School of Molecular Sciences
ARIZONA STATE UNIVERSITY

SOLVATION
DIELECTRICS
Ranko Richert
LIQUIDS ... GLASSES

# *Techniques of Time-Resolved Dielectric Relaxation Measurements in the Nonlinear Regime*


## Ranko Richert


Tutorial on "Physics of Dielectrics - Basic Principles and Applications"

Pisa, Italy
11 September 2016

- ► non-linear basics
- ► experimental techniques
- ► chemical effects
- ► energy absorption
- ► entropy effects
- ► NDE summary

# dielectric relaxation: static permittivity

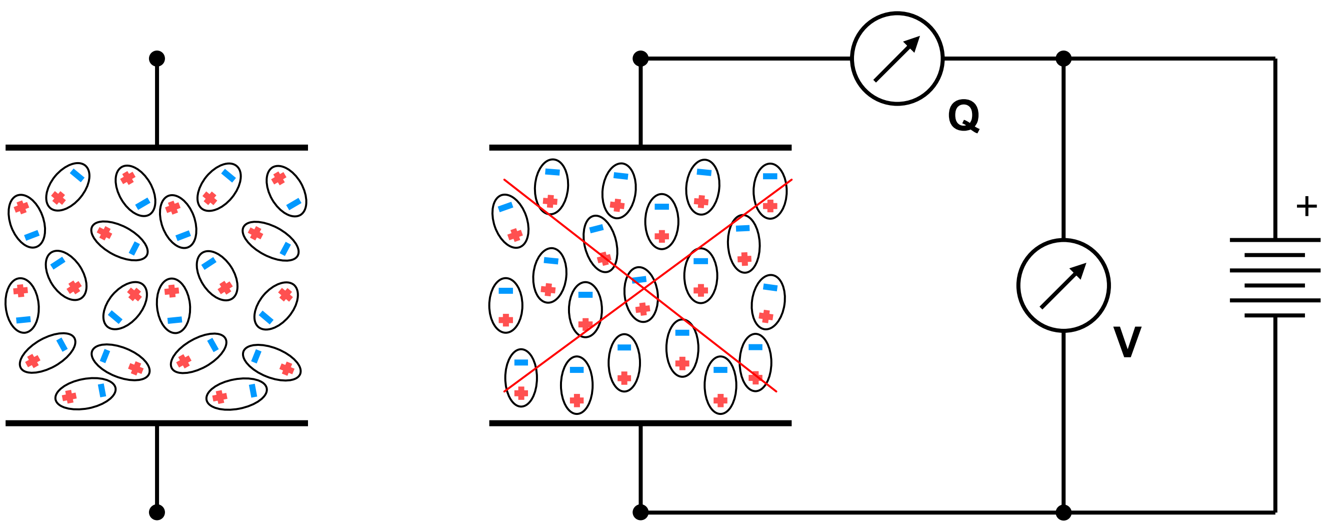
$$\mathbf{D} = \varepsilon \ \varepsilon_0 \ \mathbf{E}$$

*dielectric displacement*

$$\mathbf{D} \equiv \frac{\mathbf{Q}}{\mathbf{A}} = \varepsilon \varepsilon_0 \frac{\mathbf{V}}{\mathbf{d}} \equiv \varepsilon \varepsilon_0 \mathbf{E}$$

*electric field*

$\mathbf{E} \approx \mathbf{0}$ $\mathbf{E} > \mathbf{0}$




$$\mu E << k_B T$$

R. Richert, Adv. Chem. Phys. 156 (2015) 101

# Nonlinear Basics

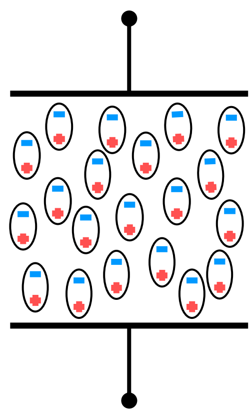
# limits to linear dielectric behavior

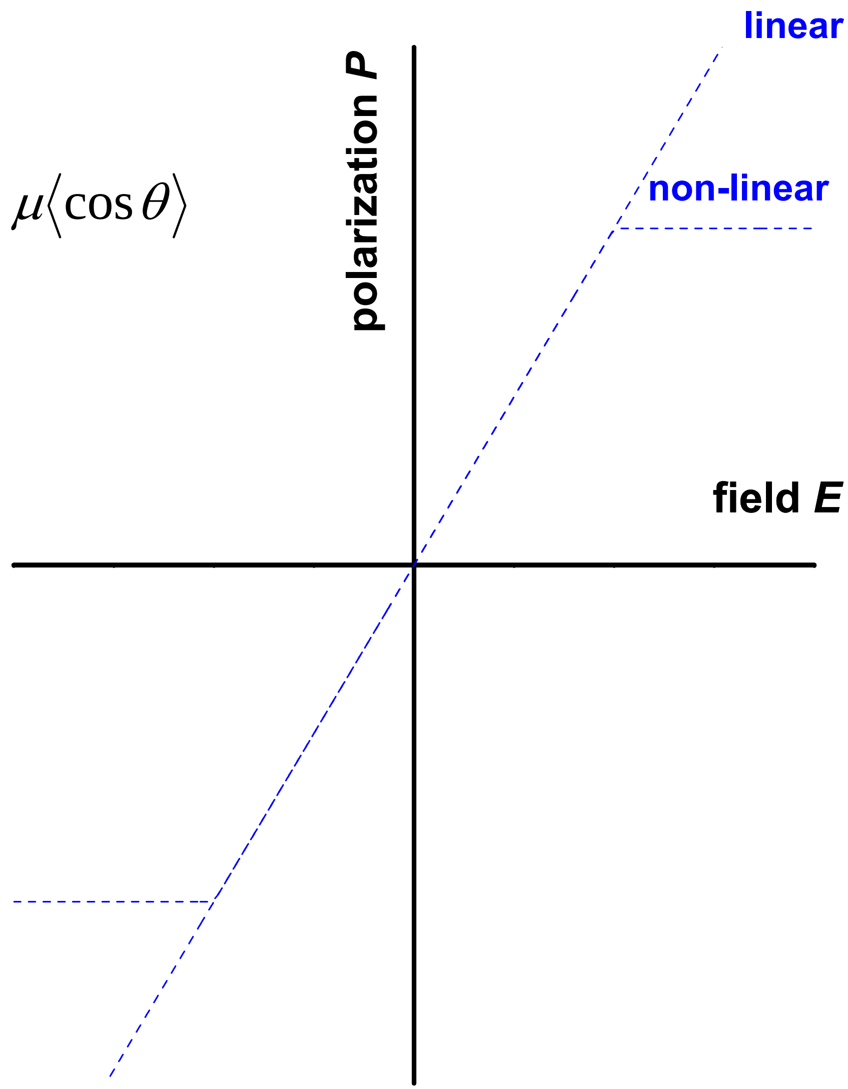
$$P = \frac{\rho N_A}{M}\left(\alpha_{el} + \alpha_{or}\right)E$$

$$\alpha_{or} = \frac{\mu\langle\cos\theta\rangle}{E}$$

$$P \propto \alpha_{el}E + \mu\langle\cos\theta\rangle$$

$$\langle\cos\theta\rangle = 1$$






A real dipolar system is limited to: $\langle\cos\theta\rangle \leq 1$

**Langevin saturation effect**
(for dipole gas)

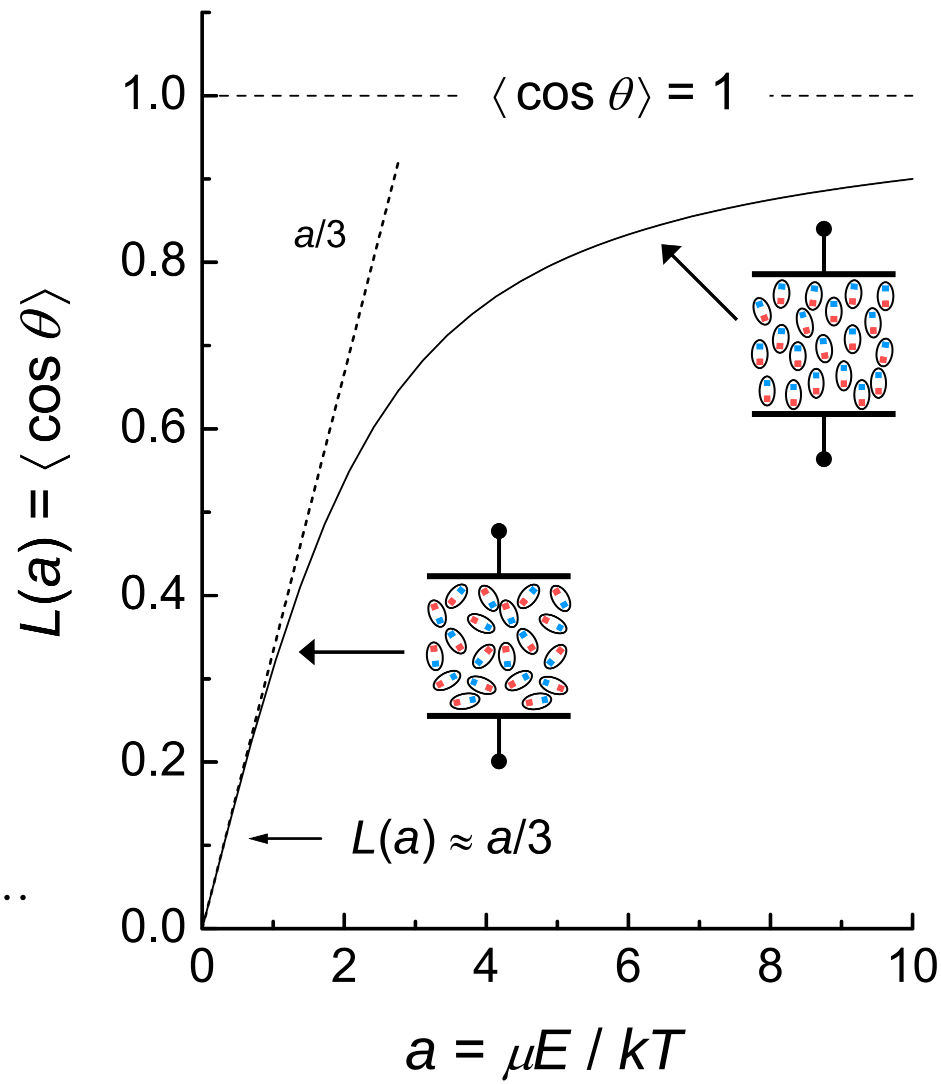
$$\langle \cos\theta \rangle = \frac{\iint_{4\pi} \cos\theta \, e^{\mu E \cos\theta / kT} \, d\Omega}{\iint_{4\pi} e^{\mu E \cos\theta / kT} \, d\Omega}$$

$\Rightarrow$

Langevin function, $a = \mu E / kT$ :

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

$$L(a) \approx \frac{1}{3}a - \frac{1}{45}a^3 + \frac{2}{945}a^5 - \frac{2}{9450}a^7 + \ldots$$



