



Nonlinear Dielectric Effects in Simple Fluids

LINEAR RESPONSE - THEORY AND PRACTICE

*Søminestationen, Holbæk, Denmark
1 - 8 July 2007*

High-Field Dielectric Response:

Coulombic stress

Langevin effect

homogeneous 'heating'

heterogeneous 'heating'

Ranko Richert

definitions of dielectric and electric quantities

V voltage	I current	Q charge
D displacement	E electric field	P polarization
ε dielectric function	M electric modulus	χ susceptibility
j current density	σ conductivity	ρ resistivity

‘permittivity of vacuum’

$$\begin{aligned}\varepsilon_0 &= 8.854 \times 10^{-12} \text{ F m}^{-1} \\ &= 8.854 \times 10^{-12} \text{ A s V}^{-1} \text{ m}^{-1} \\ &= 8.854 \times 10^{-14} \text{ S s cm}^{-1}\end{aligned}$$

steady state relations

$$D = \varepsilon \varepsilon_0 E \quad E = \frac{M}{\varepsilon_0} D$$

$$P = D - \varepsilon_0 E = (\varepsilon - 1) \varepsilon_0 E = \chi \varepsilon_0 E \quad \chi = \varepsilon - 1$$

$$D = \frac{Q}{A} \quad E = \frac{V}{d} \quad Q = \int_0^t I(t') dt'$$

$\hat{\varepsilon} = \varepsilon' - i\varepsilon''$	\leftarrow	$\hat{\sigma} = i\omega\varepsilon_0\hat{\varepsilon}$	\rightarrow	$\hat{\sigma} = \sigma' + i\sigma''$
\uparrow				\uparrow
$\hat{M} = 1/\hat{\varepsilon}$				$\hat{\rho} = 1/\hat{\sigma}$
\downarrow				\downarrow
$\hat{M} = M' + iM''$	\leftarrow	$\hat{\rho} = \hat{M} / i\omega\varepsilon_0$	\rightarrow	$\hat{\rho} = \rho' - i\rho''$

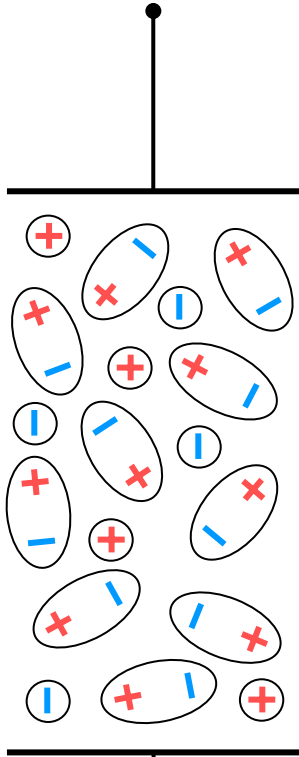
free charges

$$j = \frac{I}{A}$$

$$j = \sigma E = j_\sigma + j_\varepsilon = j_\sigma + \dot{D}$$

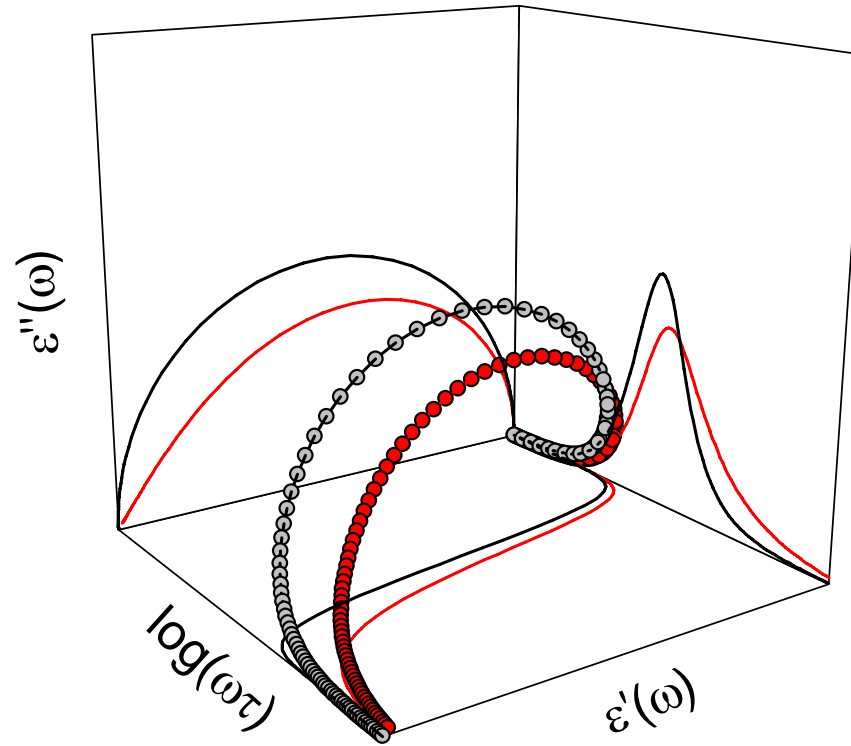
$$E = \rho j \quad j = \dot{D}$$

dielectric relaxation techniques



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

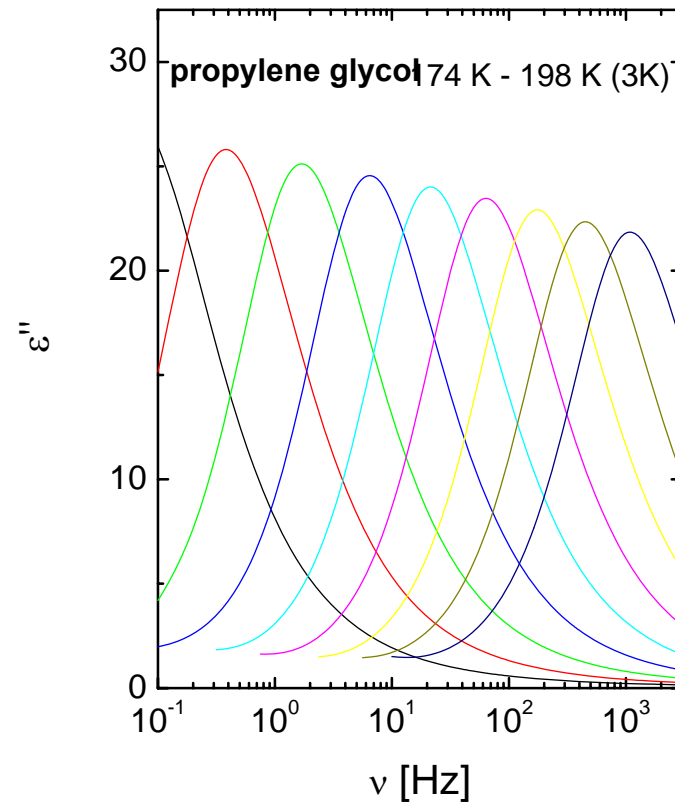
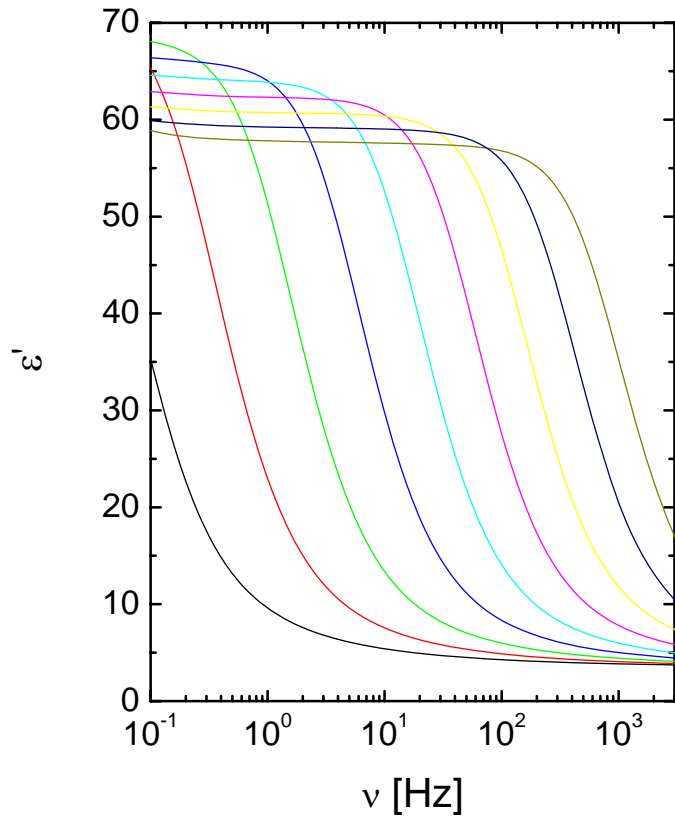
dielectric displacement $\mathbf{D} \equiv \frac{\mathbf{Q}}{\mathbf{A}} \propto \frac{\mathbf{V}}{\mathbf{d}} \equiv \mathbf{E}$ electric field



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

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

typical case near the glass transition



non-linear susceptibility

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

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 :

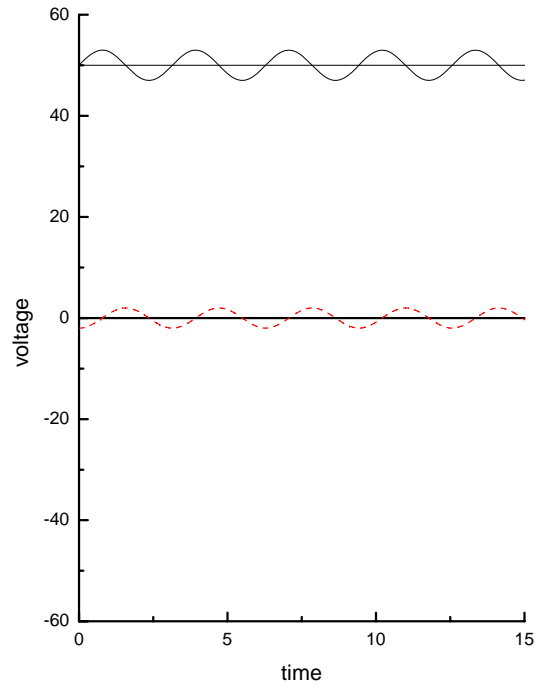
$$\Delta \varepsilon_s / E^2 = -\lambda \varepsilon_s$$

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

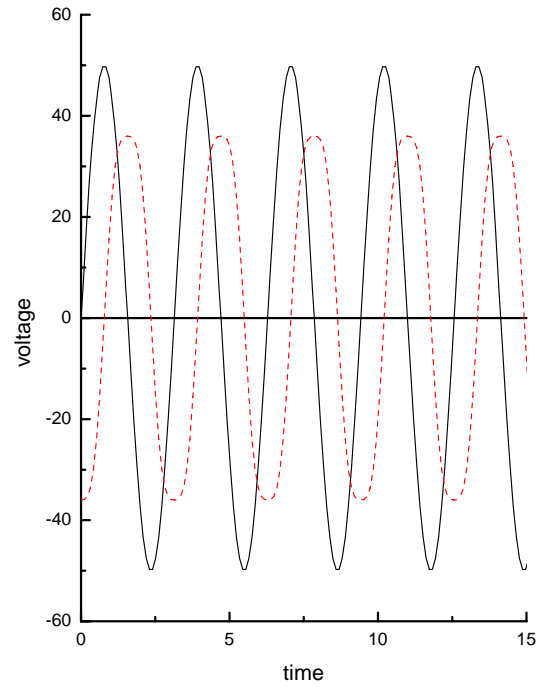
M.S. Green, R. Kubo (1950's) : linear transport coefficients $L_{F_e=0}$ are related to auto - correlation function of the equilibrium fluctuations in the conjugate flux J

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

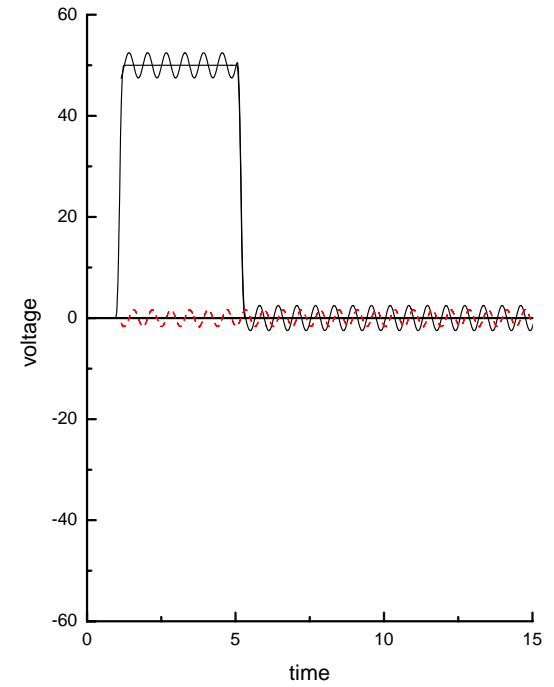
variety of high field techniques



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)

from nonlinearity to cooperativity length scale ?

Physical Review B 72, 064204 (2005)

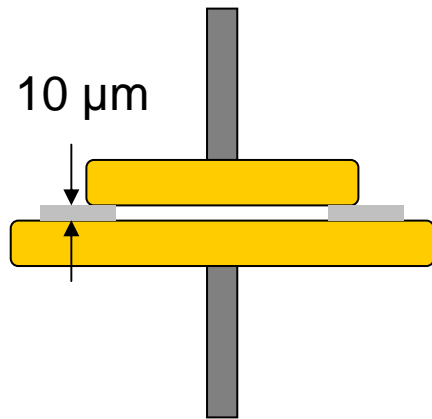
Nonlinear susceptibility in glassy systems: A probe for cooperative dynamical length scales

Jean-Philippe Bouchaud and Giulio Biroli

We argue that for generic systems close to a critical point, an extended fluctuation-dissipation relation connects the low frequency nonlinear (cubic) susceptibility to the four-point correlation function. In glassy systems, the latter contains interesting information on the heterogeneity and cooperativity of the dynamics. Our result suggests that if the abrupt slowing down of glassy materials is indeed accompanied by the growth of a cooperative length l , then the nonlinear, 3ω response to an oscillating field (at frequency ω) should substantially increase and give direct information on the temperature (or density) dependence of l . **The analysis of the nonlinear compressibility or the dielectric susceptibility in supercooled liquids, or the nonlinear magnetic susceptibility in spin-glasses, should give access to a cooperative length scale, that grows as the temperature is decreased or as the age of the system increases.** Our theoretical analysis holds exactly within the modecoupling theory of glasses.

Coulombic stress

Coulombic stress exercise



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

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

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

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

$$Q = CV$$

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

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

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

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

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

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

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

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

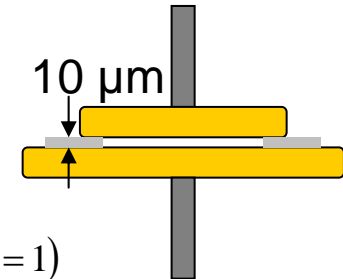
Young's modulus $E = \frac{[\text{stress}]}{[\text{strain}]} = \frac{L_0}{\Delta L} \frac{F}{A}$

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

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

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

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



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

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

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

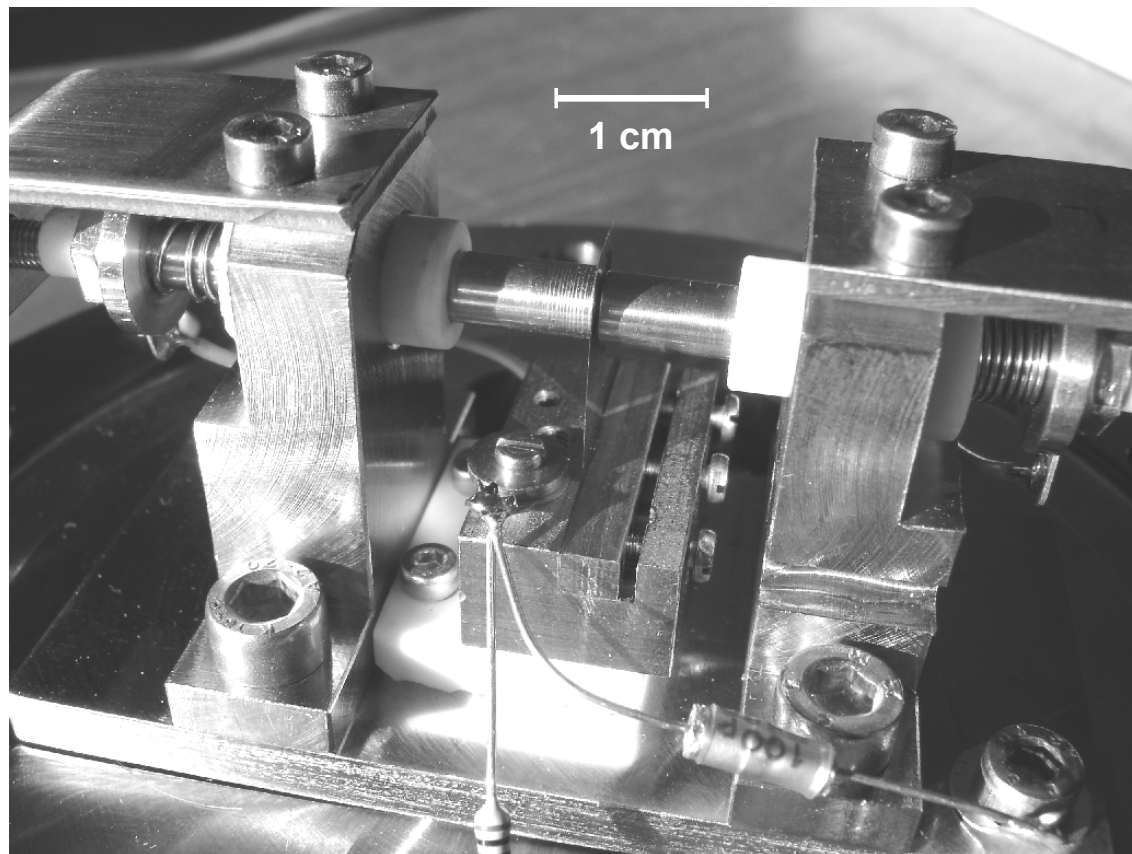
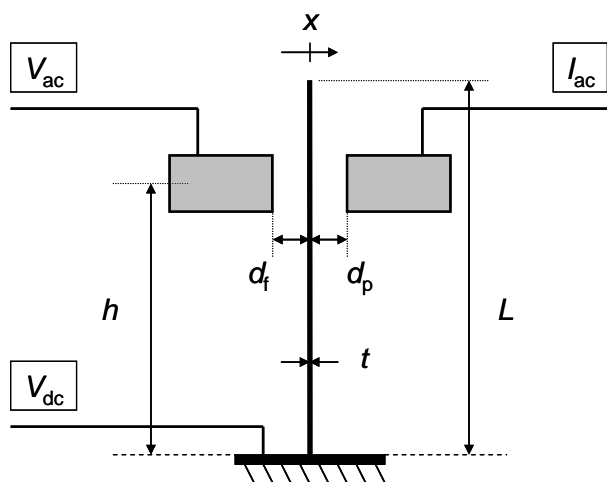
$$Y = 1 \text{ GPa (Teflon)}$$

