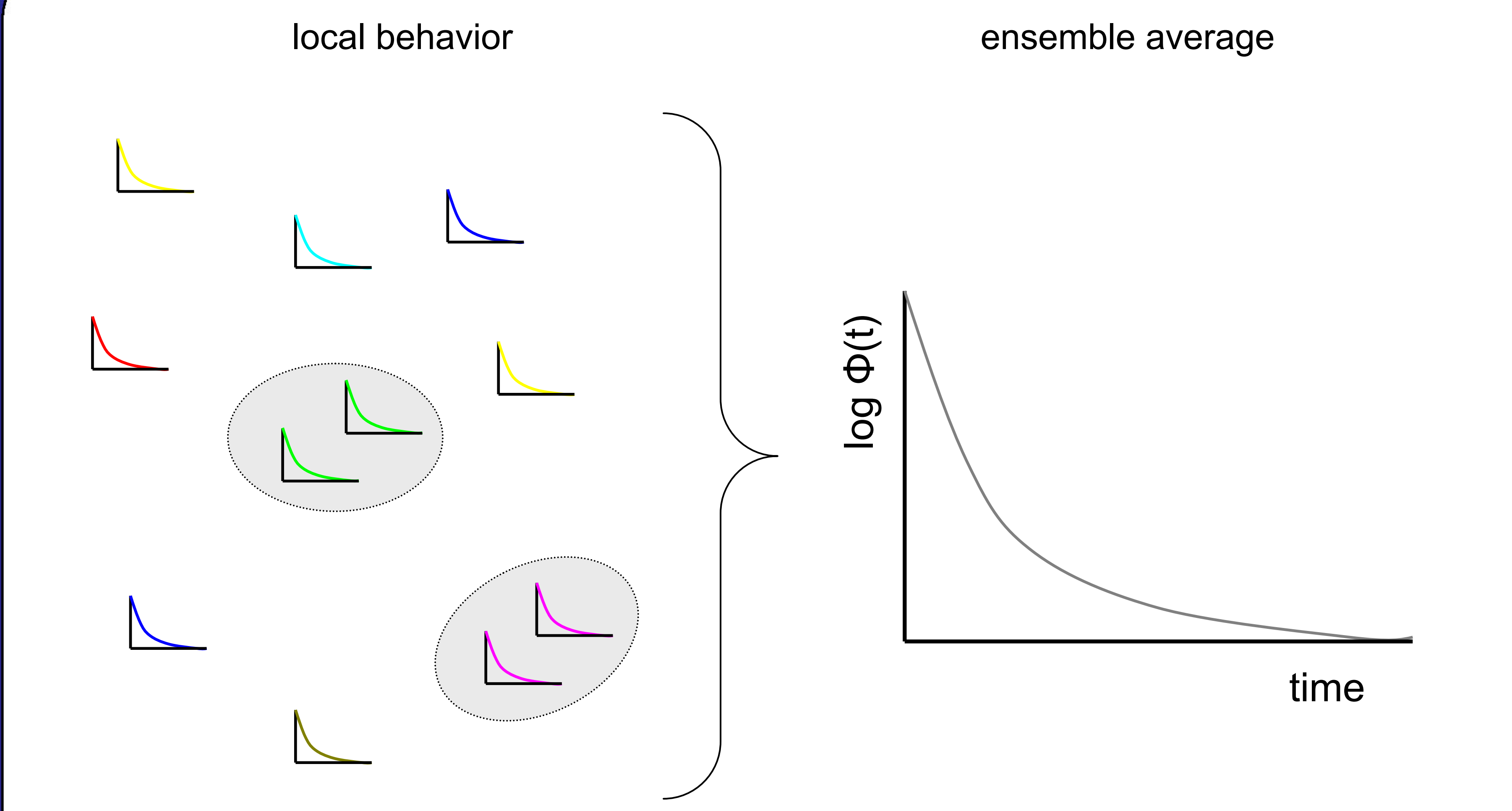
$$E(t) = E_b \sin(\omega_b t)$$

$$\Delta Q = \pi \varepsilon_0 \, \varepsilon''(\omega_b) \, E_b^2$$

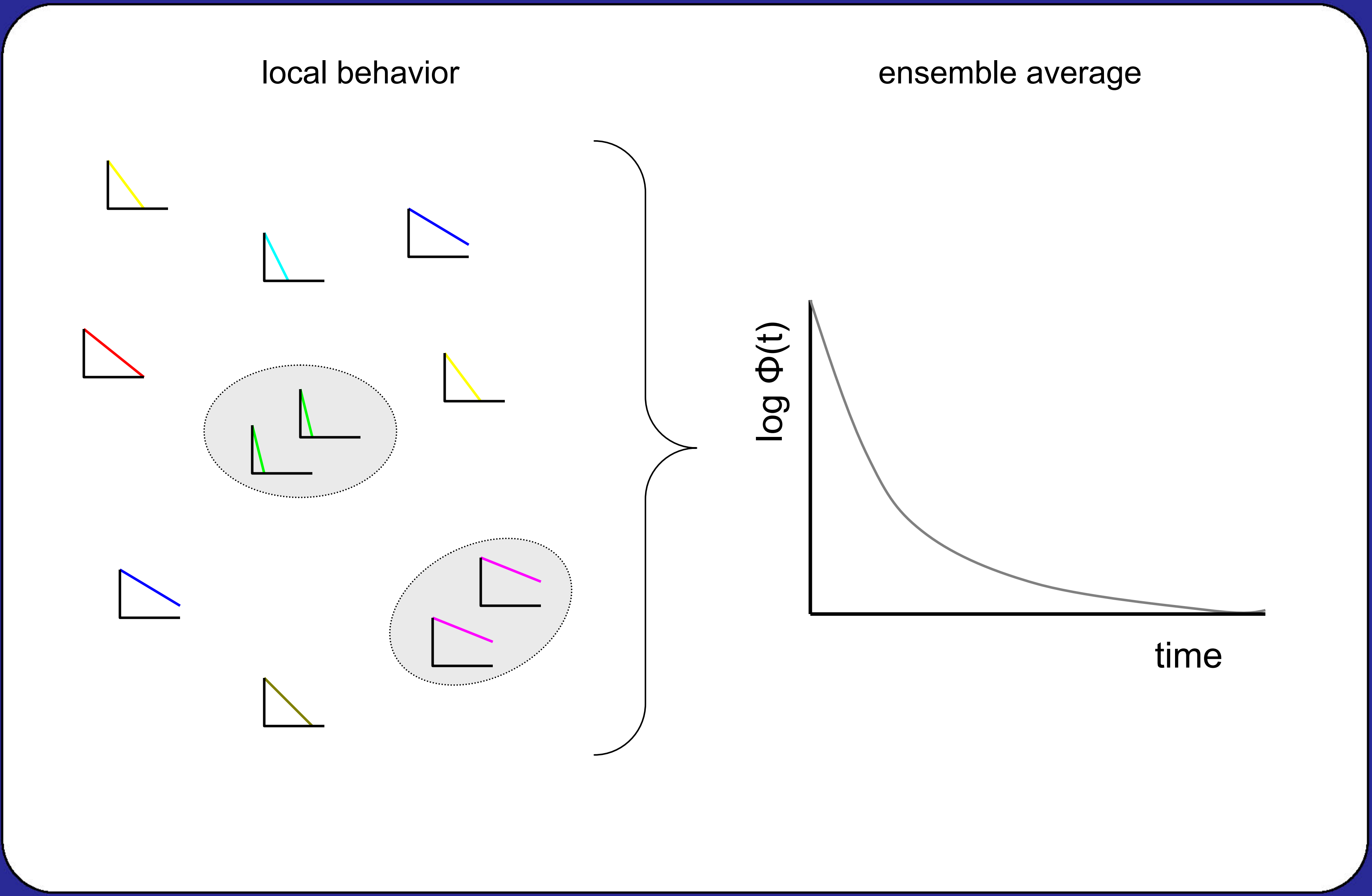


B. Schiener, R. Böhmer, A. Loidl, R. V. Chamberlin, Science 274 (1996) 752
B. Schiener, R. V. Chamberlin, G. Diezemann, R. Böhmer, J. Chem. Phys. 107 (1997) 7746

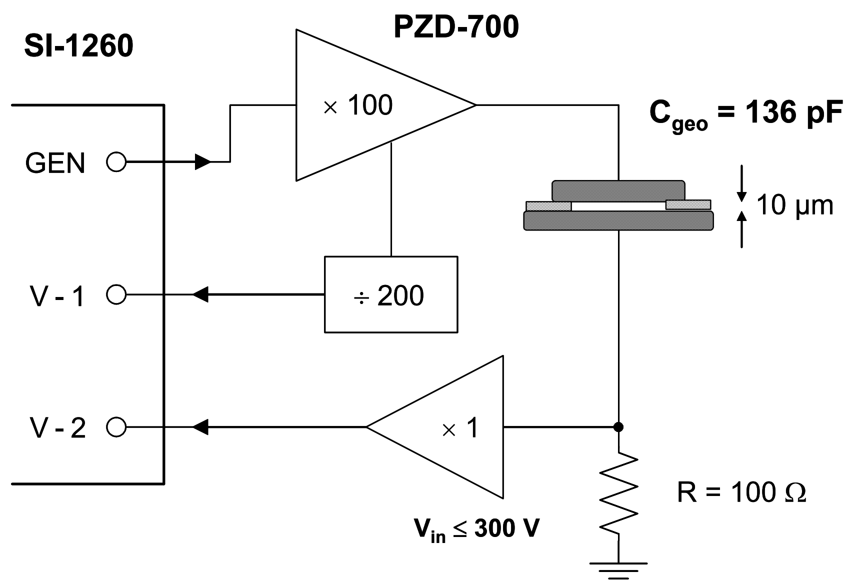
features of homogeneous dynamics

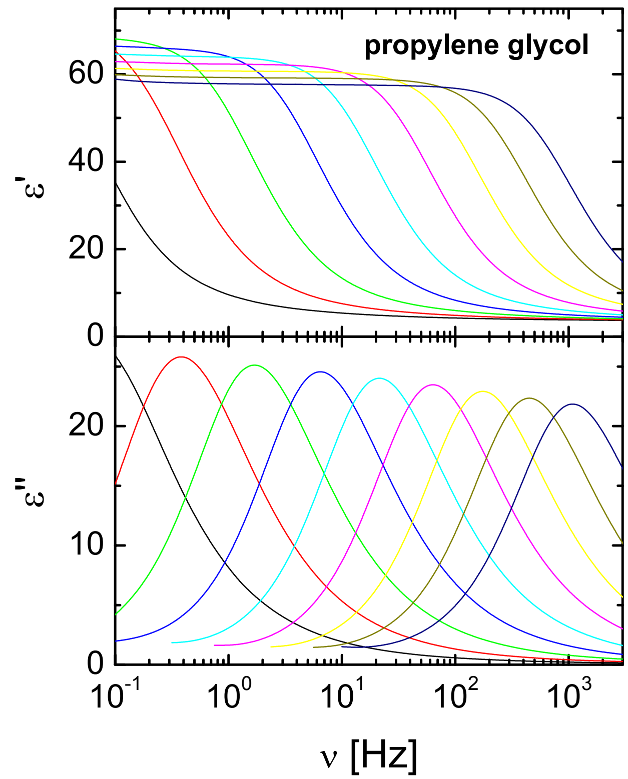


features of heterogeneous dynamics



high field impedance - beyond the linear regime





fields up to 450 kV/cm

µE* up to 0.082 *kT

0.1 Hz to 50 kHz range

$$\frac{\mathbf{P}}{\varepsilon_0} = \underbrace{\chi^{electret}}_{\substack{=0\\ \text{causality}}} + \chi\mathbf{E} + \underbrace{\chi^{(1)}E\mathbf{E}}_{\substack{=0\\ \text{symmetry}}} + \underbrace{\chi^{(2)}E^2\mathbf{E}}_{\substack{\text{usually}\\ \text{too small}}} + \underbrace{\chi^{(3)}E^3\mathbf{E}}_{\substack{=0\\ \text{symmetry}}} + \underbrace{\chi^{(4)}E^4\mathbf{E}}_{\substack{\text{usually}\\ \text{way too small}}} + \ldots$$

