

Nonlinear Dielectric Effects in Simple Fluids

NON-LINEAR DIELECTRIC EXPERIMENTS

*Roma, Dielectric Tutorial
30 August 2009*

High-Field Dielectric Response:

Coulombic stress

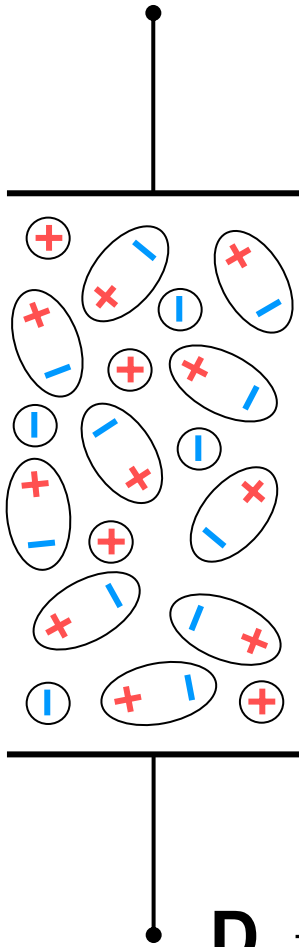
Langevin effect

Energy absorption

Time-resolved technique

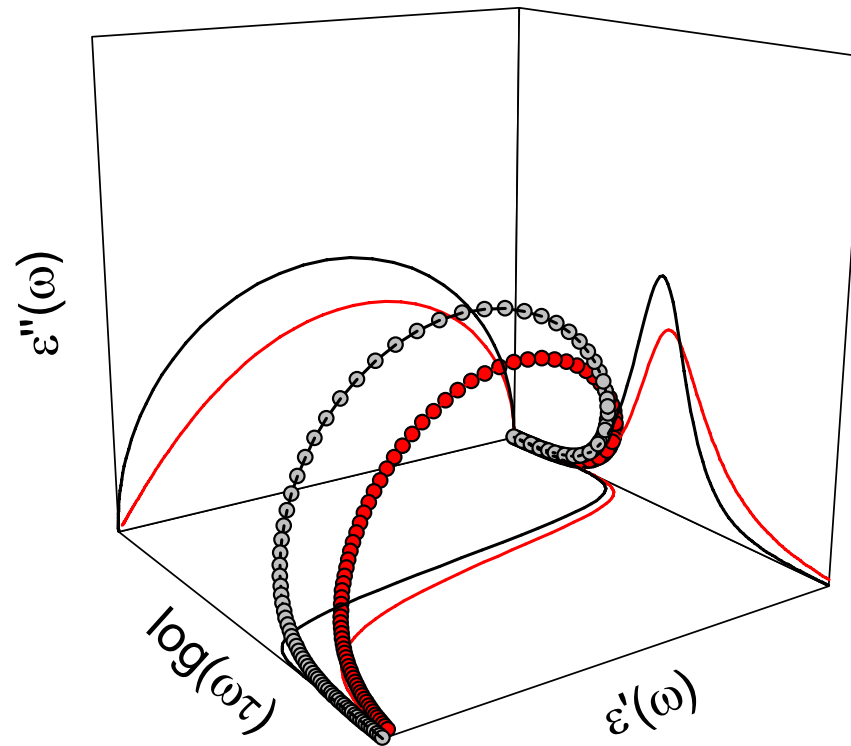
Ranko Richert

dielectric relaxation techniques



$$\mathbf{D} = \epsilon \epsilon_0 \mathbf{E}$$

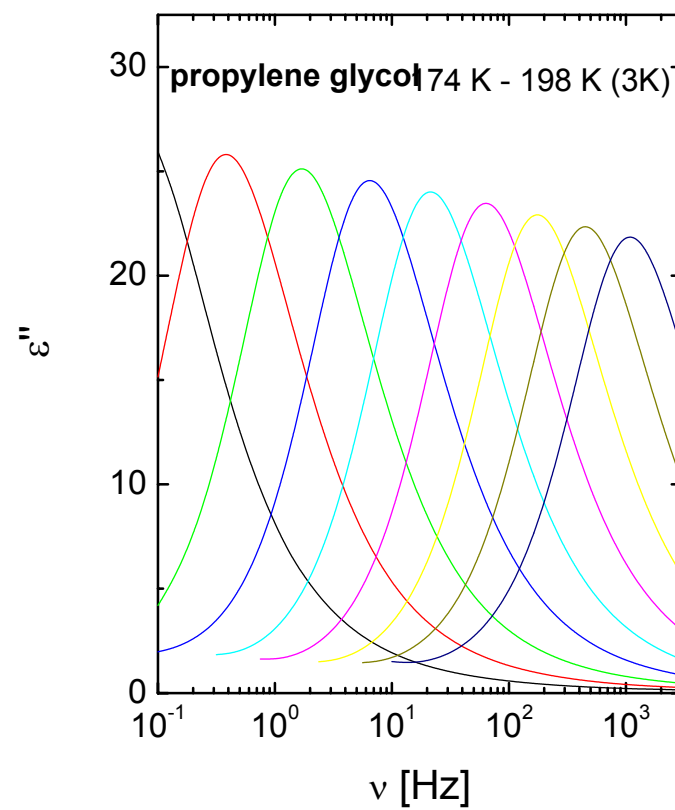
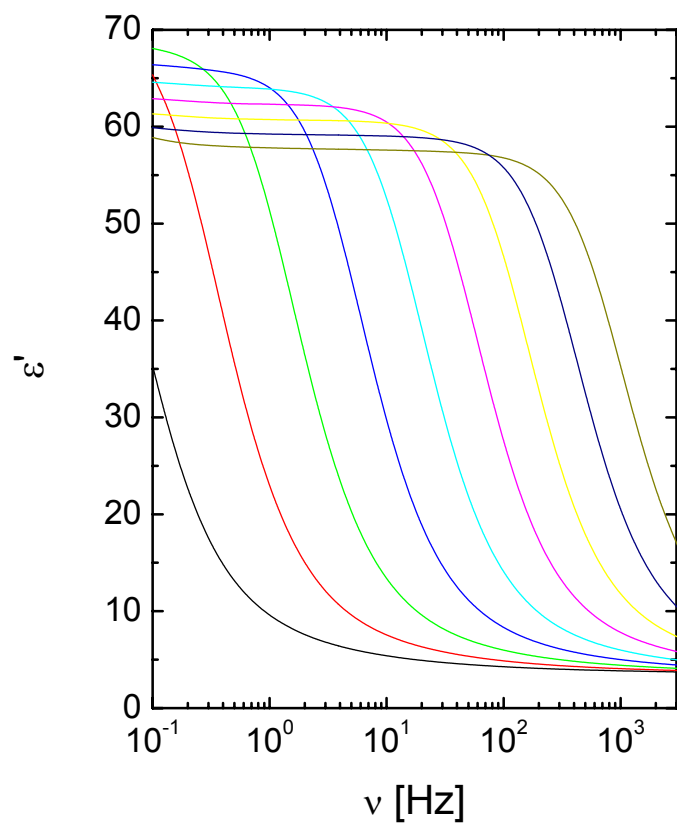
dielectric displacement $\mathbf{D} \equiv \frac{\mathbf{Q}}{\mathbf{A}} \propto \frac{\mathbf{V}}{\mathbf{d}} \equiv \mathbf{E}$ electric field



$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau} \quad \{\text{Debye}\}$$

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\gamma} \quad \left\{ \begin{array}{l} \text{Havriliak} \\ \text{- Negami} \end{array} \right\}$$

typical case near the glass transition



non-linear susceptibility

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

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

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

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

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

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

Piekara factor :

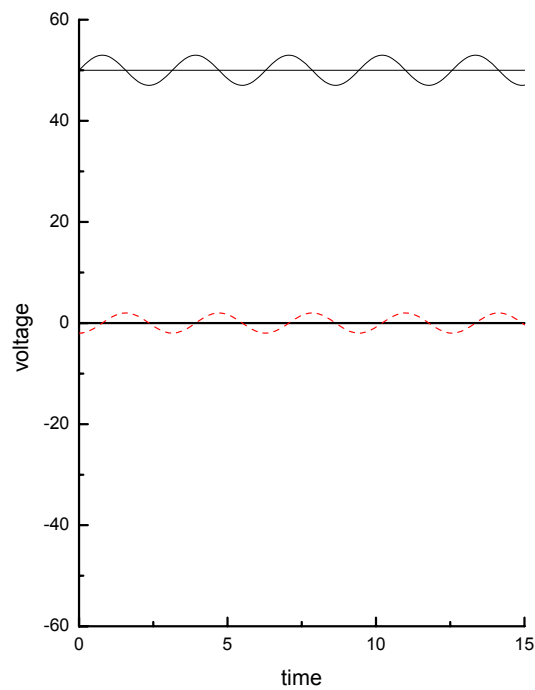
$$\Delta \varepsilon_s / E^2 = -\lambda \varepsilon_s$$

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

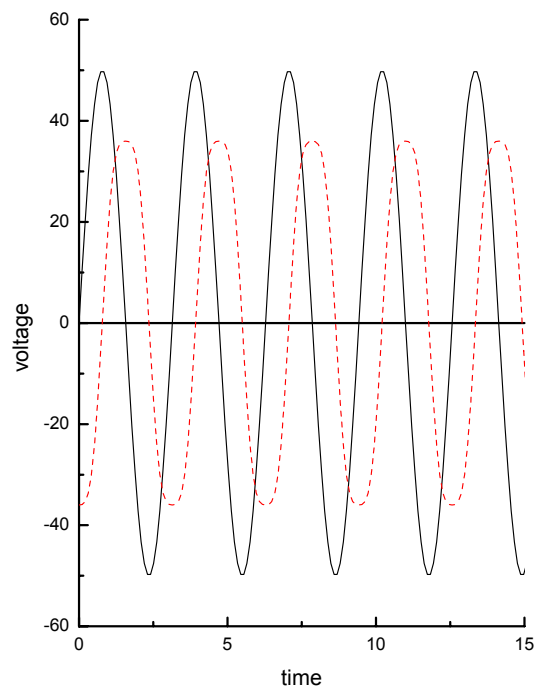
M. S. Green, R. Kubo (1950's) : linear transport coefficients $L_{F_e=0}$ are related to auto - correlation function of the equilibrium fluctuations in the conjugate flux J

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

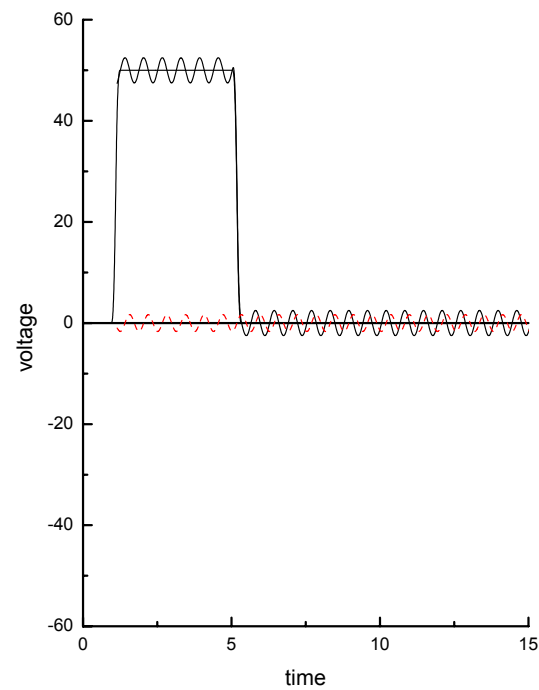
variety of high field techniques



high DC field
low AC field
mainly 1ω



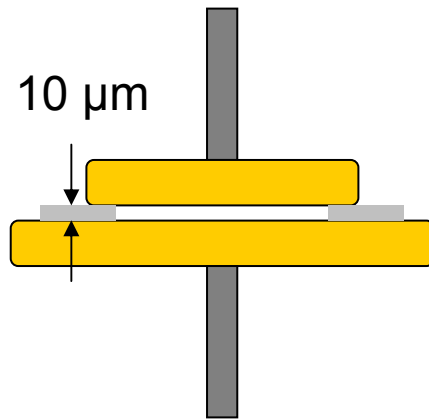
high AC field
no bias
 $1\omega + 3\omega$



low AC field
on high pulse
 $NDE(t)$

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

$$\mathbf{F}_{SI} = \frac{qq'}{4\pi\epsilon_0 r^3} \mathbf{r}$$

$$\mathbf{F}_{cgs} = \frac{qq'}{r^3} \mathbf{r}$$

$$C = \frac{Q}{V}$$

$$Q = CV$$

$$C = \frac{\epsilon_0 \epsilon A}{d}$$

$$\text{Energy} = \frac{1}{2} QV$$

calculate force resulting from voltage $V(t)$

$$V(t) = V_0 \sin(\omega t)$$

calculate effect on measured ϵ

assume Teflon spacer with

Young's modulus $E = 1 \text{ GPa}$

$$\text{mechanical modulus} \equiv \frac{[\text{stress}]}{[\text{strain}]} = \frac{L_0}{\Delta L} \frac{F}{A}$$

Coulombic stress solutions

work $Fd = \text{energy } \frac{1}{2}QV$

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

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

$$F = \frac{1}{2}V^2\varepsilon_0 A \frac{\partial d^{-1}}{\partial d} = \frac{\varepsilon_0 A}{2d^2}V^2 = \frac{\varepsilon_0 A}{2d^2}(V_{dc} + V_{ac})^2$$

$$F = \frac{\varepsilon_0 A}{2d^2}[V_{dc} - V_0 \sin(\omega t)]^2$$

$$= \frac{\varepsilon_0 A}{2d^2}\left(V_{dc}^2 - 2V_{dc}V_0 \sin(\omega t) + \frac{V_0^2}{2}[1 - \cos(2\omega t)]\right)$$

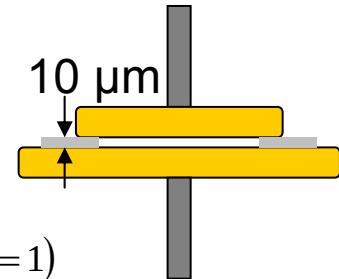
Young's modulus $E = \frac{[\text{stress}]}{[\text{strain}]} = \frac{L_0}{\Delta L} \frac{F}{A}$

$$\mathbf{F}_{SI} = \frac{qq'}{4\pi\varepsilon_0 r^3} \mathbf{r}$$

$$C = \frac{Q}{V}$$

$$C = \frac{\varepsilon_0 A}{d} \quad (\varepsilon = 1)$$

$$E = \frac{1}{2}QV$$



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

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

$$a = 4.7 \times 10^{-5} \text{ m}^2 \text{ (Teflon ring, } d = 14\text{--}16 \text{ mm)}$$