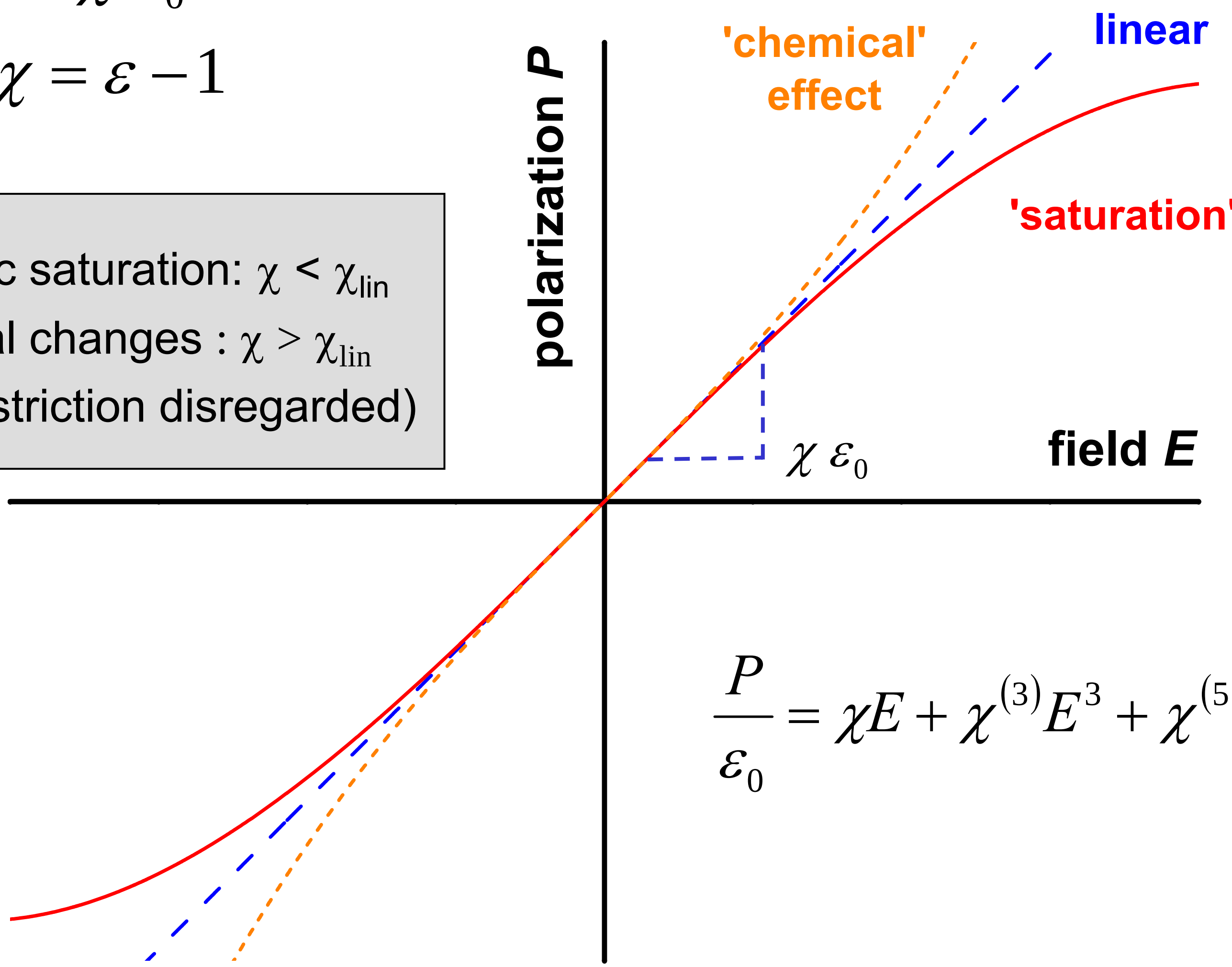

C.J.F. Böttcher, Theory of Electric Polarization Vol.1 (Elsevier, 1973)

# non-linear dielectric effects: static limit

$$P \approx \chi\, \varepsilon_0\, E$$

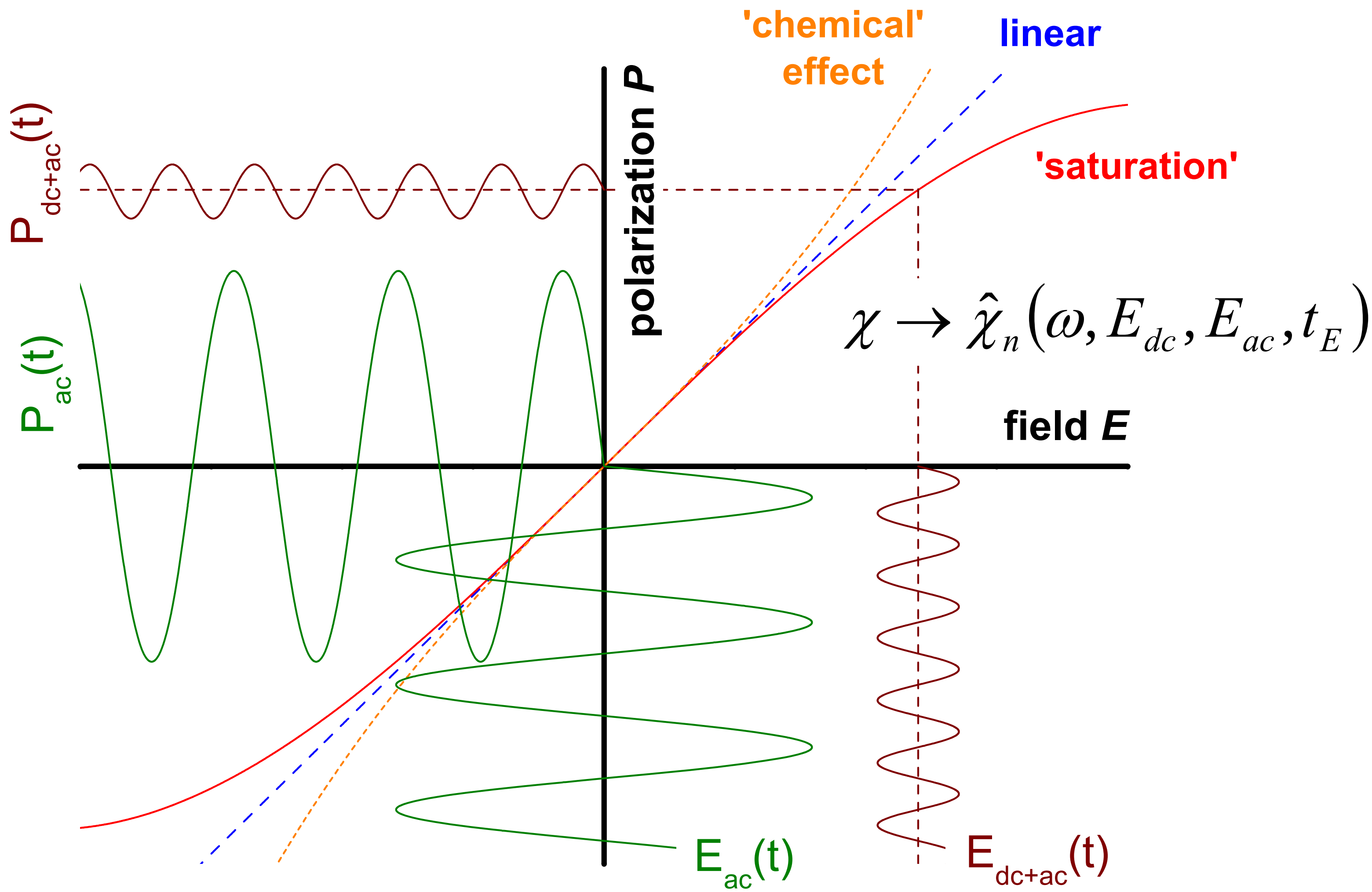
$$\chi = \varepsilon - 1$$

dielectric saturation: $\chi < \chi_{lin}$
chemical changes : $\chi > \chi_{lin}$
(electrostriction disregarded)

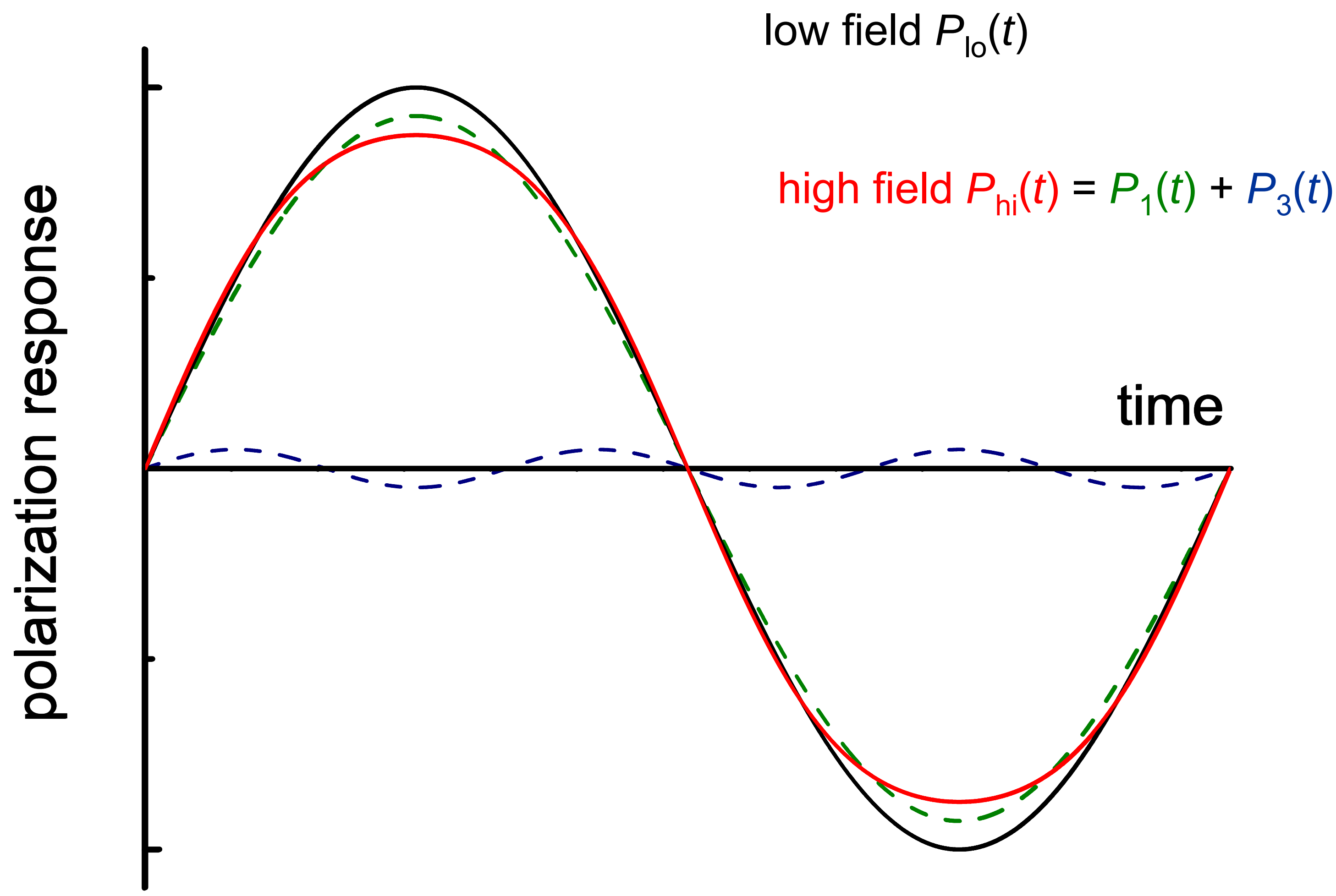



$$\frac{P}{\varepsilon_0} = \chi E + \chi^{(3)} E^3 + \chi^{(5)} E^5 + \ldots$$

# beyond the static limit: ac- versus dc-field approach




R. Richert, Phys. Rev. E 88 (2013) 062313 gauging deviation from linear dielectric response



# Fourier analysis of polarization

high field $P_{hi}(t) = P_1(t) + P_3(t)$

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

$$P_n'(\omega) = \underbrace{\frac{\omega}{\pi} \int_t^{t+k2\pi/\omega} \sin(n\omega t') P(t') dt'}_{\text{in-phase component}} \quad , \quad P_n''(\omega) = \underbrace{\frac{\omega}{\pi} \int_t^{t+k2\pi/\omega} \cos(n\omega t') P(t') dt'}_{\text{out-of-phase component}}$$

$$\left.\begin{aligned} \varepsilon'(\omega) &= 1 + \frac{\sqrt{P_1'^2 + P_1''^2}}{\varepsilon_0 E_0} \times \cos \arctan(P_1''/P_1') \\ \varepsilon''(\omega) &= -\frac{\sqrt{P_1'^2 + P_1''^2}}{\varepsilon_0 E_0} \times \sin \arctan(P_1''/P_1') \end{aligned}\right\} \quad \hat{\varepsilon}(\omega) = 1 + \hat{\chi}(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