S. Weinstein, R. Richert, Phys. Rev. B 75 (2007) 064302
S. Weinstein, R. Richert, J. Phys.: Condens. Matter 19 (2007) 205128

analyzer input protection

ANALOG DEVICES

Ultralow, Input-Bias Current
Operational Amplifier

AD549

AD 549 L

$R_{in} = 10^{15}\ \Omega$

$C_{in} = 0.8$ pF

$I_{bias} = 40$ fA

In the corresponding version of this scheme for a follower, shown in Figure 38, R_P and the capacitance at the positive input terminal produce a pole in the signal frequency response at a f = ½πRC. Again, the Johnson noise, R_P, adds to the amplifier's input voltage noise.

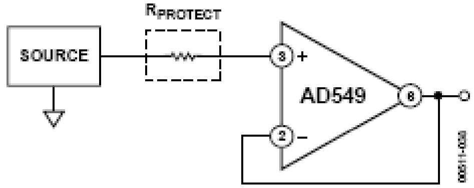
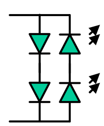
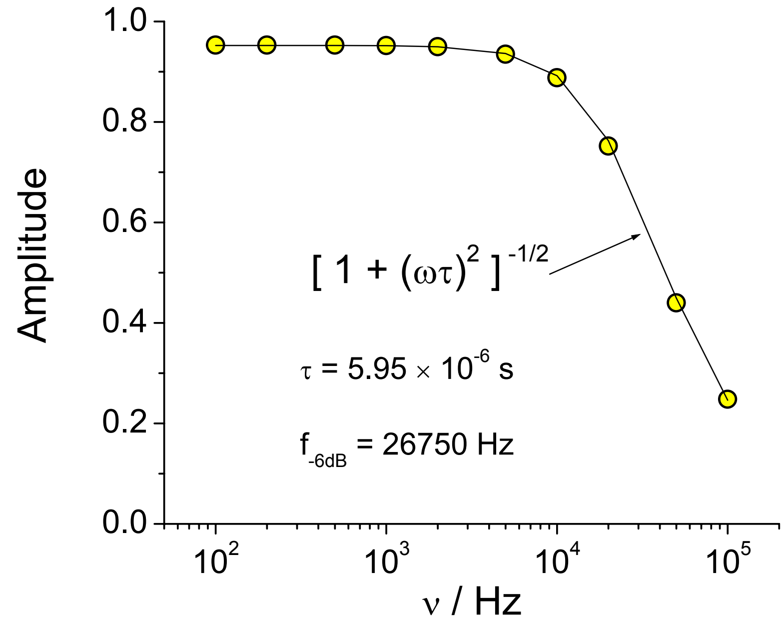


Figure 38. Follower with Input Current Limit

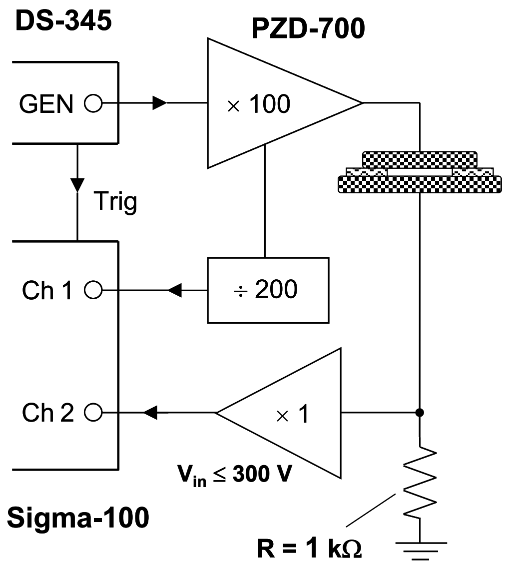


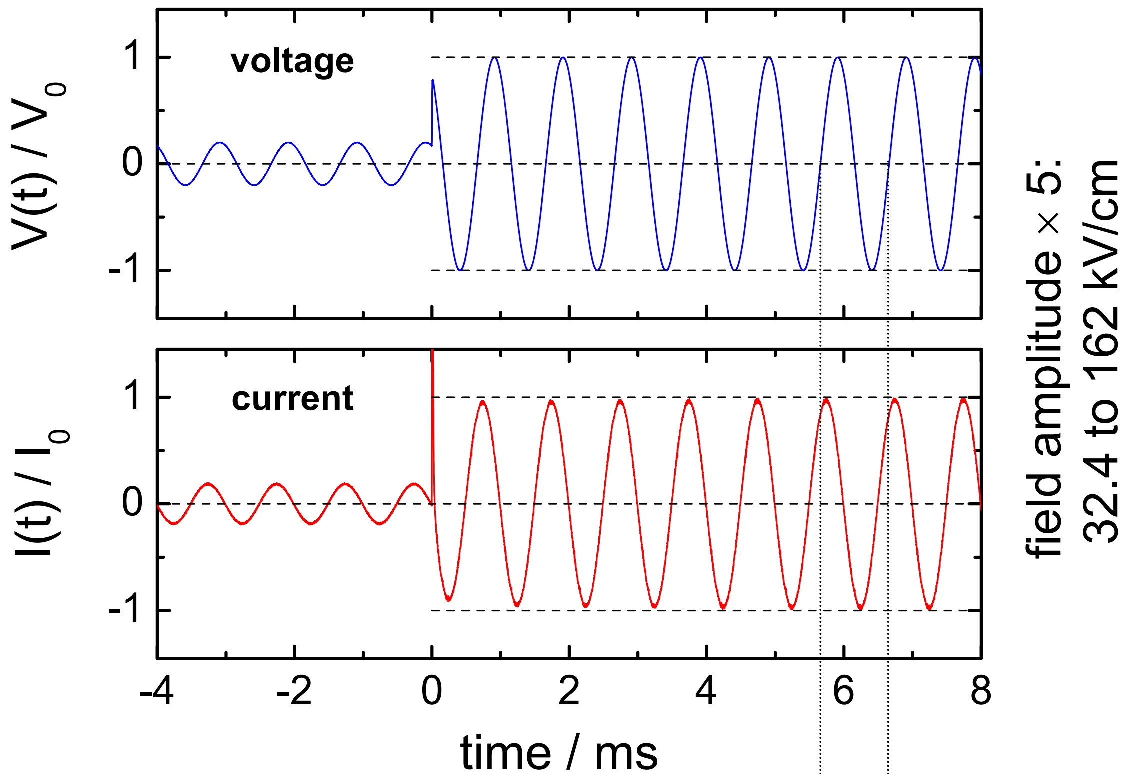


$R_{PROTECT} = 3\ \mathrm{M}\Omega$:
protects against 300 V (no time limit)

S. Weinstein, R. Richert, Phys. Rev. B 75 (2007) 064302
S. Weinstein, R. Richert, J. Phys.: Condens. Matter 19 (2007) 205128

adding time-resolution capabilities to high-field technique





$$\underline{S(t) = V(t) \text{ or } I(t)}$$

$$R = \frac{\omega}{\pi}\int_0^{2\pi/\omega} \sin(\omega t) S(t)\,dt = A\cos(\varphi)$$

$$I = \frac{\omega}{\pi}\int_0^{2\pi/\omega} \cos(\omega t) S(t)\,dt = A\sin(\varphi)$$

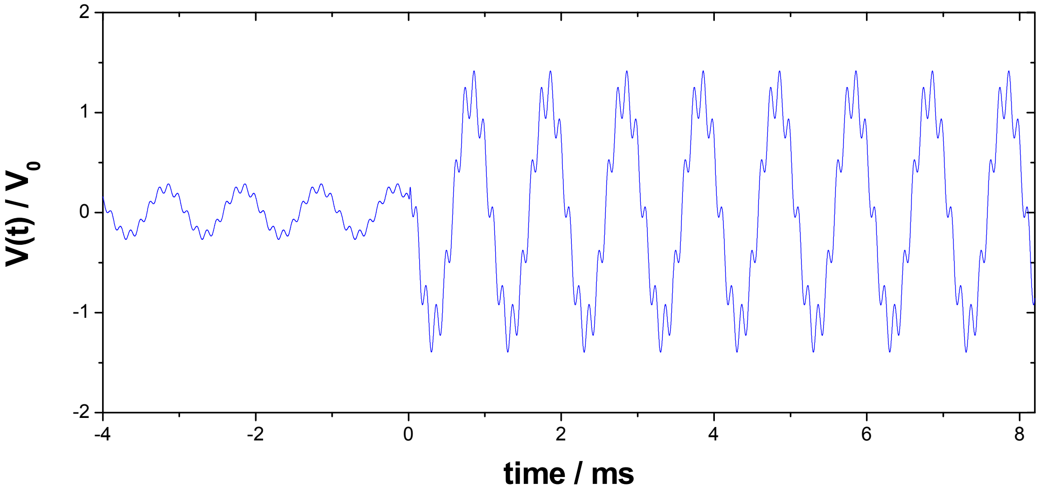
$$A = \sqrt{R^2 + I^2} \qquad \varphi = \arctan\left(\frac{I}{R}\right)$$