$$Y = 1 \text{ GPa (Teflon)}$$

$$F_0 = 31 \text{ N}$$

$$F_0/a = 0.67 \text{ MPa}$$

$$\Delta \ln \varepsilon = -\frac{\Delta d}{d} \leq 6.7 \times 10^{-4}$$

dielectric saturation

expected non-linearity: dielectric saturation, Langevin effect

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

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

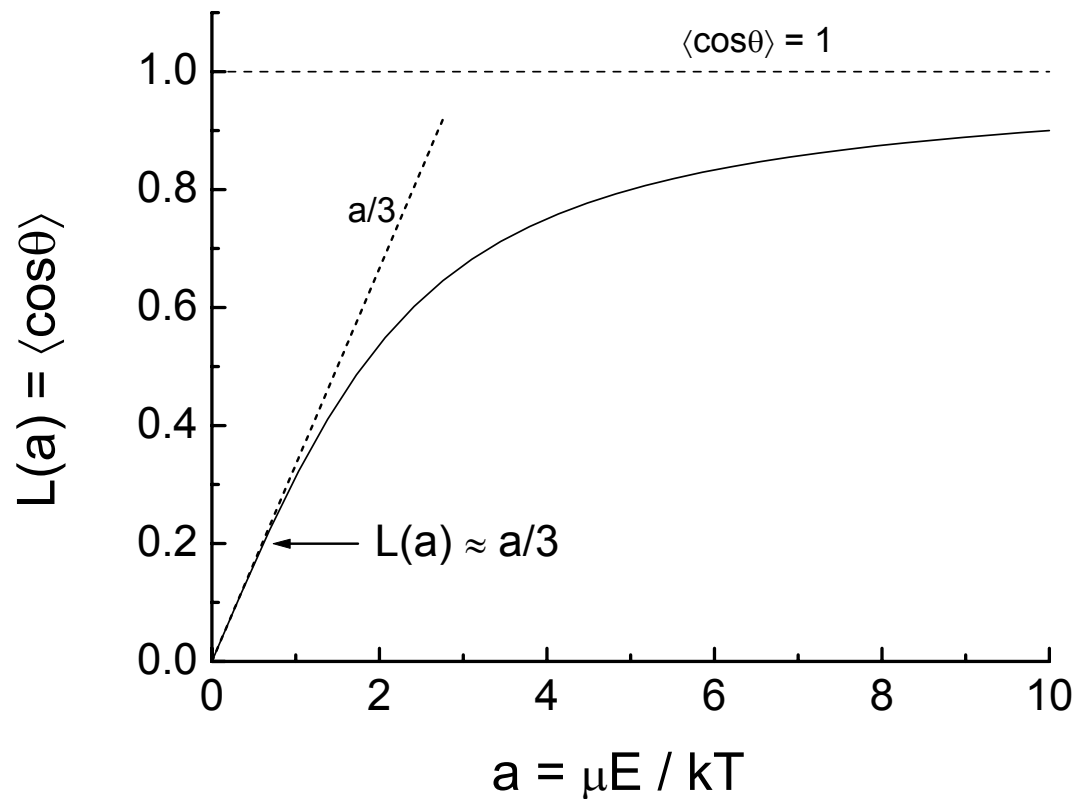
$$\langle \cos \theta \rangle = L\left(\frac{\mu E}{kT}\right) \quad \left(\begin{array}{l} \text{Langevin} \\ \text{function} \end{array} \right)$$

$$\text{with } a = \frac{\mu E}{kT}$$

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

$$\text{if } \mu E \ll kT \text{ or } a \ll 1$$

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



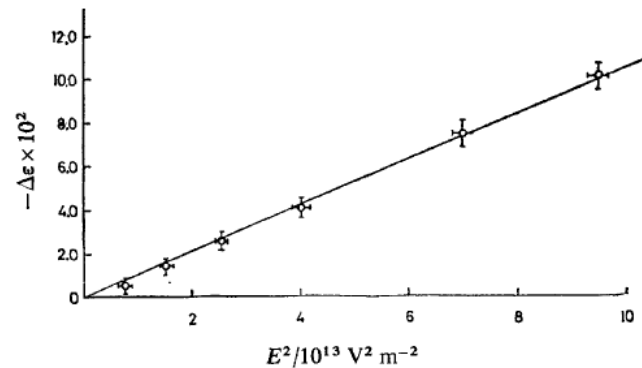
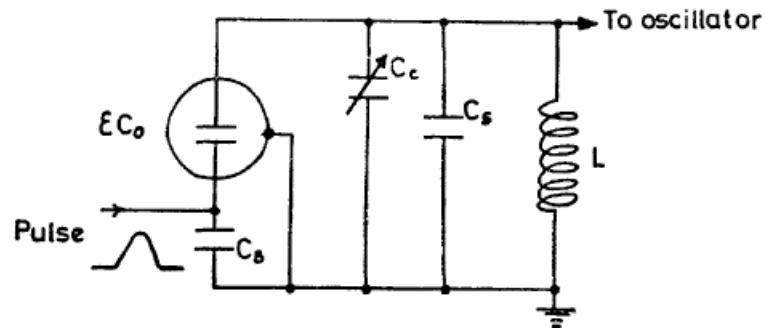
saturation in water at 293 K

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

vanVleck
$$\frac{\Delta\epsilon_s}{E^2} = \frac{\epsilon_s(E^2) - \epsilon_s(0)}{E^2} = -\frac{N\mu^4}{45\epsilon_0 V(kT)^3} \times \frac{\epsilon_s^4(\epsilon_\infty + 2)^4}{(2\epsilon_s + \epsilon_\infty)^2(2\epsilon_s^2 + \epsilon_\infty^2)}$$

J. H. van Vleck, J. Chem. Phys. 5 (1937) 556

A. Piekara, Acta Phys. Polon. 18 (1959) 361



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

time resolved NDE experiments

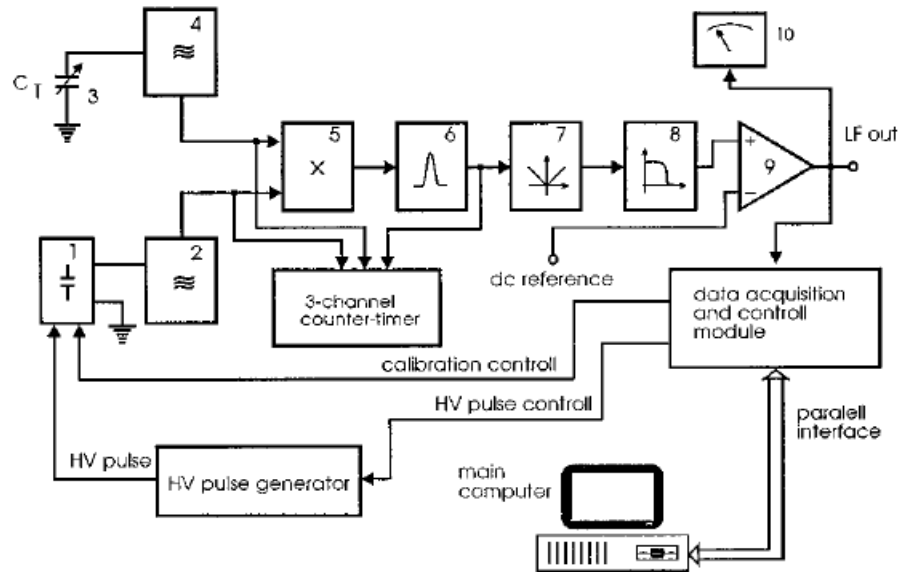
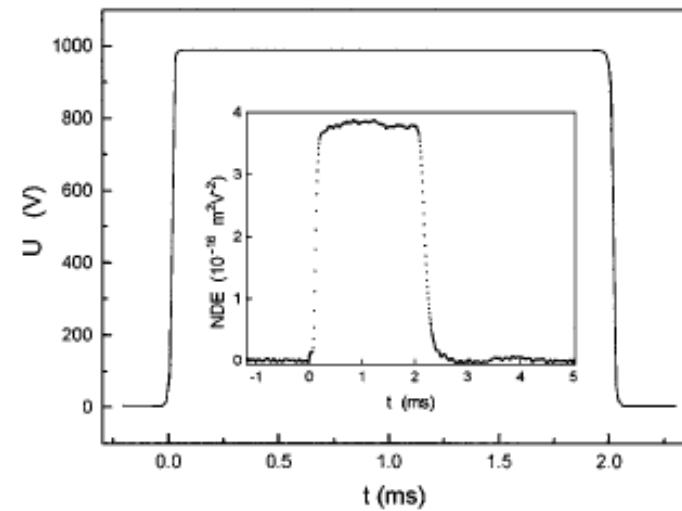
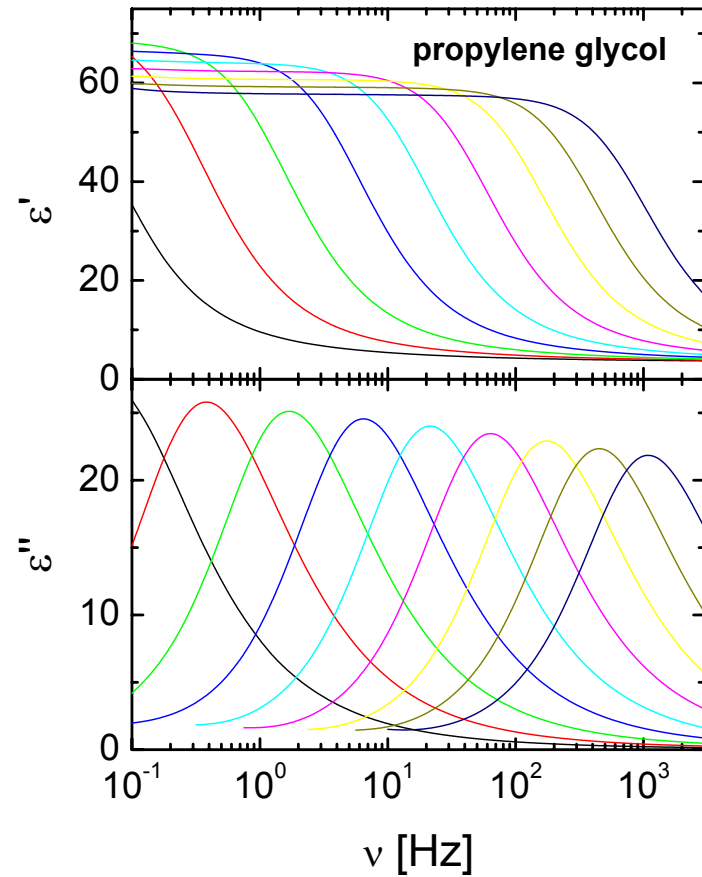
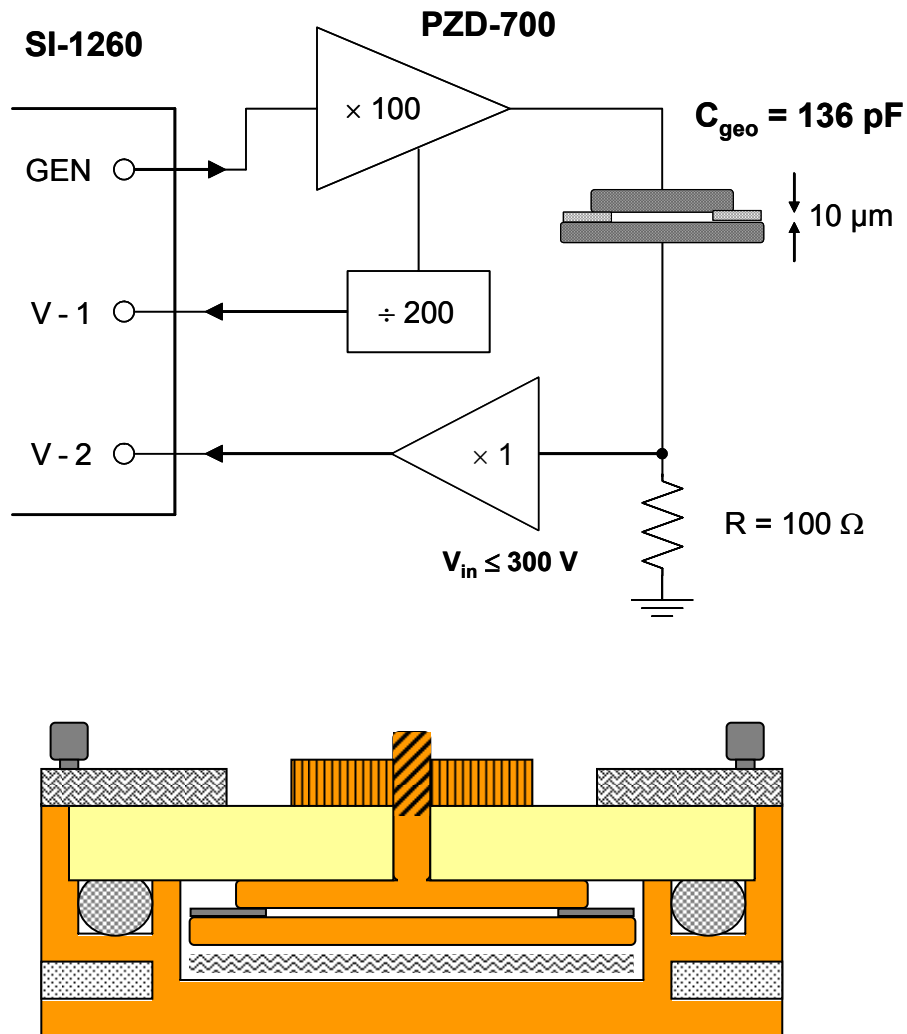


FIG. 1. The NDE measurement setup: 1—Measurement capacitor; 2—measurement generator (G_1 , freq. $f_1 + \Delta f$); 3,4—reference generator (G_2 , freq. f_2) with tuning capacitor; 5—mixer (freq. Δf); 6—bandpass filter; 7—rectifier; 8—low-pass filter; 9—amplifier; 10—indicator of the tuning of G_2 to $f_2 = f_1 + \Delta f$. The elements 2 and 4–10 are contained in one measurement unit.



high field impedance



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

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

analyzer input protection



Ultralow, Input-Bias Current
Operational Amplifier

AD549

AD 549 L

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

$$C_{in} = 0.8 \text{ pF}$$

$$I_{bias} = 40 \text{ fA}$$

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 $f = 1/2\pi RC$. Again, the Johnson noise, R_P , adds to the amplifier's input voltage noise.

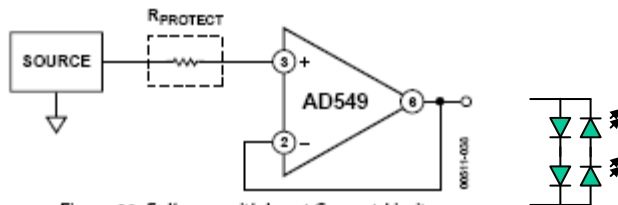
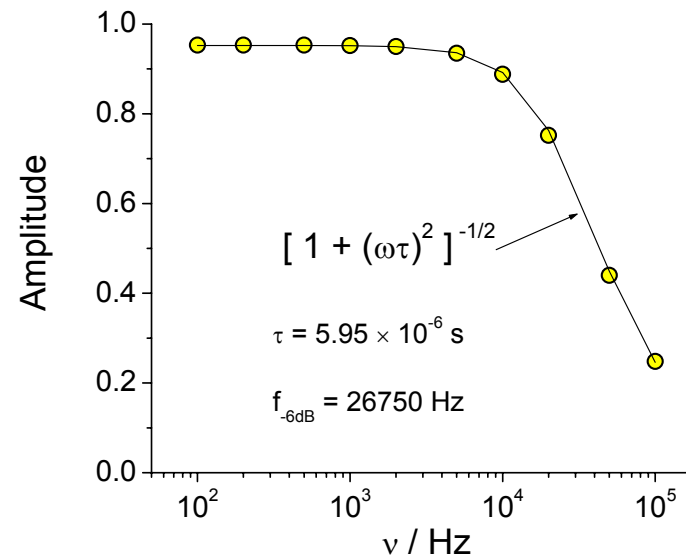


Figure 38. Follower with Input Current Limit

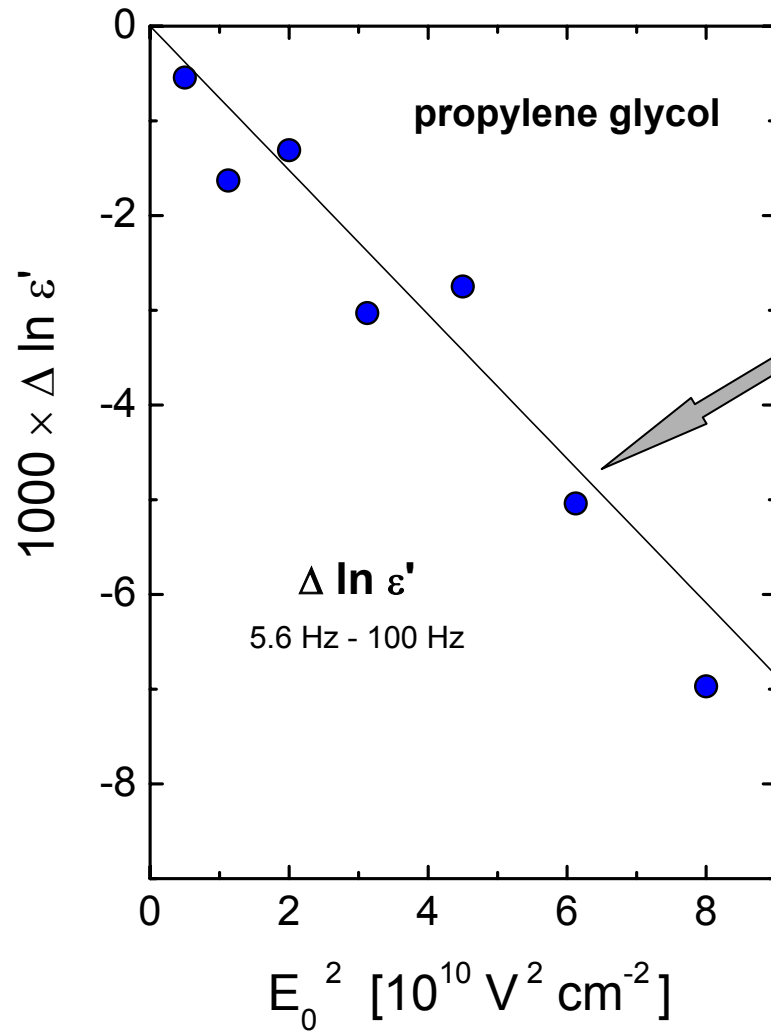


$R_{PROTECT} = 3 \text{ M}\Omega$:
protects against 300 V (no time limit)