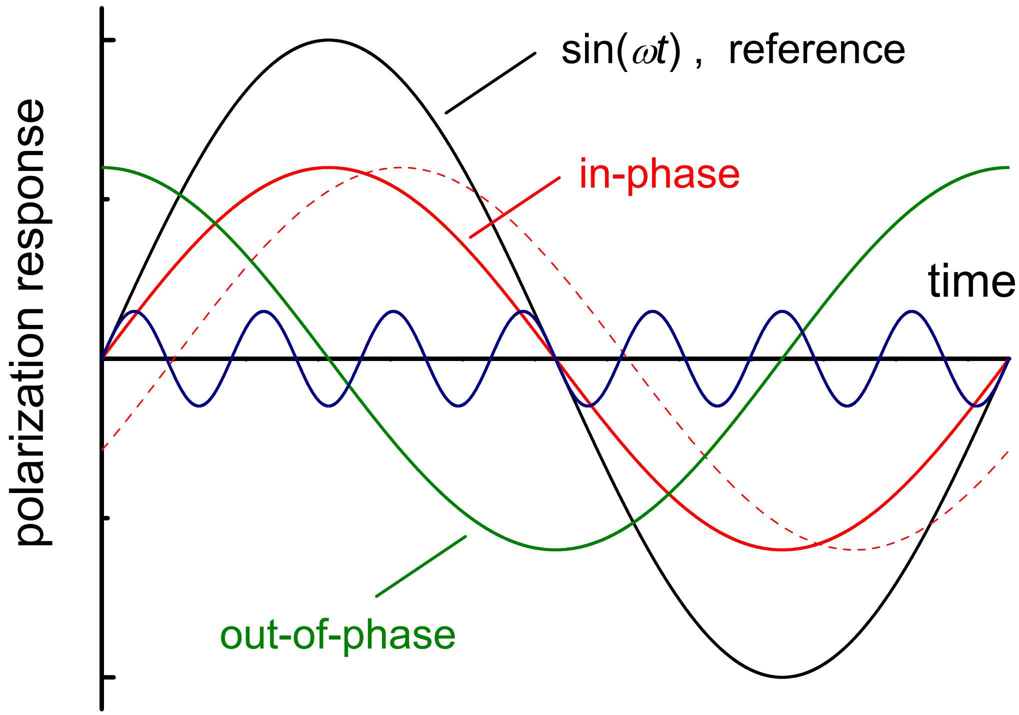
$$|\chi_n(\omega)| E_0^{n-1} = \frac{\sqrt{P_n'^2 + P_n''^2}}{\varepsilon_0 E_0}$$

P. Kim, A. R. Young-Gonzales, R. Richert, J. Chem. Phys. 145 (2016) 064510

# Fourier analysis of polarization

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

$$P_n'(\omega) = \underbrace{\frac{\omega}{\pi} \int_t^{t+k2\pi/\omega} \sin(n\omega t')P(t')dt'}_{\text{in-phase component}} \; , \quad P_n''(\omega) = \underbrace{\frac{\omega}{\pi} \int_t^{t+k2\pi/\omega} \cos(n\omega t')P(t')dt'}_{\text{out-of-phase component}}$$




$$\sin(\omega t \pm \varphi) = \underbrace{\cos\varphi}_{\substack{\text{in-phase}\\ \text{amplitude}}} \sin(\omega t) \pm \underbrace{\sin\varphi}_{\substack{\text{out-of-phase}\\ \text{amplitude}}} \cos(\omega t)$$

# appearence of $\chi_n$'s in first eight Fourier components

$$E(t) = E_B + E_0 \cos(\omega t)$$

$$\frac{P(t)}{\varepsilon_0} = \hat{\chi}^{(1)}(\omega)E(t) + \hat{\chi}^{(3)}(\omega)E^3(t) + \ldots$$

---

$$\frac{\hat{P}_0(0)}{\varepsilon_0 E_B} = \hat{\chi}_0(0) + \left(E_B^2 + \frac{3}{2}E_0^2\right)\hat{\chi}_0^{(3)}(0)$$

$$\frac{\hat{P}_1(\omega)}{\varepsilon_0 E_0} = \hat{\chi}_1(\omega) + 3\left(E_B^2 + \frac{1}{4}E_0^2\right)\hat{\chi}_1^{(3)}(\omega)$$

$$\frac{\hat{P}_2(2\omega)}{\varepsilon_0 E_B} = \frac{3}{2}E_0^2\hat{\chi}_2^{(3)}(\omega)$$

$$\frac{\hat{P}_3(3\omega)}{\varepsilon_0 E_0} = \frac{1}{4}E_0^2\hat{\chi}_3^{(3)}(\omega)$$

---

**$E_B = 0$:**

$$\Delta_E \frac{\hat{P}_1(\omega)}{\varepsilon_0 E_0} = \underbrace{\hat{\chi}_1(\omega) + \frac{3}{4}E_0^2\hat{\chi}_1^{(3)}(\omega)}_{\text{high field}} - \underbrace{\hat{\chi}_1(\omega)}_{\text{low field}} = \frac{3}{4}E_0^2\hat{\chi}_1^{(3)}(\omega)$$

$\updownarrow$

$$\frac{\hat{P}_3(\omega)}{\varepsilon_0 E_0} = \frac{1}{4}E_0^2\hat{\chi}_3^{(3)}(\omega)$$

R. Richert, Phys. Rev. E 88 (2013) 062313

# perturbation approach to nonlinear dielectric response

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

$$\langle P_1(\cos\theta)\rangle = \frac{\mu}{3kT\tau}\int_{-\infty}^{t} e^{-\frac{t-t_1}{\tau}} E(t_1)\,dt_1$$

$$-\frac{1}{15}\left(\frac{\mu}{kT\tau}\right)^3 \iiint_{-\infty<t_3\le t_2\le t_1\le t} e^{-\frac{t-t_1}{\tau}} e^{-3\frac{t_1-t_2}{\tau}} e^{-\frac{t_2-t_3}{\tau}} E(t_3)E(t_2)E(t_1)\,dt_3\,dt_2\,dt_1$$

$$+\frac{6}{175}\left(\frac{\mu}{kT\tau}\right)^5 \int\!\!\int\!\!\int\!\!\int\!\!\int_{-\infty<t_5\le\ldots\le t_1\le t} e^{-\frac{t-t_1}{\tau}} e^{-3\frac{t_1-t_2}{\tau}} e^{-6\frac{t_2-t_3}{\tau}} e^{-3\frac{t_3-t_4}{\tau}} e^{-\frac{t_4-t_5}{\tau}} E(t_5)E(t_4)E(t_3)E(t_2)E(t_1)\,dt_5\,dt_4\,dt_3\,dt_2\,dt_1$$

$$-\ldots$$

with limit to third order we find "after considerable algebra":

$$\langle P_1(\cos\theta)\rangle = \frac{1}{3}\frac{\mu E_0}{kT}\times\left[\frac{\cos(\omega t)}{1+\omega^2\tau^2}+\frac{\omega t\sin(\omega t)}{1+\omega^2\tau^2}\right]$$

$$-\frac{1}{3}\left(\frac{\mu E_0}{kT}\right)^3\times\left[\frac{(27-13\omega^2\tau^2)}{540(1+\omega^2\tau^2)(1+4\omega^2\tau^2/9)}\times\frac{\cos(\omega t)}{1+\omega^2\tau^2}+\frac{(21+\omega^2\tau^2)}{270(1+\omega^2\tau^2)(1+4\omega^2\tau^2/9)}\times\frac{\omega t\sin(\omega t)}{1+\omega^2\tau^2}\right]$$

$$-\frac{1}{3}\left(\frac{\mu E_0}{kT}\right)^3\times\left[\frac{(3-17\omega^2\tau^2)}{180(1+\omega^2\tau^2)(1+4\omega^2\tau^2/9)}\times\frac{\cos(3\omega t)}{1+(3\omega)^2\tau^2}+\frac{(7-3\omega^2\tau^2)}{90(1+\omega^2\tau^2)(1+4\omega^2\tau^2/9)}\times\frac{\omega t\sin(3\omega t)}{1+(3\omega)^2\tau^2}\right]$$

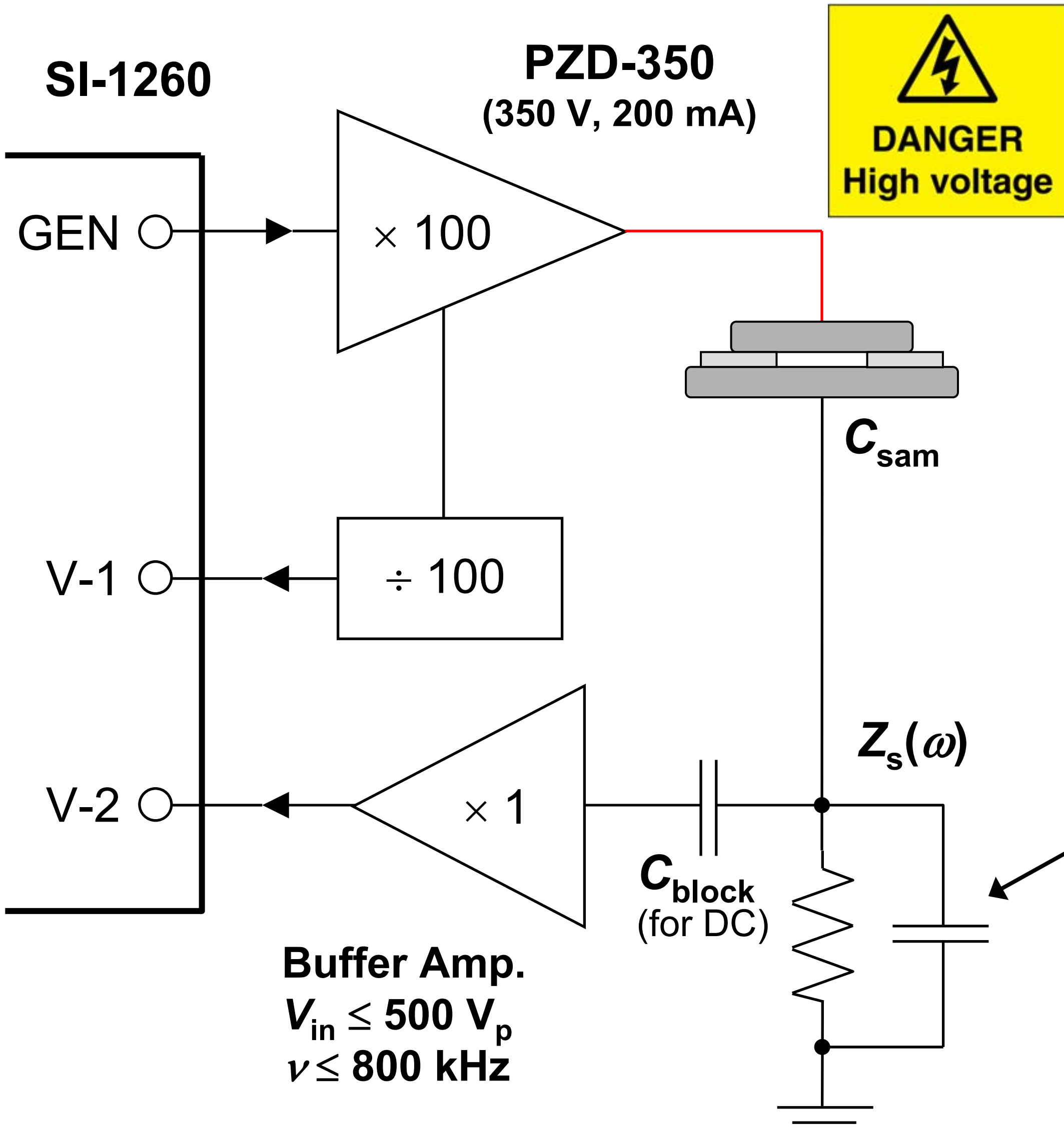
**limited to:** **third order effect, non-interacting dipoles, Debye type response, stationary state**