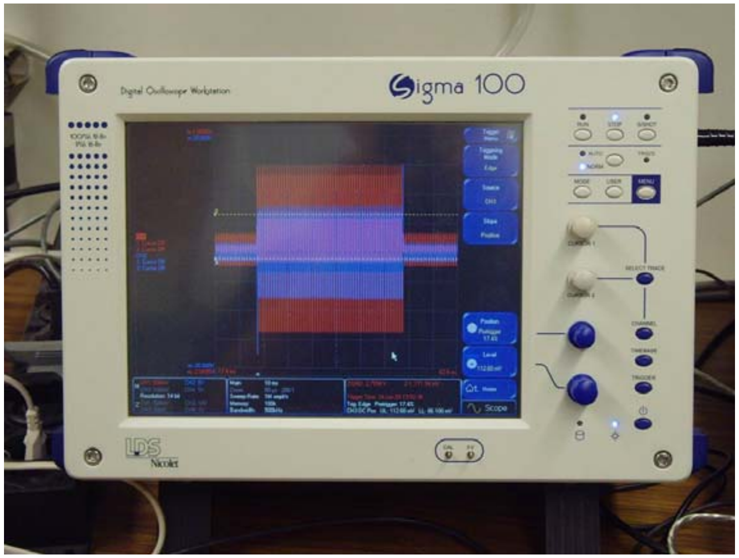
$$\tan\delta = \tan\left(\frac{\pi}{2} - \Delta\varphi\right)$$

L.-M. Wang, R. Richert, Phys. Rev. Lett. 99 (2007) 185701
W. Huang, R. Richert, J. Phys.Chem. B 112 (2008) 9909

single / multiple frequency technique

Stanford Research DS-345 Generator





Nicolet Sigma 100 Digital Oscilloscope

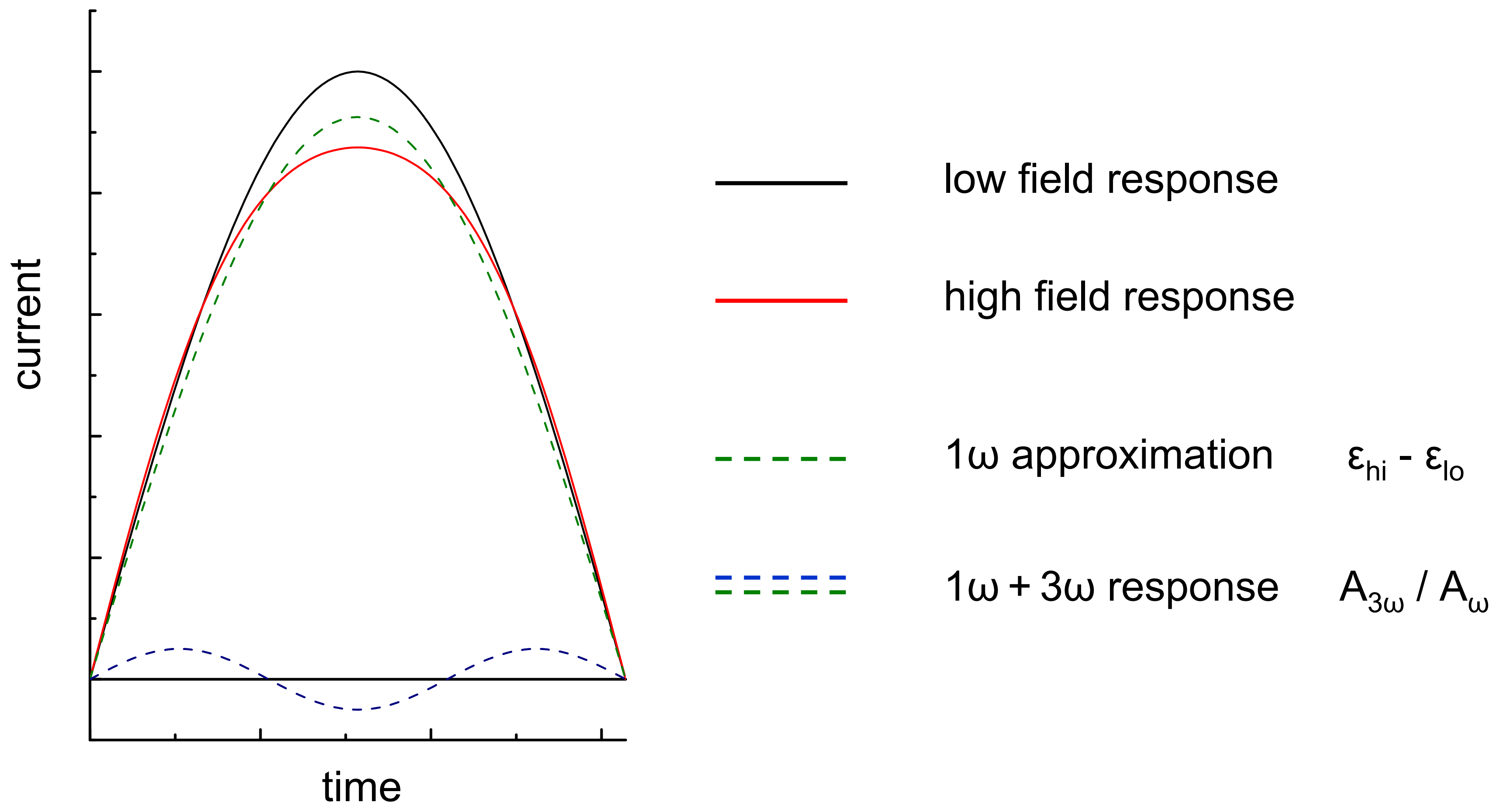
4 channels

1 Ms depth

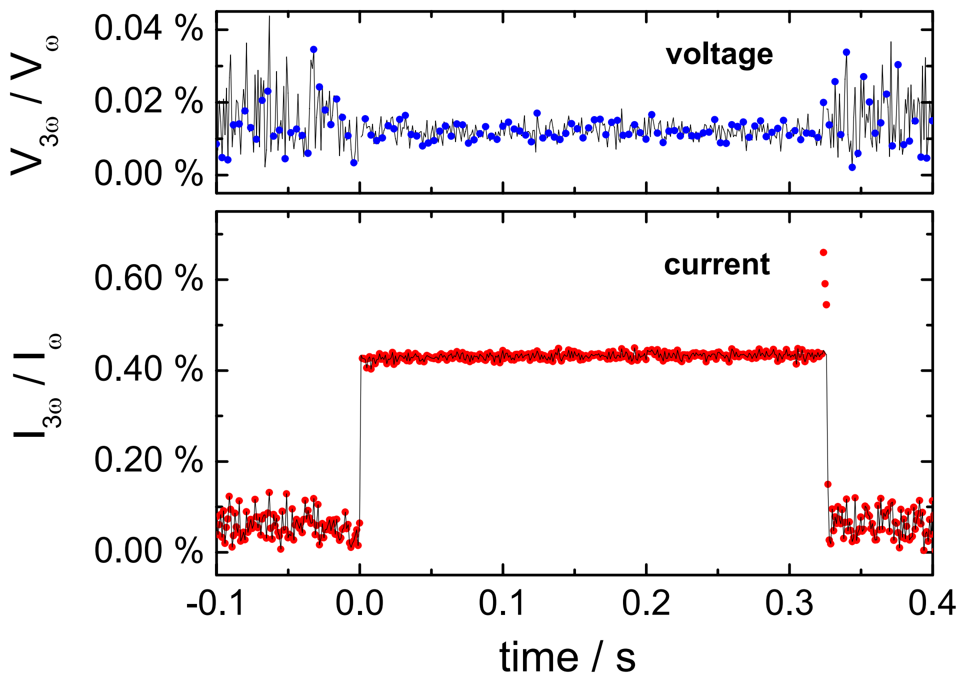
12 bit @ 100 Ms/s
14 bit @ 1 Ms/s

W. Huang, R. Richert, J. Chem. Phys. 130 (2009) 194509

1ω versus 3ω data analysis



3ω signal during field change: 32.4 to 162 kV/cm



$$D_0 = \varepsilon\varepsilon_0 E_0 + \lambda\varepsilon\varepsilon_0 E_0^3$$
$$= \varepsilon\varepsilon_0 E_0 \times \left(1 + \lambda E_0^2\right)$$
$$\lambda = \Delta \ln \varepsilon / E_0^2$$

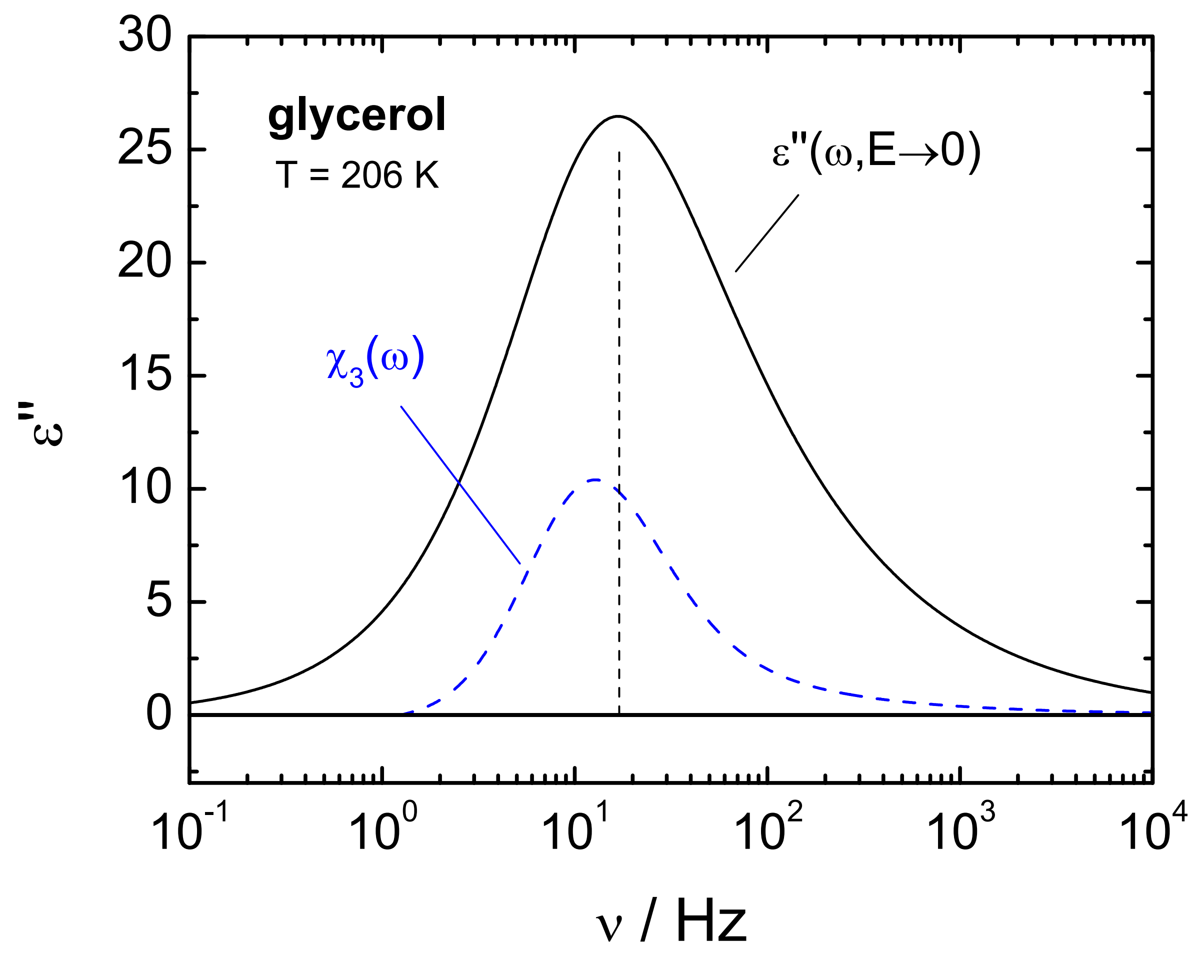
$$E = E_0 \sin(\omega t)$$
$$D_\omega(t) = \varepsilon\varepsilon_0 E_0 \sin(\omega t) + \lambda\varepsilon\varepsilon_0 E_0^3 \tfrac{3}{4} \sin(\omega t)$$
$$\Rightarrow \qquad A_\omega \approx \varepsilon\varepsilon_0 E_0$$
$$D_{3\omega}(t) = -\lambda\varepsilon\varepsilon_0 E_0^3 \tfrac{1}{4} \sin(3\omega t)$$
$$\Rightarrow \qquad A_{3\omega} = \tfrac{1}{4} \varepsilon\varepsilon_0 E_0 \Delta \ln \varepsilon$$