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

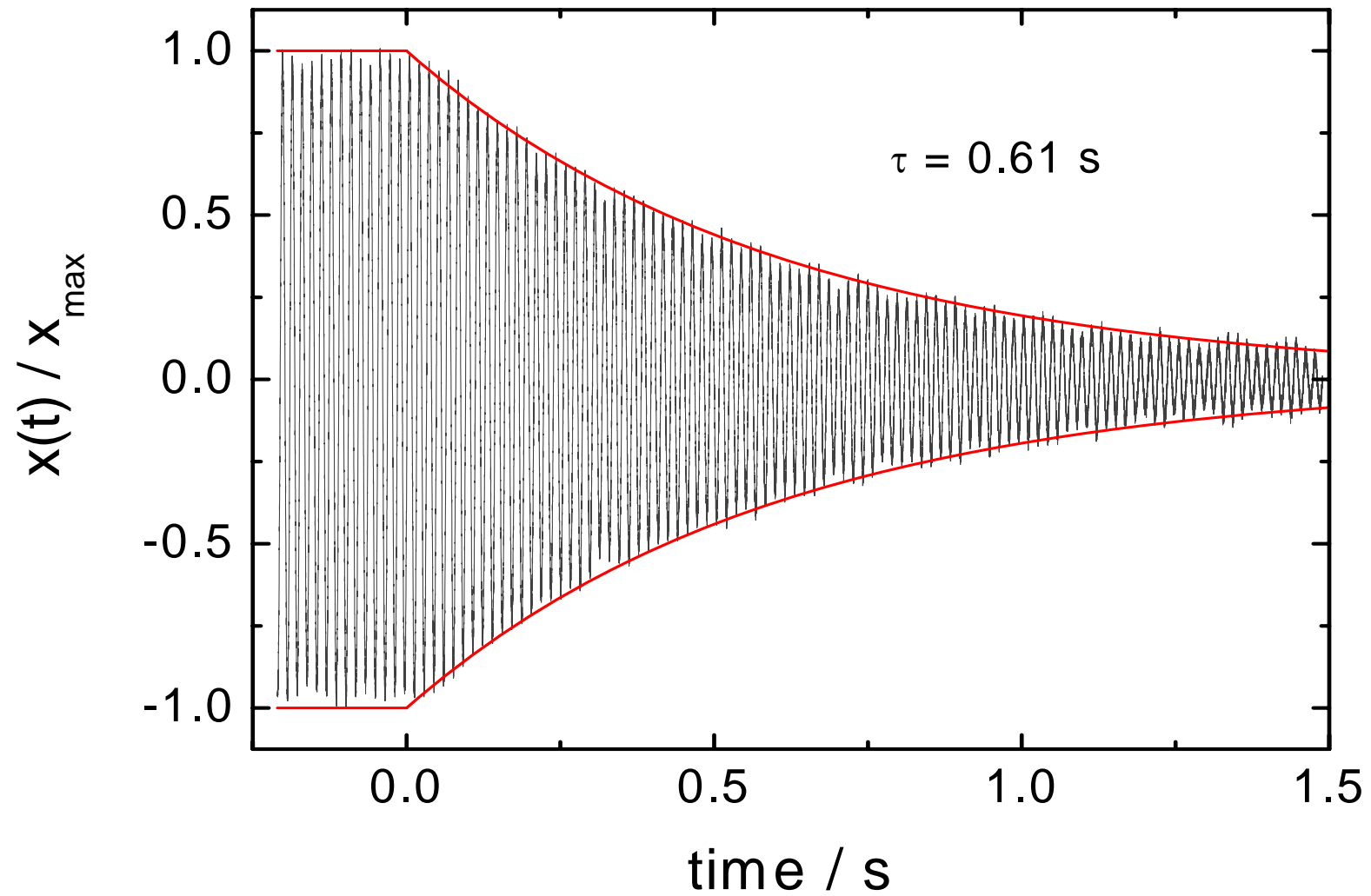
$$F_0/a = 0.67 \text{ MPa}$$

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

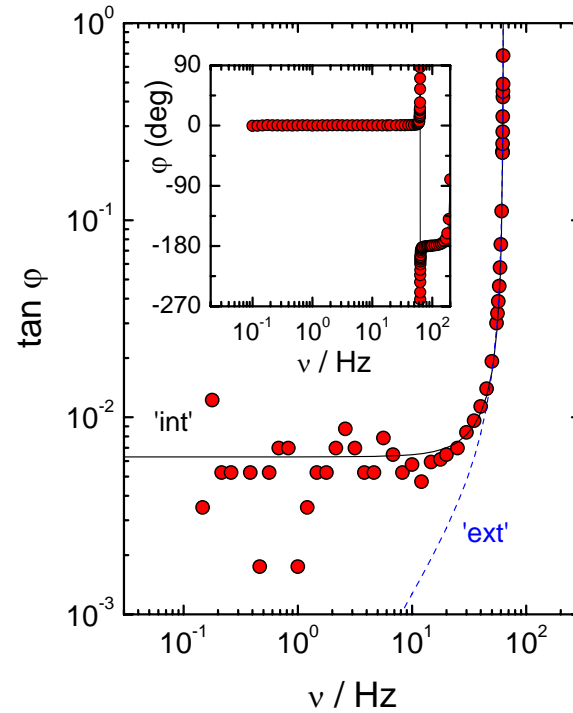
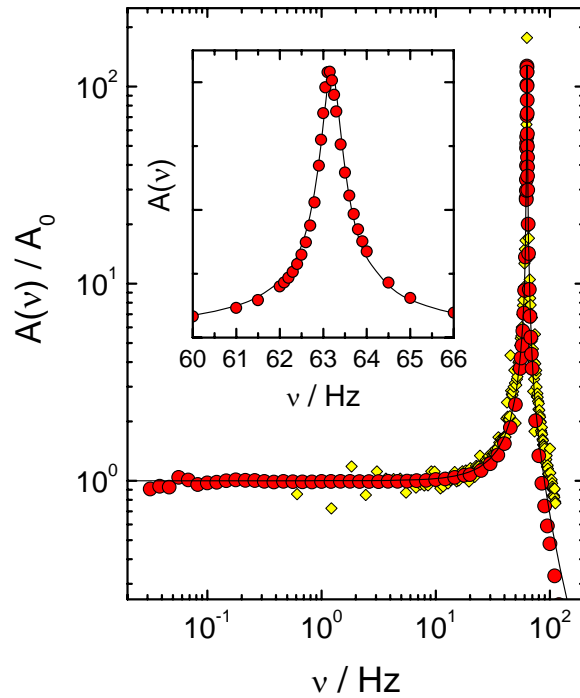
impedance approach to mechanical loss in a cantilever



ringdown of cantilever at resonance frequency



k' and k'' across 3.5 decades in frequency



$$m\ddot{x} + \rho\dot{x} + kx = F_0 e^{i\omega t}, \quad x = Ae^{i\omega t}$$

$$A(\omega) = \frac{A_0}{\sqrt{(1 - \mu^2)^2 + D_{\text{ext}}^2 \mu^2}}$$

$$\tan \varphi(\omega) = D_{\text{ext}} \frac{\mu}{1 - \mu^2}$$

$$m\ddot{x} + \hat{k}x = m\ddot{x} + k'x + ik''x = F_0 e^{i\omega t}, \quad x = Ae^{i\omega t}$$

$$A(\omega) = \frac{A_0}{\sqrt{(1 - \mu^2)^2 + D_{\text{int}}^2}}$$

$$\tan \varphi(\omega) = \frac{k''}{k' - k\mu^2}$$

$$\mu = \omega/\omega_0 = \omega\sqrt{m/k}$$

$$D_{\text{ext}} = \rho/\sqrt{mk}$$

$$D_{\text{int}} = k''/k' = E''/E'$$

dielectric saturation

expected non-linearity: dielectric saturation, Langevin effect

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

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

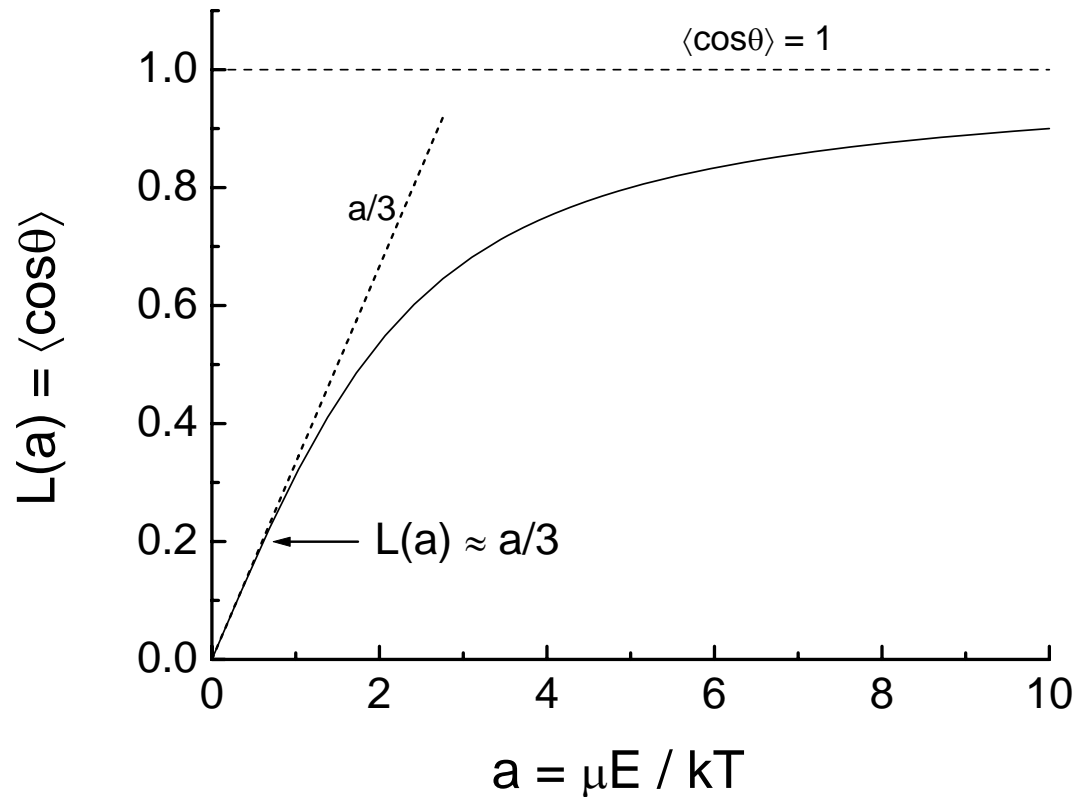
$$\langle \cos \theta \rangle = L\left(\frac{\mu E}{kT}\right) \quad \left(\begin{array}{l} \text{Langevin} \\ \text{function} \end{array} \right)$$

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

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

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

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

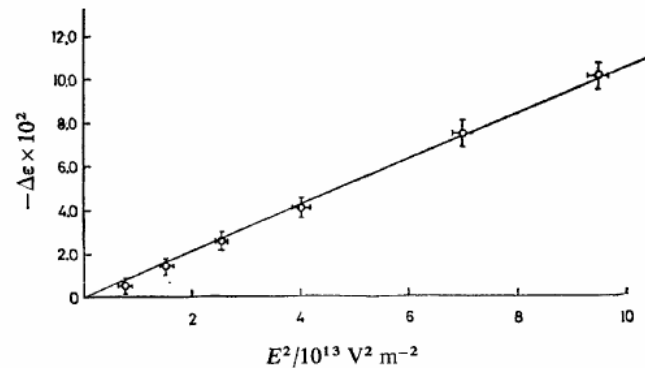
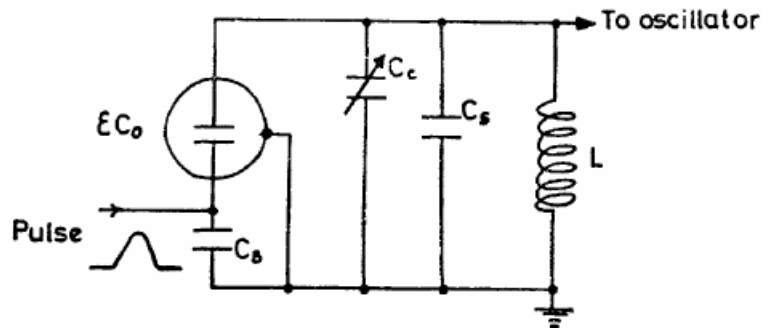


saturation in water at 293 K

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

Langevin and chemical NDE's

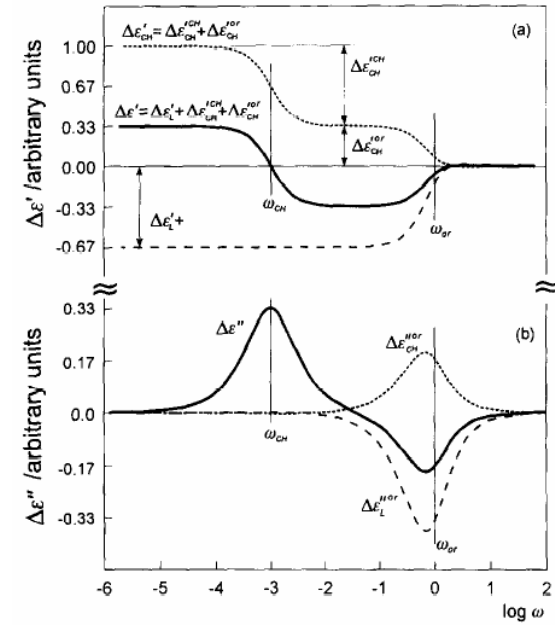
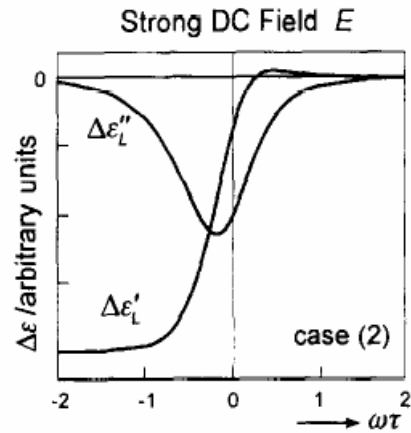
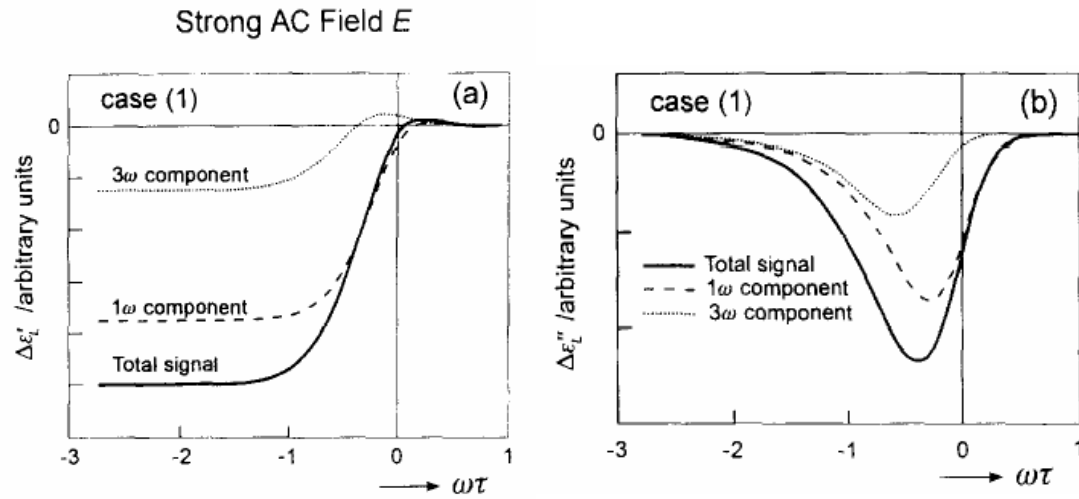


Fig. 7. Total relaxation spectrum for dipolar system with chemical equilibrium. Chemical ($\Delta\epsilon_{CH}$) and orientational ($\Delta\epsilon_L$) contributions are drawn separately.

$$dG = -S dT + V dp - P dE - A d\xi$$

time resolved NDE experiments

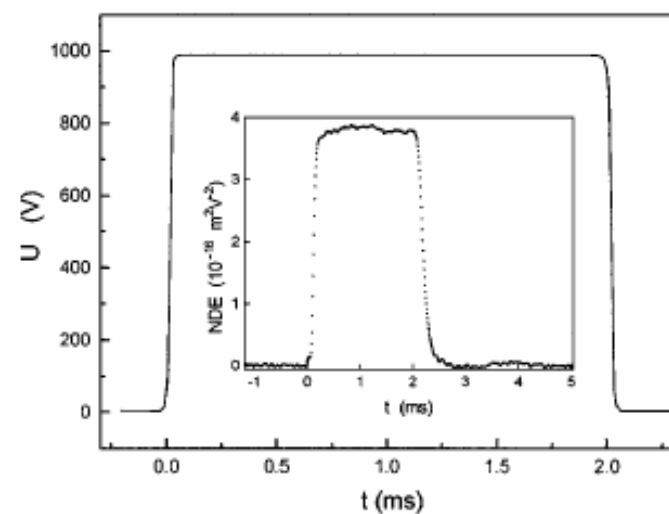
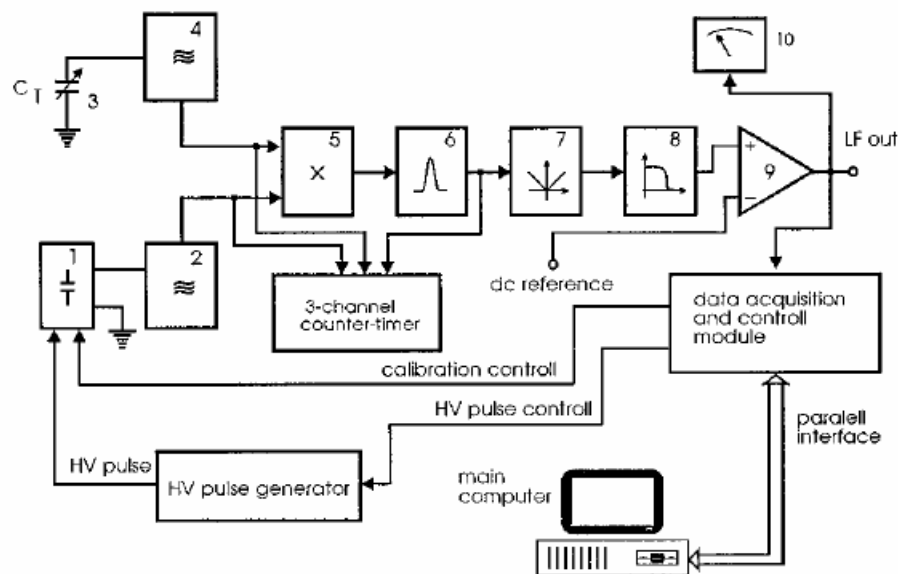
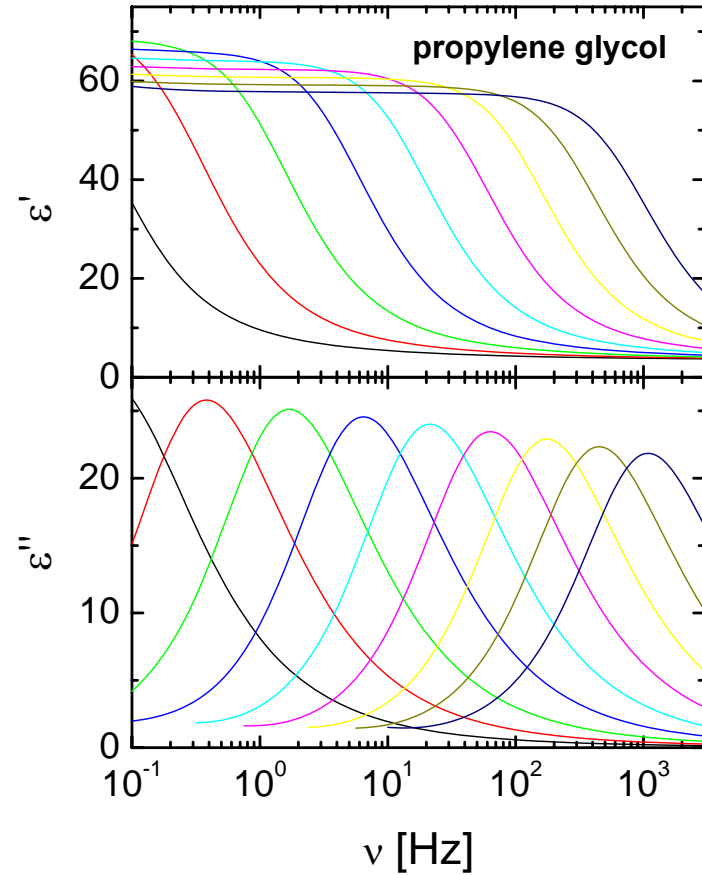
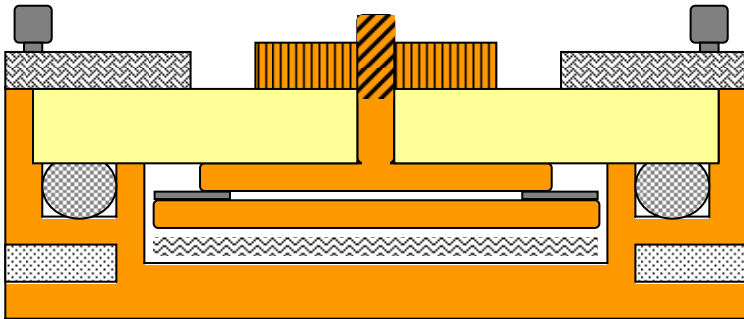
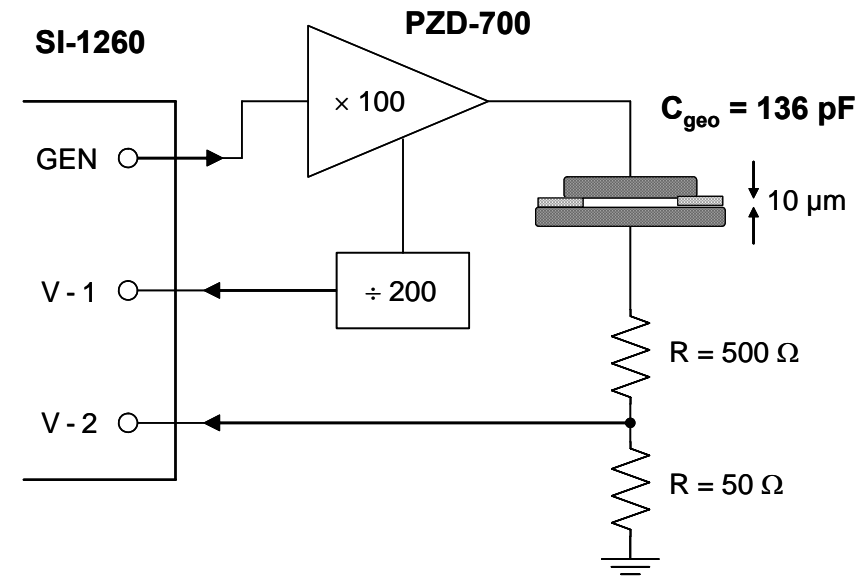