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

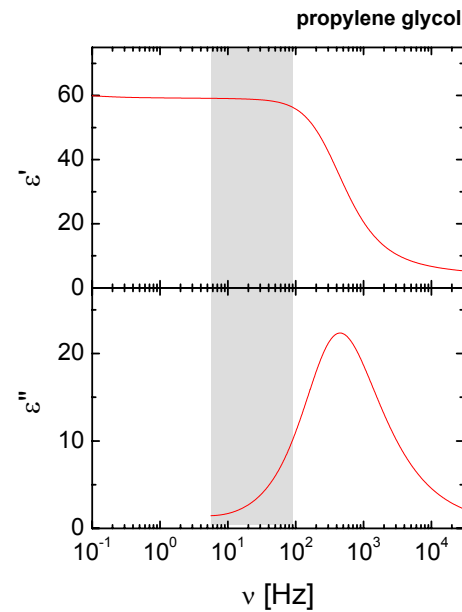
S. Weinstein, R. Richert, J. Phys.: Condens. Matter 19 (2007) 205128

field effect results for propylene glycol
[71 - 282 kV/cm steady state harmonic measurement]



$$\frac{\Delta \epsilon_s}{E^2} = -\frac{N\mu^4}{45\epsilon_0 V (kT)^3} \times \frac{\epsilon_s^4 (\epsilon_\infty + 2)^4}{(2\epsilon_s + \epsilon_\infty)^2 (2\epsilon_s^2 + \epsilon_\infty^2)}$$

(van Vleck)



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

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

energy absorbtion

(less) expected non-linearity: sample heating via dielectric loss

$$\frac{q_{eq}}{\nu} = \pi \epsilon_0 E_0^2 \epsilon''(\omega)$$

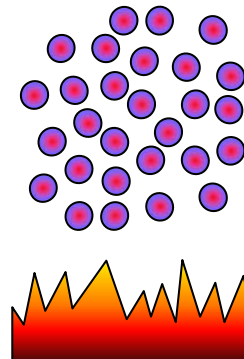
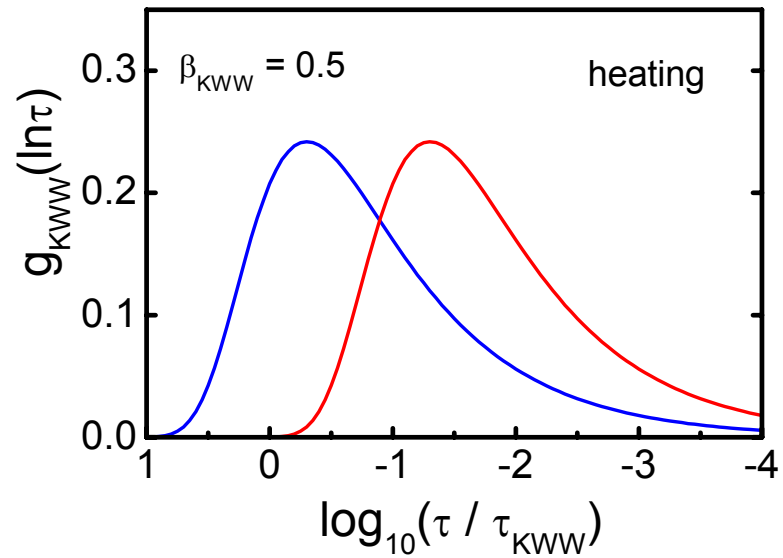
$$\epsilon'' \approx 10$$

$$E_0 = 28.2 \text{ MVm}^{-1}$$

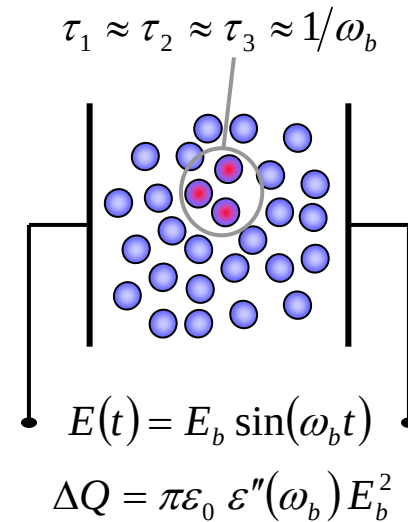
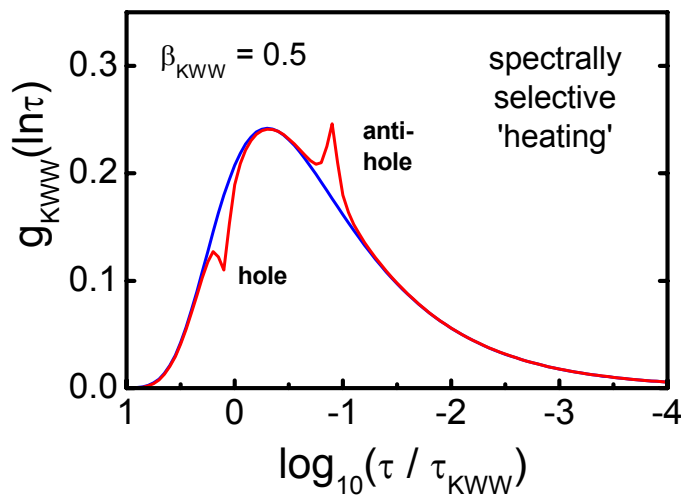
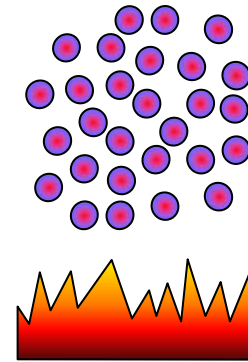
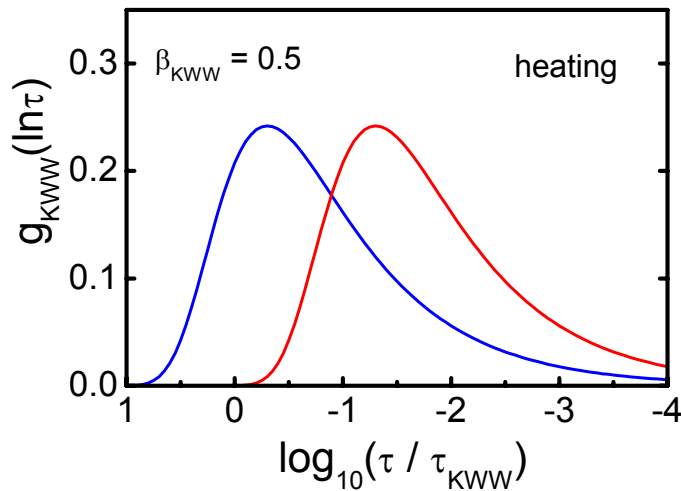
$$\frac{q_{eq}}{\nu} = 0.22 \text{ J cm}^{-3}$$

$$\frac{c_p}{\nu} \approx 2 \text{ J K}^{-1} \text{ cm}^{-3}$$

$$\Delta T = \frac{q_{eq}}{c_p} \approx 0.1 \text{ K}$$



spectrally selective dielectric experiments

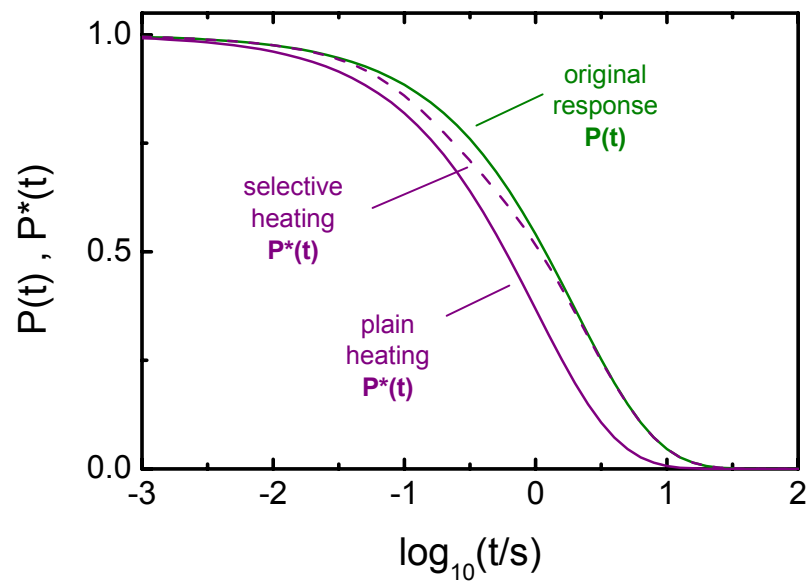
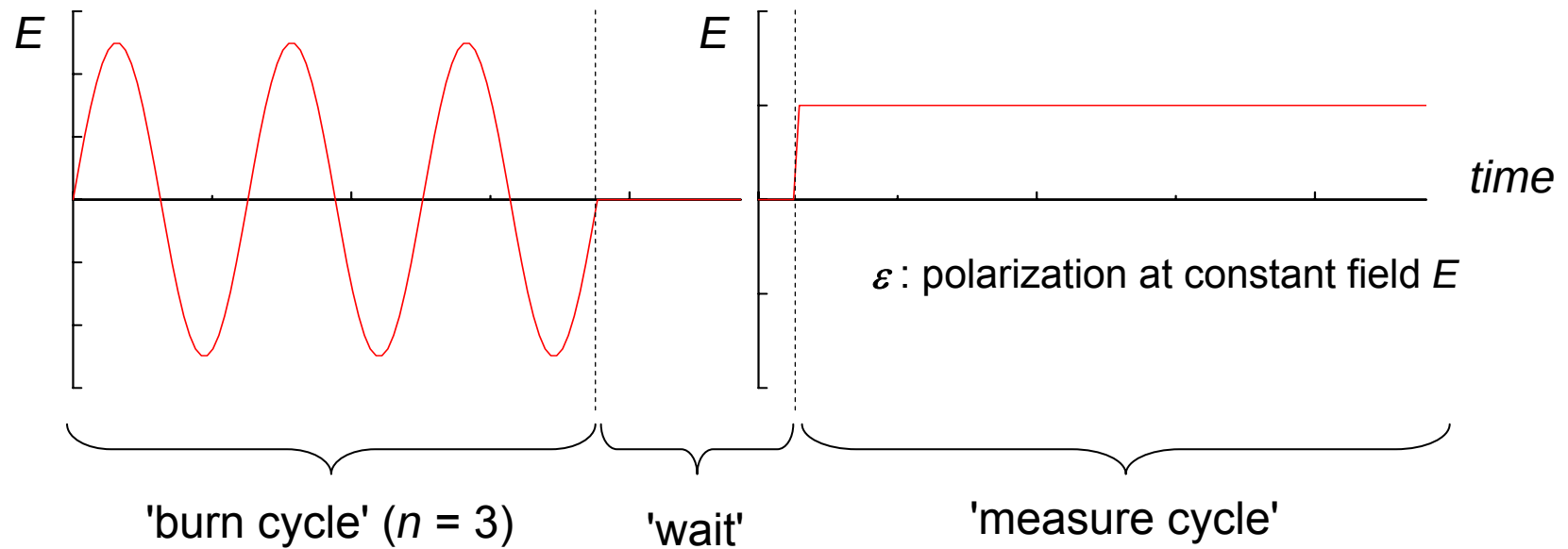


B. Schiener, R. Böhmer, A. Loidl, R. V. Chamberlin, *Science* 274 (1996) 752

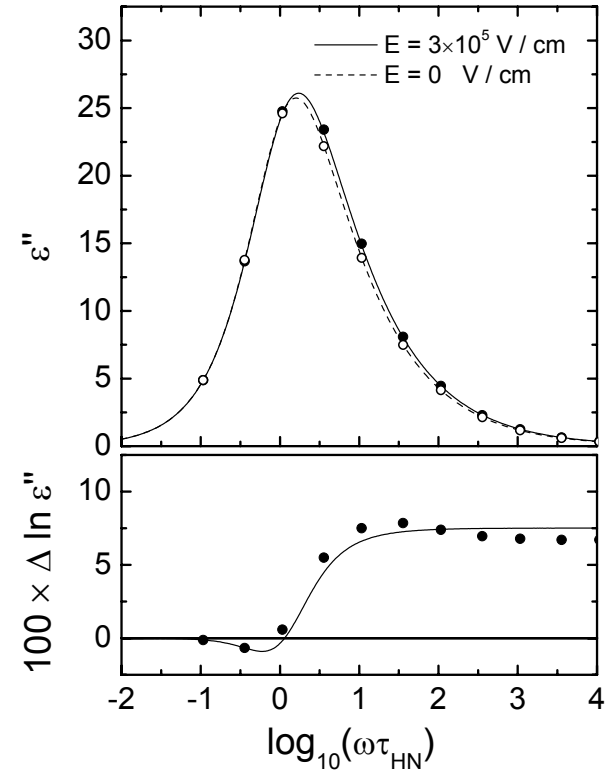
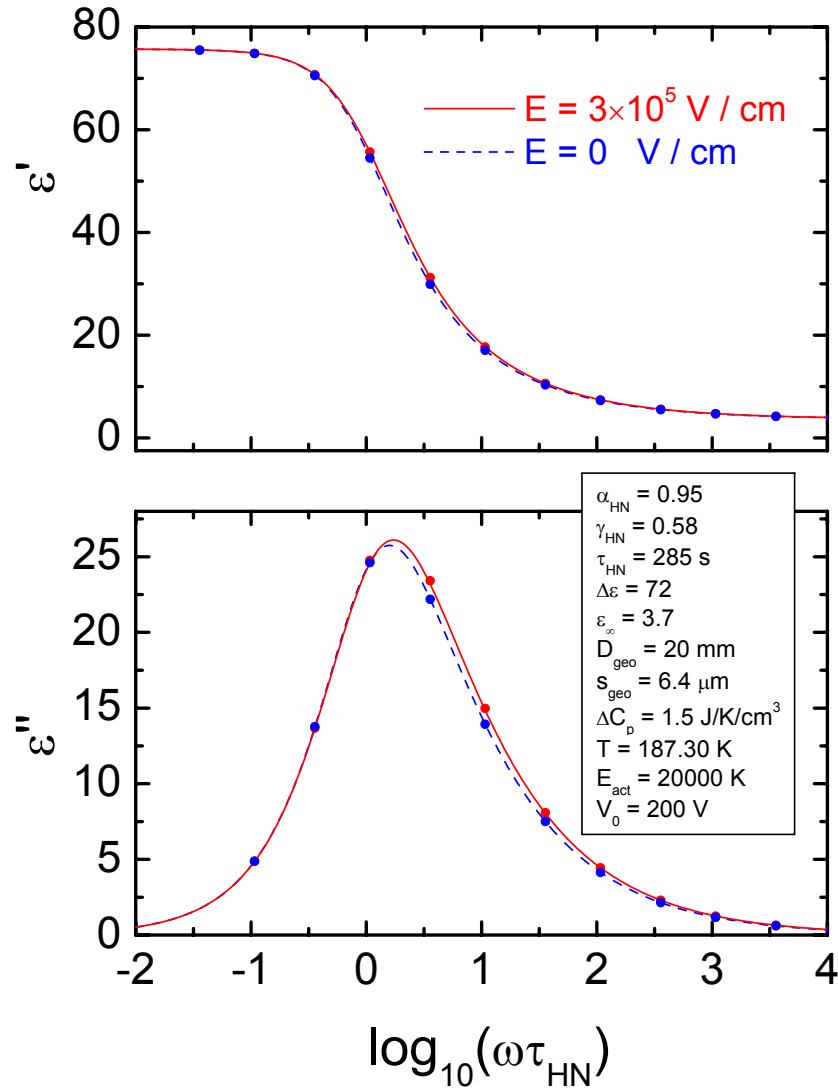
B. Schiener, R. V. Chamberlin, G. Diezemann, R. Böhmer, *J. Chem. Phys.* 107 (1997) 7746

R. V. Chamberlin, B. Schiener, R. Böhmer, *Mat. Res. Soc. Symp. Proc.* 455 (1997) 117

dielectric hole-burning technique: what do we look for?