$$\left.\begin{aligned} R &= \frac{\omega}{\pi} \int_0^{2\pi/\omega} \sin(3\omega t) V(t)\, dt \\ I &= \frac{\omega}{\pi} \int_0^{2\pi/\omega} \cos(3\omega t) V(t)\, dt \end{aligned}\right\} A = \sqrt{R^2 + I^2}$$

$$\frac{A_{3\omega}}{A_\omega} = \frac{\Delta \ln \varepsilon}{4}$$

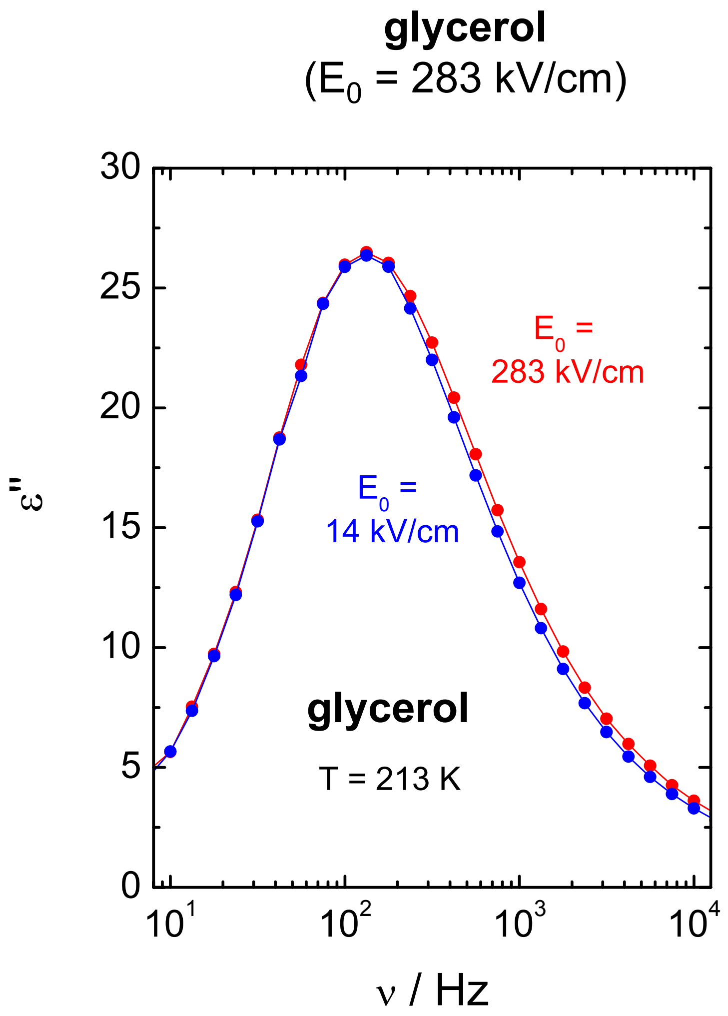
W. Huang, R. Richert, Eur. Phys. J. B 66 (2008) 217

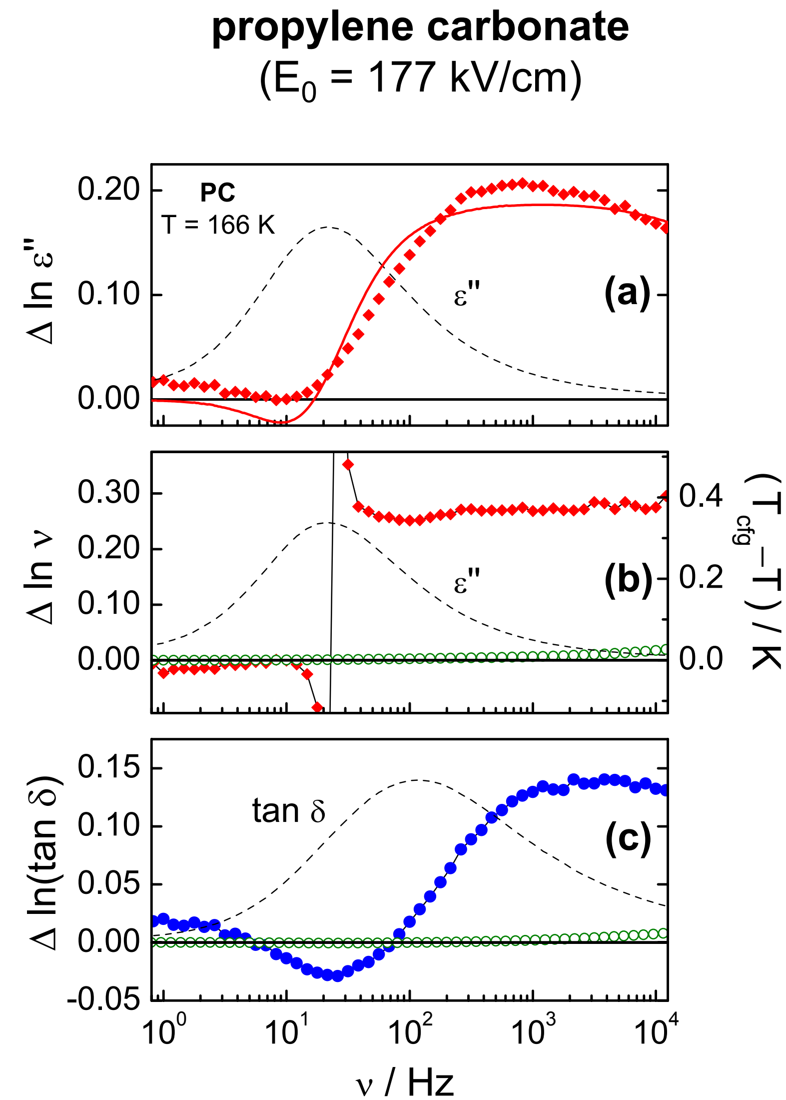
calculated frequency dependence of χ_3



R. Richert, J. Non-Cryst. Solids (in press)

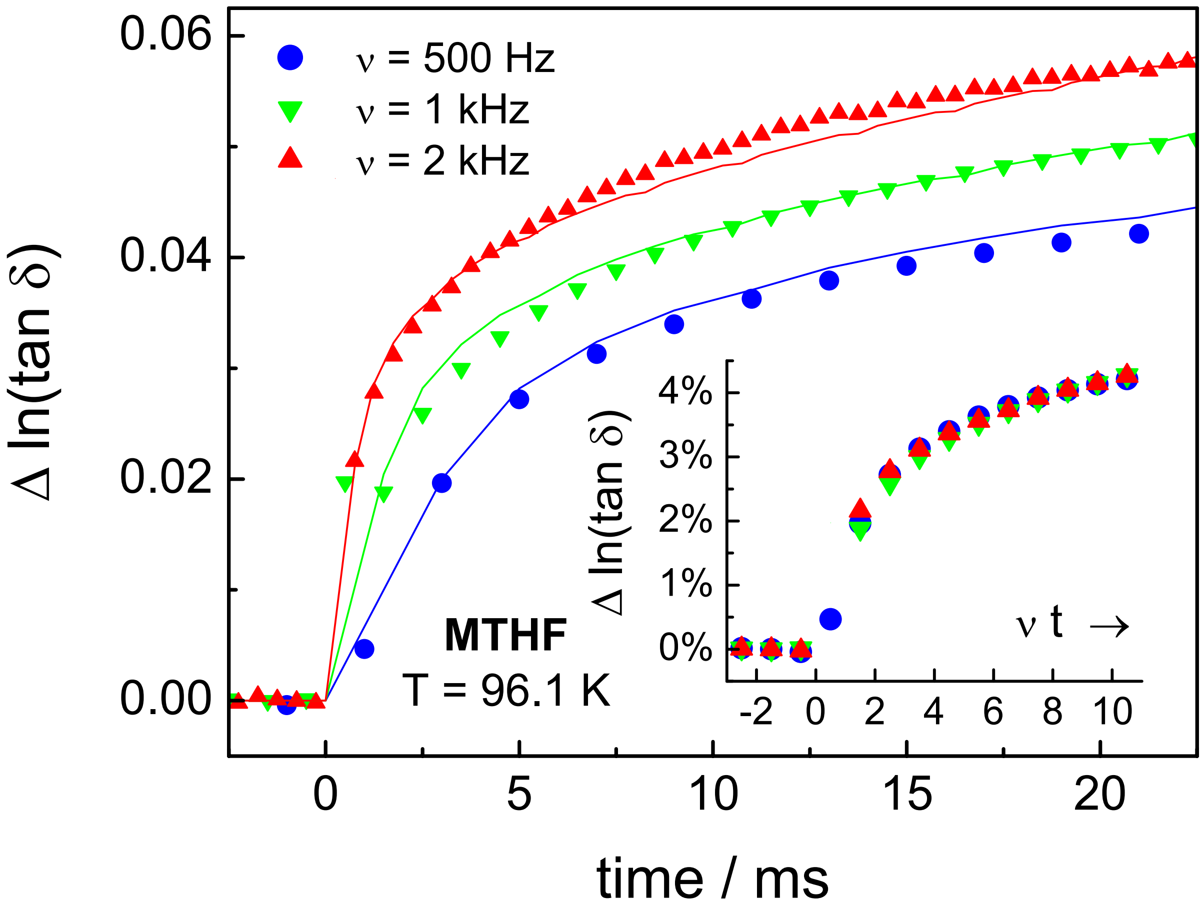
high field impedance of glycerol and propylene carbonate