FIG. 1. The NDE measurement setup: 1—Measurement capacitor; 2—measurement generator (G_1 , freq. $f_1 + \Delta f$); 3,4—reference generator (G_2 , freq. f_2) with tuning capacitor; 5—mixer (freq. Δf); 6—bandpass filter; 7—rectifier; 8—low-pass filter; 9—amplifier; 10—indicator of the tuning of G_2 to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

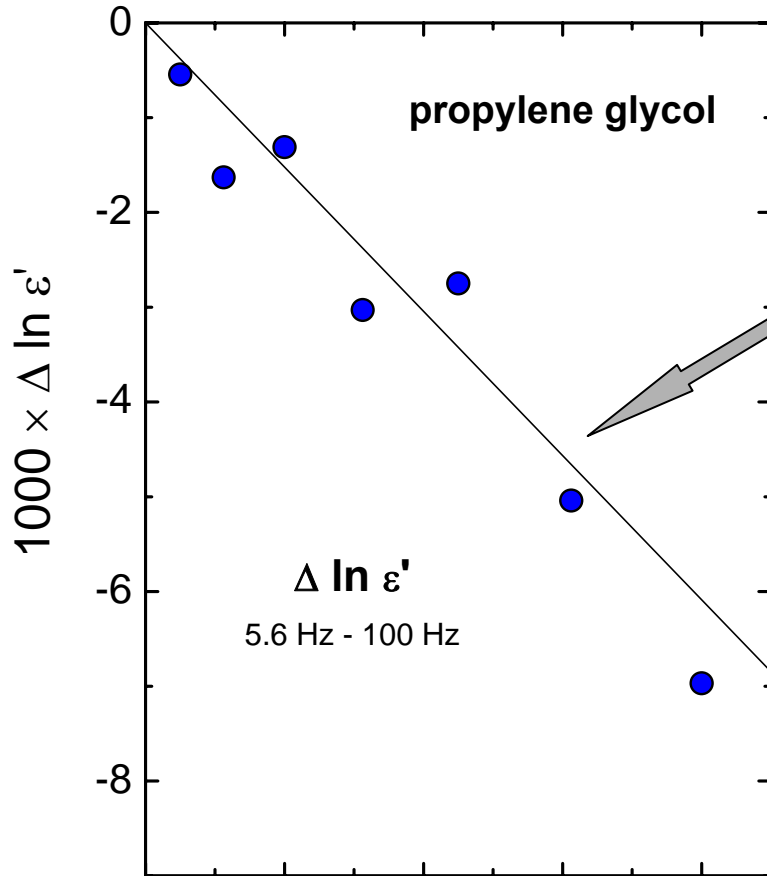
high field impedance



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

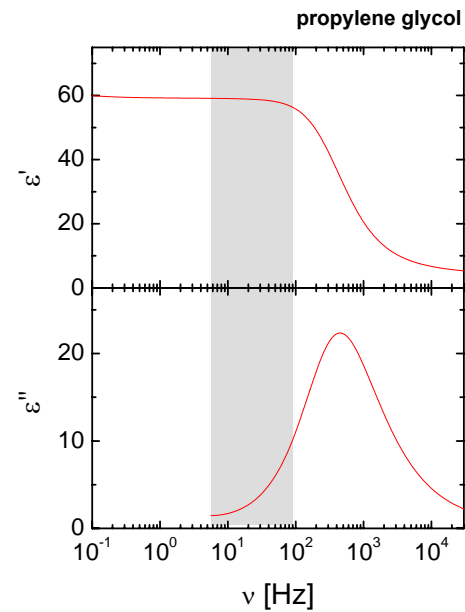
S. Weinstein, R. Richert, J. Phys.: Condens. Matter 19 (2007) 205128

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

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

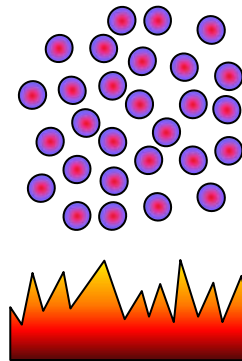
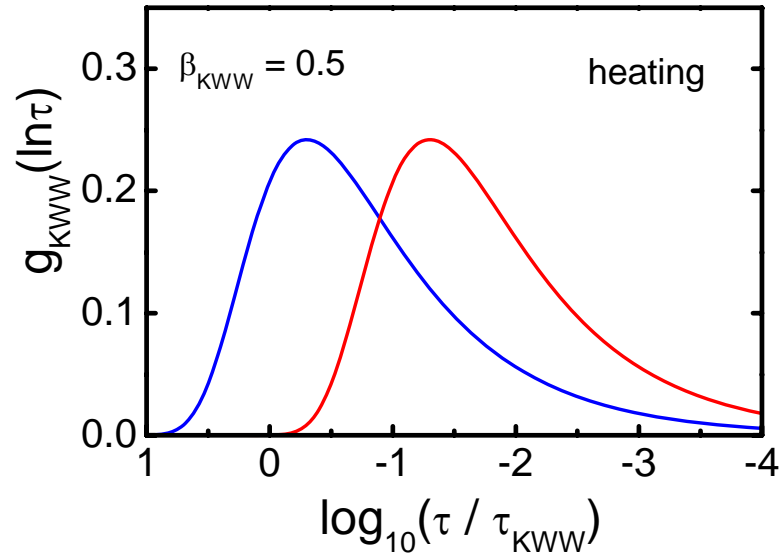
$$\epsilon'' \approx 10$$

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

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

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

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



predicted heating/temperature effects

temperature dependence :

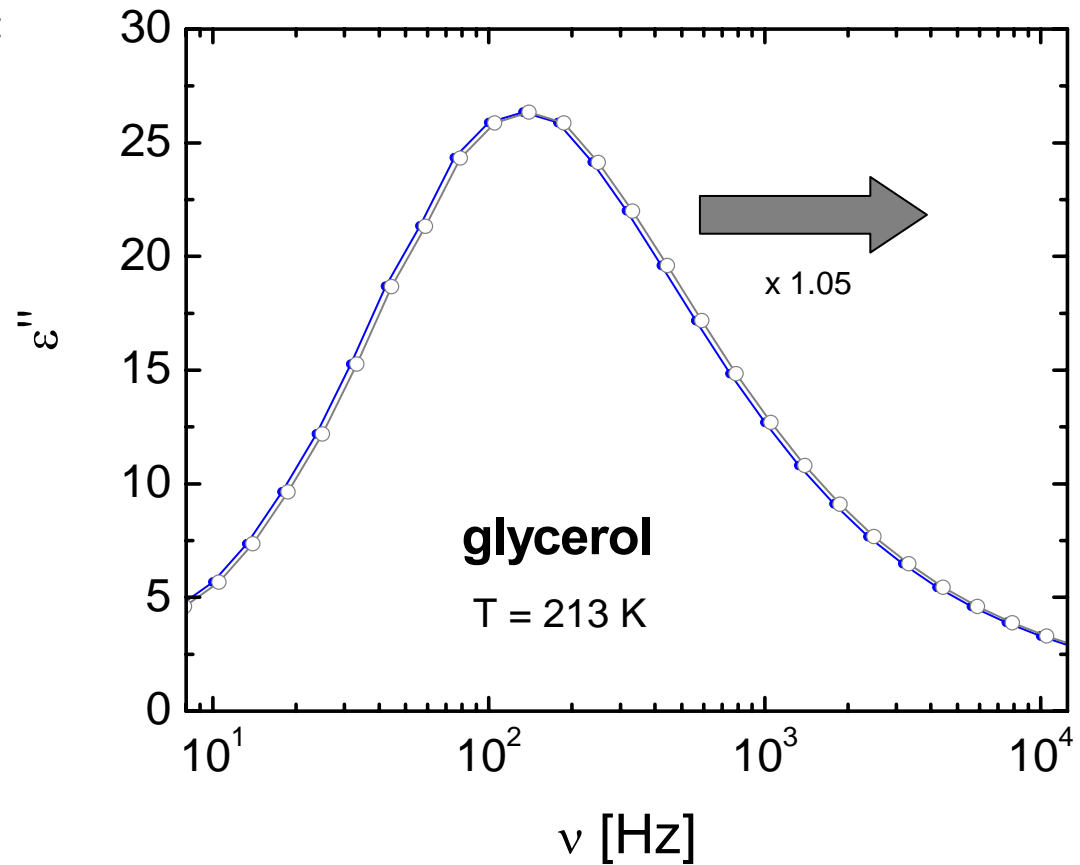
$$\tau(T) \approx \tau_0 \exp\left(\frac{E_A}{k_B T}\right)$$

$$\Delta \ln \tau = -\frac{\Delta T}{T} \frac{E_A}{k_B T}$$

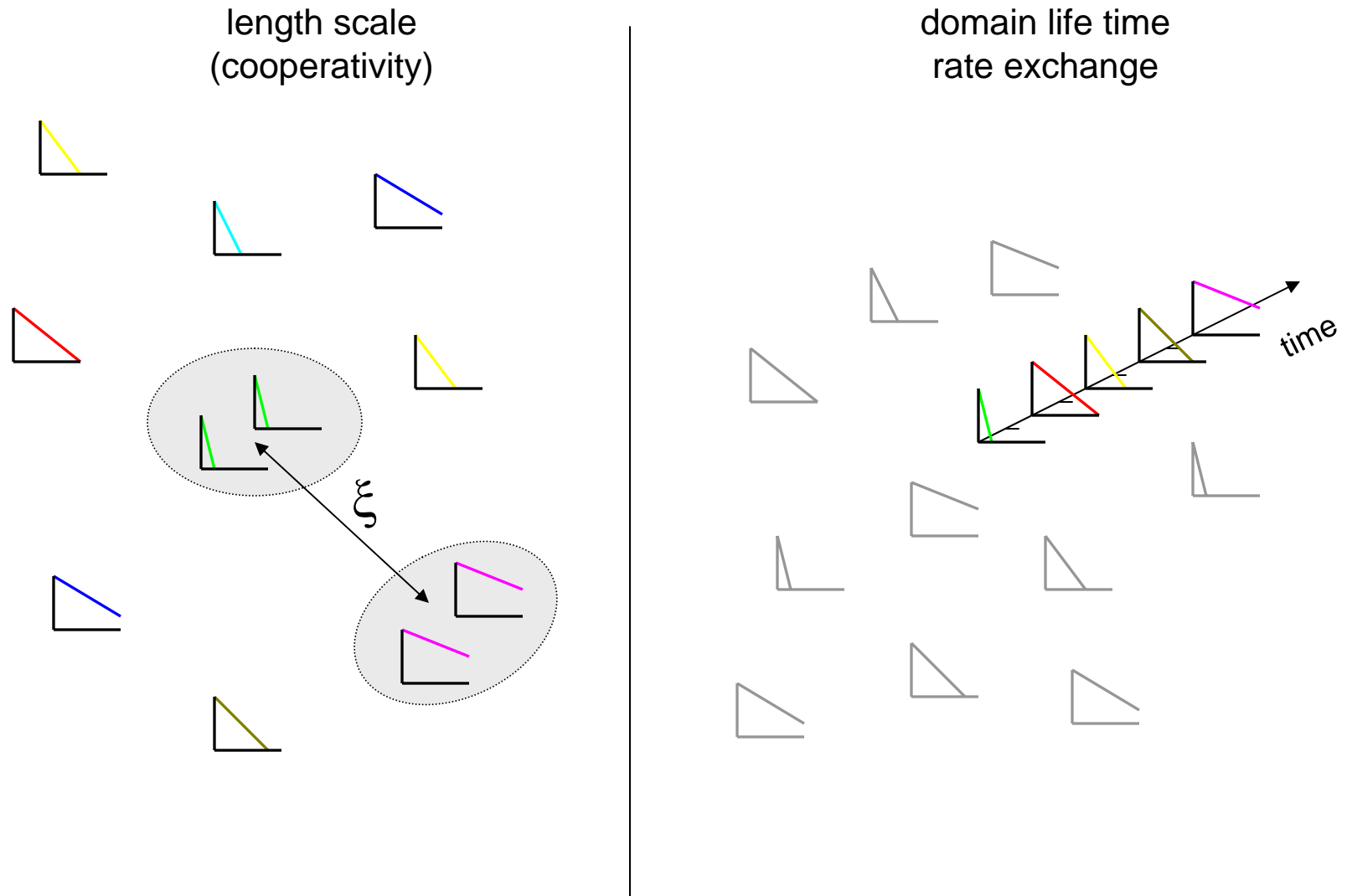
$$\frac{E_A}{k_B} \approx 20\,000 \text{ K}$$

$$\Delta T \approx 0.1 \text{ K}$$

$$\Delta \ln \tau = \frac{\Delta \tau}{\tau} \approx 0.05$$



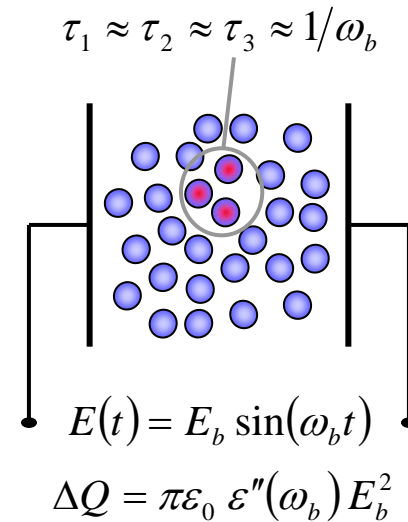
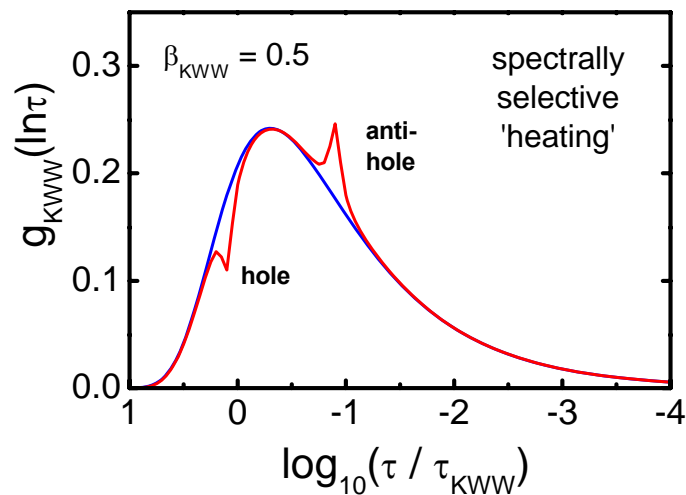
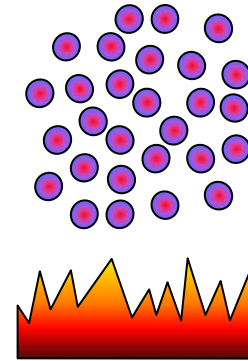
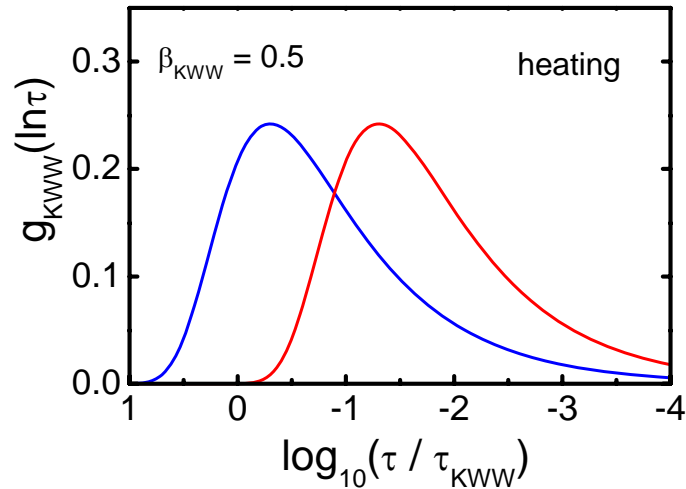
features of heterogeneous dynamics



***DIELECTRIC HOLE-BURNING
IDEA AND METHOD***



spectrally selective dielectric experiments



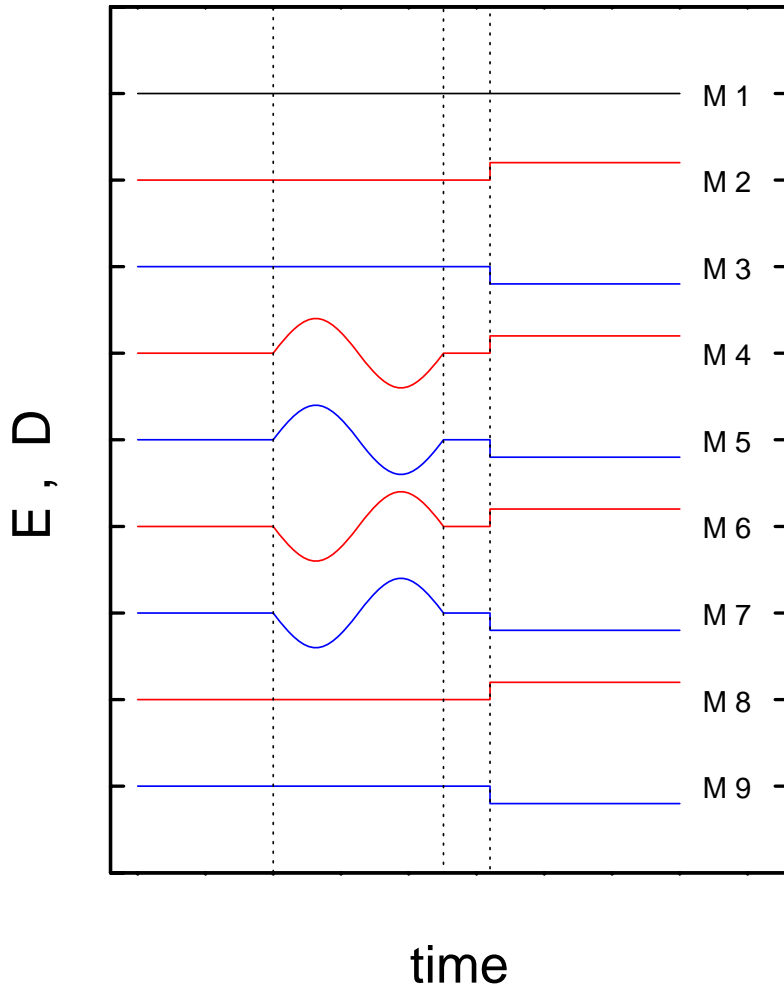
B. Schiener, R. Böhmer, A. Loidl, R. V. Chamberlin, *Science* 274 (1996) 752