W. T. Coffey, B. V. Paranjape, Proc. R. Ir. Acad. 78 (1978) 17

# Experimental Techniques

(polar viscous liquids)

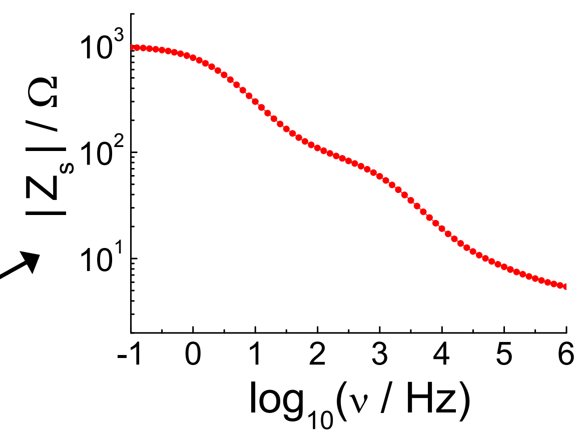
# experimental techniques: high field impedance




$E_0 \leq 650$ kV/cm

$\mu E \leq 0.1\ kT$

$\nu = 0.1$ Hz ... 350 kHz

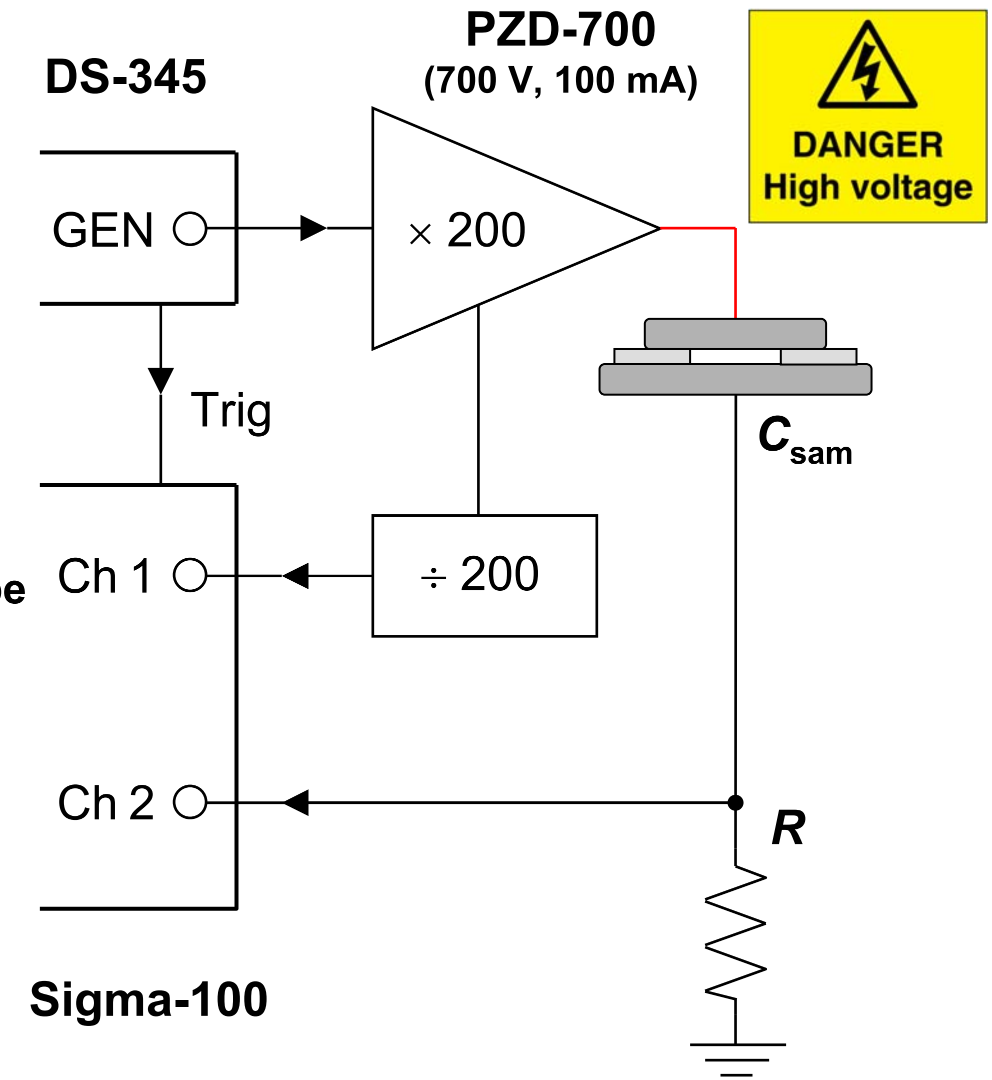



U. Pathak, R. Richert, Colloid Polym. Sci. 292 (2014) 1905

# experimental techniques: time resolved techniques

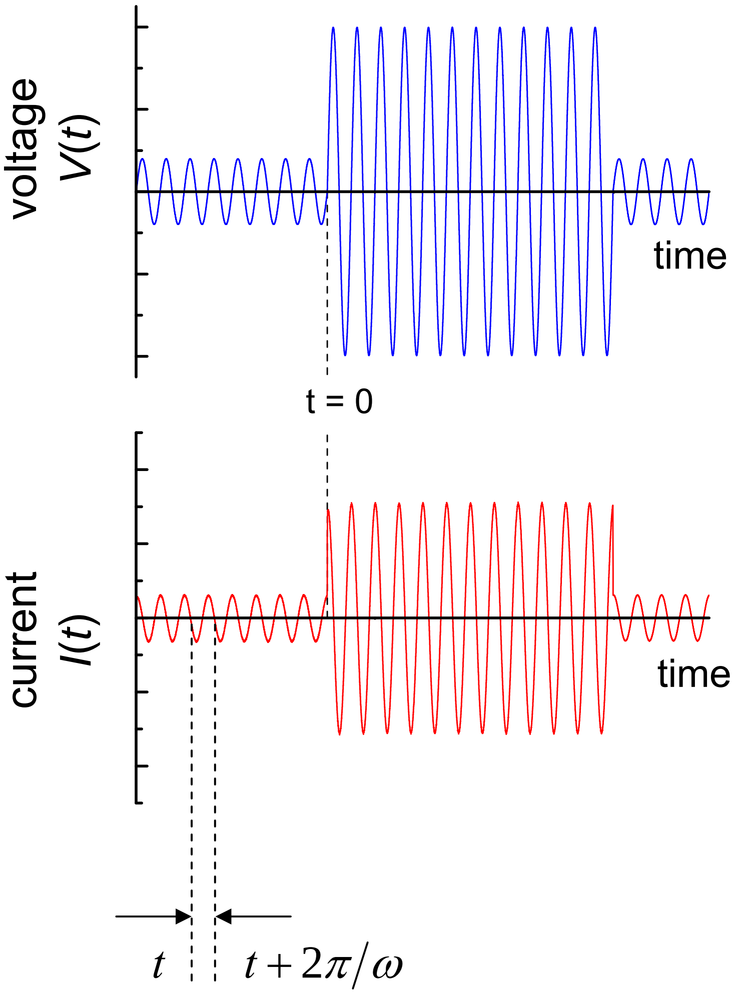
**SRS DS-345:**
**Arbitrary Waveform Signal Generator**
(16300 points, 12 bit)
10 μHz ≤ $\nu$ ≤ 30 MHz

**Nicolet Sigma 100:**
**Digital Storage Oscilloscope**
4 channels, 100 MS/s
vertical: 14 bit
horizontal: $10^6$ points




U. Pathak, R. Richert, Colloid Polym. Sci. 292 (2014) 1905

# adding time-resolution capabilities to high-field technique: ac




Fourier analysis for each period: $t \ldots t + 2\pi/\omega$

$$V' = \frac{\omega}{\pi} \int_{t}^{t+2\pi/\omega} \sin(\omega t') V(t') dt'$$

$$V'' = \frac{\omega}{\pi} \int_{t}^{t+2\pi/\omega} \cos(\omega t') V(t') dt'$$

$$A_V = \sqrt{V'^2 + V''^2}$$

$$\varphi_V = \arctan(V''/V')$$

$$I' = \frac{\omega}{\pi} \int_{t}^{t+2\pi/\omega} \sin(\omega t') I(t') dt'$$

$$I'' = \frac{\omega}{\pi} \int_{t}^{t+2\pi/\omega} \cos(\omega t') I(t') dt'$$

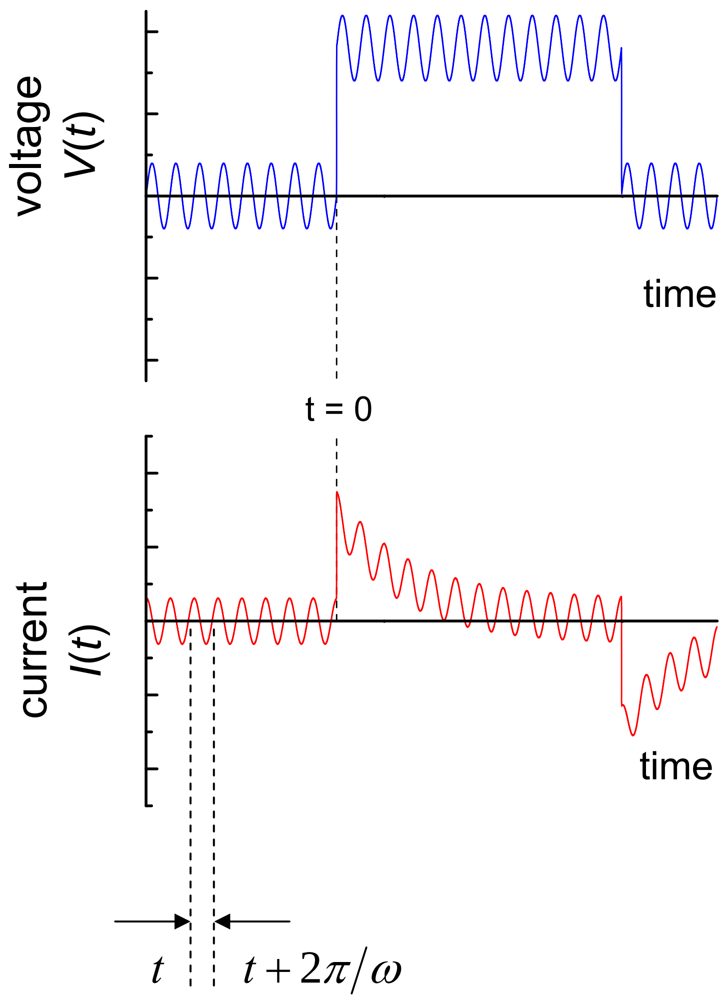
$$A_I = \sqrt{I'^2 + I''^2}$$

$$\varphi_I = \arctan(I''/I')$$

$$e'(t) = \left| \frac{A_I \sin(\varphi_I - \varphi_V)}{\omega A_V C_0} \right| , \quad e''(t) = \left| \frac{A_I \cos(\varphi_I - \varphi_V)}{\omega A_V C_0} \right|$$