R. Richert, S. Weinstein, Phys. Rev. Lett. 97 (2006) 095703
W. Huang, R. Richert, J. Chem. Phys. 130 (2009) 194509

rise of configurational temperature for different frequencies



hallmark of heterogeneity regarding τ_T or $c_p(\omega)$

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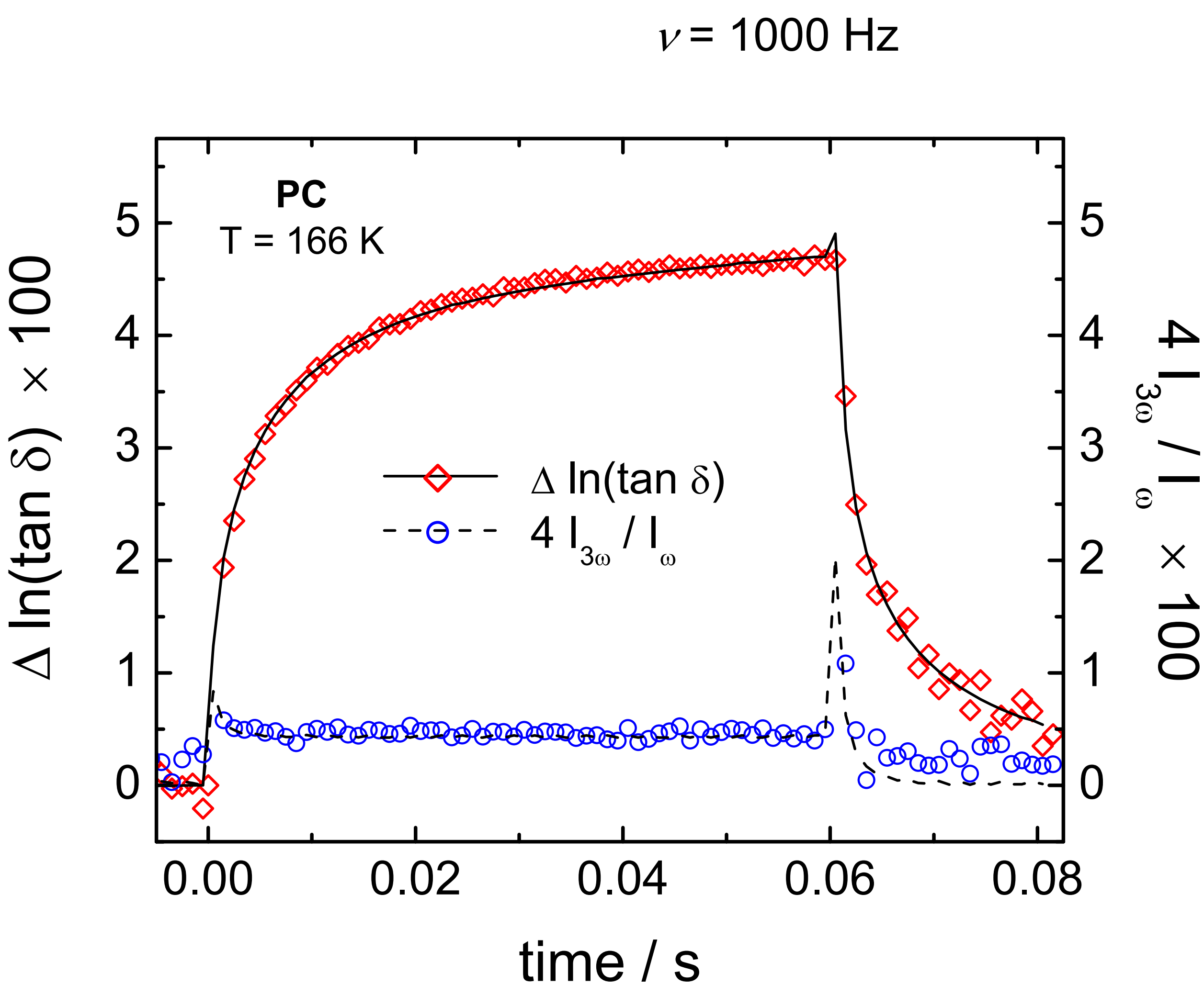
agreement between experiment and model



$$R = \frac{\omega}{\pi}\int_0^{2\pi/\omega} \sin(n\omega t) S(t)\, dt$$

$$I = \frac{\omega}{\pi}\int_0^{2\pi/\omega} \cos(n\omega t) S(t)\, dt$$

$$A = \sqrt{R^2 + I^2}$$

$$\varphi = \arctan\left(\frac{I}{R}\right)$$

$$\tan\delta = \tan\left(\frac{\pi}{2} - \Delta\varphi\right)$$

$$\frac{A_{3\omega}}{A_{\omega}} = \frac{\Delta \ln \varepsilon}{4}$$

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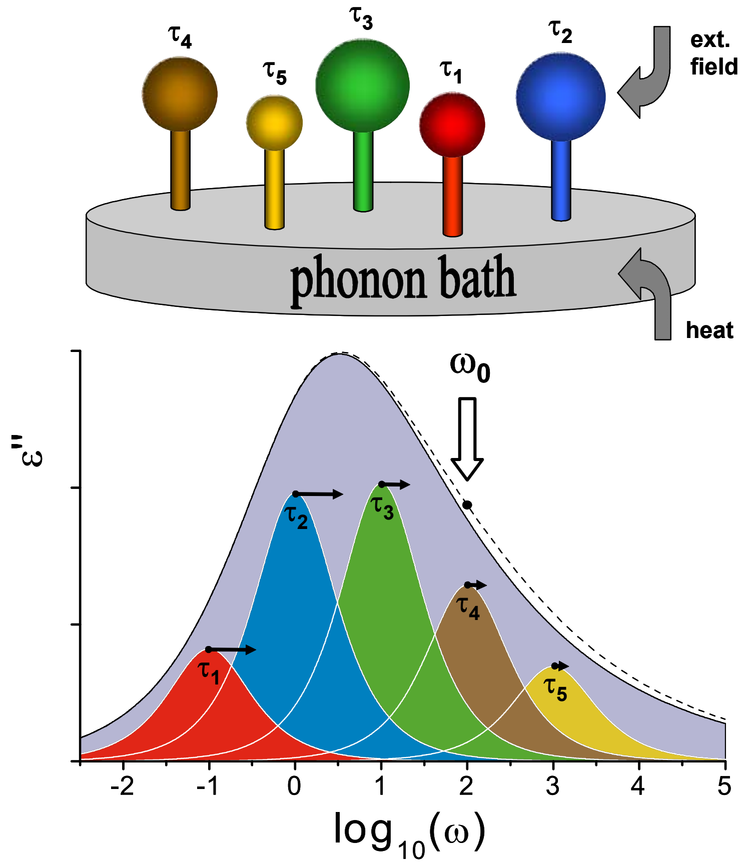
non-steady state version of 'box'-model



separately for each domain *i*

$$\Delta\varepsilon_i = \Delta\varepsilon g(\tau) d\tau \Rightarrow \sum_i \Delta\varepsilon_i = \Delta\varepsilon$$

$$\Delta C_{p,i} = \Delta C_p g(\tau) d\tau \Rightarrow \sum_i \Delta C_{p,i} = \Delta C_p$$

initial conditions :

$$D_i(0) = 0 \text{ and } T_i(0) = T$$

$$\frac{dD_i(t)}{dt} = j_i(t) = \frac{\varepsilon_0 E(t) \Delta\varepsilon_i}{\tau_i(t)} - \frac{D_i(t)}{\tau_i(t)}$$

$$\frac{dT_i(t)}{dt} = \frac{j_i^2(t)\tau_i(t)V}{\varepsilon_0 \Delta\varepsilon_i \Delta C_{p,i}} - \frac{T_i(t)-T}{\tau_i(t)}$$

$$\tau_i(t) = \tau_i(0)\left[1 - \frac{T_i(t)-T}{T}\left(\frac{E_A}{k_B T}\right)\right]$$

$$\frac{dT}{dt} = \sum_i \frac{T_i(t)-T}{\tau_i(t)} \frac{\Delta C_{p,i}}{C_{p,\infty}} \text{ for adiabatic case}$$

$$V(t) = E(t)d$$

$$I(t) = Aj_\infty + A\sum j_i(t) = A\left(\varepsilon_0\varepsilon_\infty \frac{dE(t)}{dt} + \sum j_i(t)\right)$$

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non-steady state version of 'box'-model

$$E(t) = E_0 \sin(\omega t)$$

for each mode 'i'

$$\Delta\varepsilon_i = \Delta\varepsilon g(\tau) d\tau \Rightarrow \sum_i \Delta\varepsilon_i = \Delta\varepsilon$$

$$\Delta C_{p,i} = \Delta C_p g(\tau) d\tau \Rightarrow \sum_i \Delta C_{p,i} = \Delta C_p$$

$$\text{initial conditions}: D_i(0) = 0 \text{ and } T_i(0) = T \quad \text{(equil.)}$$

$$\text{polarization}: \quad \frac{dD_i(t)}{dt} = j_i(t) = \frac{\varepsilon_0 E(t) \Delta\varepsilon_i}{\tau_i(t)} - \frac{D_i(t)}{\tau_i(t)}$$

$$\text{conf .temp.}: \quad \frac{dT_i(t)}{dt} = + \frac{j_i^2(t)\tau_i(t)V}{\varepsilon_0 \Delta\varepsilon_i \Delta C_{p,i}} - \frac{T_i(t) - T}{\tau_i(t)}$$

$$\text{adj. time const.}: \quad \tau_i(t) = \tau_i(0)\left[1 - \frac{T_i(t) - T}{T}\left(\frac{E_A}{k_B T}\right)\right]$$