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

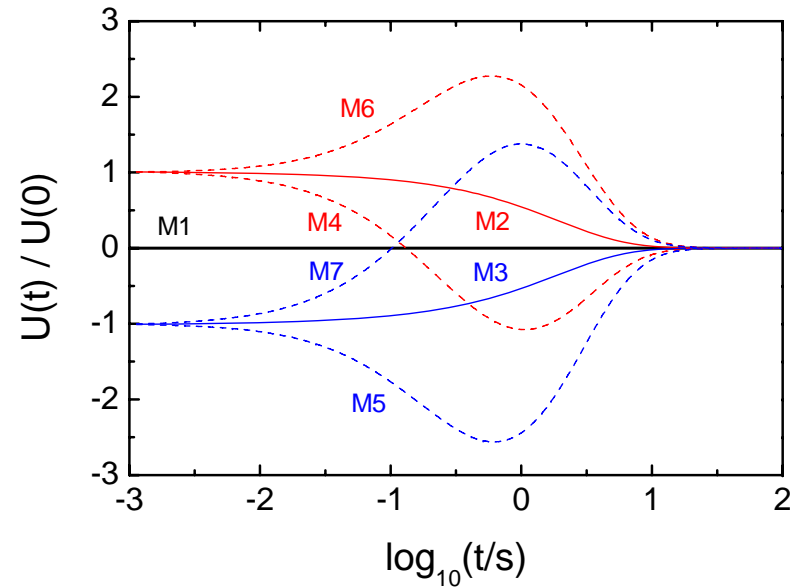
dielectric $\varepsilon(t)$ and electric $M(t)$ hole-burning

phase-cycle

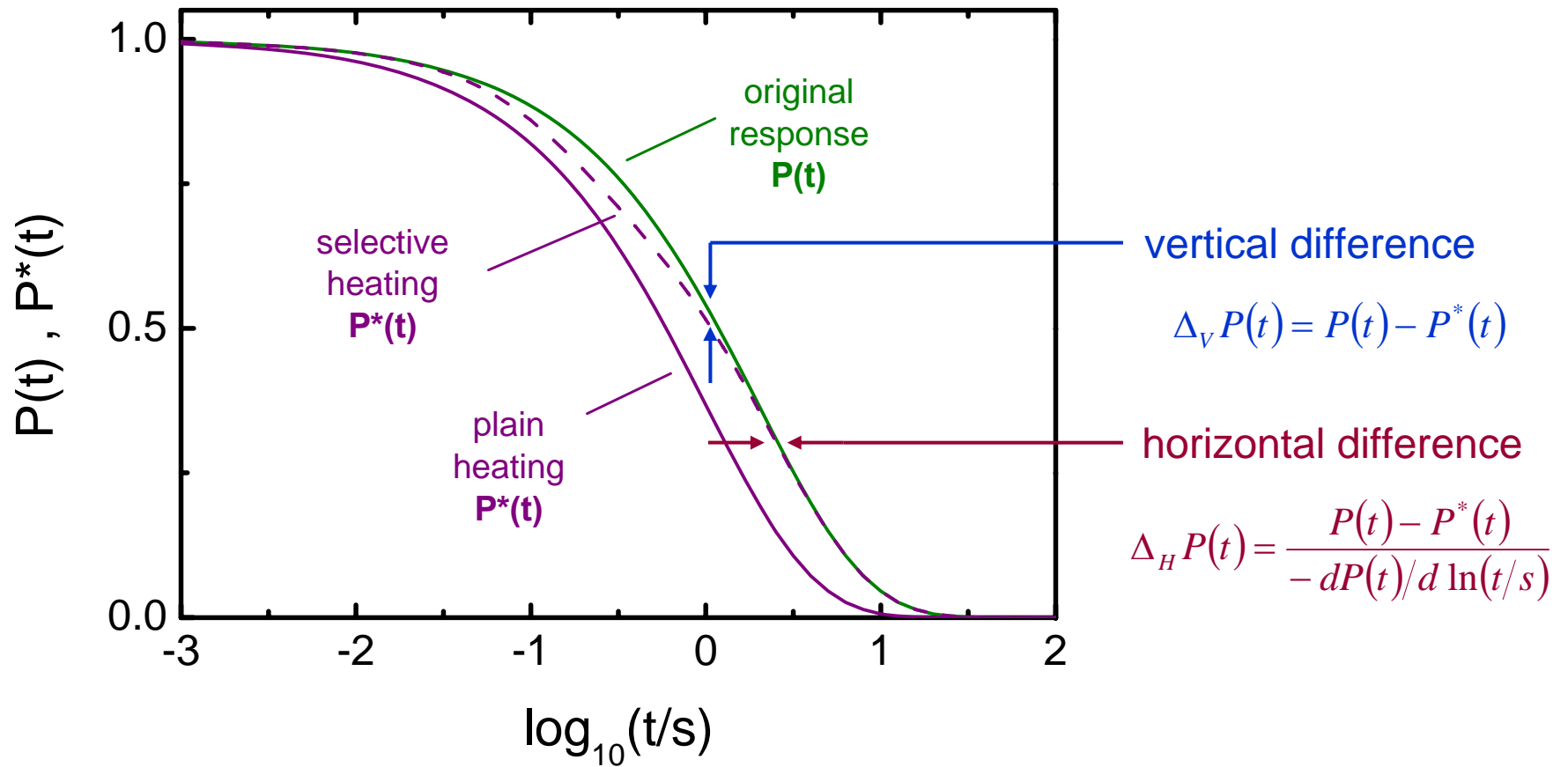


$$\phi_{idle}(t) = \frac{M_2(t) - M_3(t) + M_8(t) - M_9(t)}{M_2(t_0) - M_3(t_0) + M_8(t_0) - M_9(t_0)}$$

$$\phi_{burn}(t) = \frac{M_4(t) - M_5(t) + M_6(t) - M_7(t)}{M_4(t_0) - M_5(t_0) + M_6(t_0) - M_7(t_0)}$$



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

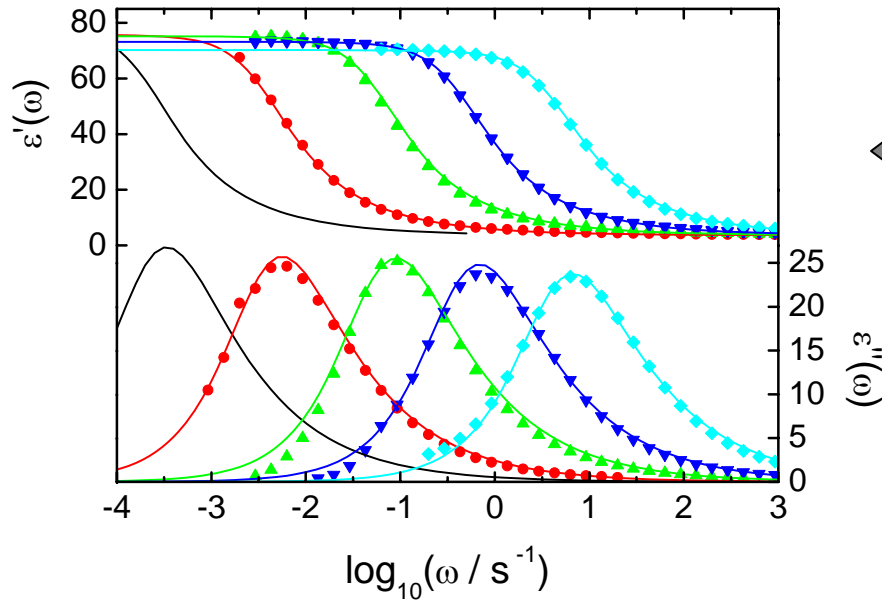


DIELECTRIC HOLE-BURNING EXPERIMENTS



dielectric relaxation and retardation in viscous glycerol

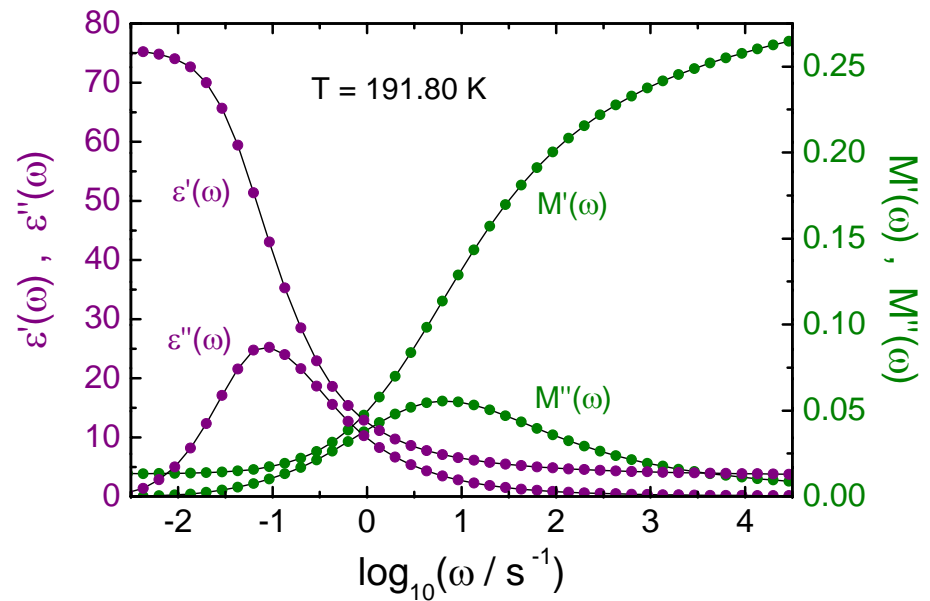
sample thickness: 6.4 μm



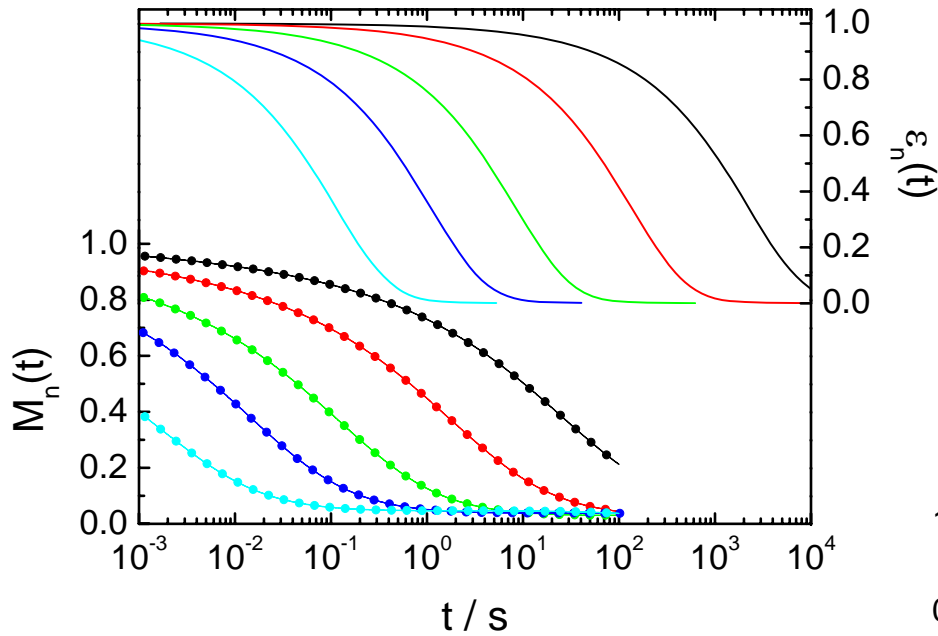
frequency domain data $\epsilon^*(\omega, T)$

- $T = 183.50 \text{ K}$
- $T = 187.30 \text{ K}$
- $T = 191.80 \text{ K}$
- $T = 195.80 \text{ K}$
- $T = 200.50 \text{ K}$

$\epsilon^*(\omega)$ versus $M^*(\omega)$



exploiting M(t) for high frequency hole-burning



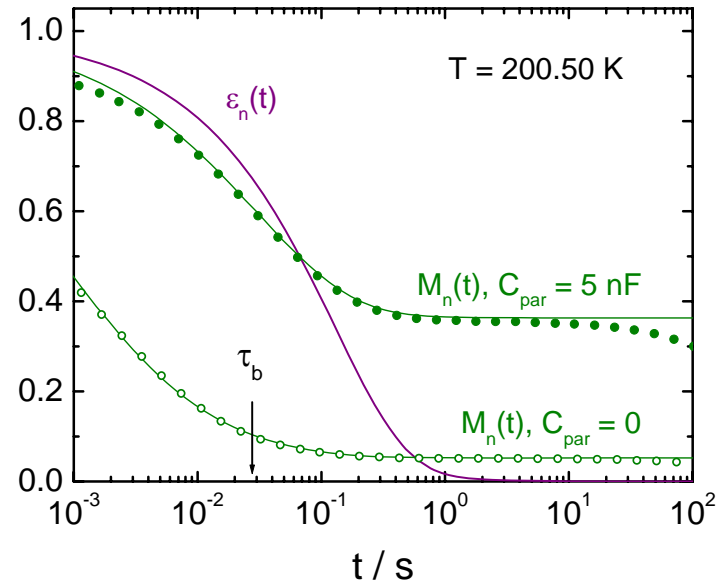
- $T = 183.50 \text{ K}$
- $T = 187.30 \text{ K}$
- $T = 191.80 \text{ K}$
- $T = 195.80 \text{ K}$
- $T = 200.50 \text{ K}$

$$\tau_M \approx \frac{1}{80} \times \tau_\epsilon$$

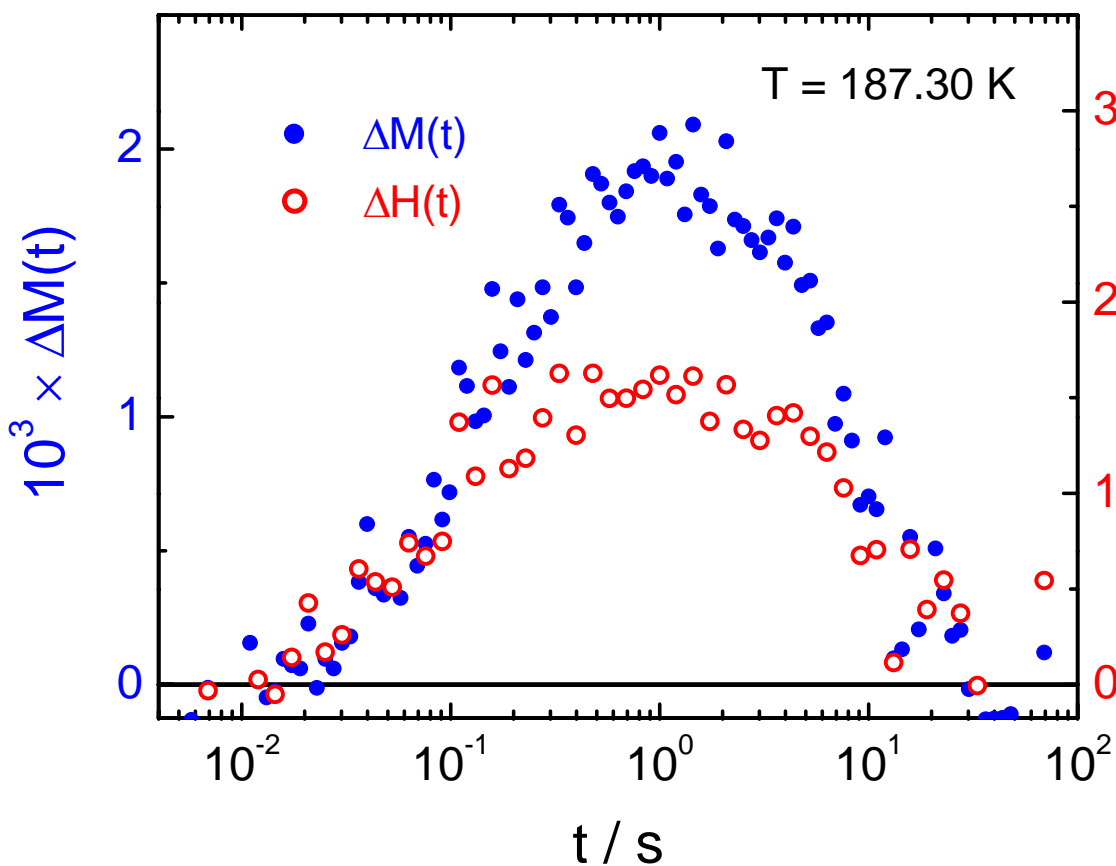
variable τ : $\tau_M \dots \tau_\epsilon$
using parallel capacitance

$$\frac{\tau_M}{\tau_\epsilon} \approx \frac{\epsilon_\infty}{\epsilon_s} \rightarrow \frac{\epsilon_\infty + \epsilon_{par}}{\epsilon_s + \epsilon_{par}} \rightarrow 1$$

$M_n(t), \epsilon_n(t)$



DHB results for glycerol: vertical and horizontal differences



vertical & horizontal
signal at:

$$n = 6$$

$$t_w = 1 \text{ s}$$

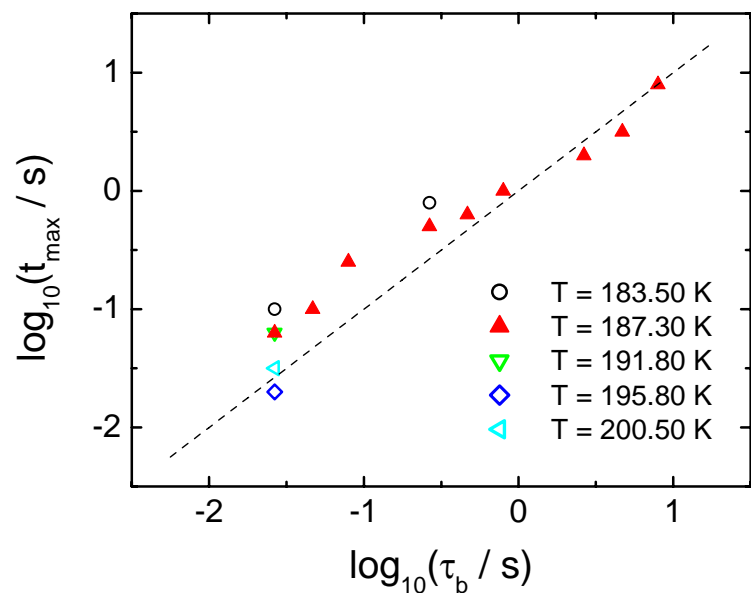
$$f_b = 0.2 \text{ Hz}$$

$$V_b = 90 \text{ V}$$

$$E_b = 140 \text{ kV/cm}$$

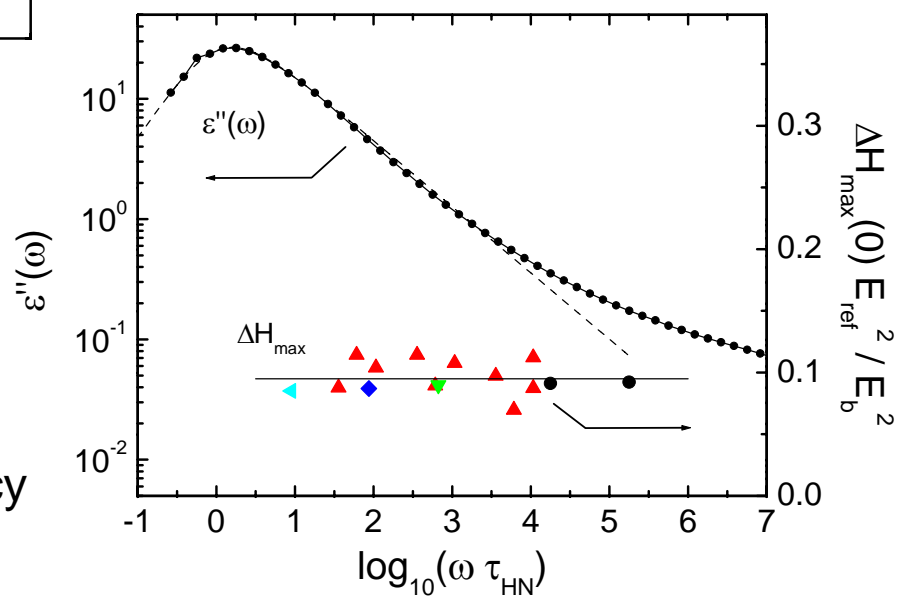
$$T = 187.30 \text{ K}$$

DHB results for glycerol: burn-frequency dependence

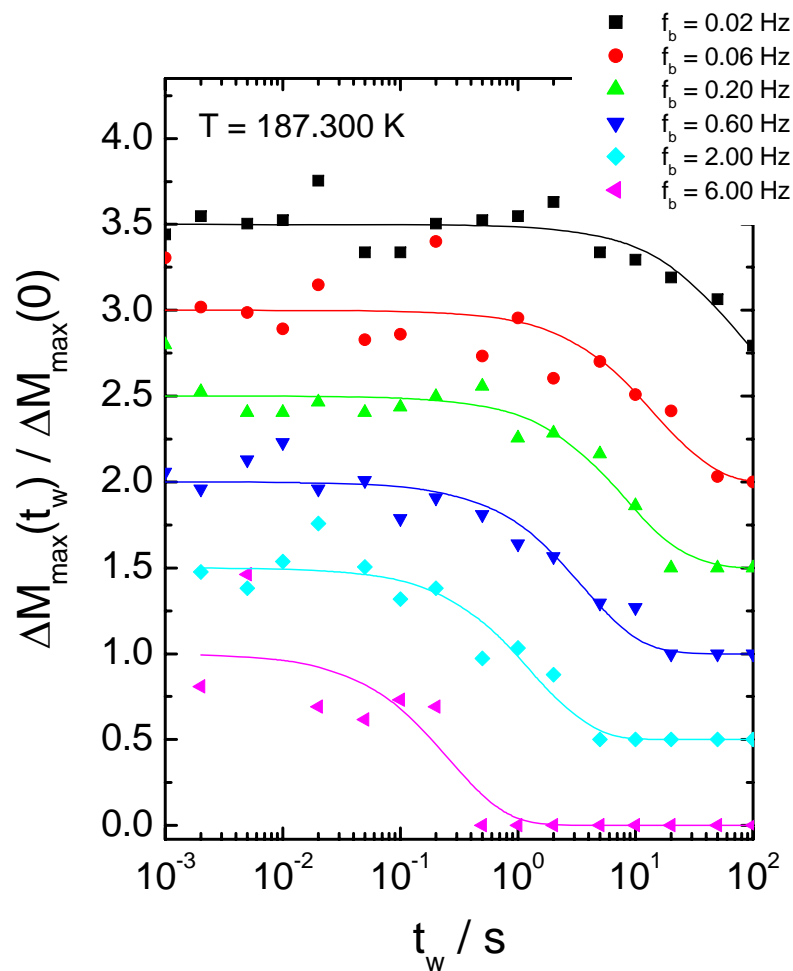


amplitude of horizontal hole
versus
relative burn frequency

position of vertical hole
versus
burn frequency



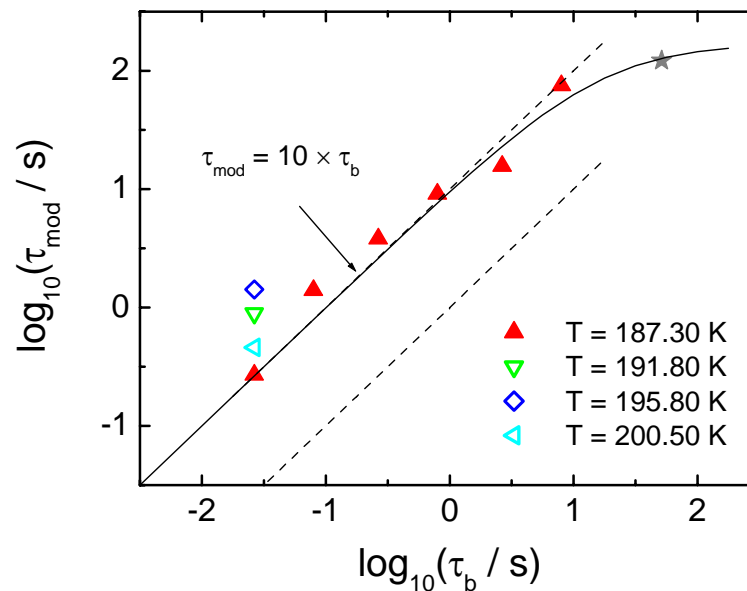
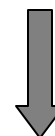
DHB results for glycerol: waiting-time dependence



pump - wait - probe

t_w

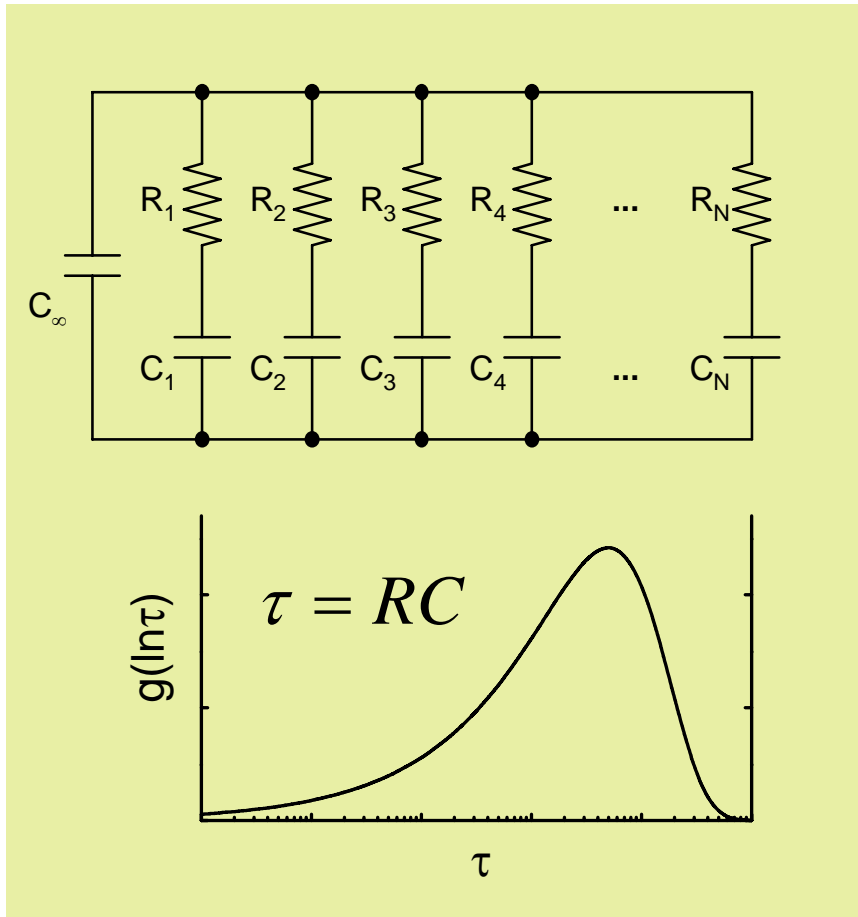
$$\frac{\Delta M_{\max}(t_w)}{\Delta M_{\max}(0)} = \exp\left(-\frac{t_w}{\tau_{\text{mod}}}\right)$$



DIELECTRIC HOLE-BURNING MODEL



calculation of energy loss (heating) for RC network



external voltage $V_X(t)$ applied:

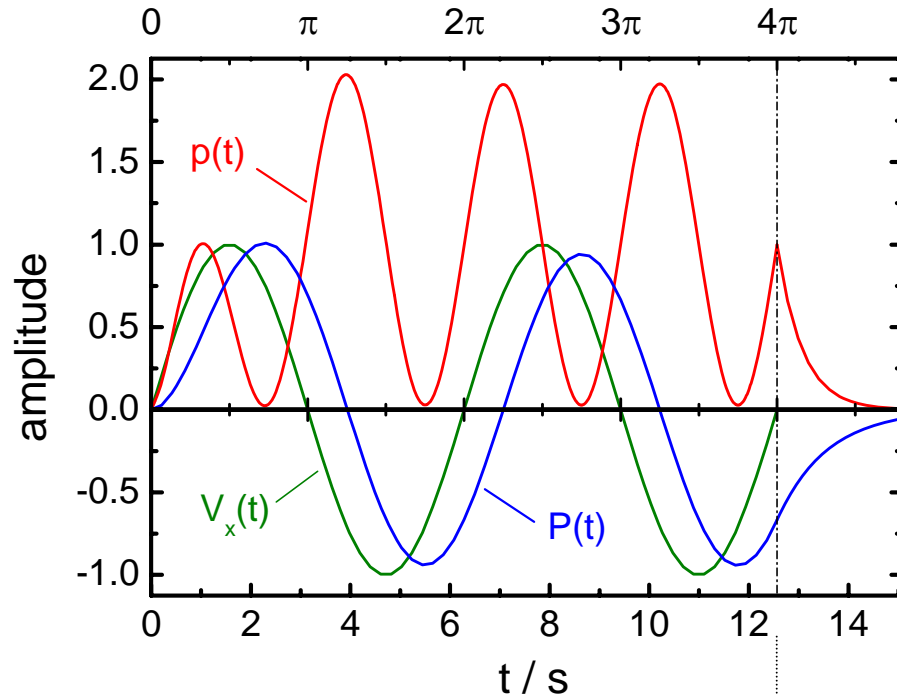
$$\frac{dV_C(t)}{dt} = \frac{1}{C} I_R(t) = \frac{V_X(t) - V_C(t)}{RC}$$

$$P(t) \propto Q_C(t) = CV_C(t) \quad \text{polarization}$$

$$\frac{dT_R(t)}{dt} = \frac{V_R(t)I_R(t)}{c_p} - \frac{T_R(t)}{RC} \quad \text{power}$$

$$R(t) = R_B \left[1 - \frac{T_R(t)}{T} \left(\frac{E_A}{k_B T} \right) \right]$$

calculation of heating $p(t)$ for RC network



steady state case:

$$q_{eq} = \pi \varepsilon_0 \nu E_0^2 \varepsilon''(\omega_b)$$

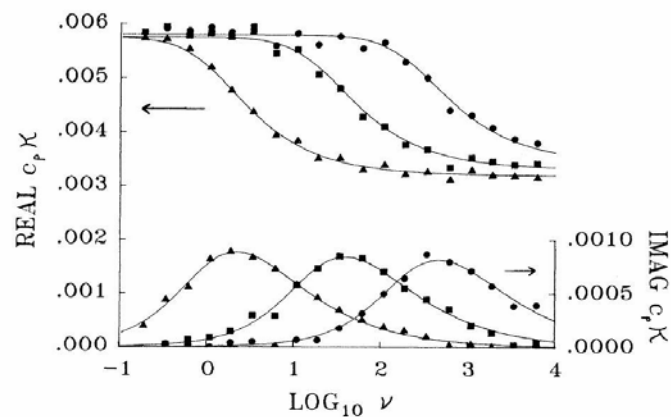
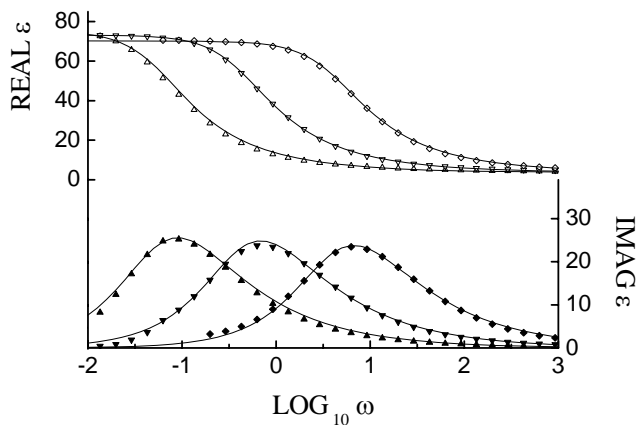
$$0 \leq t \leq n2\pi/\omega_b$$

$$E_x(t) = \begin{cases} E_0 \sin(\omega_b t) & , \quad 0 \leq t \leq n2\pi/\omega_b \\ 0 & , \quad \text{otherwise} \end{cases}$$

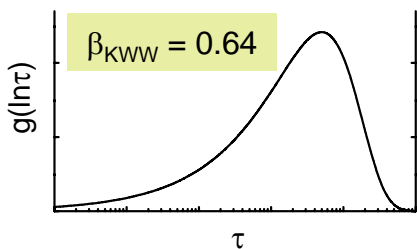
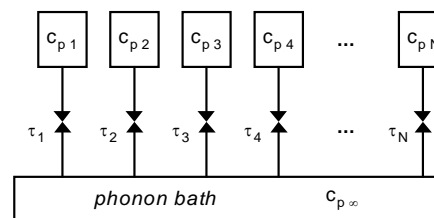
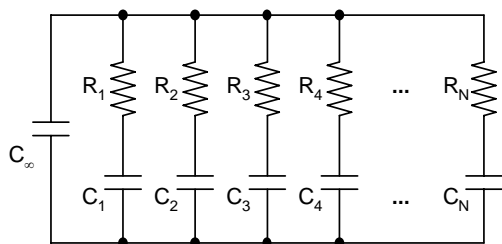
$$0 \leq t \leq n2\pi/\omega_b \quad t > n2\pi/\omega_b$$

$$p(t) = \frac{\varepsilon_0 \nu E_0^2 \varepsilon''(\omega_b) \omega_b}{1 + \omega_b^2 \tau^2} \times \begin{cases} [\omega_b \tau \sin(\omega_b t) + \cos(\omega_b t) - \exp(-t/\tau)]^2 & , \quad 0 \leq t \leq n2\pi/\omega_b \\ [1 - \exp(n2\pi/\omega_b \tau)]^2 \exp(-2t/\tau) & , \quad t > n2\pi/\omega_b \end{cases}$$

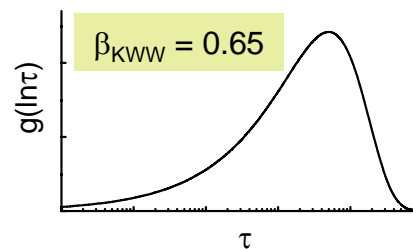
dielectric and thermal relaxation times in glycerol



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

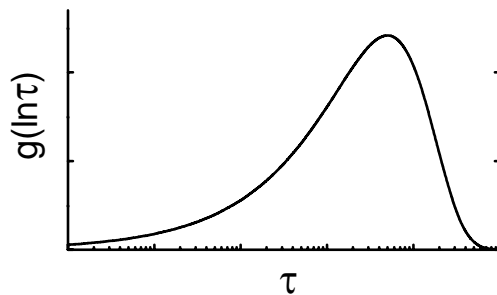
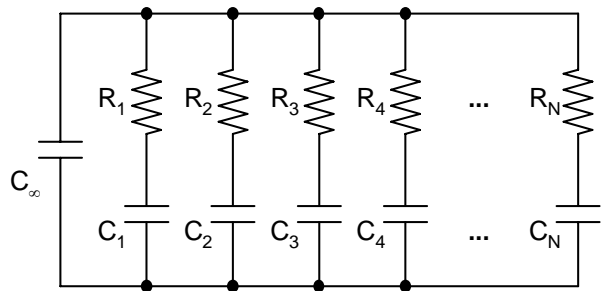
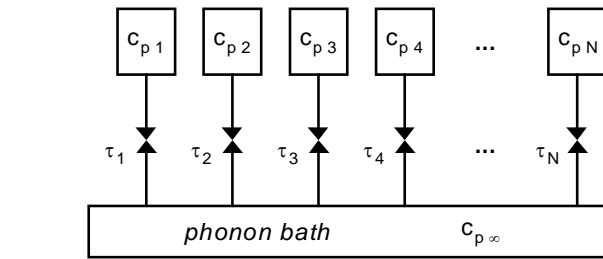


=



K. Schröter and E. Donth, J. Chem. Phys. 113 (2000) 9101

also assume: tau's are locally correlated



$$\Delta c_p = 1.5 \text{ JK}^{-1} \text{ cm}^{-3}$$

$$E_A^{eff} = \frac{\partial \ln \tau}{\partial (1/T)} = 2 \times 10^4 \text{ K}$$

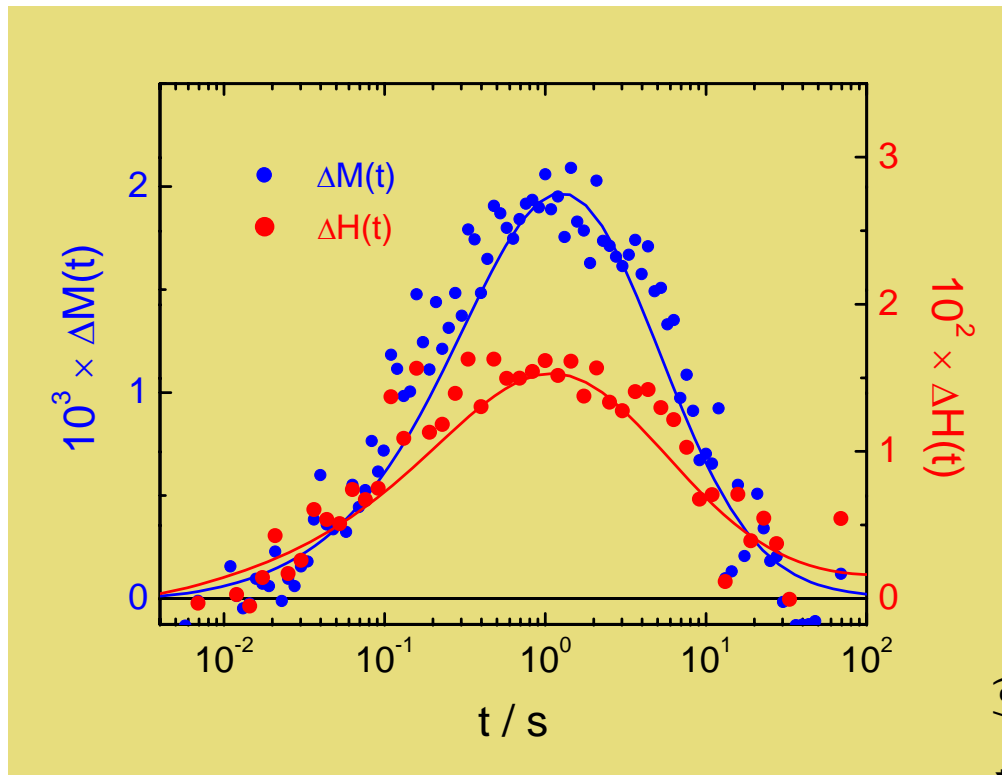
$$\varepsilon_\infty = 3.7, \varepsilon_s = 75.7$$

$$\alpha_{HN} = 0.95, \gamma_{HN} = 0.58, \tau_{HN} = 285 \text{ s}$$

Model:

locally correlated structural and thermal relaxation time heterogeneity

DHB in glycerol: calculated vs. measured results



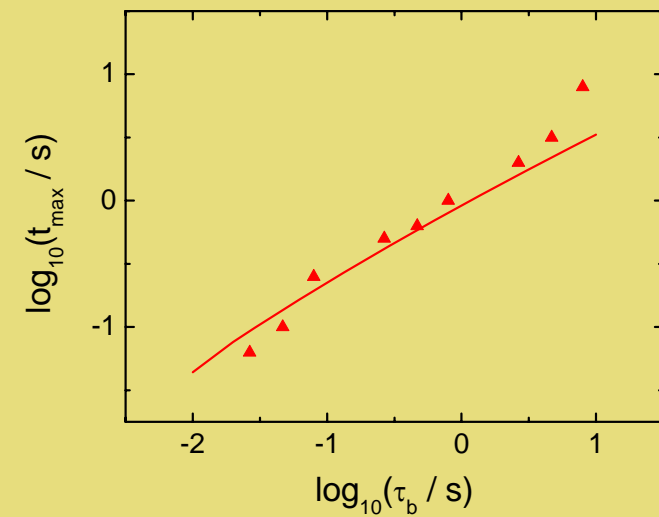
vertical & horizontal
signal at $n = 6$

$$t_w = 1 \text{ s}$$

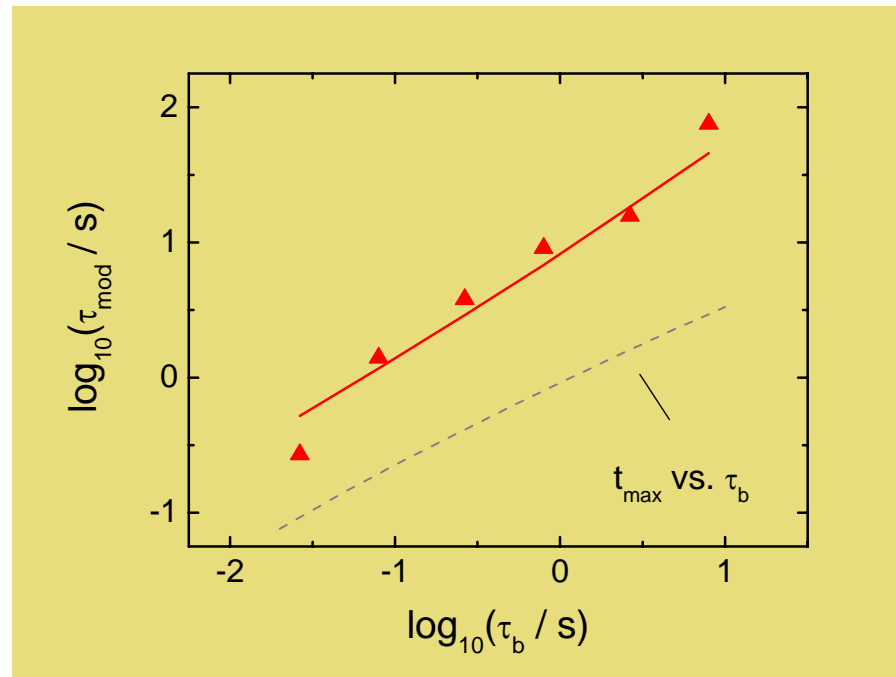
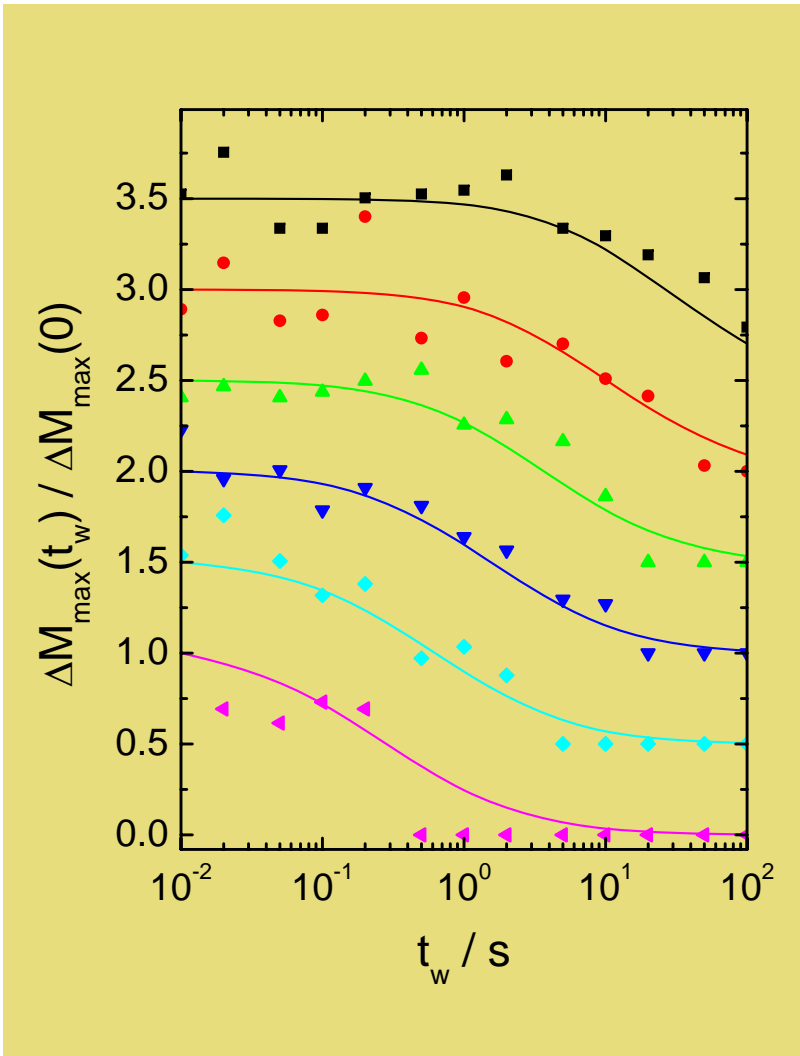
$$f_b = 0.2 \text{ Hz}$$

$$V_b = 90 \text{ V}$$

$$E_b = 140 \text{ kV/cm}$$



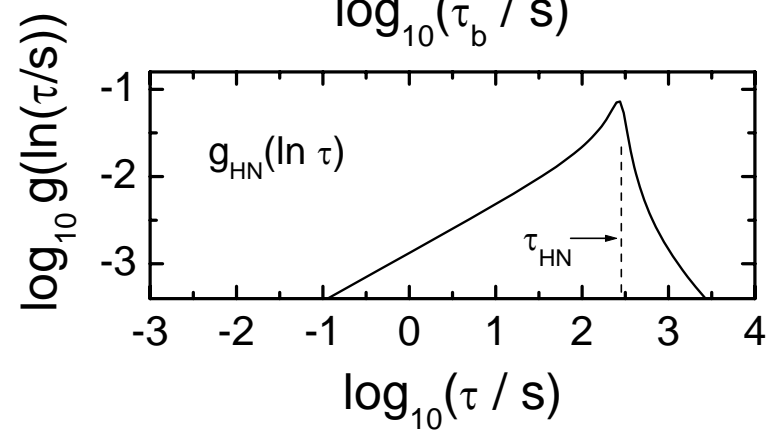
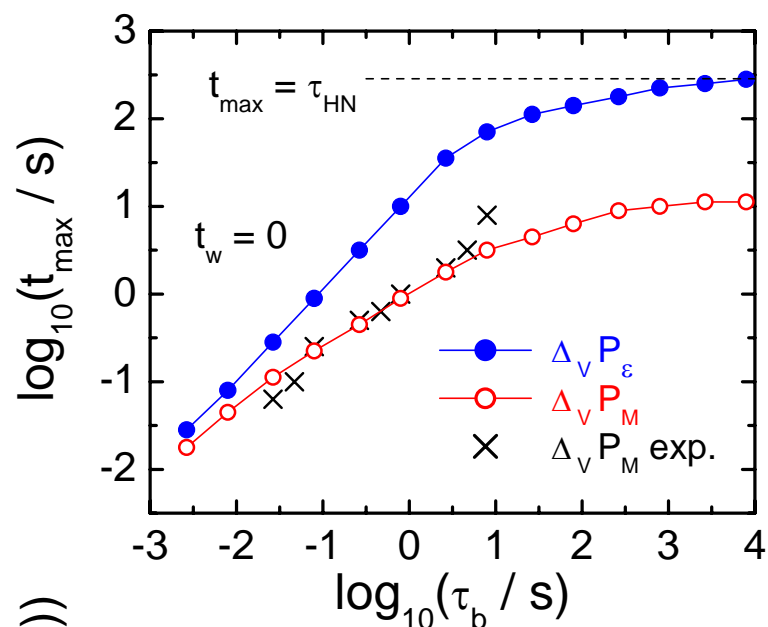
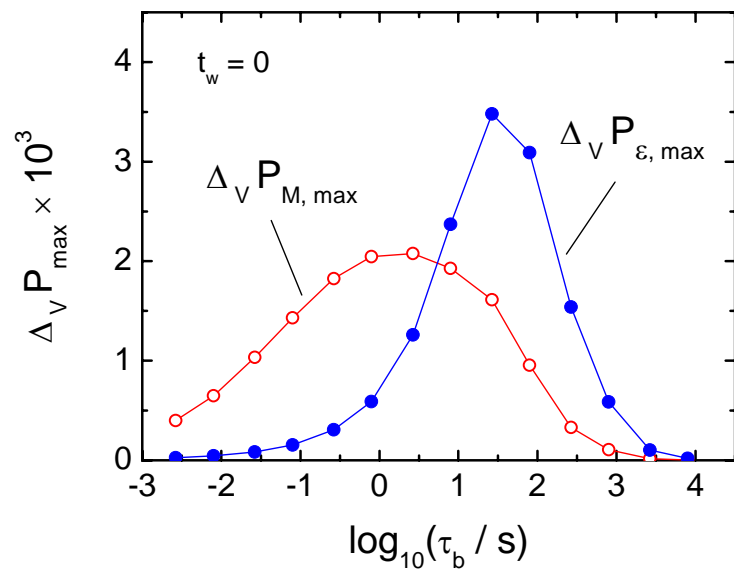
DHB in glycerol: calculated vs. measured results



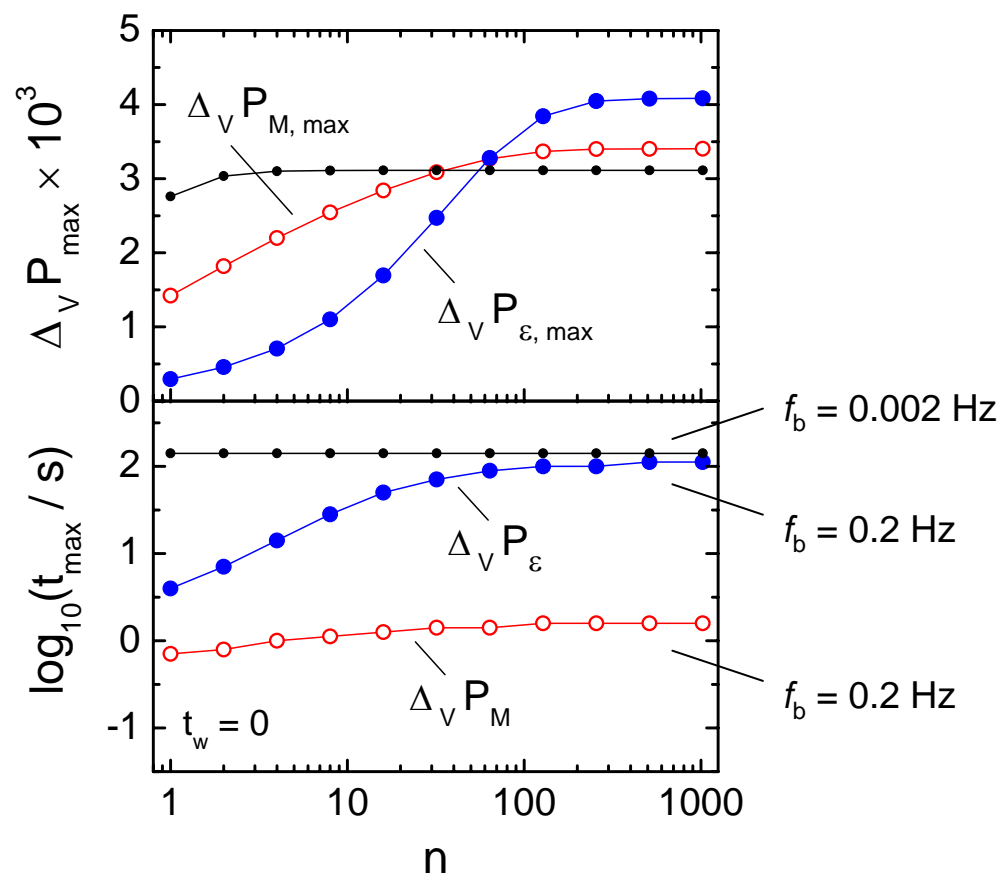
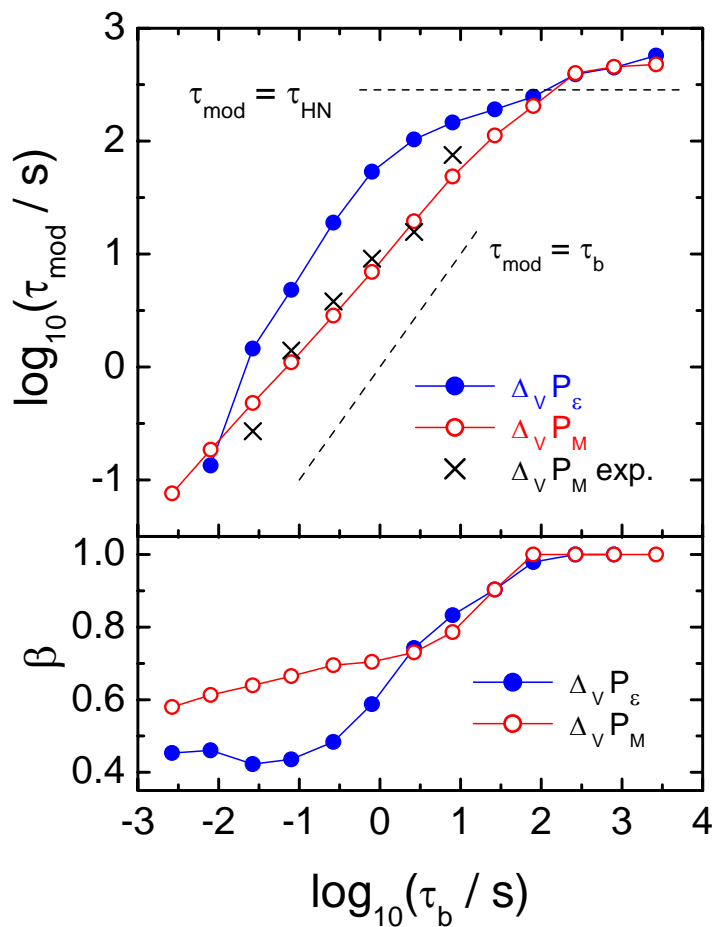
**FURTHER MODEL
'PREDICTIONS'**



DHB: insight from the model [hole amplitude and position]

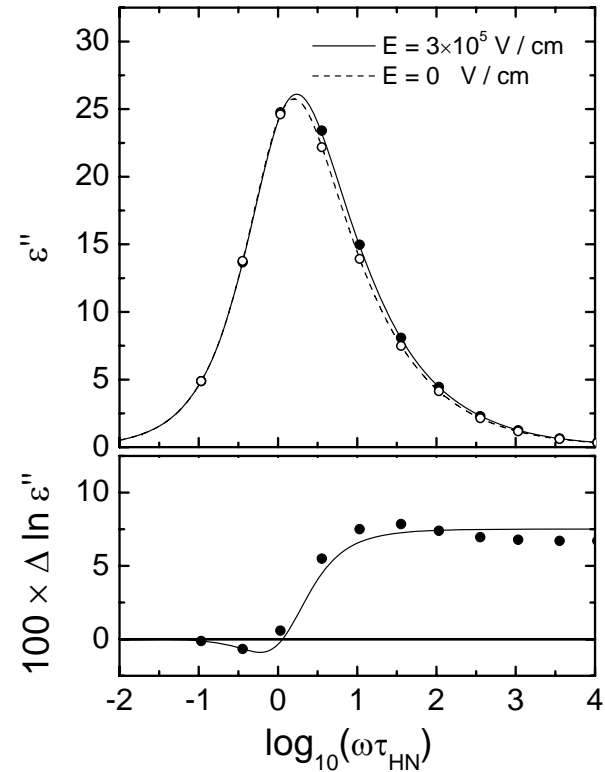
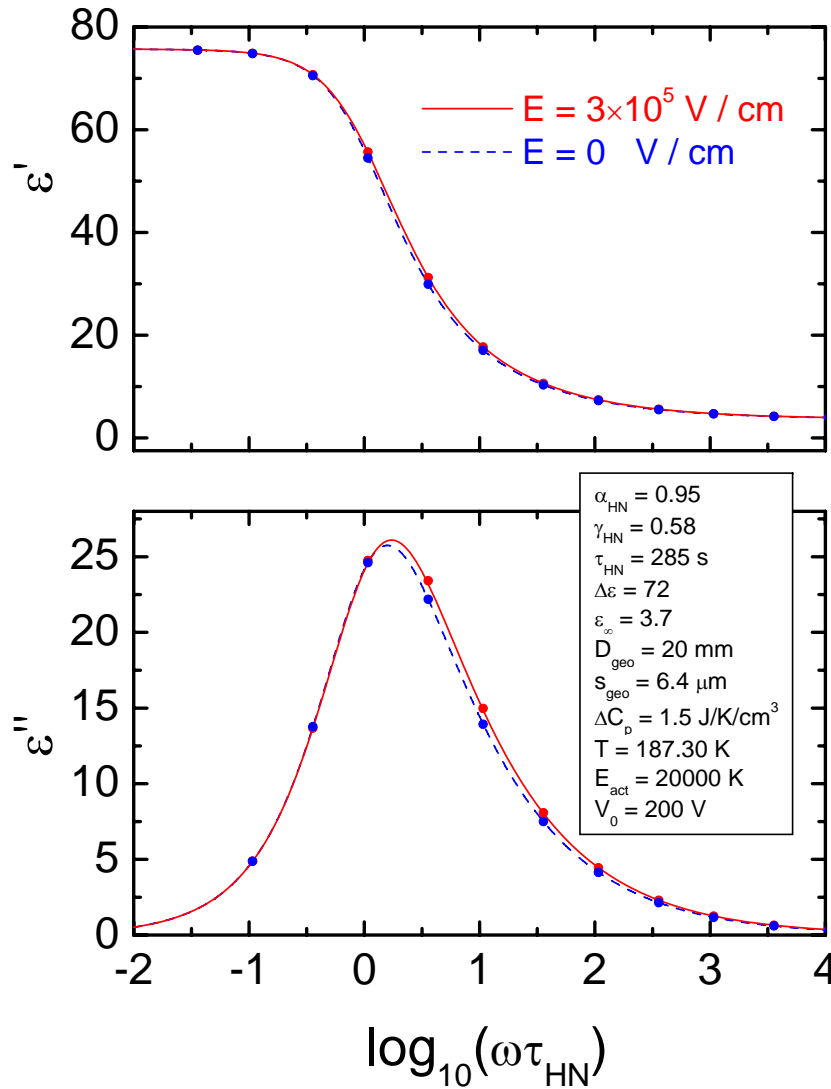


DHB: insight from the model [hole recovery and accumulation]

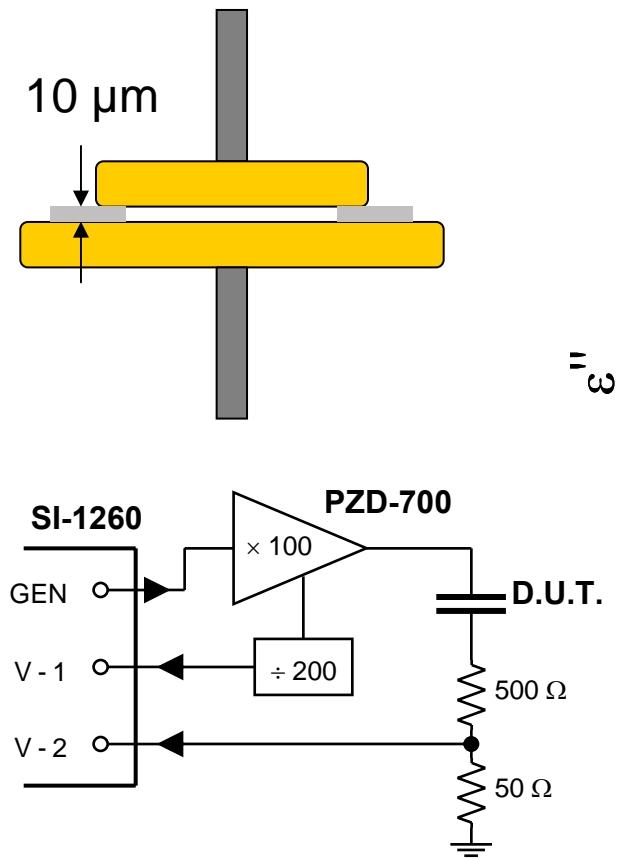


high field impedance

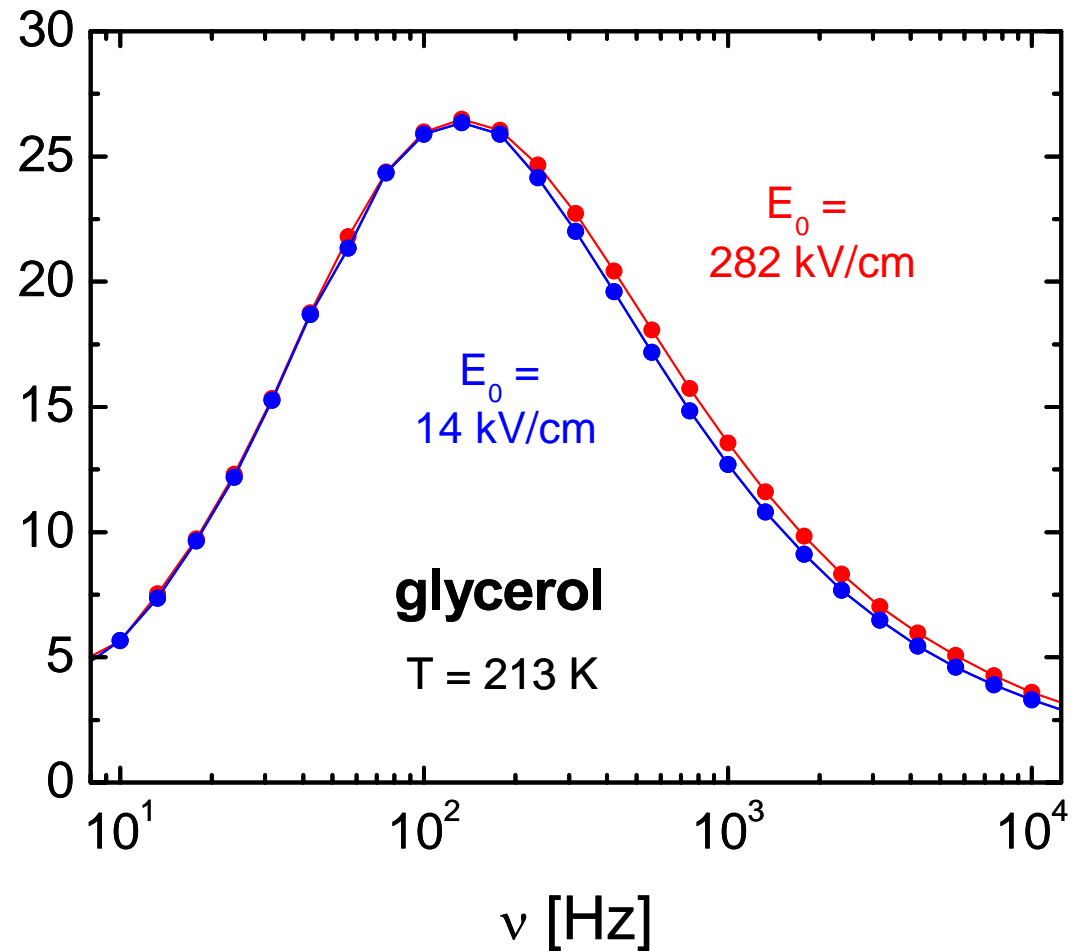
model prediction for 300 kV/cm steady state harmonic field



continuous harmonic (impedance) measurement (glycerol)