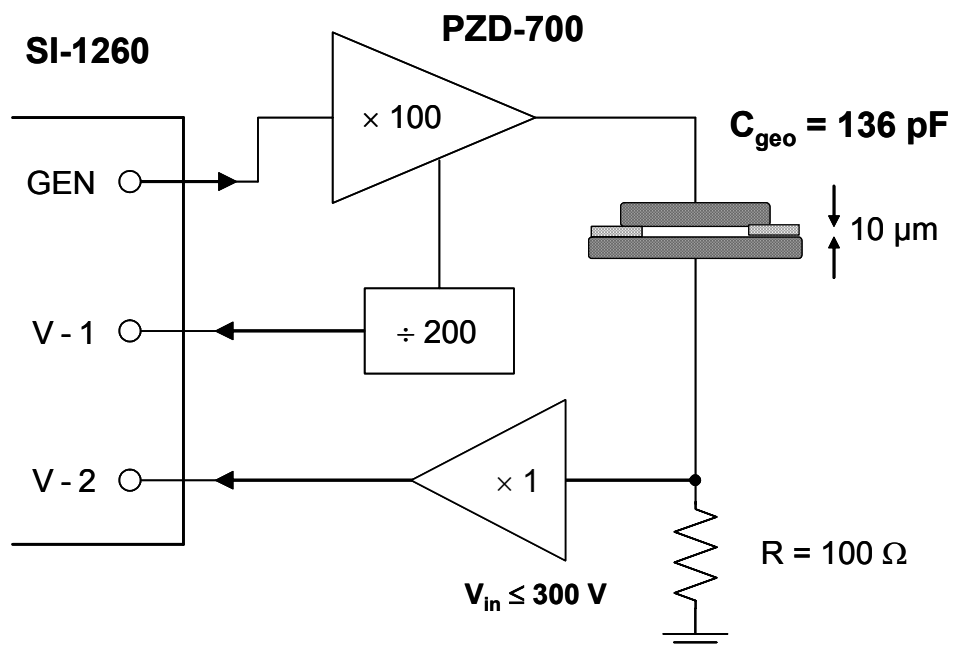


model prediction for 300 kV/cm steady state harmonic field



high field impedance

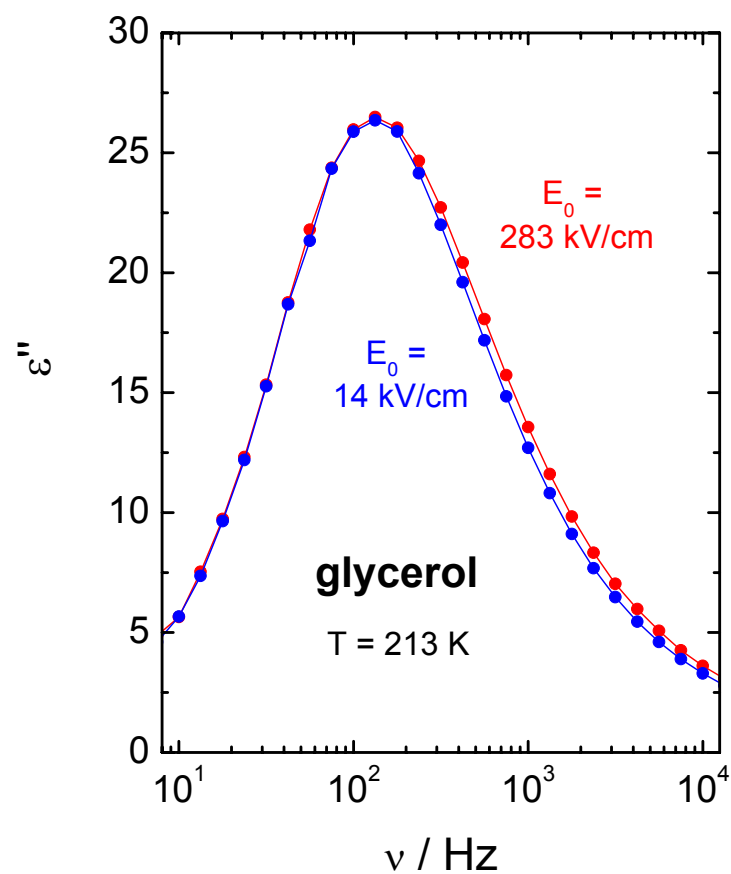
high field impedance technique



fields up to 450 kV/cm

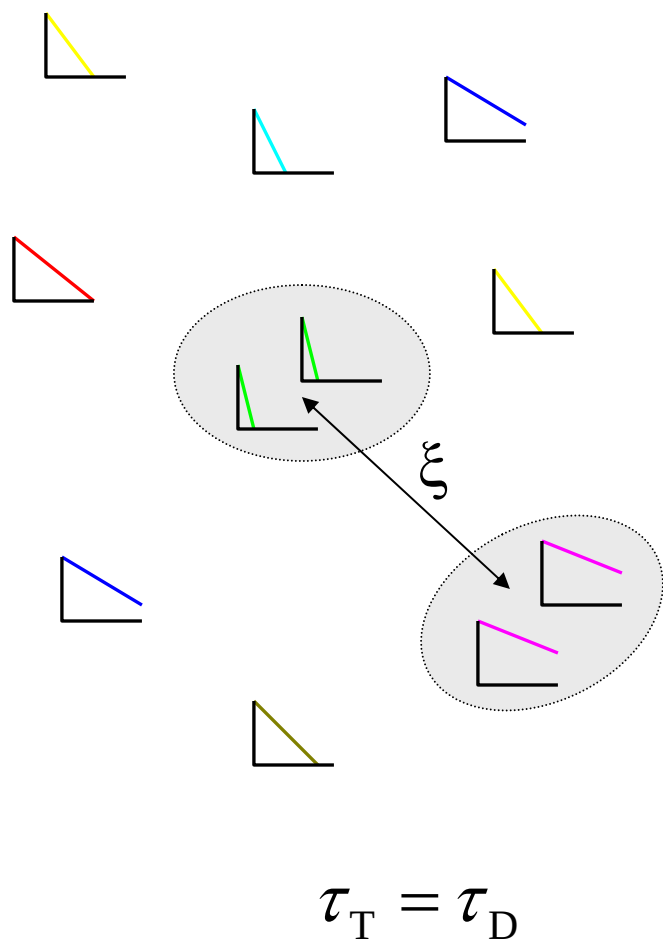
μE up to 0.082 kT

0.1 Hz to 50 kHz range

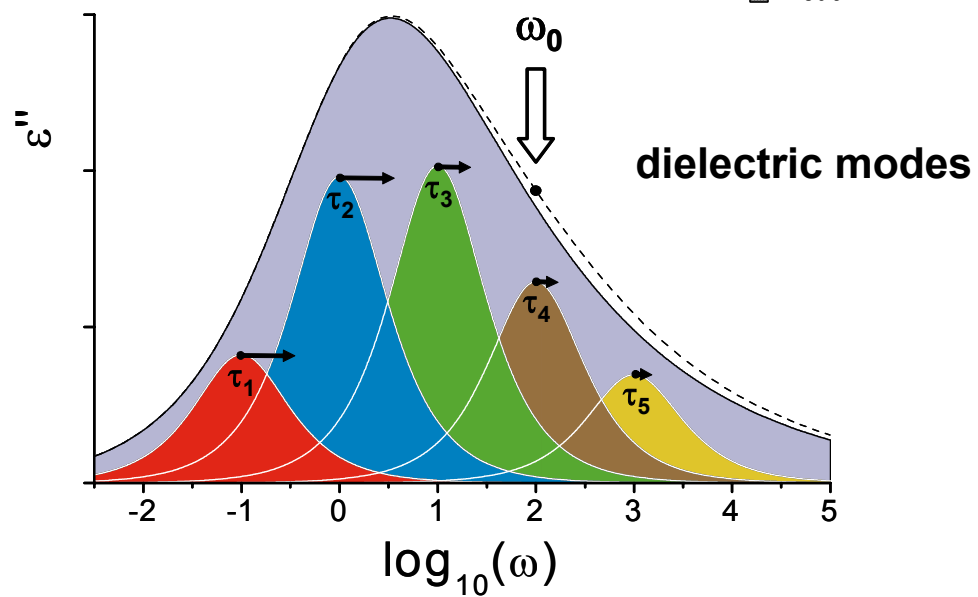
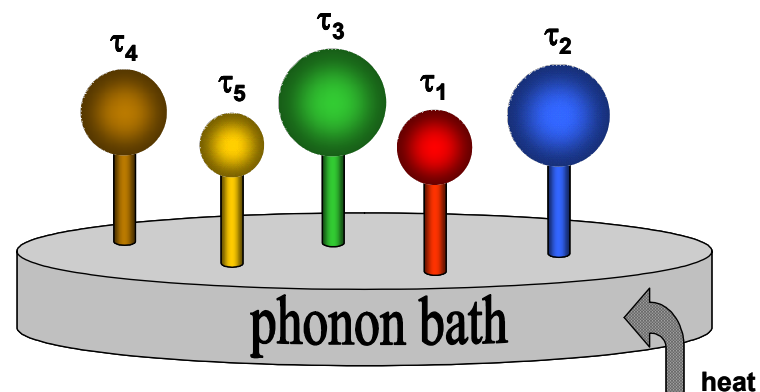


heterogeneous dynamics and configurational temperatures

dynamically correlated domains



calorimetric modes



model for high-field steady-state harmonic measurement

harmonic field $E_0 \sin(\omega_b t)$ applied:

steady state energy Q/n per period:

$$\frac{Q}{n} = \pi \epsilon_0 E_0^2 \epsilon''(\omega) V$$

power p averaged over period:

$$p = \frac{Q\omega}{2\pi} = \frac{\epsilon_0 E_0^2 \epsilon''(\omega) V \omega}{2}$$

excess configurational temperature:

$$\frac{dT_{cfg}}{dt} = \frac{p}{c_p} - \frac{T_{cfg} - T}{\tau_T} = 0 \quad \Rightarrow \quad T_{cfg} = T + \frac{\tau_T p}{c_p}$$

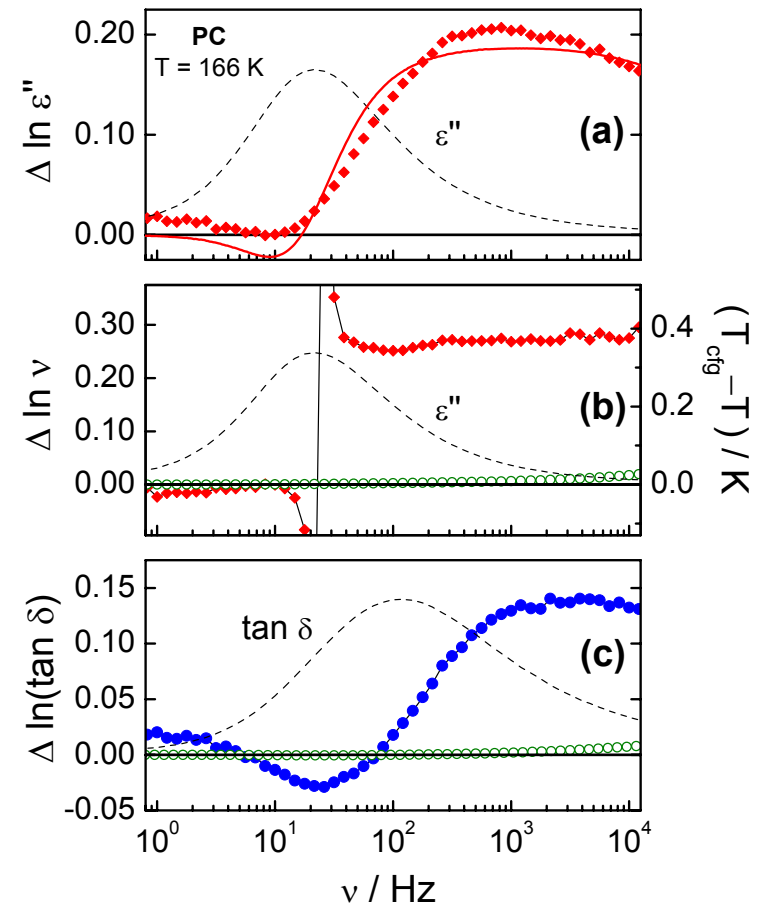
for a single domain with $\tau = \tau_T = \tau_D$:

$$T_{cfg} = T + \frac{\epsilon_0 E_0^2 \Delta \epsilon}{2 \Delta c_p} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}$$

analogous to 'box'-model:

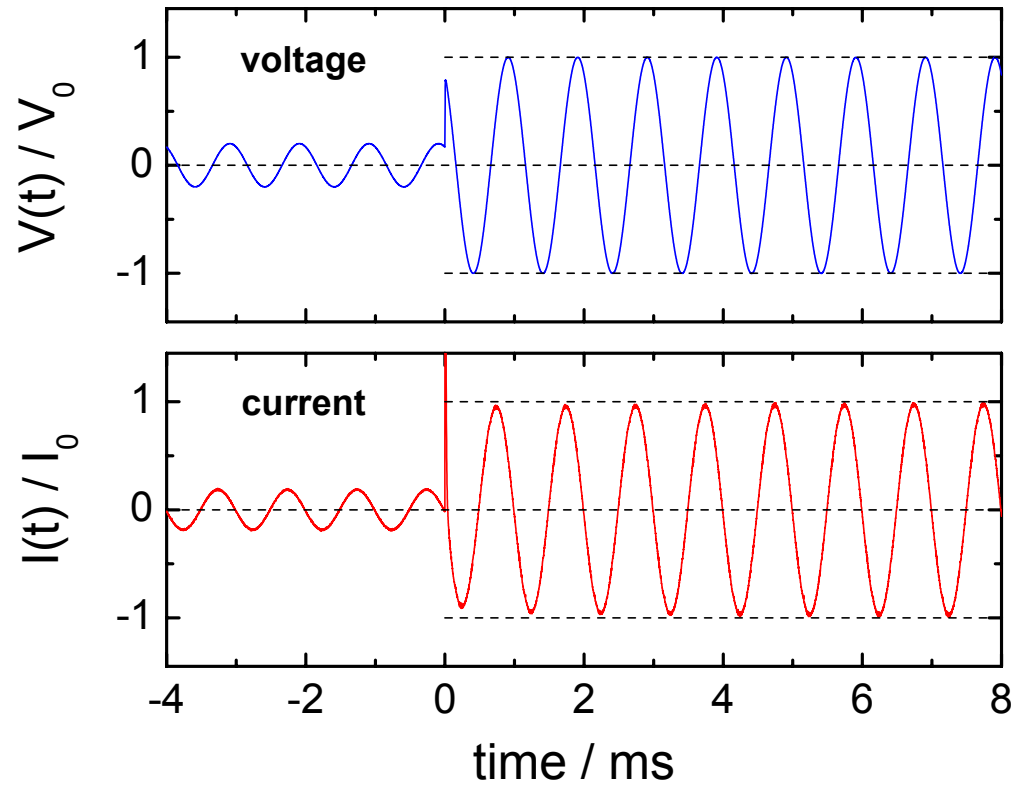
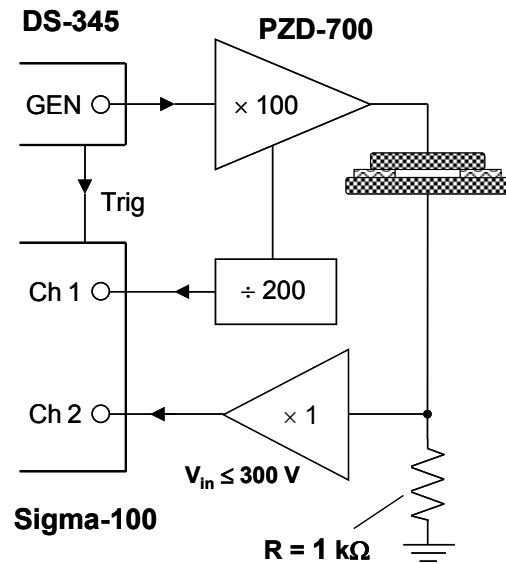
B. Schiener, R. Böhmer, A. Loidl, R. V. Chamberlin,
Science 274 (1996) 752

propylene carbonate
($E_0 = 177$ kV/cm)