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

# adding time-resolution capabilities to high-field technique: dc




Fourier analysis for each period: $t \ldots t+2\pi/\omega$

$$V' = \frac{\omega}{\pi}\int_t^{t+2\pi/\omega}\sin(\omega t')V(t')dt' \qquad A_V = \sqrt{V'^2 + V''^2}$$

$$V'' = \frac{\omega}{\pi}\int_t^{t+2\pi/\omega}\cos(\omega t')V(t')dt' \qquad \varphi_V = \arctan(V''/V')$$

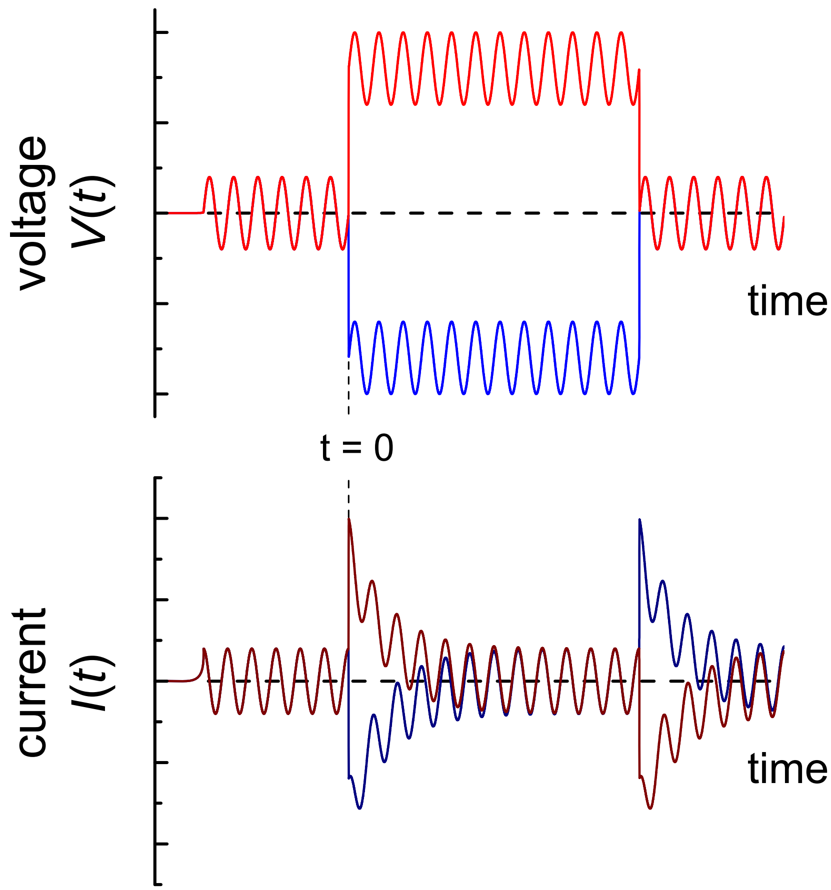
$$I' = \frac{\omega}{\pi}\int_t^{t+2\pi/\omega}\sin(\omega t')I(t')dt' \qquad A_I = \sqrt{I'^2 + I''^2}$$

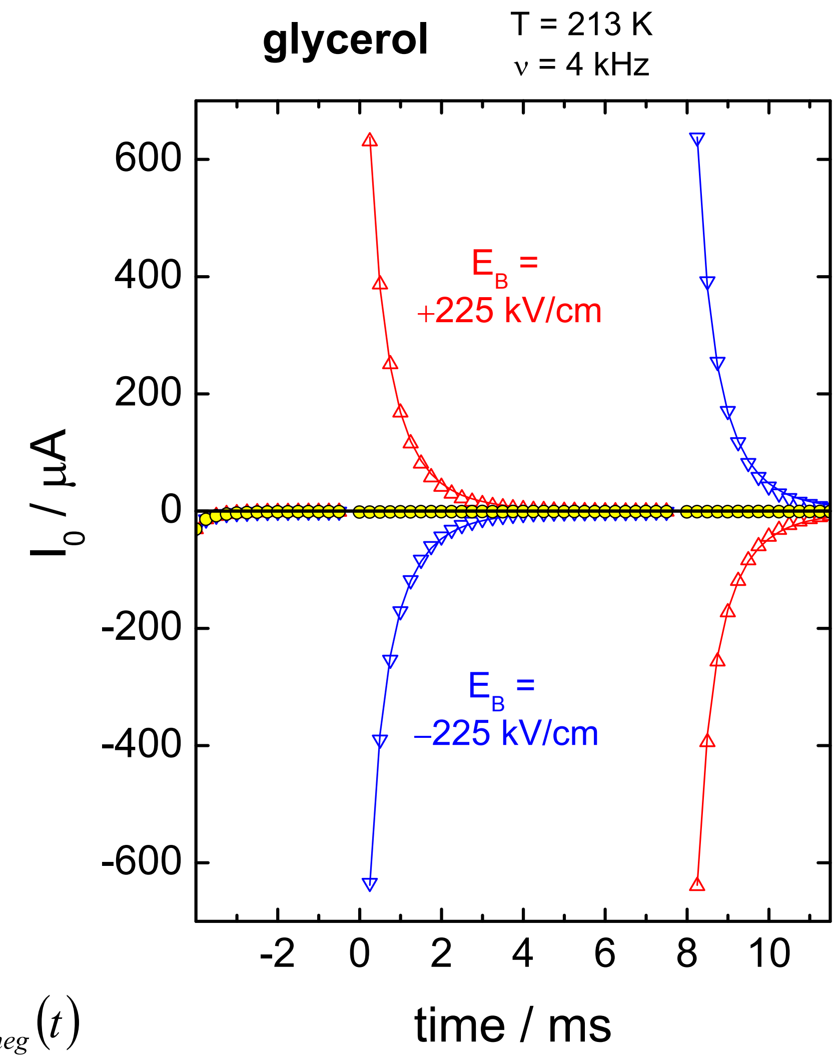
$$I'' = \frac{\omega}{\pi}\int_t^{t+2\pi/\omega}\cos(\omega t')I(t')dt' \qquad \varphi_I = \arctan(I''/I')$$

$$e'(t) = \left|\frac{A_I \sin(\varphi_I - \varphi_V)}{\omega A_V C_0}\right|, \quad e''(t) = \left|\frac{A_I \cos(\varphi_I - \varphi_V)}{\omega A_V C_0}\right|$$

S. Samanta, R. Richert, J. Chem. Phys. 142 (2015) 044504

# adding time-resolution capabilities to high-field technique: dc




$$V(t) = \frac{V_{pos}(t) + V_{neg}(t)}{2} \quad , \quad I(t) = \frac{I_{pos}(t) + I_{neg}(t)}{2}$$

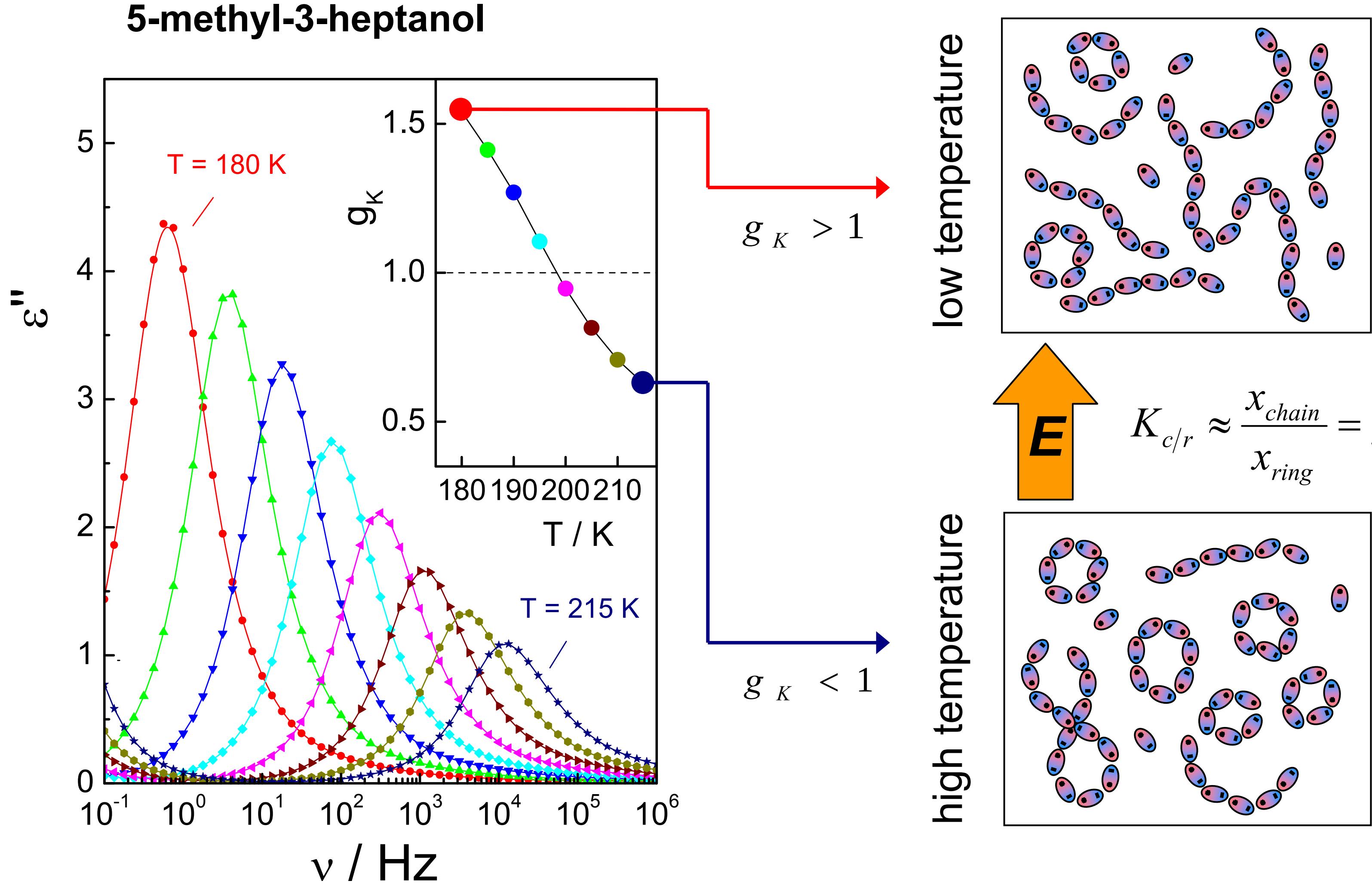
(eliminates all even Fourier components)