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



model for high-field steady-state harmonic measurement

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

steady state energy Q_∞/n per period :

$$\frac{Q_\infty}{n} = \pi \varepsilon_0 E_0^2 \varepsilon''(\omega_b) V$$

power P_R averaged over period :

$$P_R = \frac{Q_\infty \omega_b}{2\pi} = \frac{\varepsilon_0 E_0^2 \varepsilon''(\omega_b) V \omega_b}{2}$$

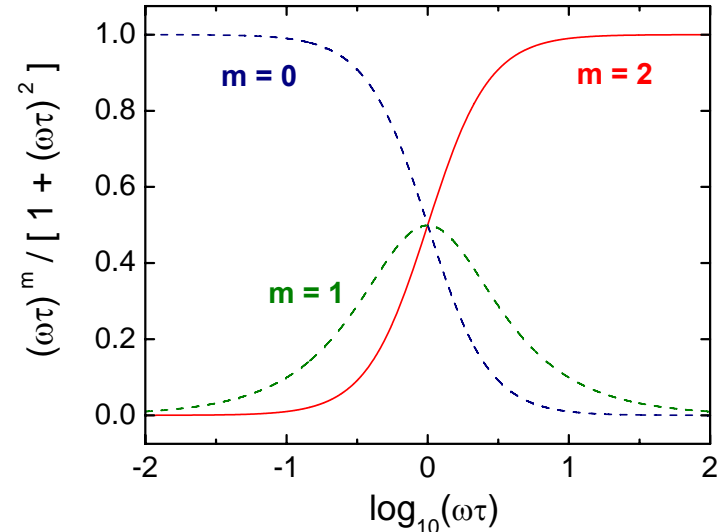
period - averaged excess T ($dT_R/dt = 0$):

$$\frac{dT_R}{dt} = \frac{P_R}{c_p} - \frac{T_R}{\tau_T} \Rightarrow T_R = \frac{\tau_T P_R}{c_p}$$

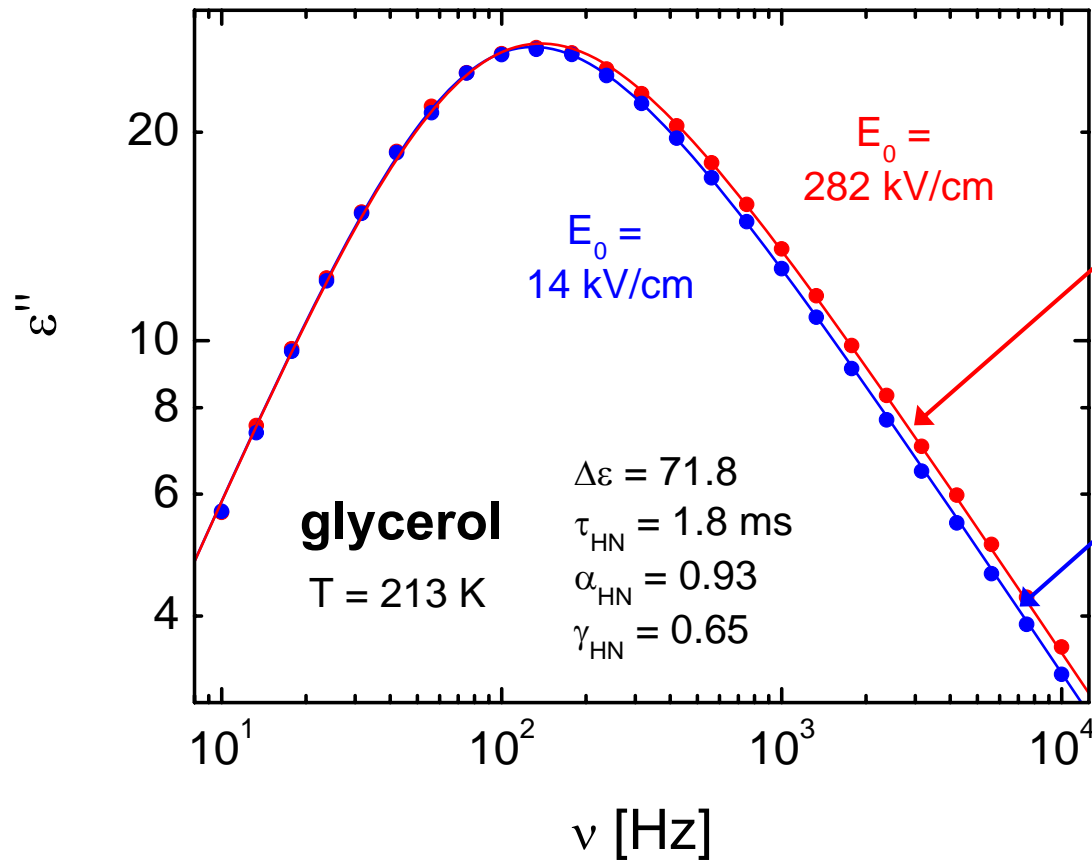
for a single domain or branch with $\tau = \tau_T = \tau_D$:

$$\varepsilon''(\omega_b) = \Delta \varepsilon \frac{\omega_b \tau}{1 + \omega_b^2 \tau^2} g(\tau) d\tau \quad c_p = \frac{C_p}{V} = \Delta c_p g(\tau) d\tau \quad \text{configurational heat capacity !}$$

$$T_R = \frac{\varepsilon_0 E_0^2 \varepsilon''(\omega_b) V \omega_b \tau}{2C_p} = \frac{\varepsilon_0 E_0^2 \Delta \varepsilon V \omega_b \tau}{2\Delta c_p V} \frac{g(\tau) d\tau}{g(\tau) d\tau} \frac{\omega_b \tau}{1 + \omega_b^2 \tau^2} = \frac{\varepsilon_0 E_0^2 \Delta \varepsilon}{2\Delta c_p} \frac{\omega_b^2 \tau^2}{1 + \omega_b^2 \tau^2}$$



high voltage impedance results for glycerol



current model:

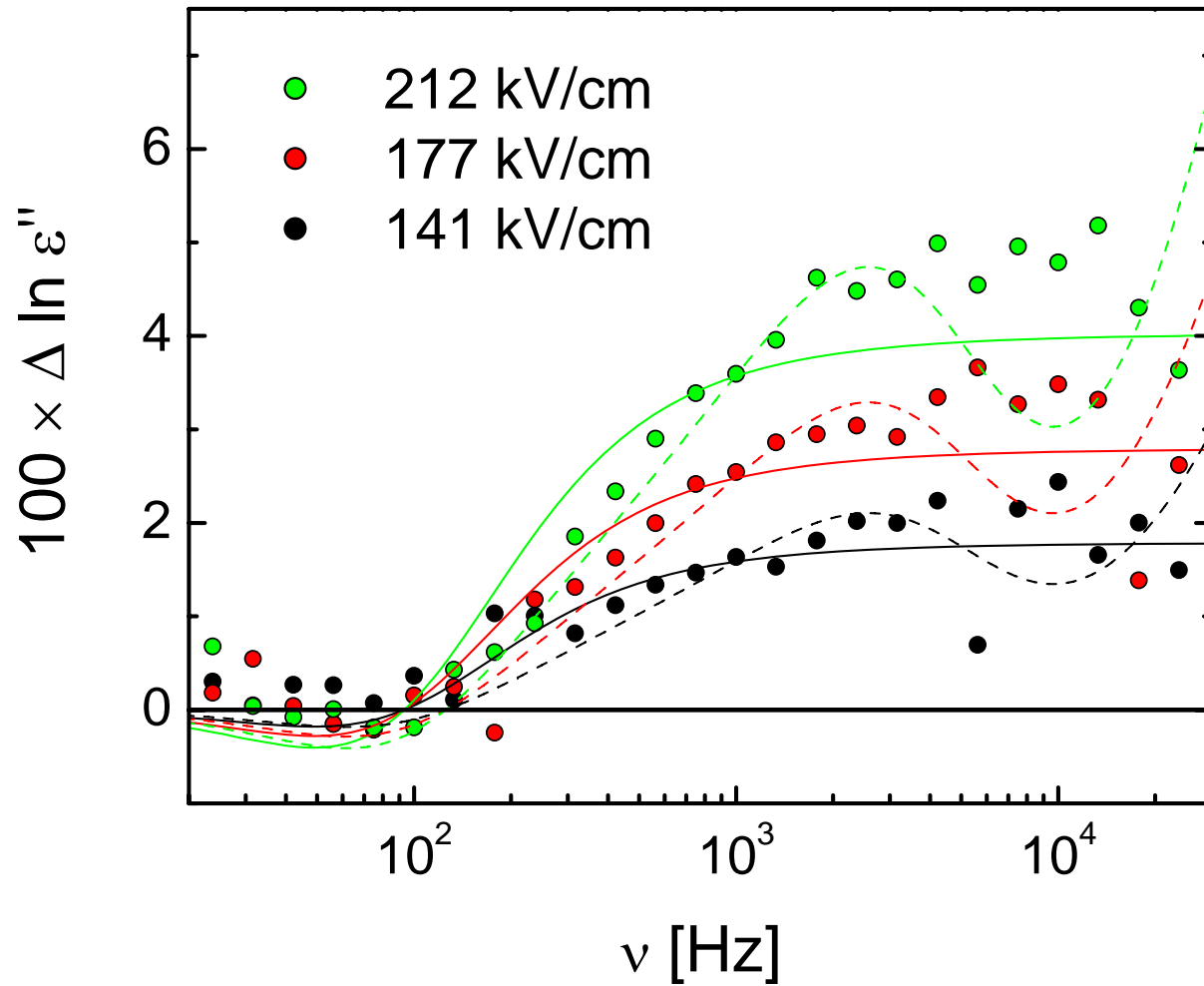
$$\ln \tau^* = \ln \tau - \frac{T_A}{T^2} \times \frac{\varepsilon_0 E_0^2 \Delta\varepsilon}{2\Delta c_p} \times \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}$$

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

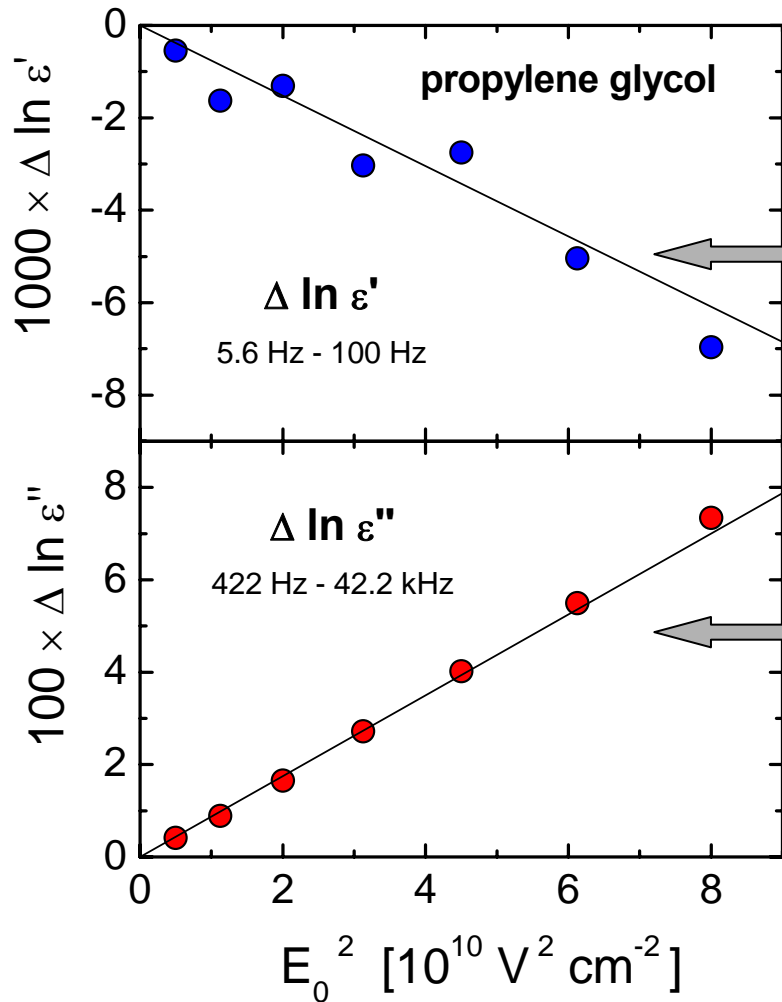
Havriliak - Negami fit:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\gamma}$$

high voltage impedance results for glycerol
[details of frequency dependent field effects]



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



Coulombic stress :

$$Fd = \frac{1}{2} QV, Q = CV, C = \epsilon \epsilon_0 A/d$$

$$F(t) = \frac{\epsilon_s \epsilon_0 A}{2} E^2(t) = \underbrace{\frac{\epsilon_s \epsilon_0 A}{4}}_{\approx 31 \text{ N}} E_0^2 - \frac{\epsilon_s \epsilon_0 A}{4} E_0^2 \cos(2\omega t)$$

dielectric saturation :

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

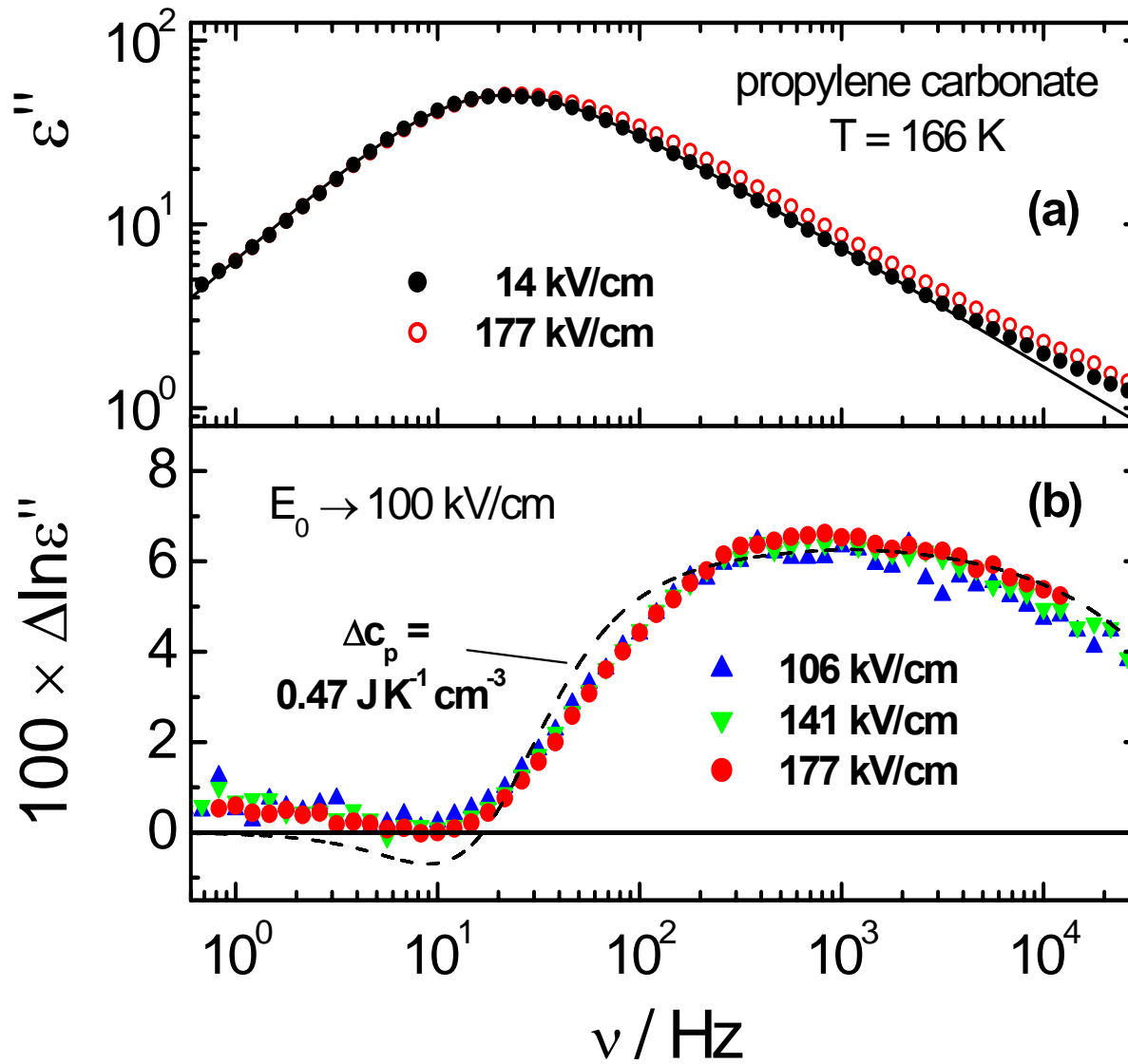
(van Vleck)

energy absorption :

$$T_e(\tau) = \frac{\epsilon_0 E_0^2 \Delta \epsilon}{2\Delta c_p} \times \frac{\omega_0^2 \tau^2}{1 + \omega_0^2 \tau^2} = T_e^0 \times \frac{\omega_0^2 \tau^2}{1 + \omega_0^2 \tau^2}$$

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

situation with other liquids: propylene carbonate



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

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

Adam-Gibbs: dynamics - thermodynamics link

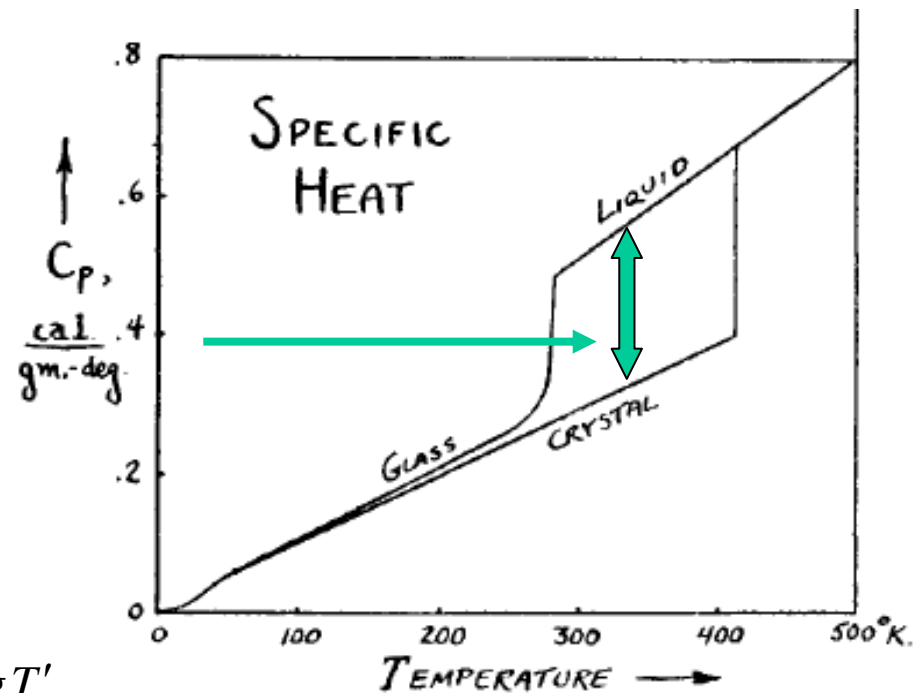
$$\tau(T) = \tau_0 \exp\left[\frac{c}{TS_{c_{fg}}(T)}\right]$$

equivalent to VFT if : $S_c(T) = S_\infty(1 - T_K/T)$

T_K is Kauzmann temperature : $\lim_{T \rightarrow T_K} S_c(T) = 0$

On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids
Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139.