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

adding time-resolution capabilities to high-field technique



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

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

$$= A \cos(\varphi)$$

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

$$= A \sin(\varphi)$$

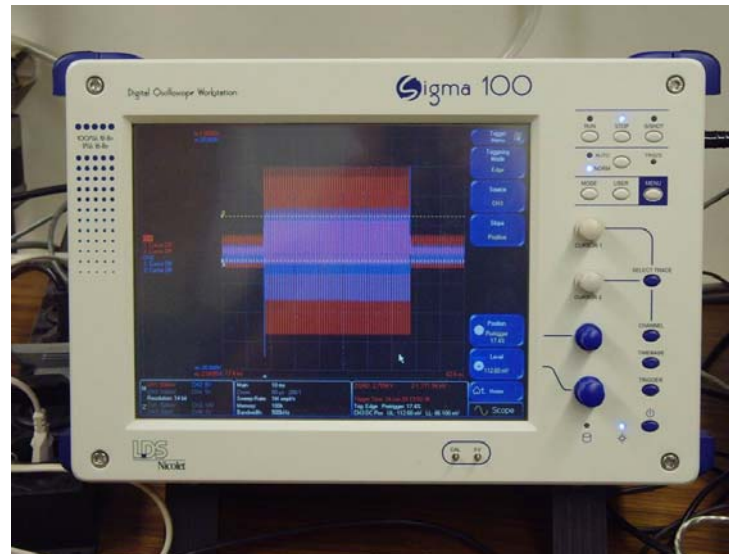
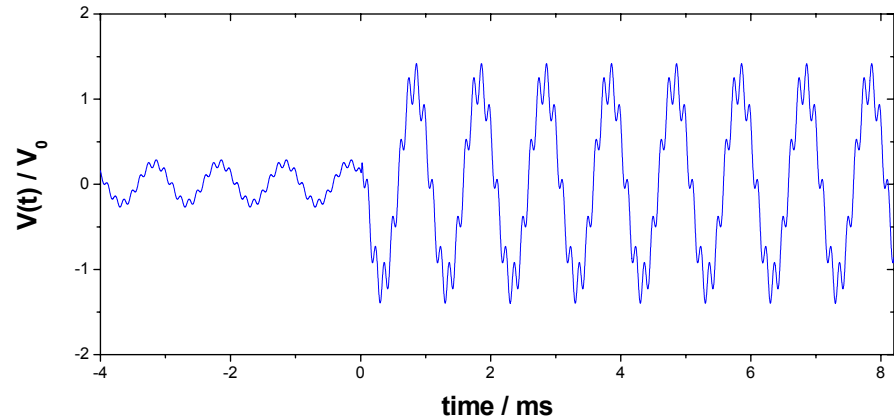
$$A = \sqrt{R^2 + I^2} \quad \varphi = \arctan\left(\frac{I}{R}\right)$$

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

single/multiple frequency technique



Stanford Research DS-345 Generator



Nicolet Sigma 100 Digital Oscilloscope

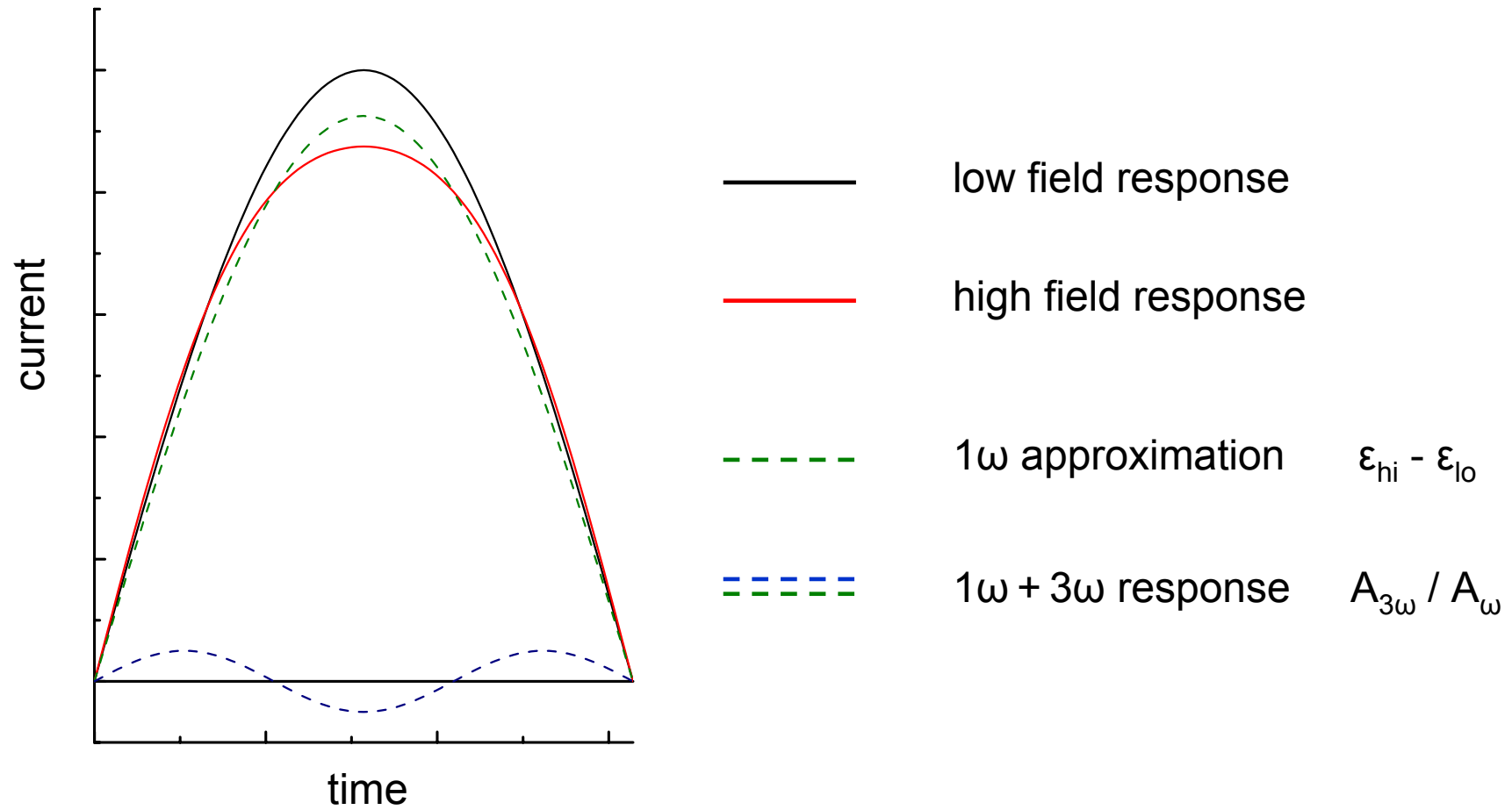
4 channels

1 Ms depth

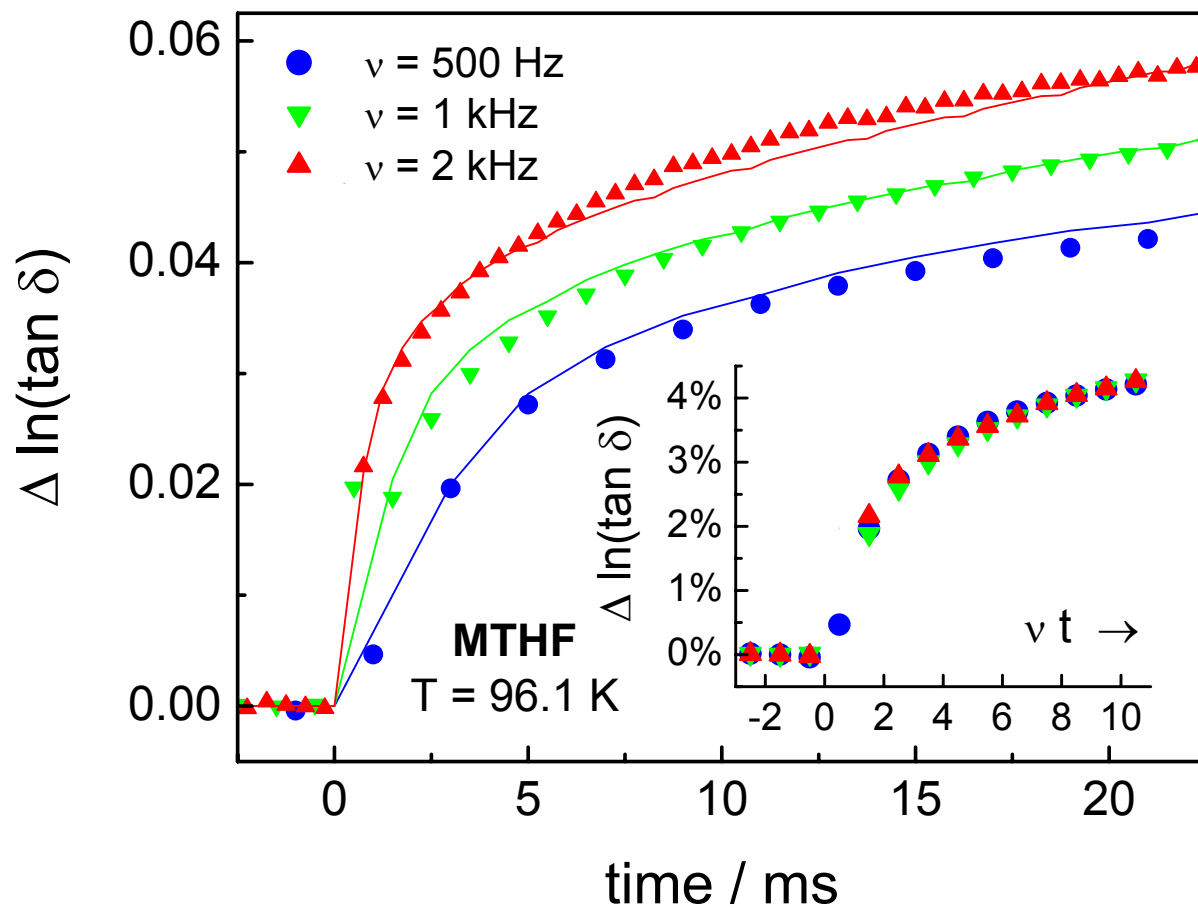
12 bit @ 100 Ms/s

14 bit @ 1 Ms/s

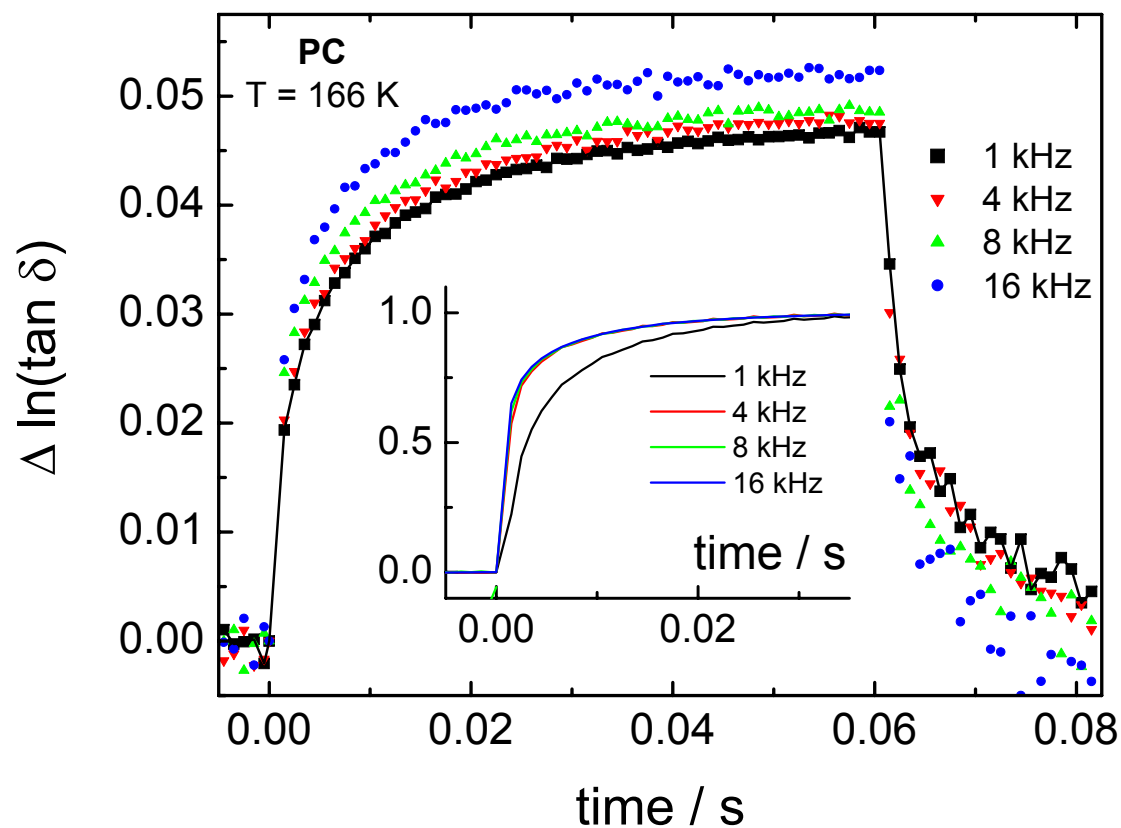
1 ω versus 3 ω data analysis



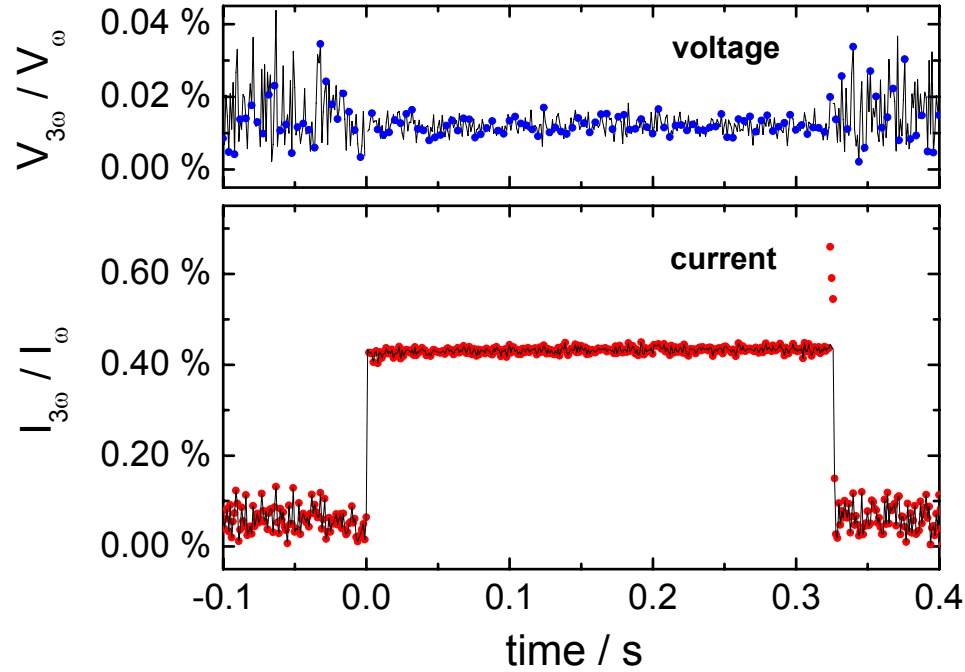
rise of configurational temperature for different frequencies



rise of configurational temperature for pumping with 1 kHz and probing at higher frequencies



3 ω signal during field change



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

$$\begin{aligned} D_0 &= \varepsilon \varepsilon_0 E_0 + \lambda \varepsilon \varepsilon_0 E_0^3 \\ &= \varepsilon \varepsilon_0 E_0 \times (1 + \lambda E_0^2) \\ \lambda &= \Delta \ln \varepsilon / E_0^2 \end{aligned}$$