S. Samanta, R. Richert, J. Chem. Phys. 142 (2015) 044504

## Chemical Effect

(Monohydroxy Alcohols)

# special case of 5-methyl-3-heptanol



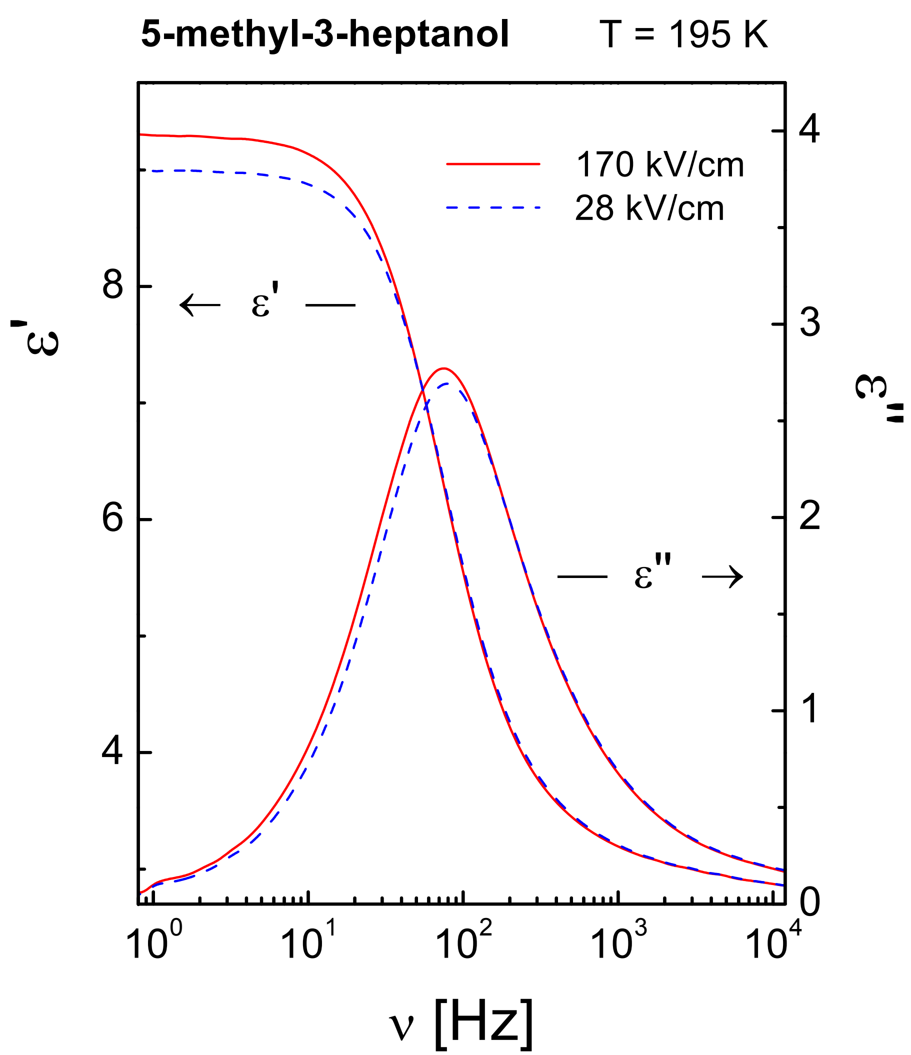

$$K_{c/r} \approx \frac{x_{chain}}{x_{ring}} = f(E)$$

$$g_K = 1 + z\langle \cos\theta \rangle$$

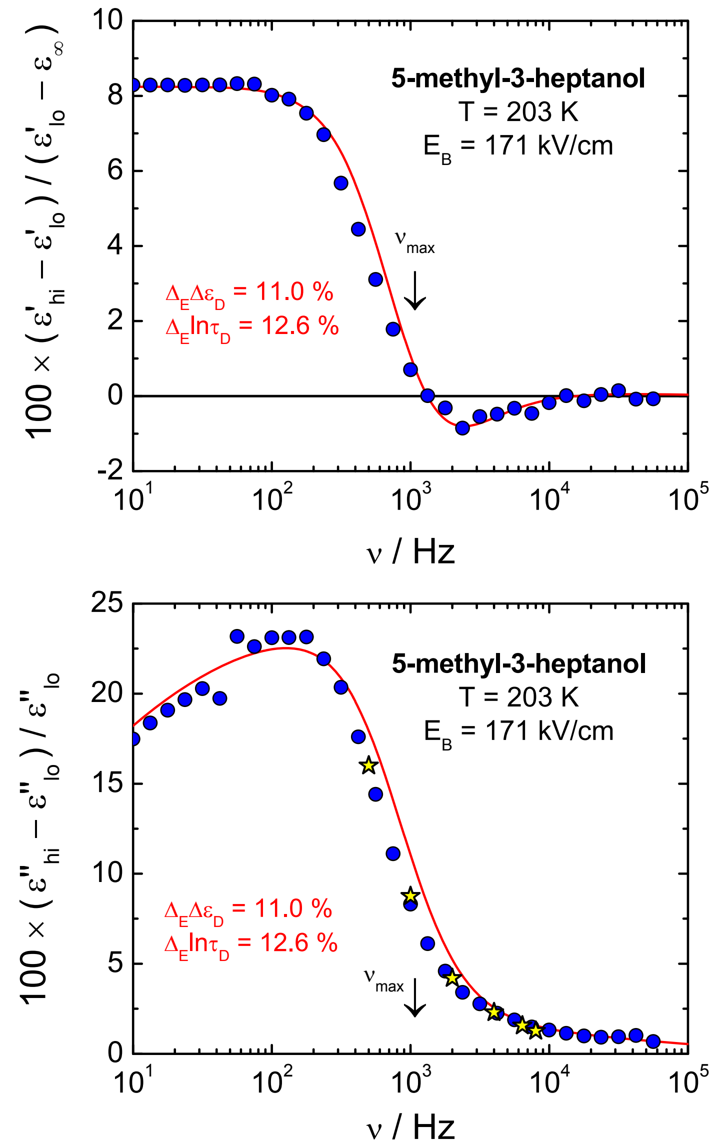
**W. Dannhauser, J. Chem. Phys. 48 (1968) 1911**