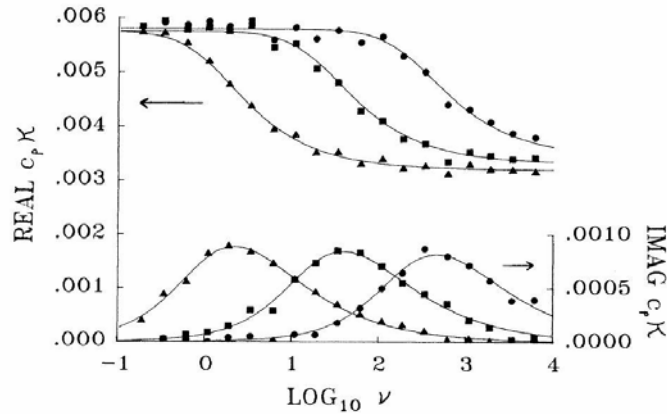
**excess specific heat =
configurational modes +
excess vibrational modes**



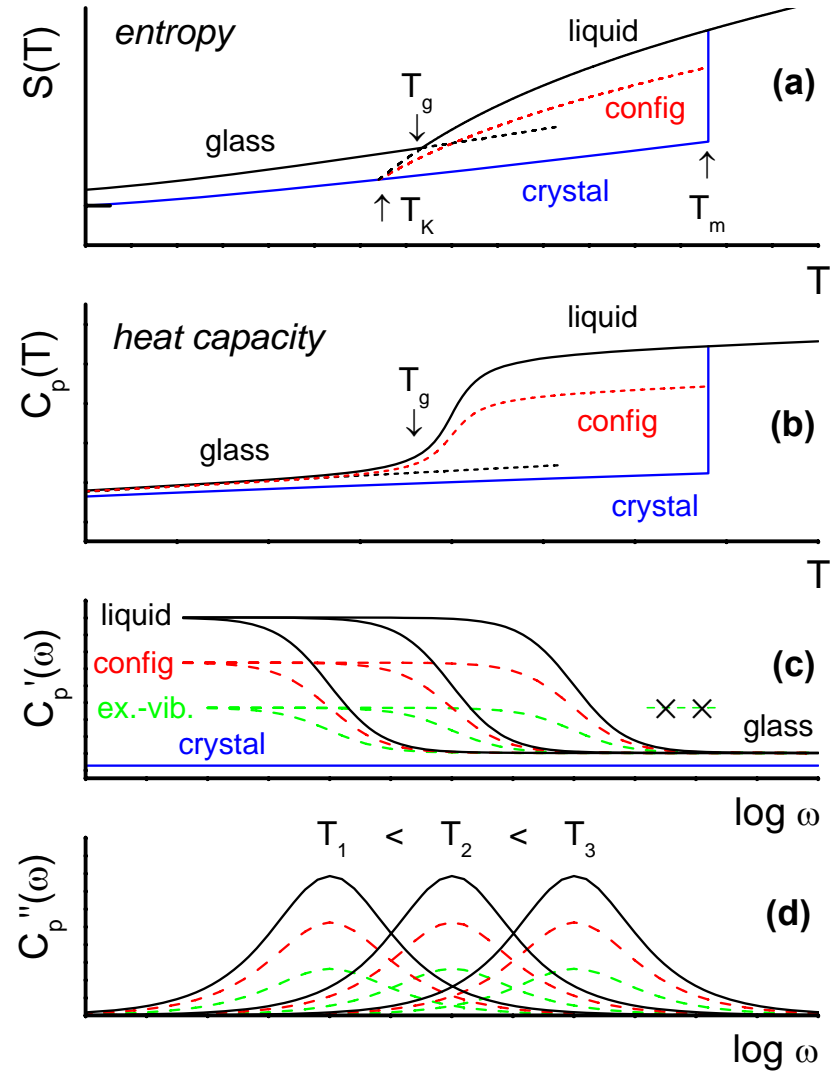
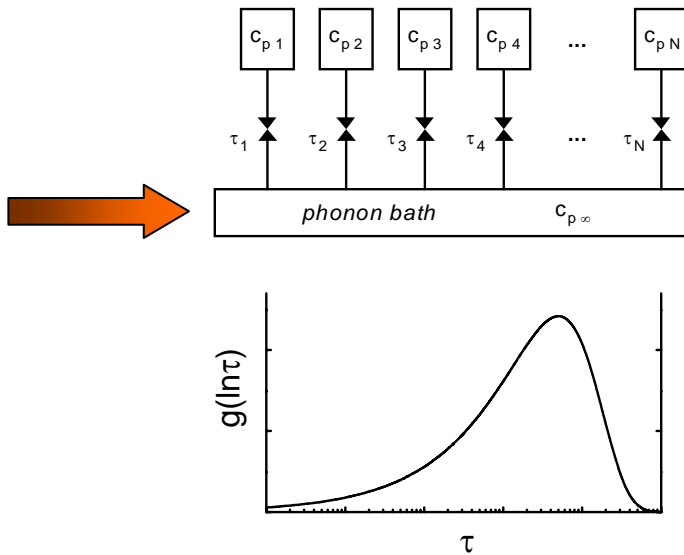
$S_{exc}(T)$ is excess entropy :

$$S_{exc}(T) = \Delta S_{fus} - \int_T^{T_{fus}} C_p^{melt}(T') - C_p^{cryst}(T') d \log T'$$

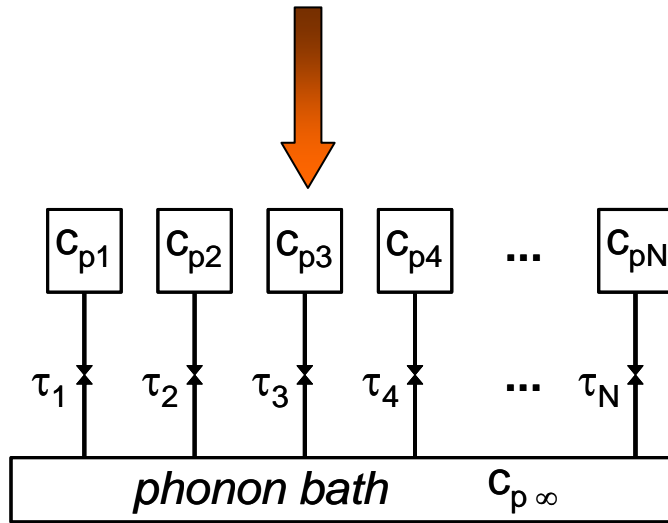
'forward' dynamic heat capacity experiment



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



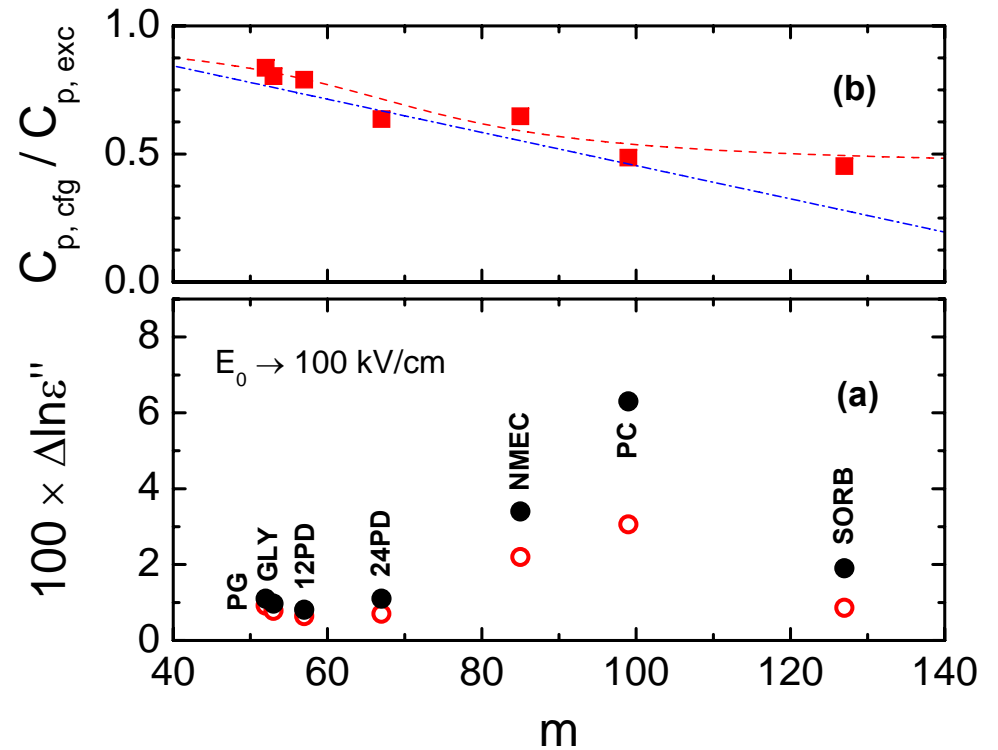
measuring the configurational heat capacity



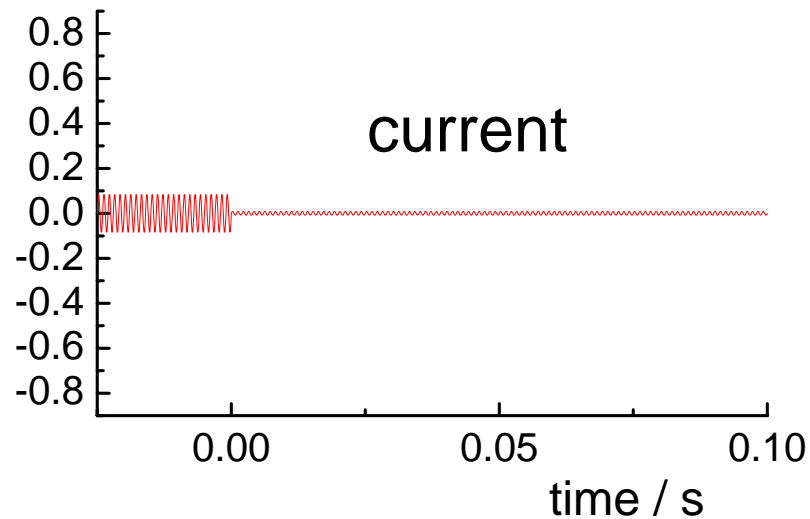
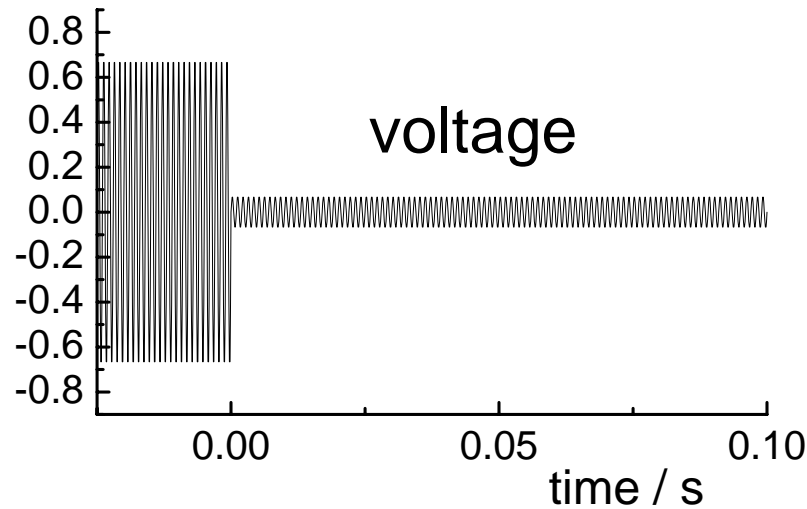
current model:

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

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



Fourier analysis of signal with field change



$$V(\omega) = A \sin(\omega t + \varphi)$$

$$R = \frac{\omega}{\pi} \int_0^{2\pi/\omega} \sin(\omega t) [A \sin(\omega t + \varphi)] dt$$

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

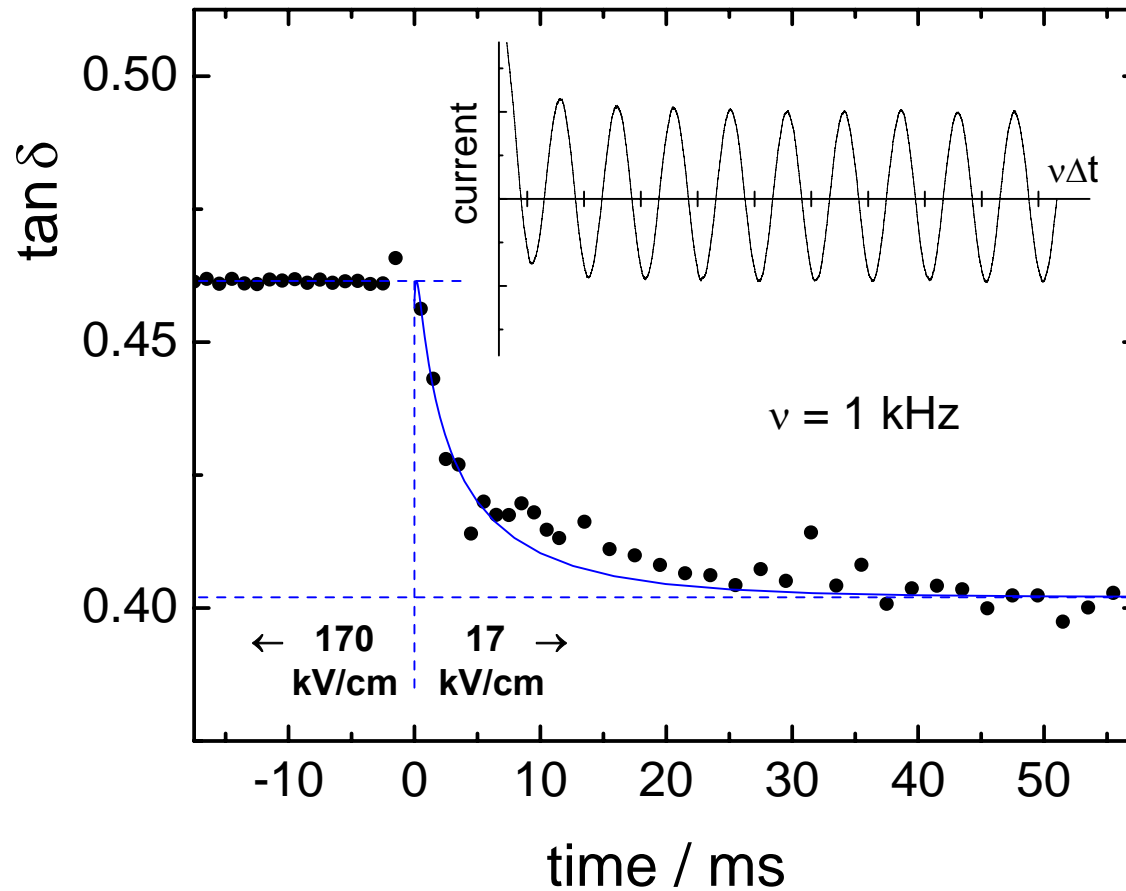
$$I = \frac{\omega}{\pi} \int_0^{2\pi/\omega} \cos(\omega t) [A \sin(\omega t + \varphi)] dt$$

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

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

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

time resolved nanoscopic heat-flow



$$V(\omega) = A \sin(\omega t + \varphi)$$

$$R = \frac{\omega}{\pi} \int_0^{2\pi/\omega} \sin(\omega t) [A \sin(\omega t + \varphi)] dt$$

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

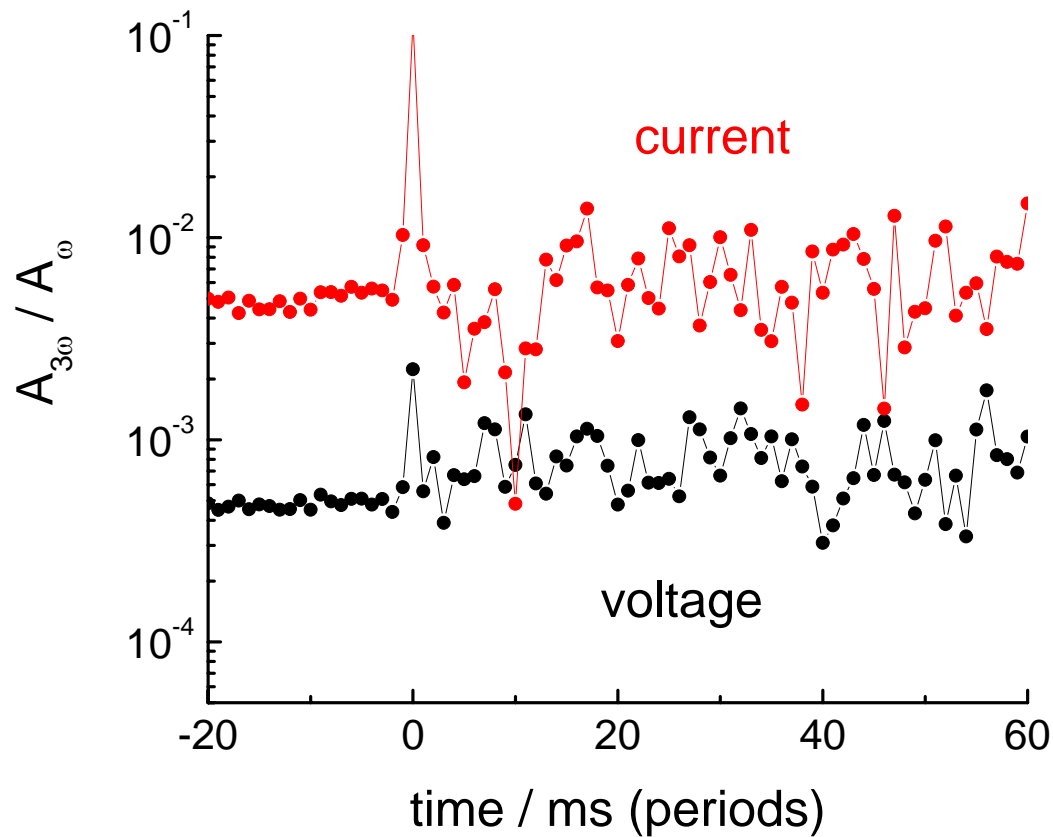
$$I = \frac{\omega}{\pi} \int_0^{2\pi/\omega} \cos(\omega t) [A \sin(\omega t + \varphi)] dt$$

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

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

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

3 ω signal during field change



$$V(\omega) = A \sin(\omega t + \varphi)$$

$$R = \frac{\omega}{\pi} \int_0^{2\pi/\omega} \sin(3\omega t) [A \sin(\omega t + \varphi)] dt$$

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

$$I = \frac{\omega}{\pi} \int_0^{2\pi/\omega} \cos(3\omega t) [A \sin(\omega t + \varphi)] dt$$

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

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