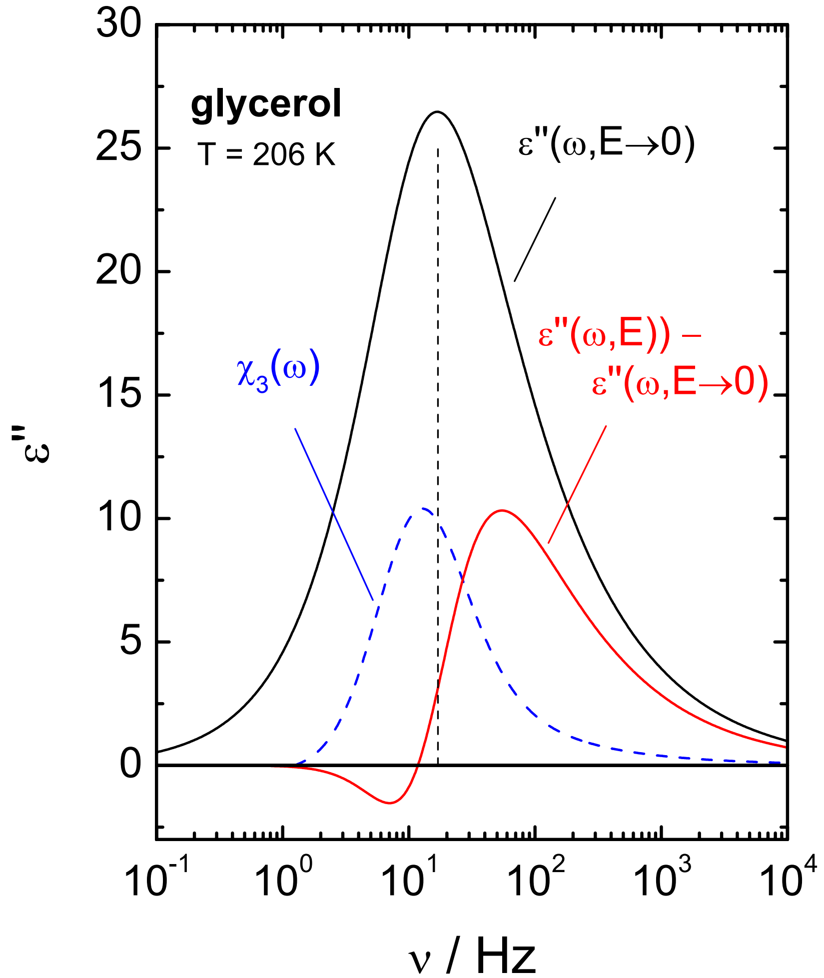
$$V(t) = E(t) d$$

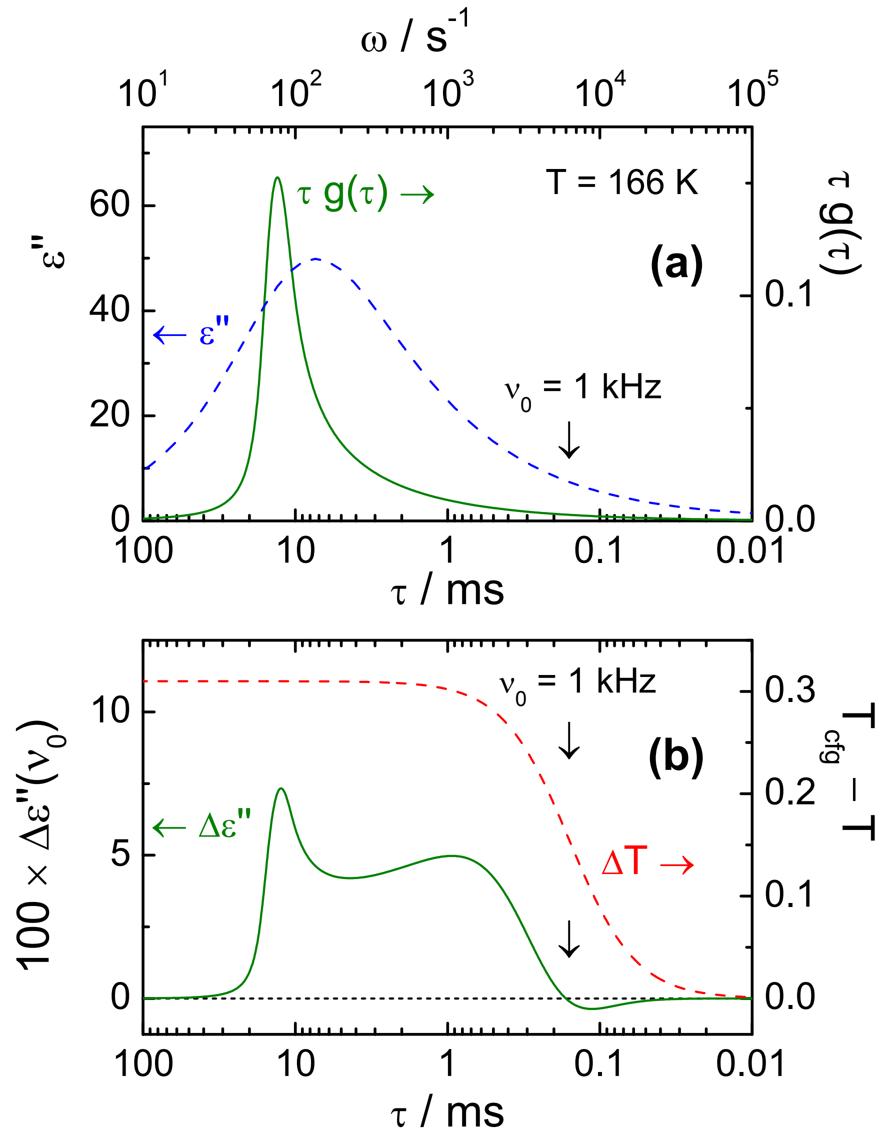
$$I(t) = Aj_\infty + A\sum j_i(t)$$

$$= A\left(\varepsilon_0 \varepsilon_\infty \frac{dE(t)}{dt} + \sum j_i(t)\right)$$

W. Huang, R. Richert, J. Chem. Phys. 130 (2009) 194509

high field impedance technique



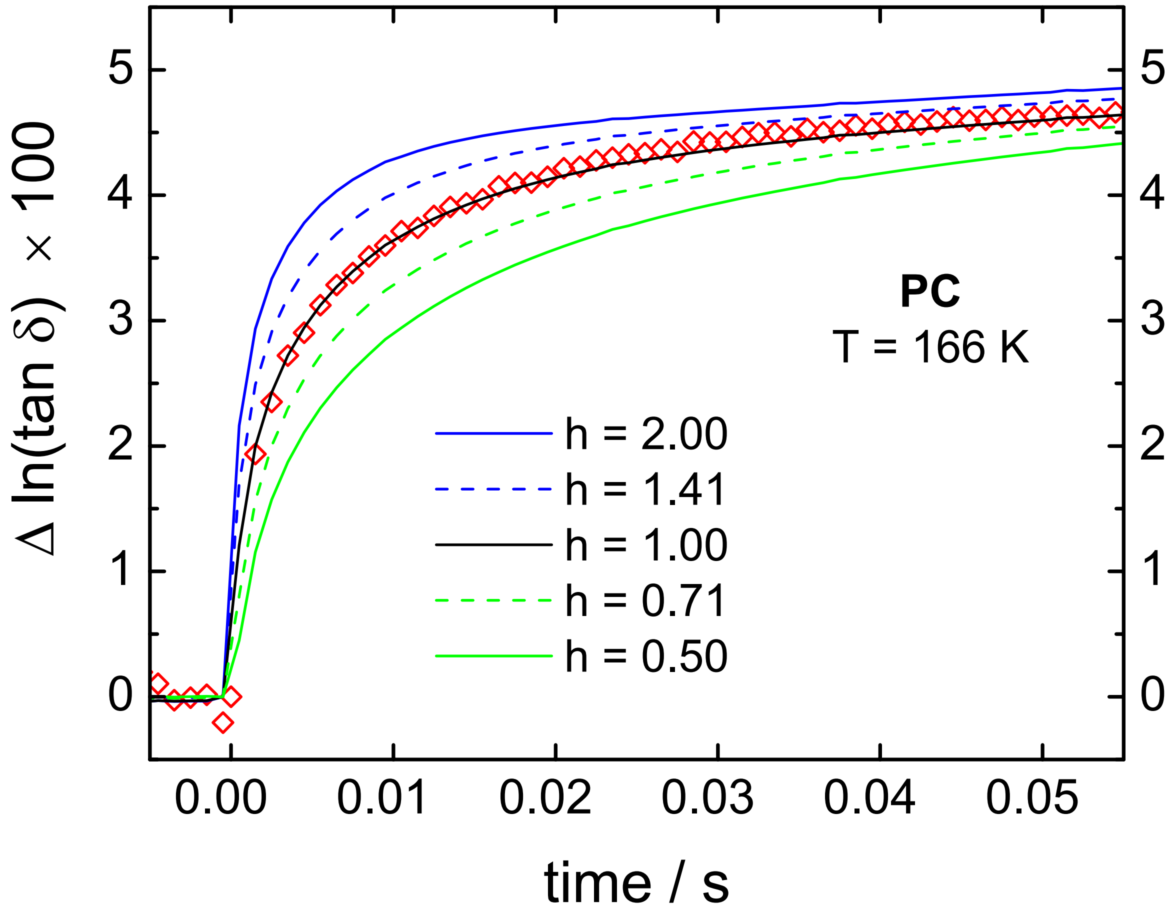


R. Richert, J. Non-Cryst. Solids (in press)

R. Richert, Thermochim. Acta (submitted)

testing the claim: $\tau_T = \tau_D$ versus $\tau_T = \tau_D/h$

$$\ln \tau_D{}^* = \ln \tau_D - \frac{E_A}{k_B T^2} \times \frac{\varepsilon_0 E_0^2 \Delta\varepsilon}{2\rho \Delta c_p} \times \frac{\omega^2 \tau_D \tau_T}{1+\omega^2 \tau_D^2}\left[1 - e^{-\frac{t}{\tau_T}}\right] = \ln \tau_D - \frac{E_A}{k_B T^2} \times \frac{\varepsilon_0 E_0^2 \Delta\varepsilon}{2\rho \Delta c_p/h} \times \frac{\omega^2 \tau_D\, \tau_D/h}{1+\omega^2 \tau_D^2}\left[1 - e^{-\frac{t}{\tau_D/h}}\right]$$