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

$$D_\omega(t) = \varepsilon \varepsilon_0 E_0 \sin(\omega t) + \lambda \varepsilon \varepsilon_0 E_0^3 \frac{3}{4} \sin(\omega t)$$

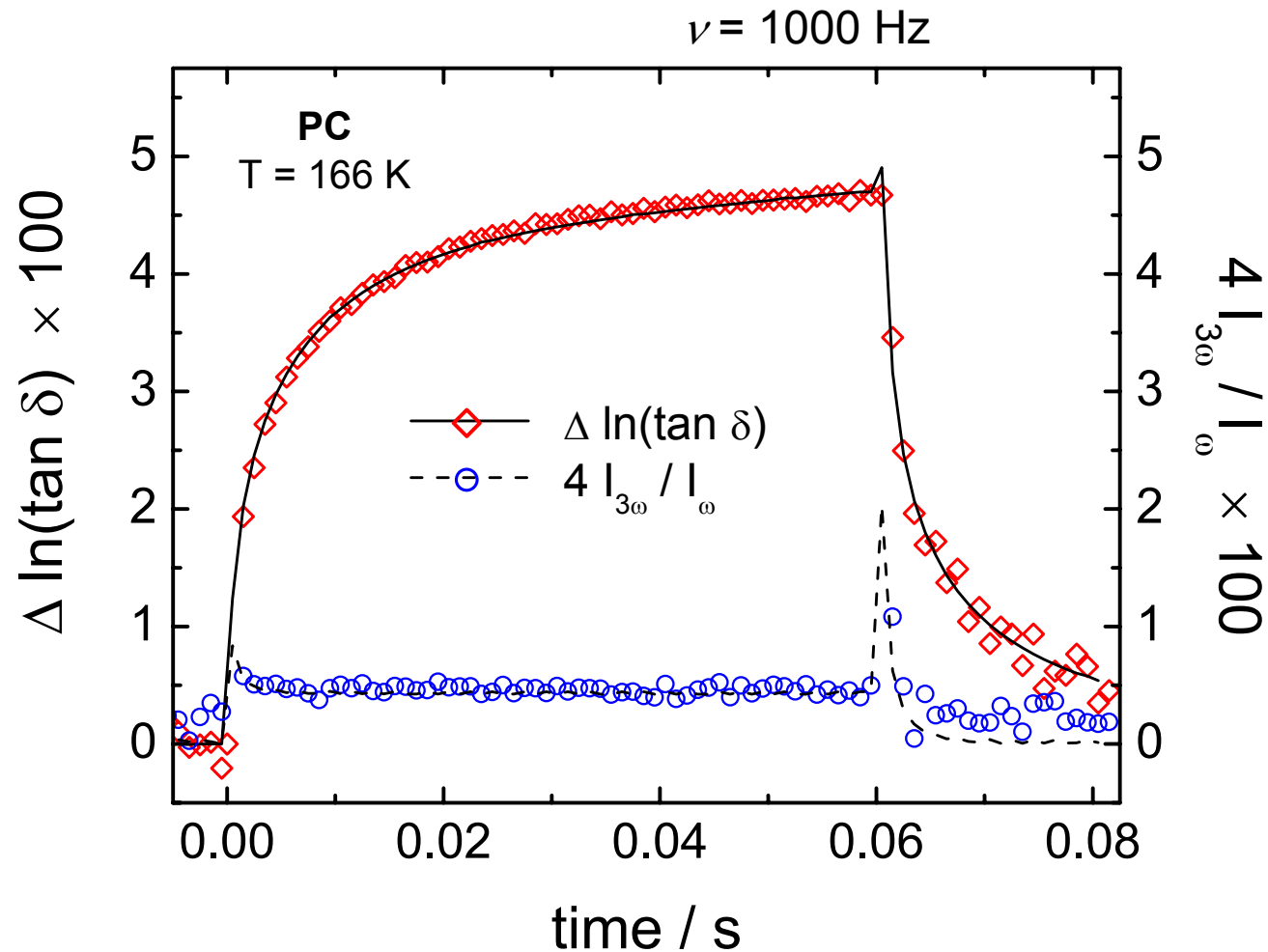
$$\Rightarrow A_\omega \approx \varepsilon \varepsilon_0 E_0$$

$$D_{3\omega}(t) = -\lambda \varepsilon \varepsilon_0 E_0^3 \frac{1}{4} \sin(3\omega t)$$

$$\Rightarrow A_{3\omega} = \frac{1}{4} \varepsilon \varepsilon_0 E_0 \Delta \ln \varepsilon$$

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

agreement between experiment and model



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

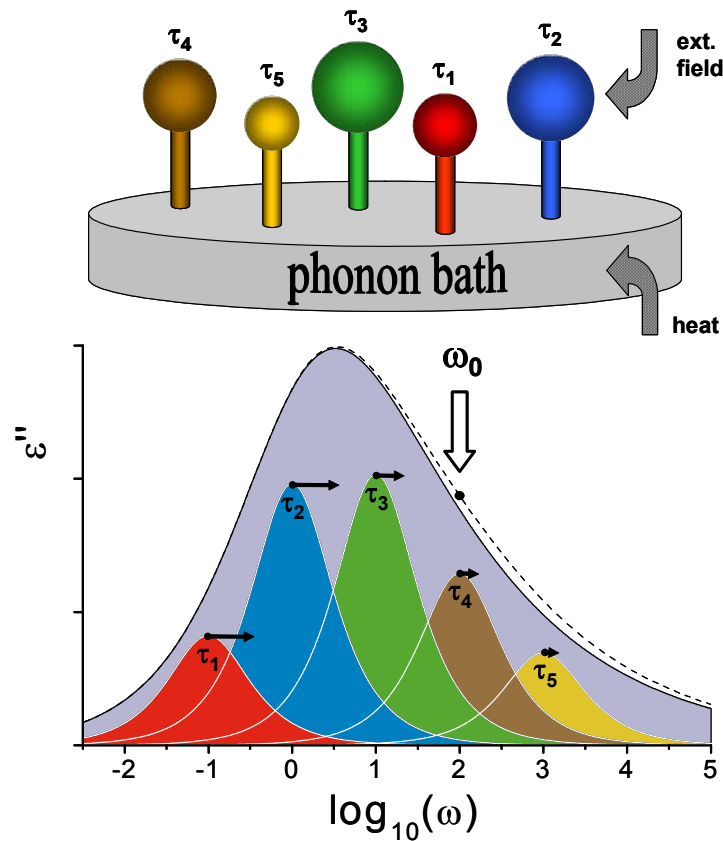
$$I = \frac{\omega}{\pi} \int_0^{2\pi/\omega} \cos(n\omega t) S(t) dt$$

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

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

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

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 :

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

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

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

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

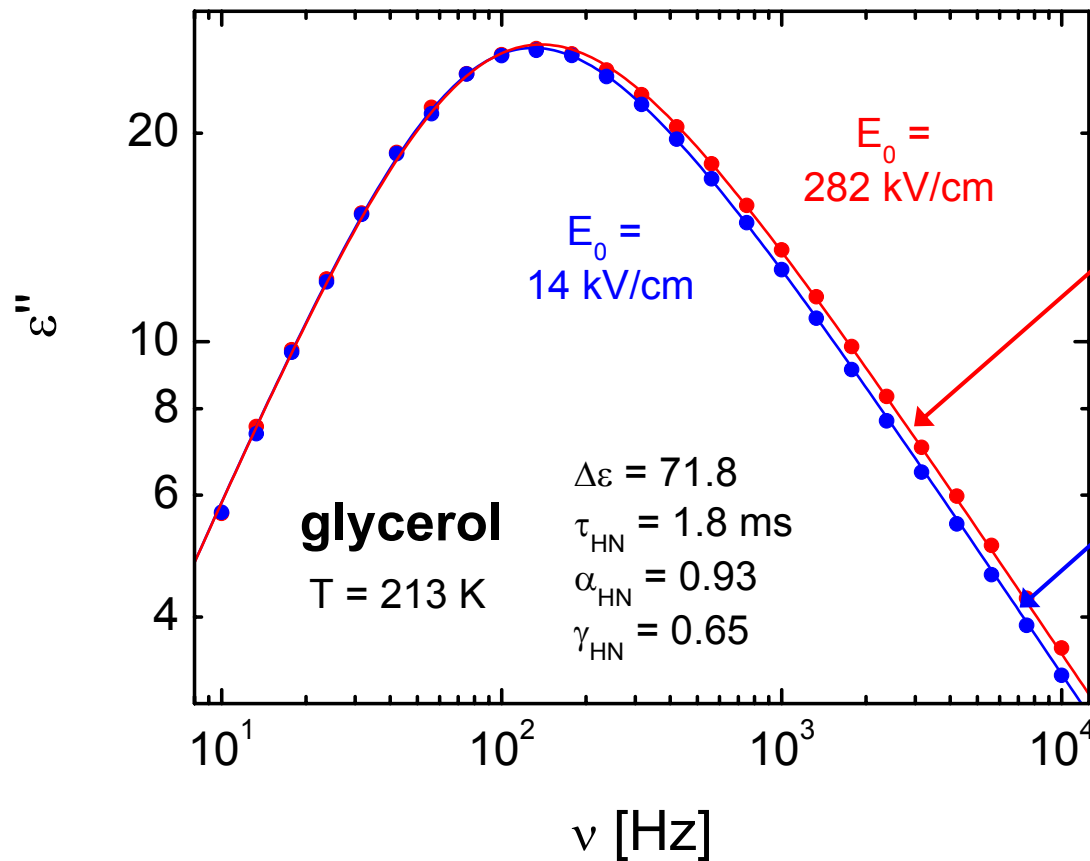
$$\frac{dT}{dt} = \sum_i \frac{T_i(t) - T}{\tau_i(t)} \frac{\Delta C_{p,i}}{C_{p,\infty}} \text{ for adiabatic case}$$

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

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

what do we learn ?

high voltage impedance results for glycerol



current model:

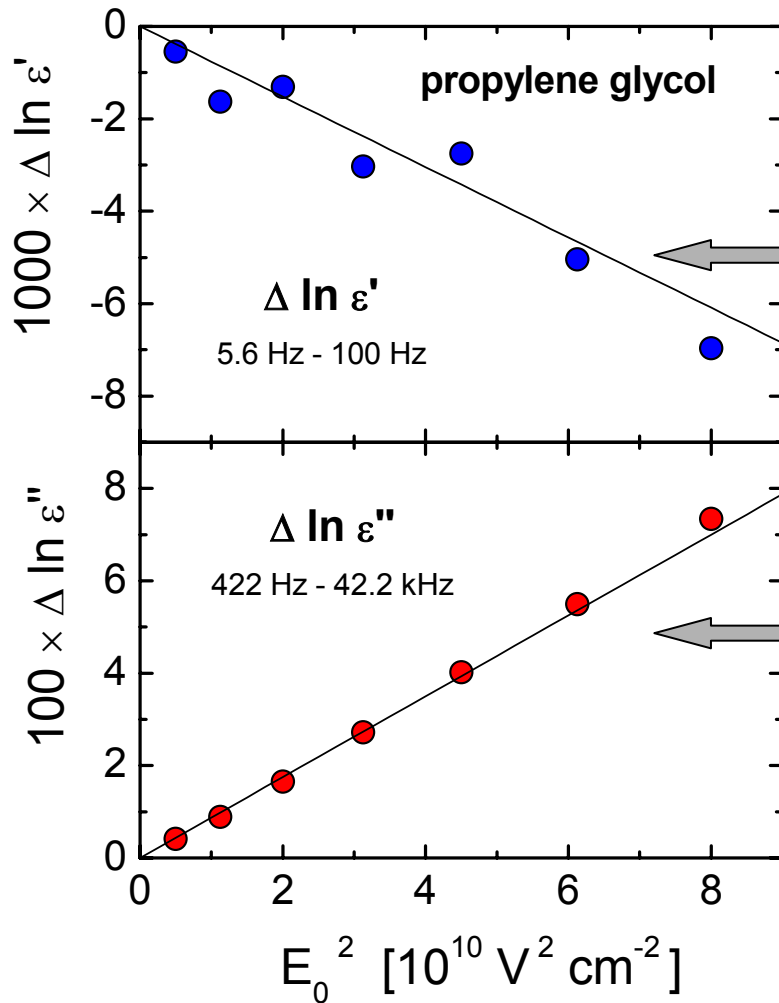
$$\ln \tau^* = \ln \tau - \frac{T_A}{T^2} \times \frac{\epsilon_0 E_0^2 \Delta\epsilon}{2\Delta c_p} \times \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}$$

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

Havriliak - Negami fit :

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{\left[1 + (i\omega\tau)^\alpha\right]^\gamma}$$

summary of relevant non-linear effects ($\sim E^2$)



Coulombic stress :

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

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

dielectric saturation :

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

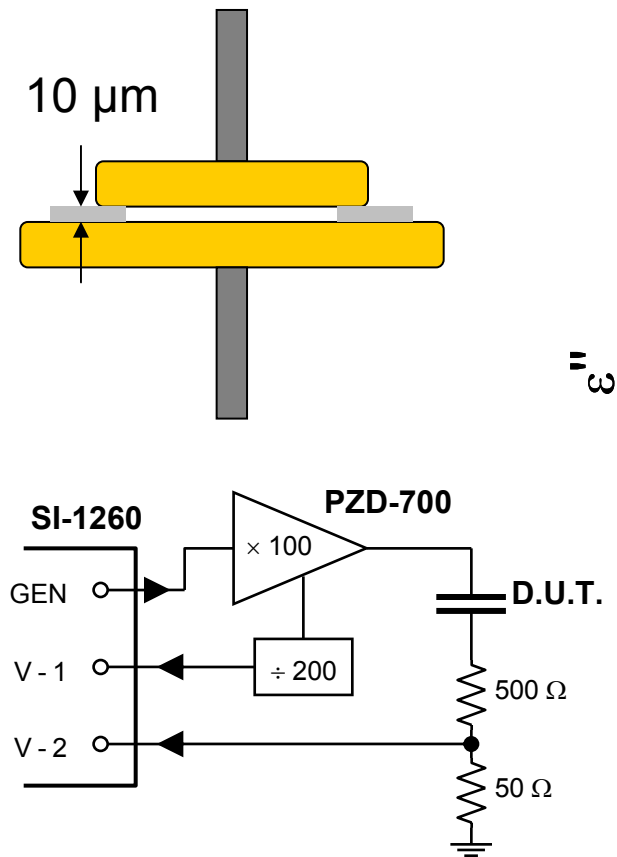
(van Vleck)

energy absorption :