A. R. Young-Gonzales, R. Richert, J. Chem. Phys. 145 (2016) 074503

# special case of 5-methyl-3-heptanol

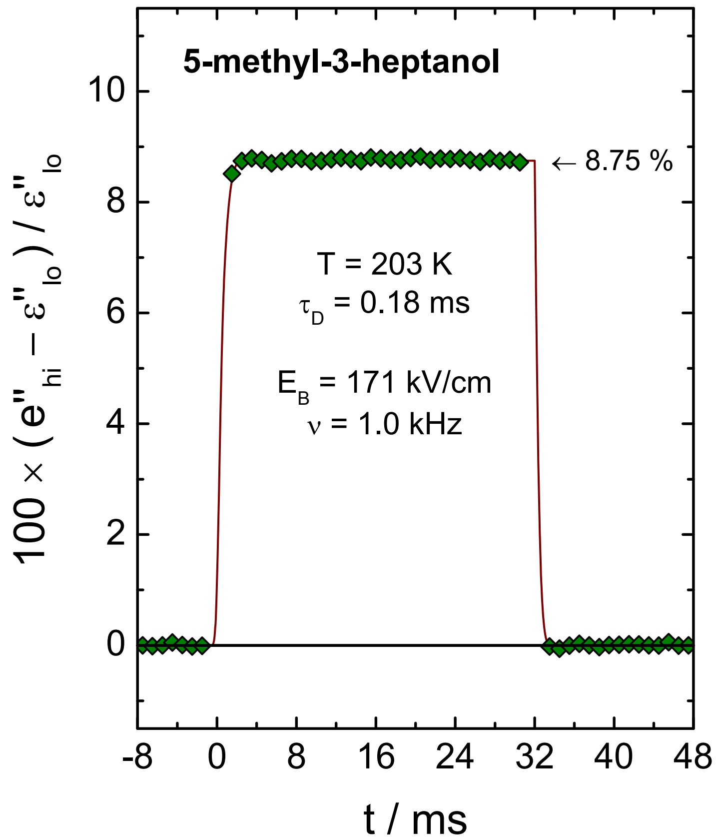


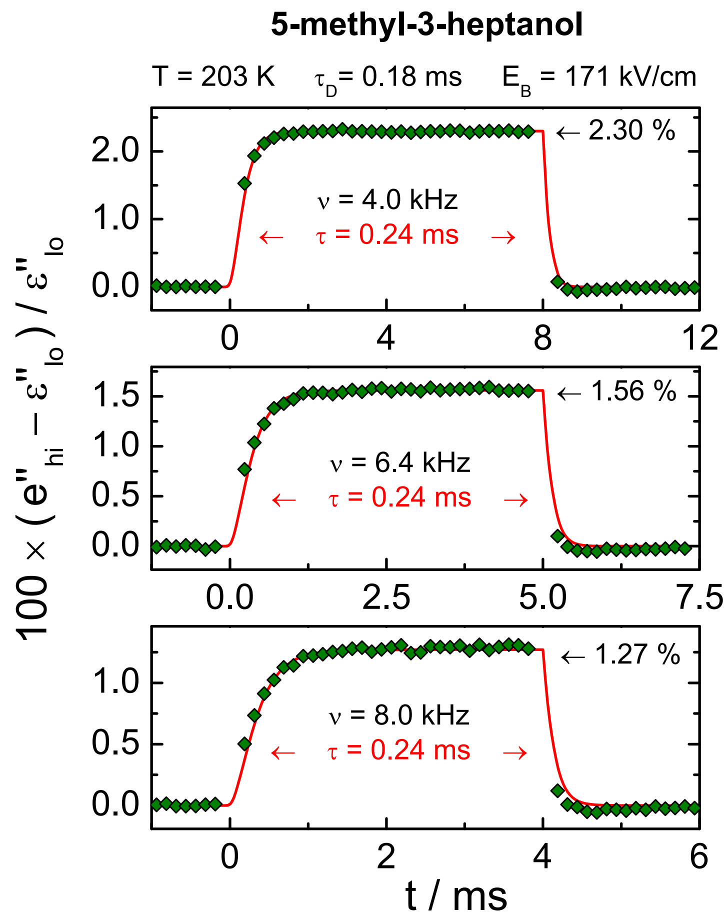

L.P. Singh, R. Richert, Phys. Rev. Lett. 1009 (2012) 167802



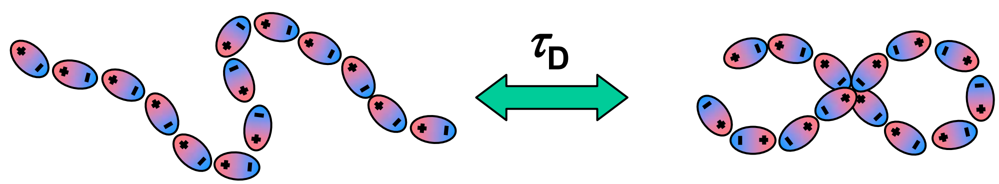

A. R. Young-Gonzales, R. Richert, J. Chem. Phys. 145 (2016) 074503

# time resolved changes: structural recovery



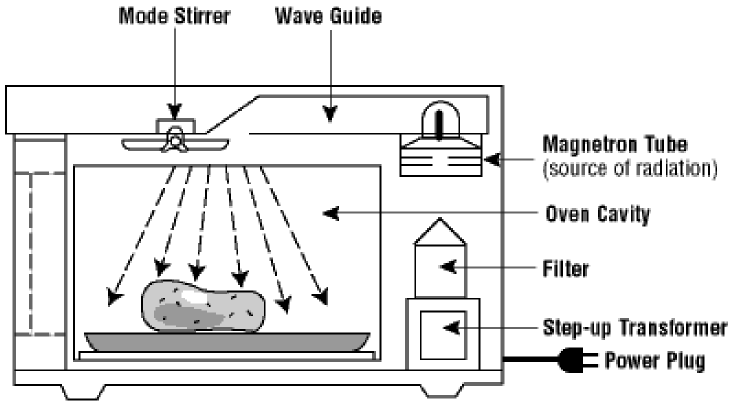




Origin of Debye peak

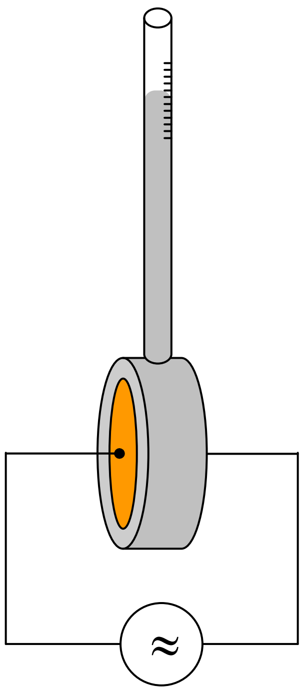


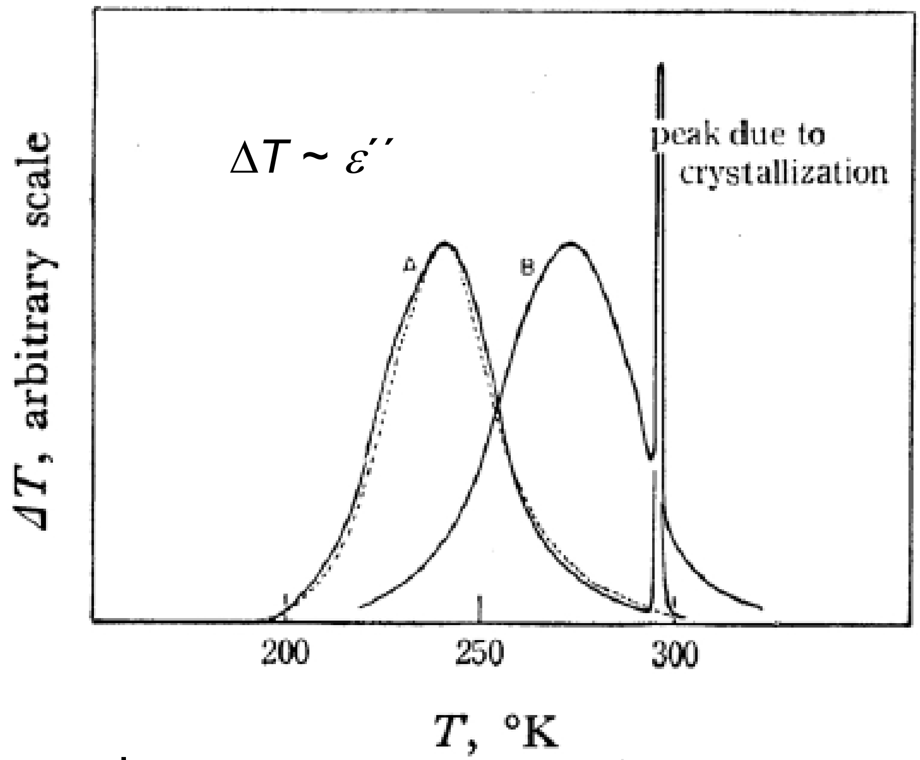

A. R. Young-Gonzales, R. Richert, J. Chem. Phys. 145 (2016) 074503

# Energy Absorption



# temperature increase as non-linear effect






cyclohexanol

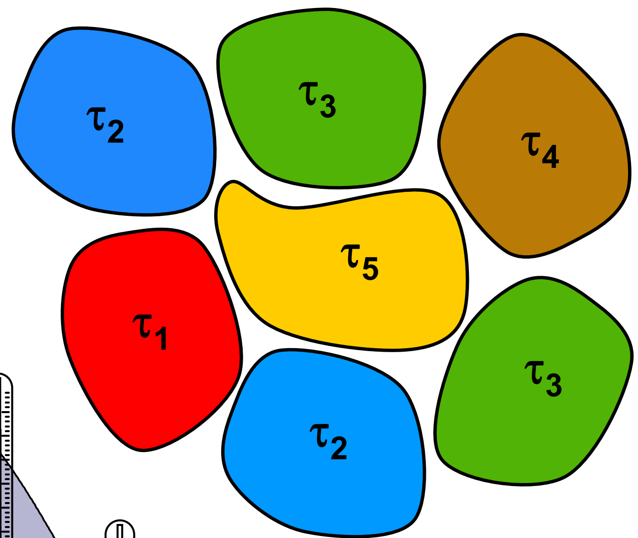
at 0.81 MHz (A)
at 10.1 MHz (B)

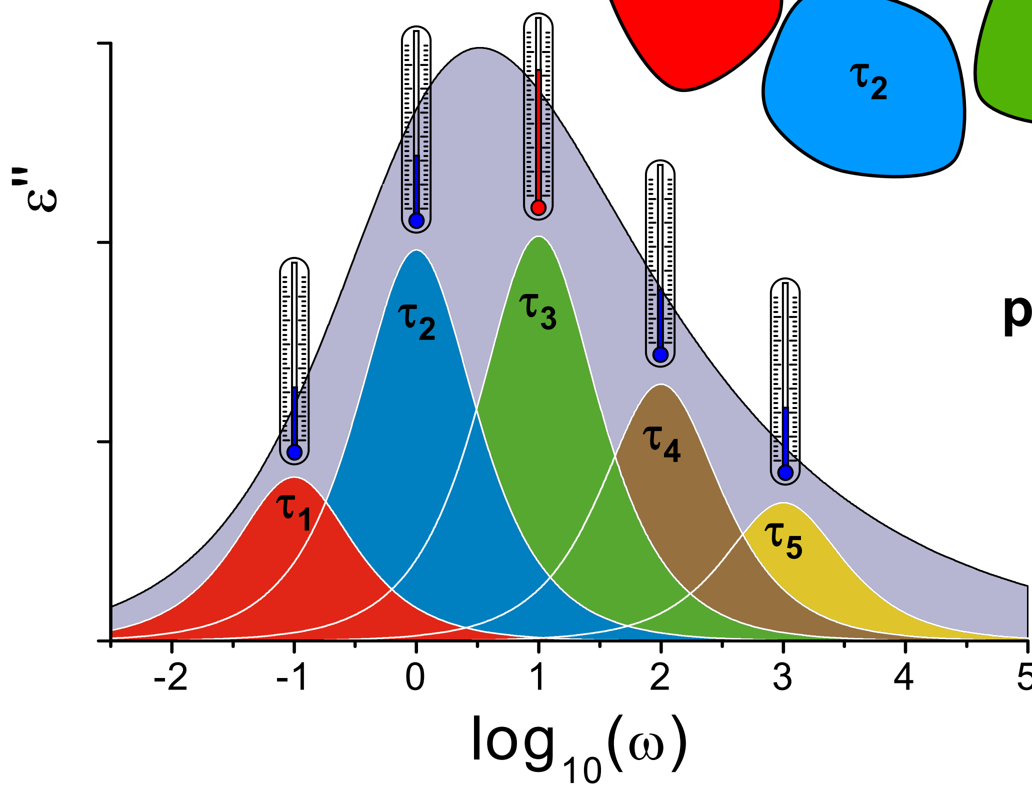
T. Matsuo, H. Suga, S. Seki, Bull. Chem. Soc. Jpn. 39 (1966) 1827

# energy absorption with heterogeneous dynamics

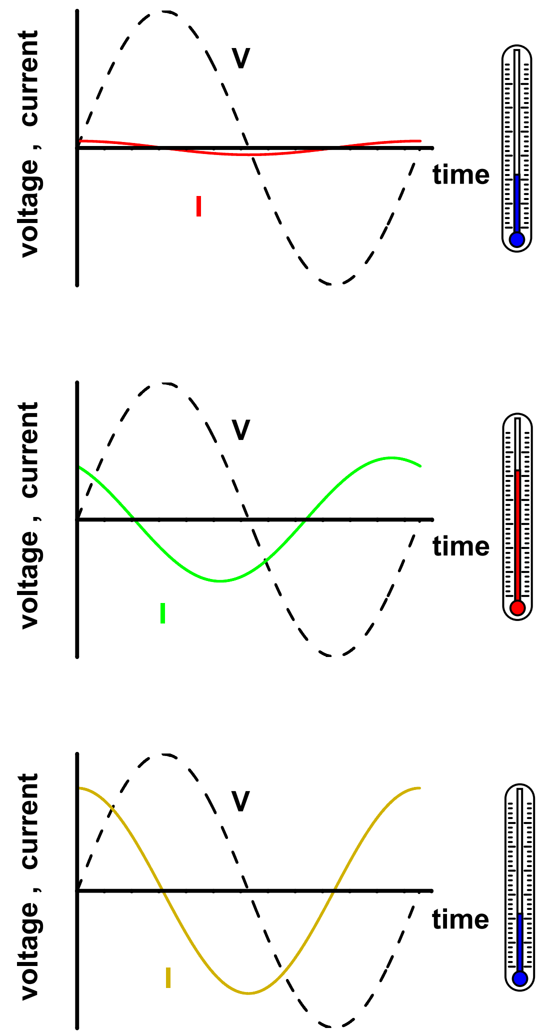
B. Schiener, R. Böhmer, A. Loidl, and R. V. Chamberlin, Science 274 (1996) 752