$\tau_T \rightarrow \tau_D/h$

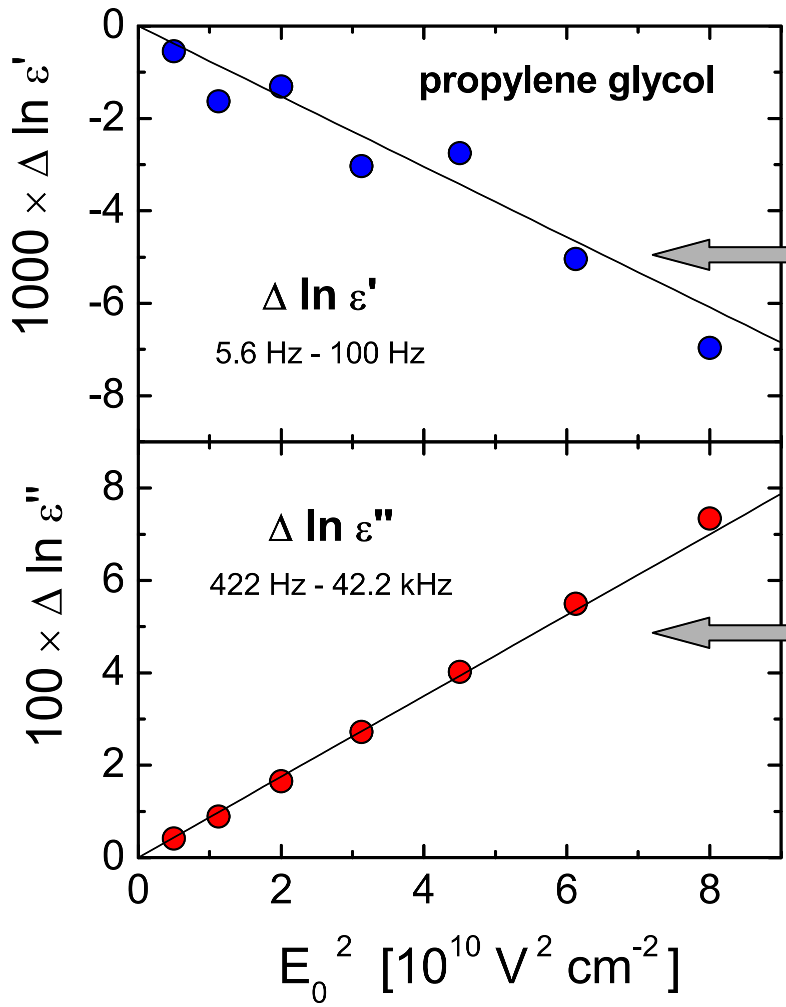
<u>result :</u>

$\tau_T = \tau_D$

$\pm 15\%$

L.-M. Wang, R. Richert, Phys. Rev. Lett. 104 (2010) 239603

summary of relevant non-linear effects (~E²)



Coulombic stress:

$$Fd = \tfrac{1}{2}QV, Q = CV, C = \varepsilon\varepsilon_0 A/d$$

$$F(t) = \frac{\varepsilon_s\varepsilon_0 A}{2}E^2(t) = \underbrace{\frac{\varepsilon_s\varepsilon_0 A}{4}E_0^2}_{\approx 31\,\mathrm{N}} - \frac{\varepsilon_s\varepsilon_0 A}{4}E_0^2\cos(2\omega t)$$

dielectric saturation:

$$\frac{\Delta\varepsilon_s}{E^2} = -\frac{N\mu^4}{45\varepsilon_0 V(kT)^3} \times \frac{\varepsilon_s^4(\varepsilon_\infty + 2)^4}{(2\varepsilon_s + \varepsilon_\infty)^2(2\varepsilon_s^2 + \varepsilon_\infty^2)}$$

(van Vleck)

energy absorption:

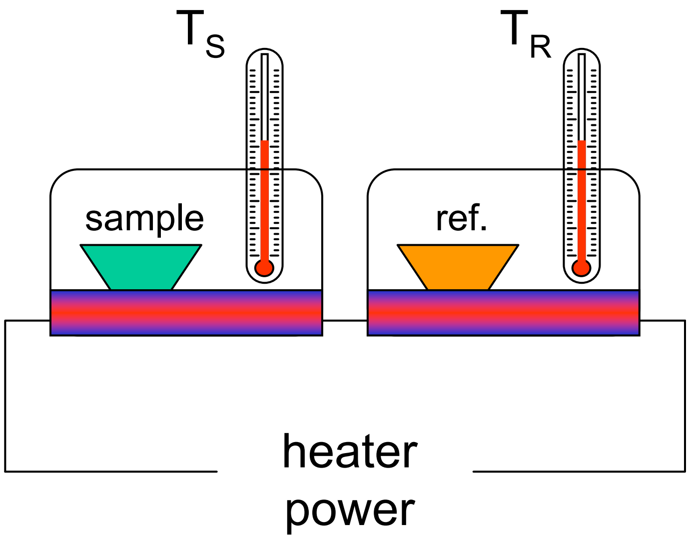
$$T_e(\tau) = \frac{\varepsilon_0 E_0^2 \Delta\varepsilon}{2\Delta c_p} \times \frac{\omega_0^2\tau^2}{1+\omega_0^2\tau^2} = T_e^0 \times \frac{\omega_0^2\tau^2}{1+\omega_0^2\tau^2}$$

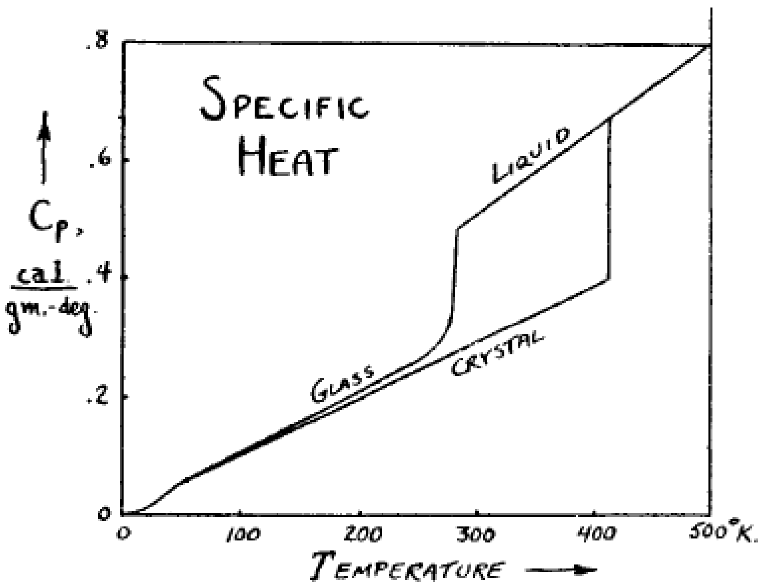
$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \Delta\varepsilon\int_0^\infty g(\tau)\frac{1}{1+i\omega\tau^*}d\tau$$