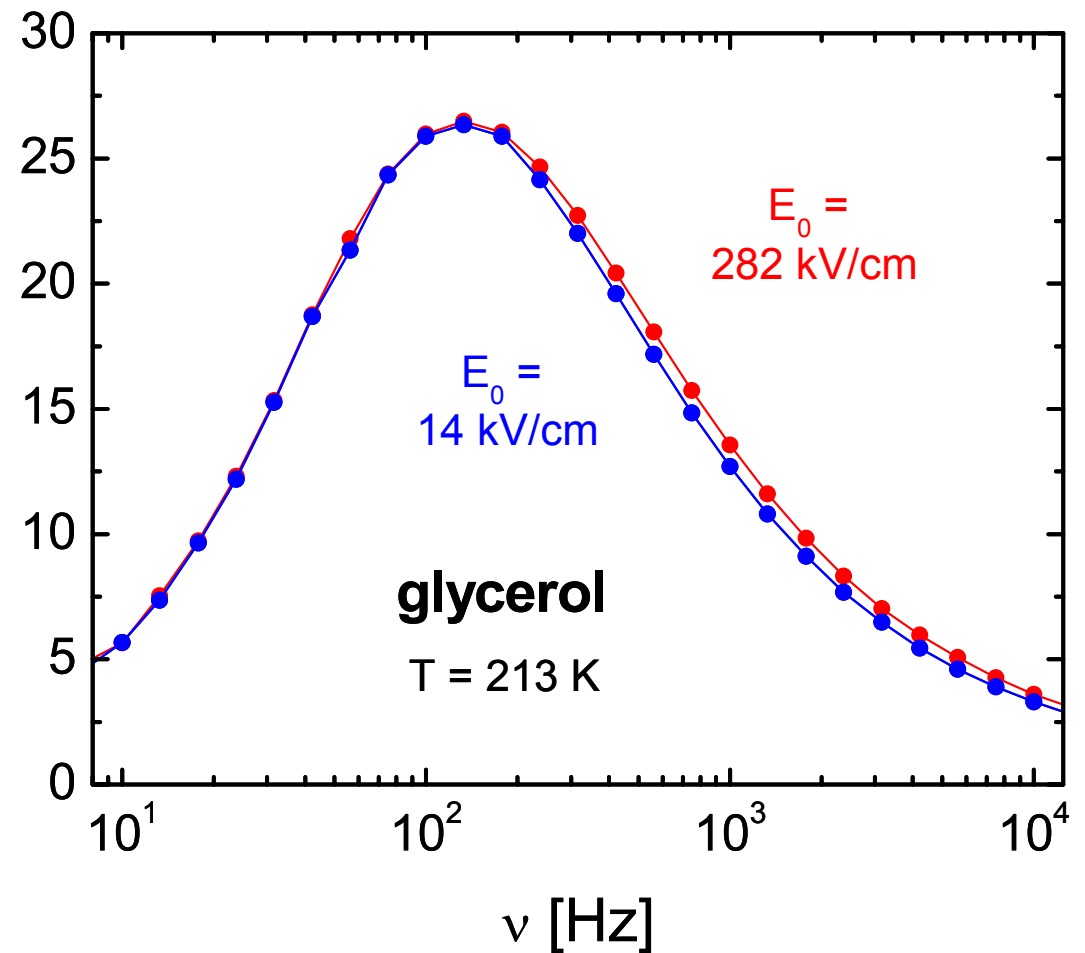
$$T_e(\tau) = \frac{\varepsilon_0 E_0^2 \Delta \varepsilon}{2\Delta C_p} \times \frac{\omega_0^2 \tau^2}{1 + \omega_0^2 \tau^2} = T_e^0 \times \frac{\omega_0^2 \tau^2}{1 + \omega_0^2 \tau^2}$$

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

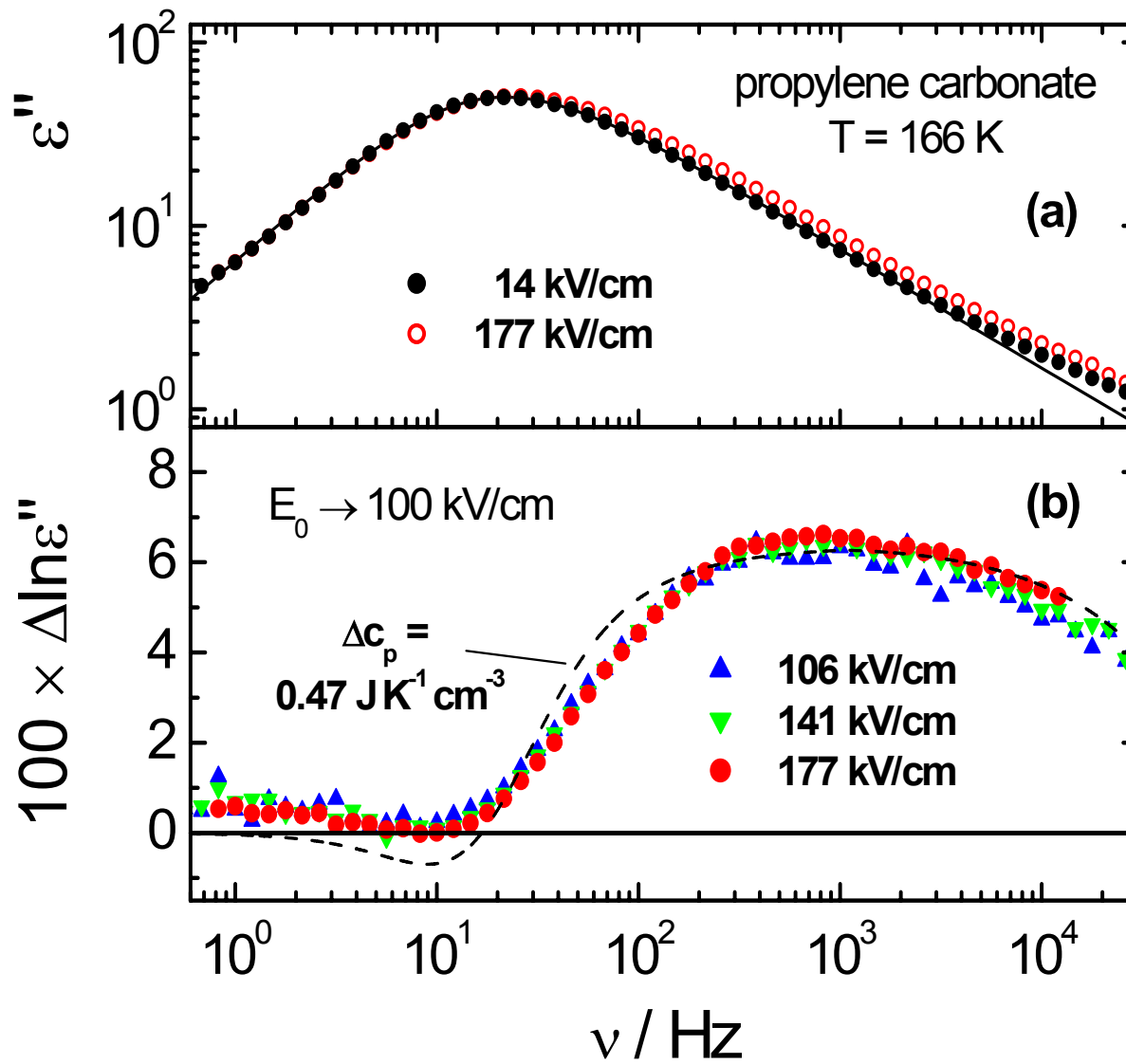
continuous harmonic (impedance) measurement (glycerol)



$$\left. \begin{array}{l} \mu_{\text{GLY}} = 2.56 \text{ D} \\ E = 28.2 \text{ MVm}^{-1} \\ T = 213 \text{ K} \end{array} \right\} \frac{\mu E}{kT} = 0.082$$



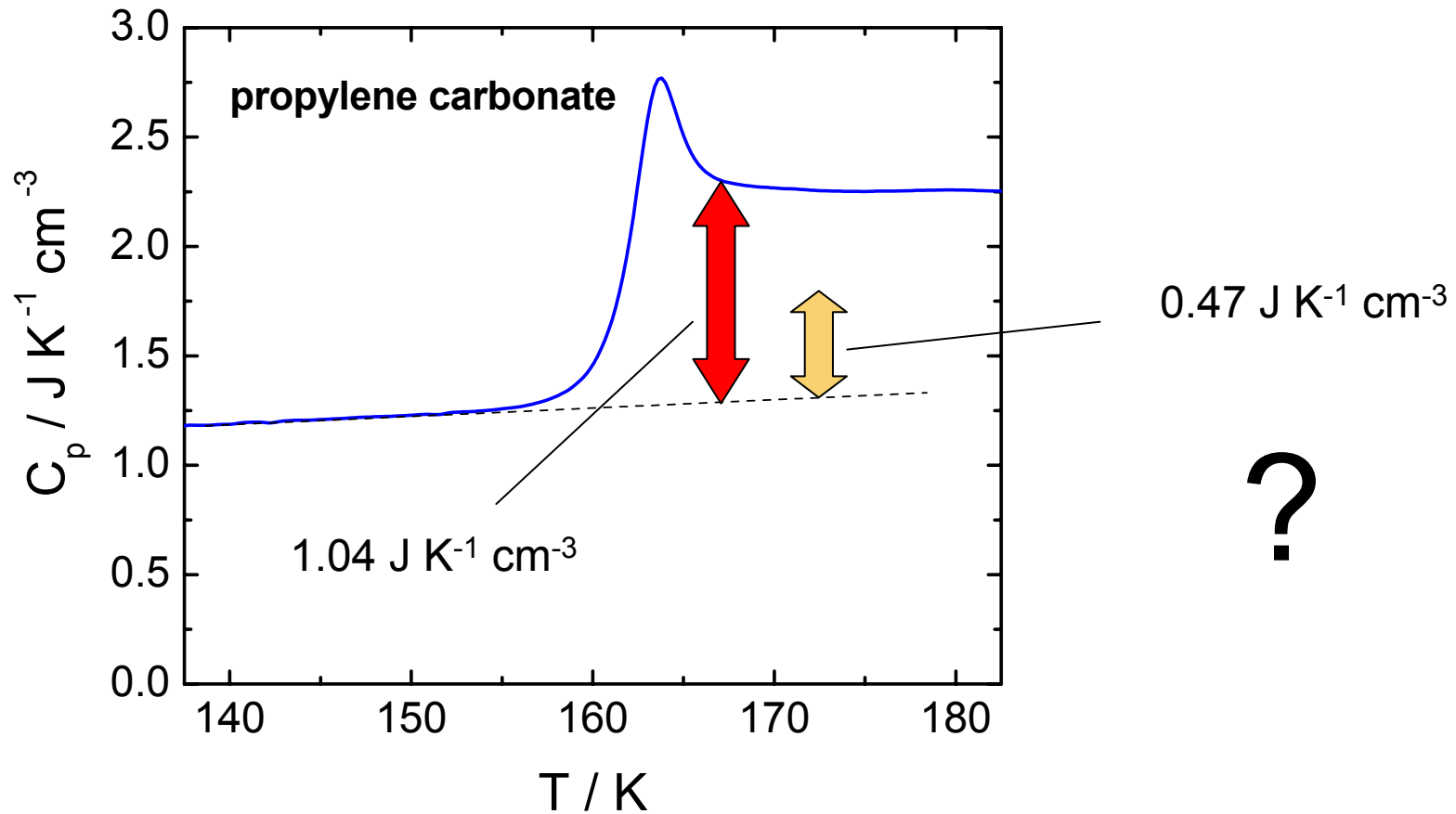
the case of propylene carbonate



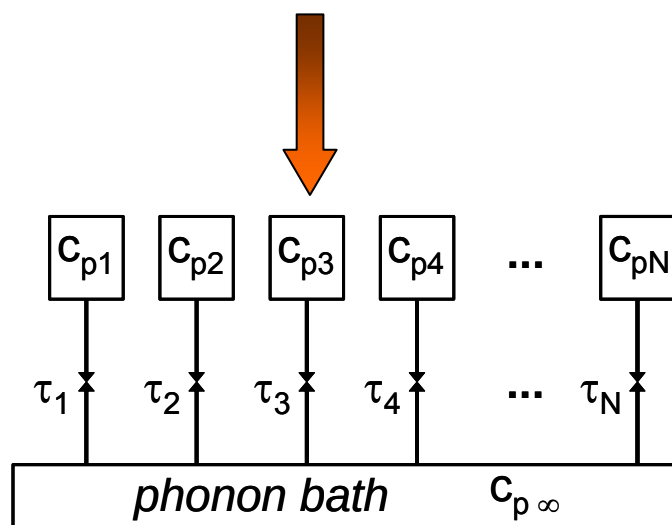
loss increases
by up to 20 %
at electric field
of 177 kV/cm

$$\Delta T_{\text{cfg}} = 0.185 \text{ K}$$

differential scanning calorimetry of propylene carbonate



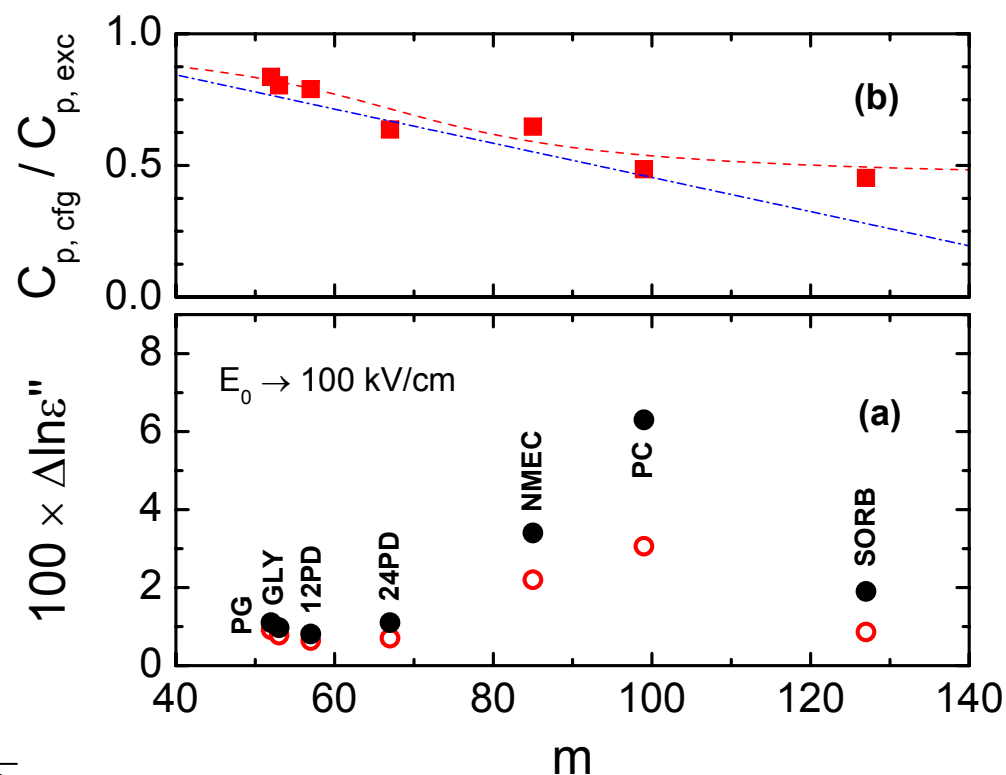
measuring the configurational heat capacity



current model:

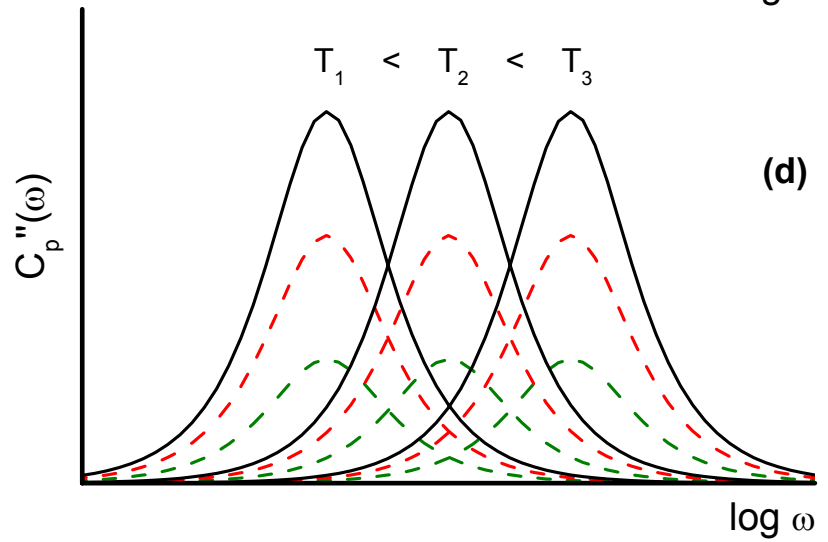
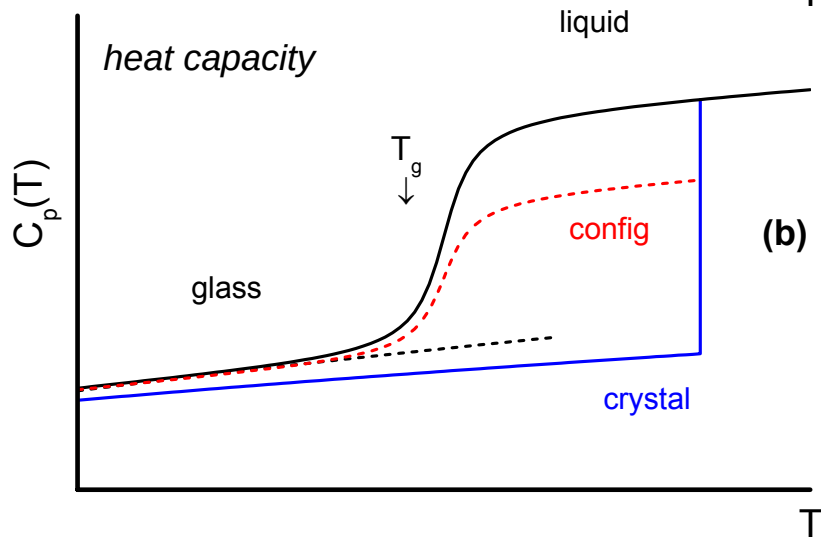
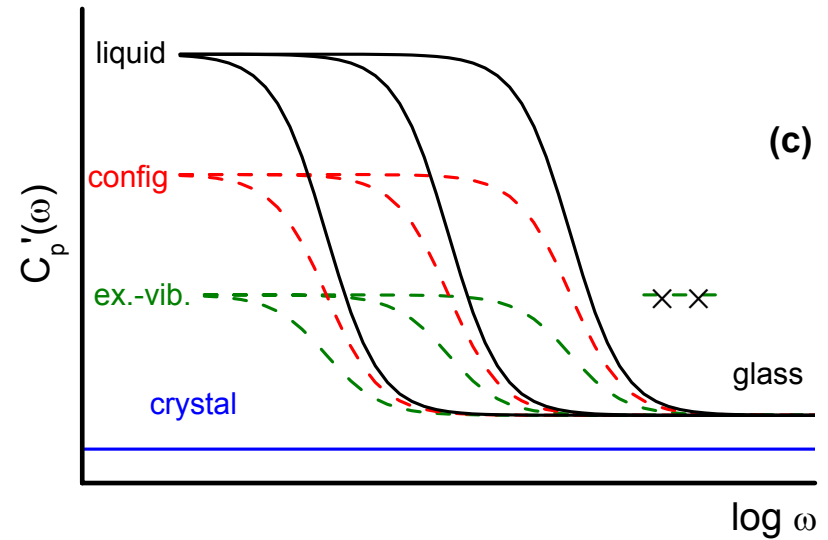
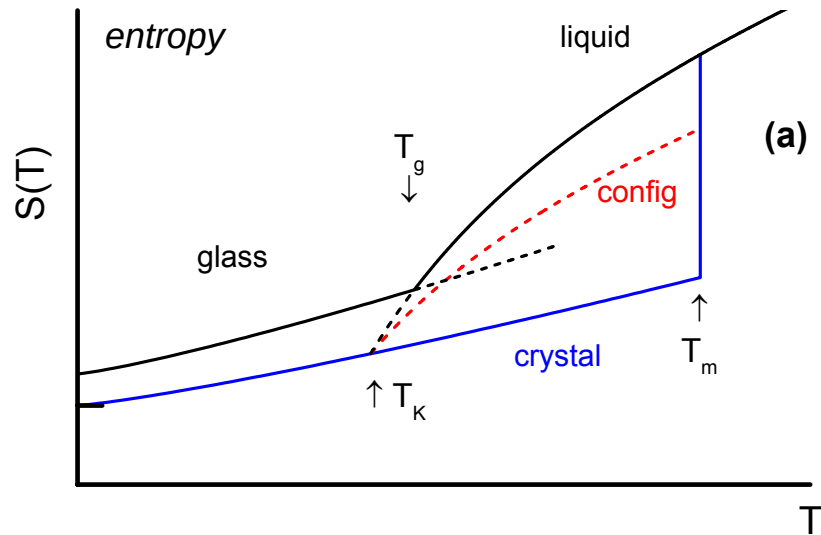
$$\ln \tau_D^* = \ln \tau_D - \frac{T_A}{T^2} \times \frac{\varepsilon_0 E_0^2 \Delta \varepsilon}{2 \Delta c_p} \times \frac{\omega^2 \tau_D \tau_T}{1 + \omega^2 \tau_D^2}$$

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



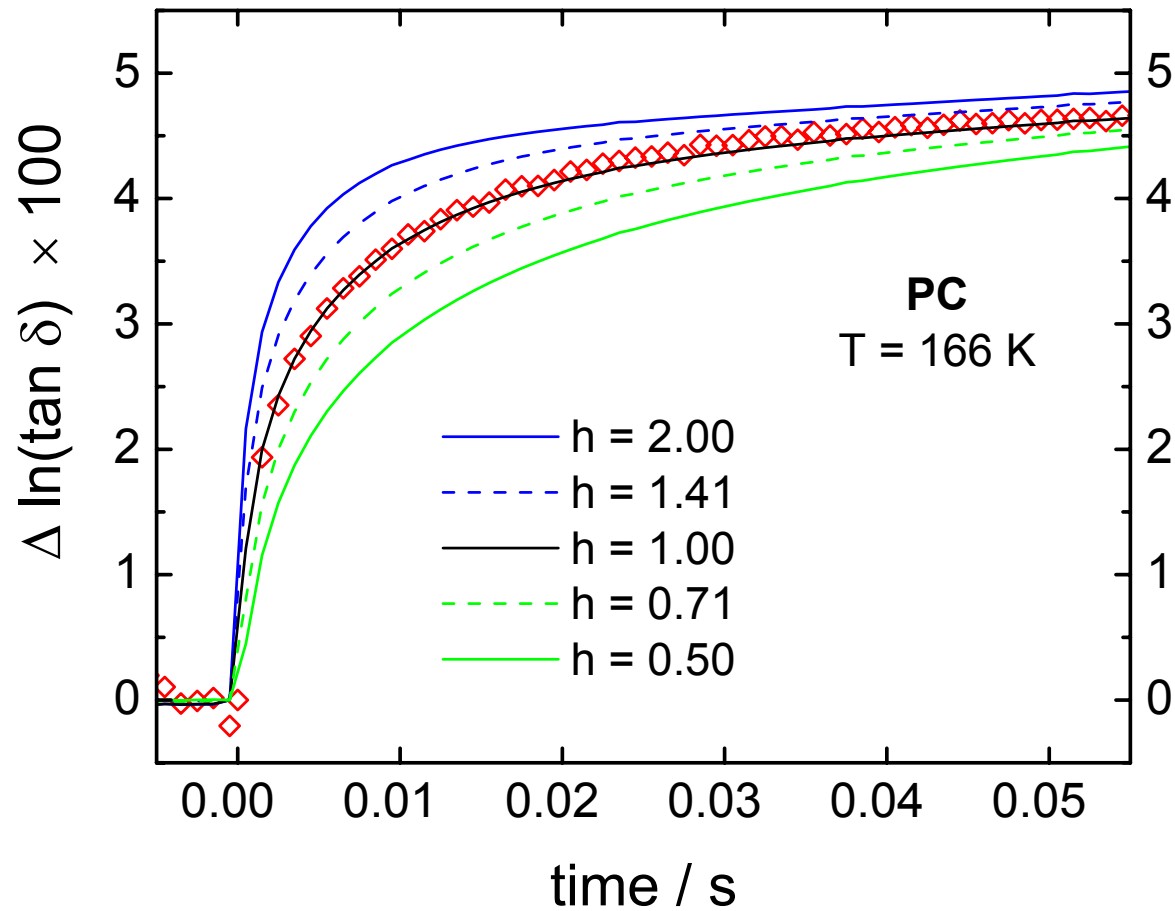
configurational heat capacity

configurational versus excess-vibrational heat capacity



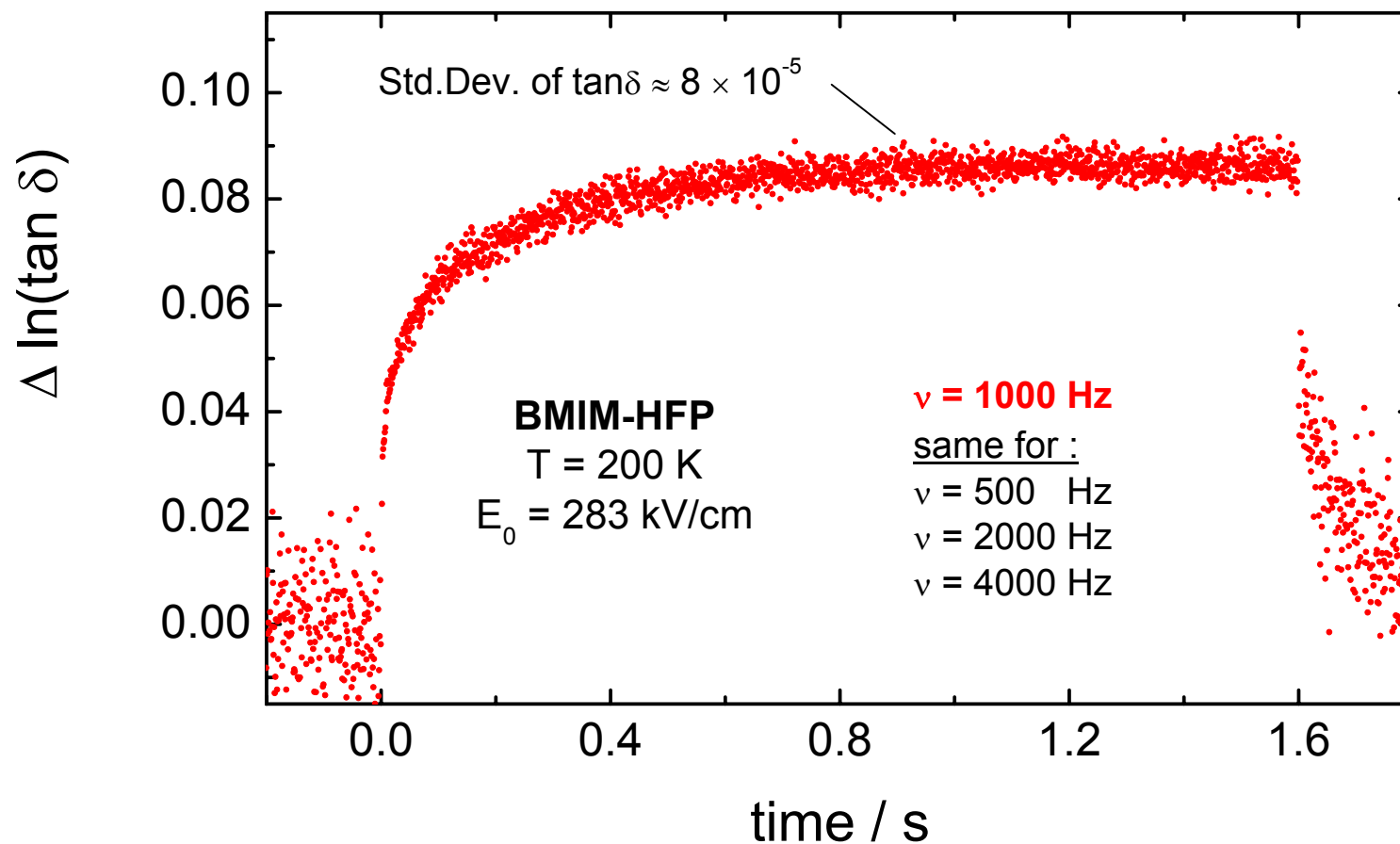
testing the claim: $\tau_T = \tau_D$ versus $\tau_T = \tau_D/h$

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

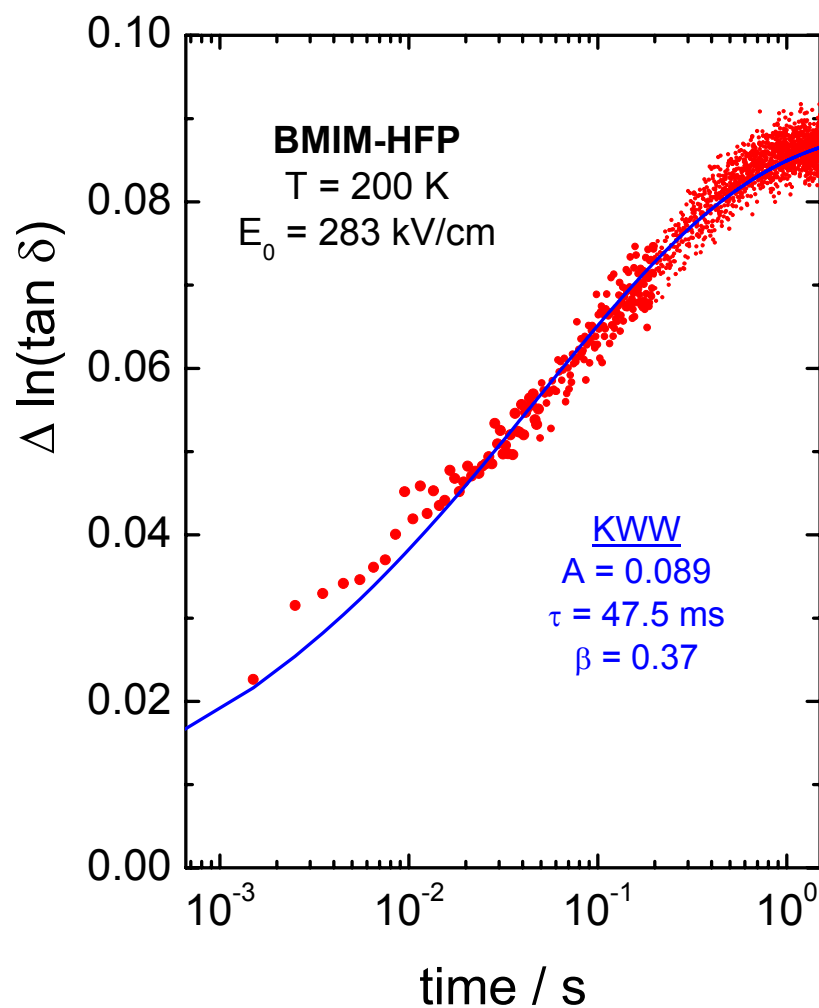
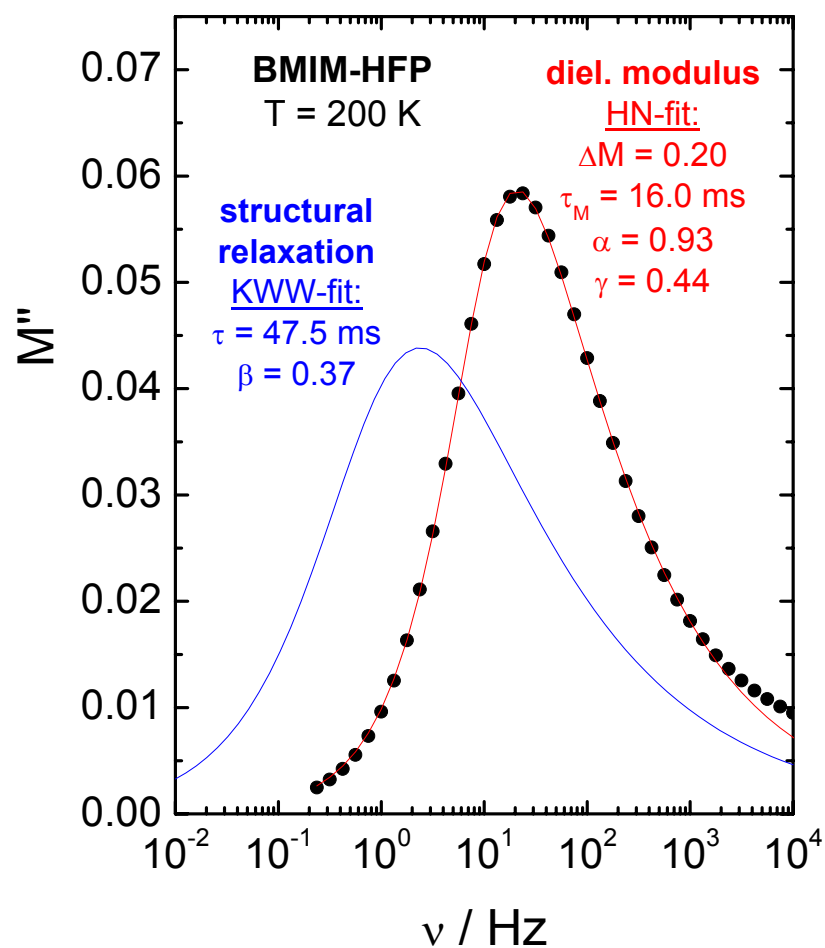


why not look at a RTIL

1-butyl-3-methyl-imidazolium + hexafluorophosphate -



explanation: mild decoupling of τ_M from τ_α



configurational temperature lifetime of Debye peak