S. Weinstein, R. Richert, Phys. Rev. B 75 (2007) 064302

<u>reverse calorimetry</u>

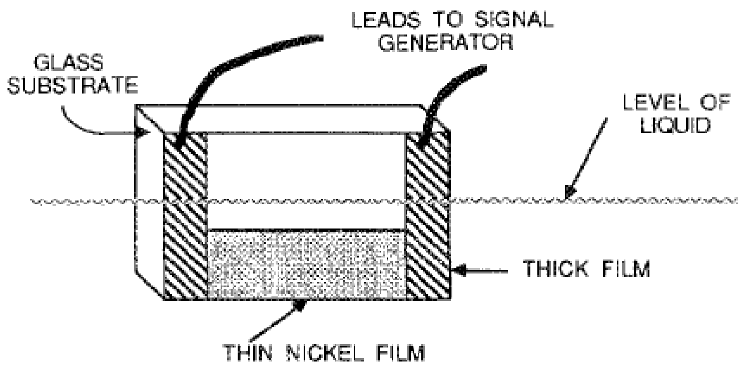
Differential Scanning Calorimetry

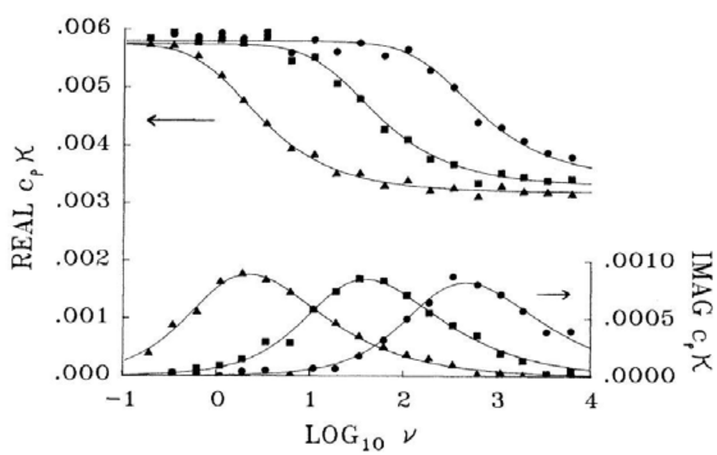


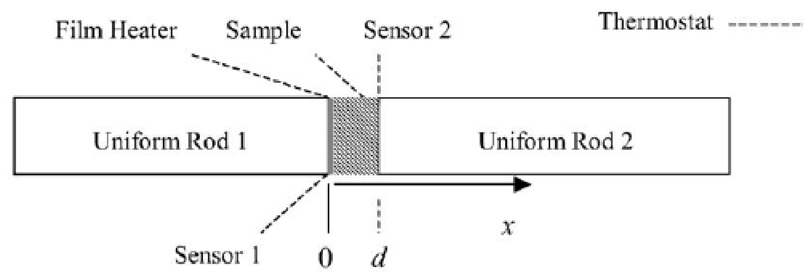


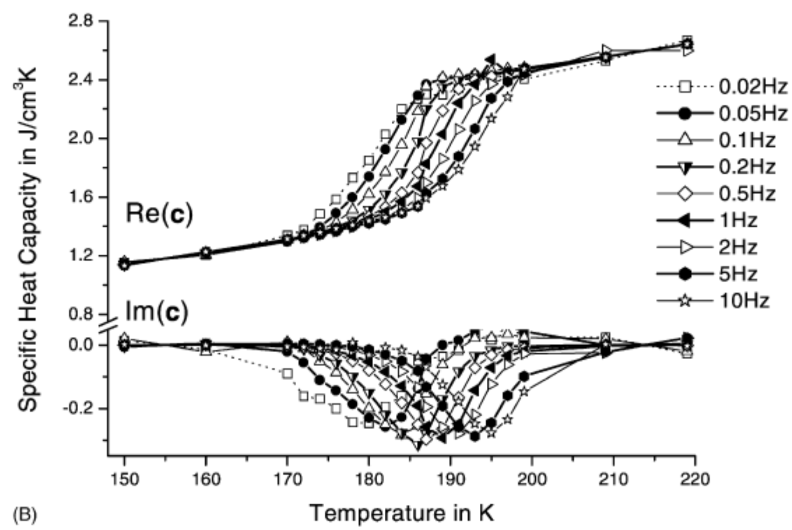
W. Kauzmann, Chem. Rev. 43 (1948) 219

dynamic heat capacity in glycerol





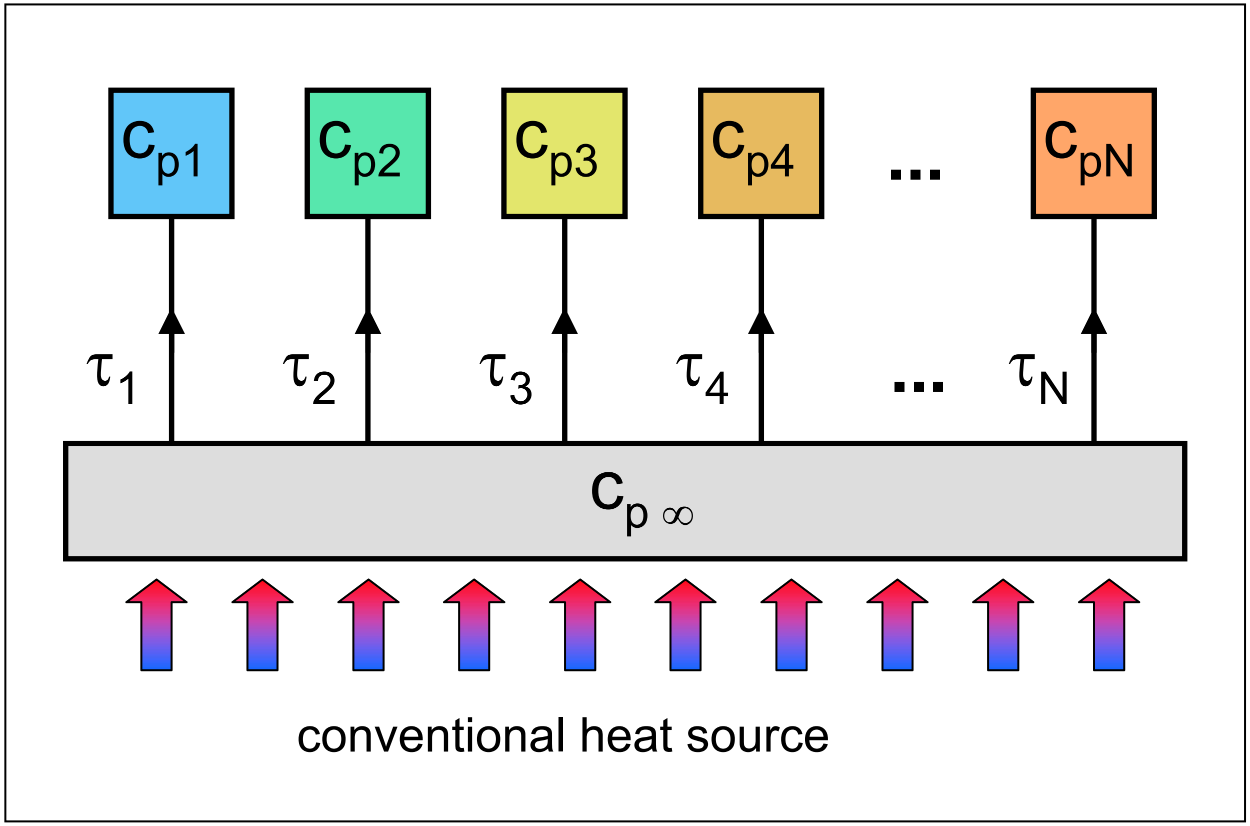




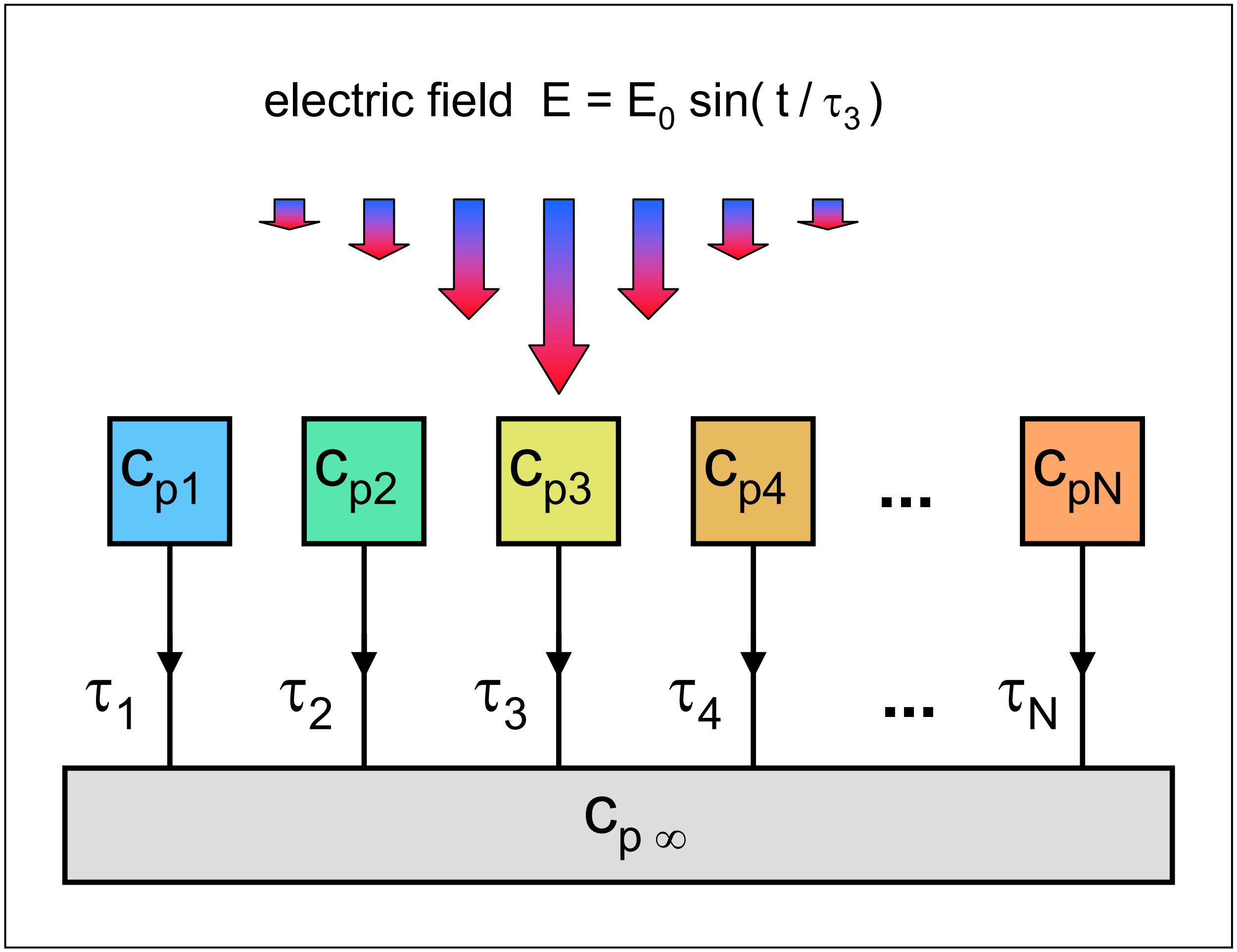
N. O. Birge, S. R. Nagel, Phys. Rev. Lett. 54 (1985) 2674

A. A. Minakov *et al.* Thermochim. Acta 403 (2003) 89

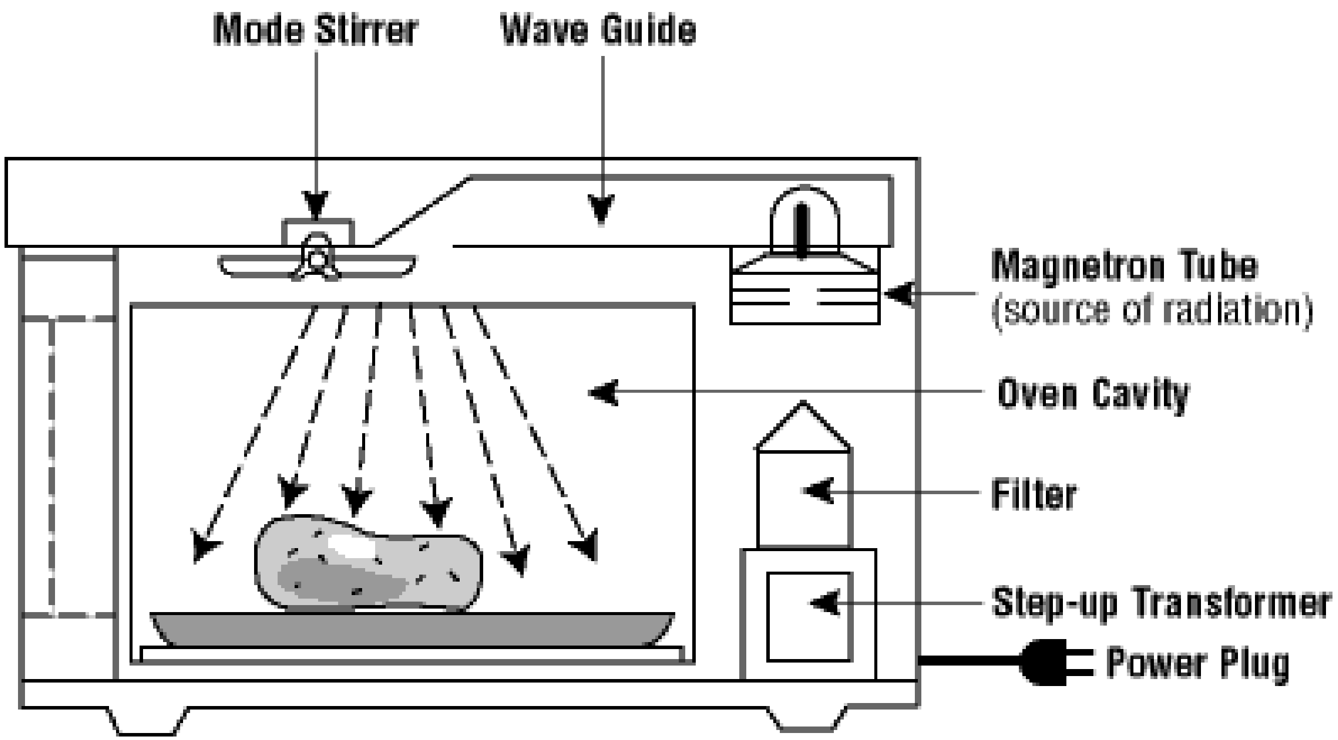
standard dynamic heat capacity



reverse dynamic heat capacity (isothermal)



reverse dynamic: microwave heating in slow motion



typical frequency: 2.45 GHz

what do we learn ?

nonlinearity from energy absorption

measure configurational C_p

thermal time scales

thermal heterogeneity

alcohols / ionic liquids

physical aging