$$E(t) = E_0 \sin(t/\tau_3)$$



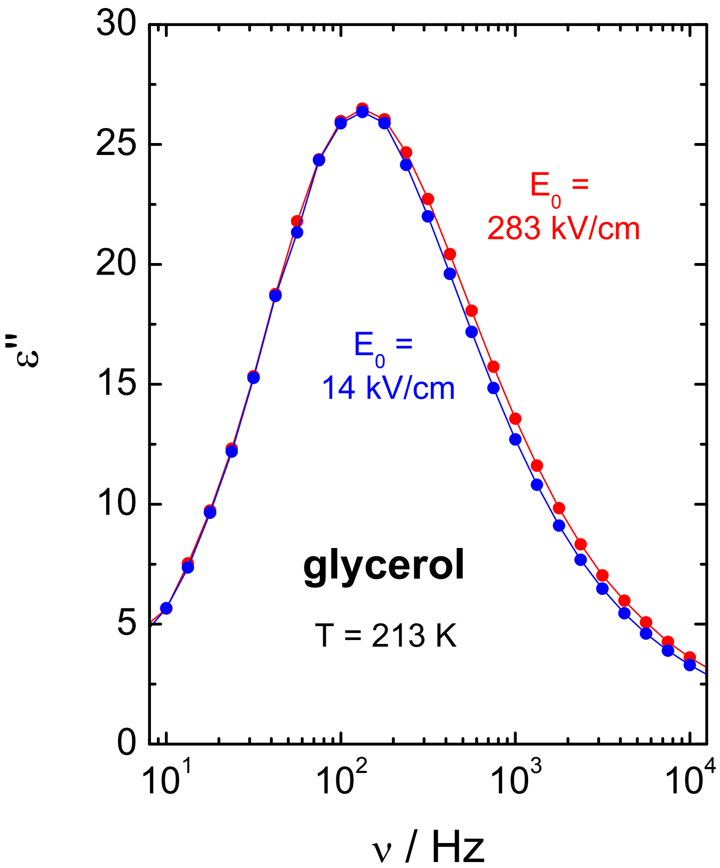

$$p = V \times I$$



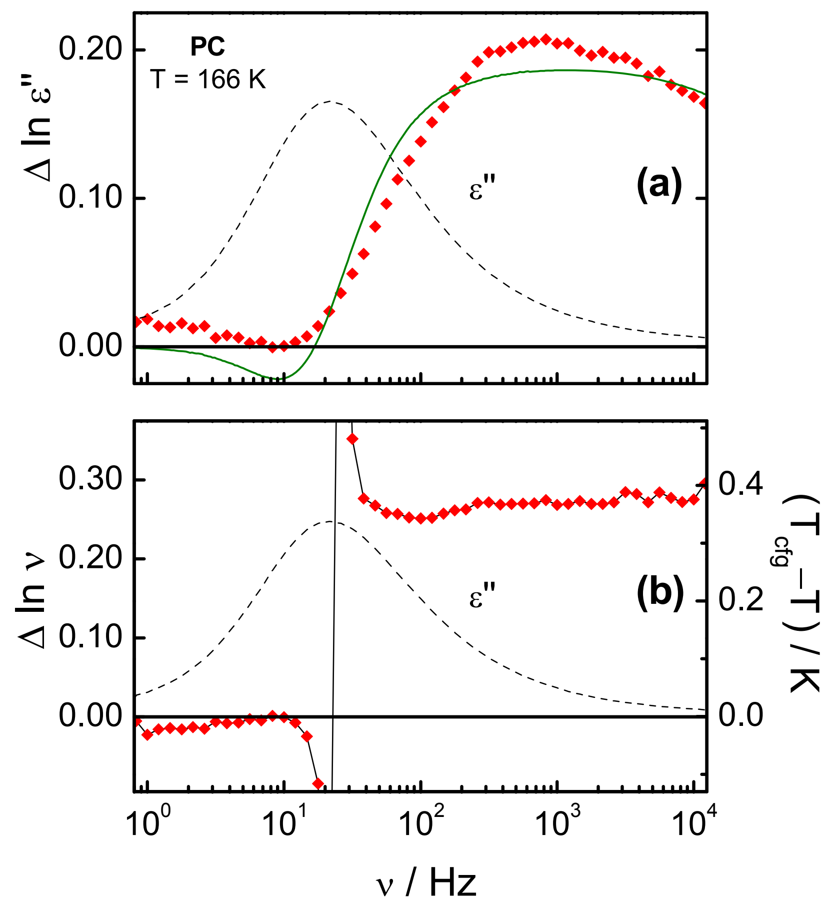

R. Richert, Eur. Phys. J. Special Topics 189 (2010) 223

# high field impedance of glycerol and propylene carbonate

**glycerol**
($E_0$ = 283 kV/cm)



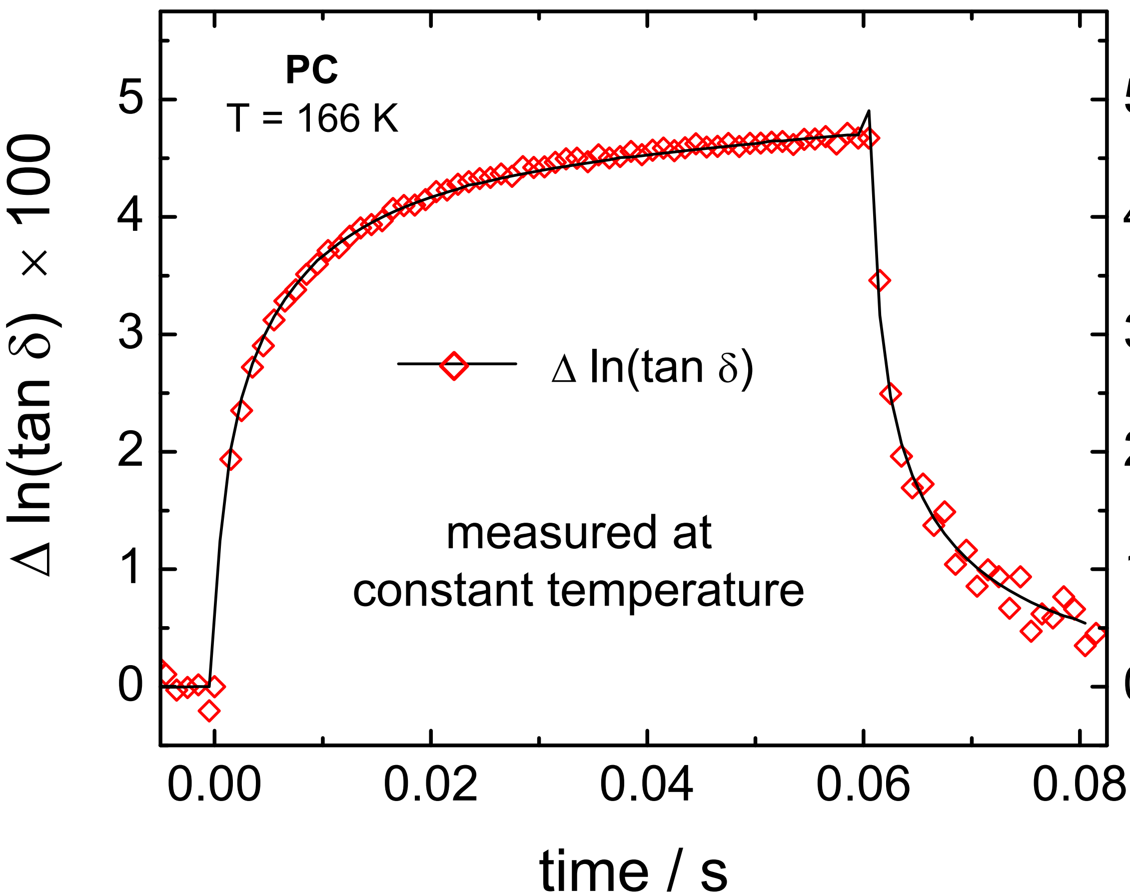

**propylene carbonate**
($E_0$ = 177 kV/cm)




R. Richert, S. Weinstein, Phys. Rev. Lett. 97 (2006) 095703

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

## agreement between experiment and model




**propylene carbonate**

($E_0$ = 177 kV/cm)

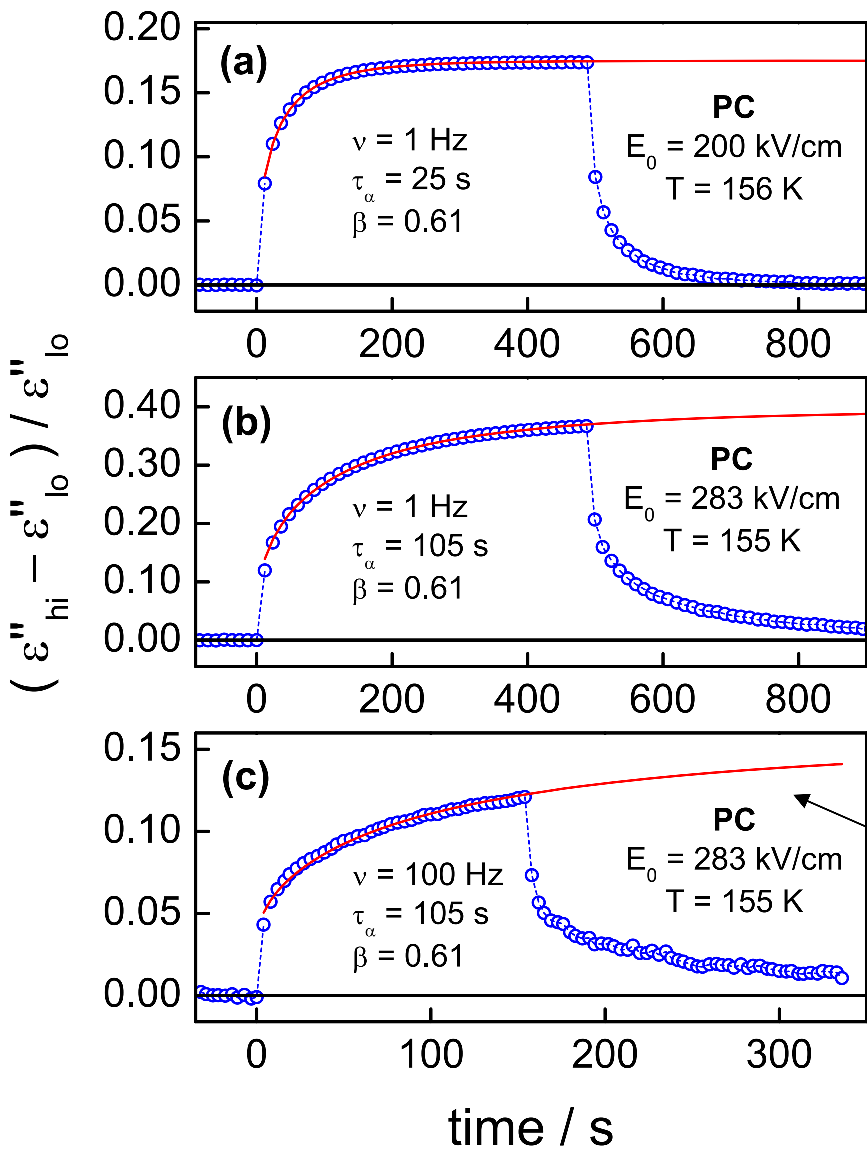
time resolved increase of fictive temperature,

at isothermal conditions

$\nu$ = 1000 Hz

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

# observations at high frequencies




$$\propto e^{-\left(\frac{t}{\langle \tau_\alpha \rangle}\right)^{\beta}}$$

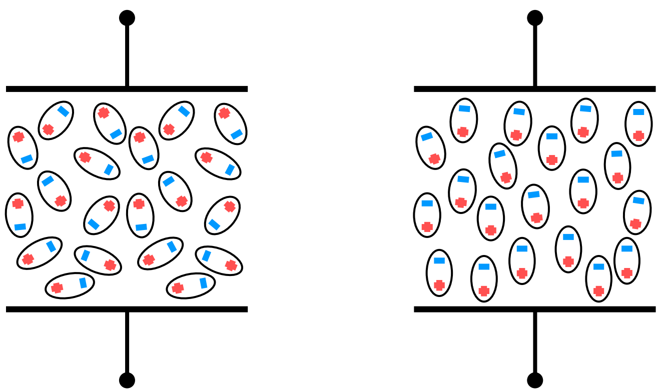
**time correlation function of τ's is structural recovery :**

**not seen in linear response experiments, homogeneous in excess wing.**

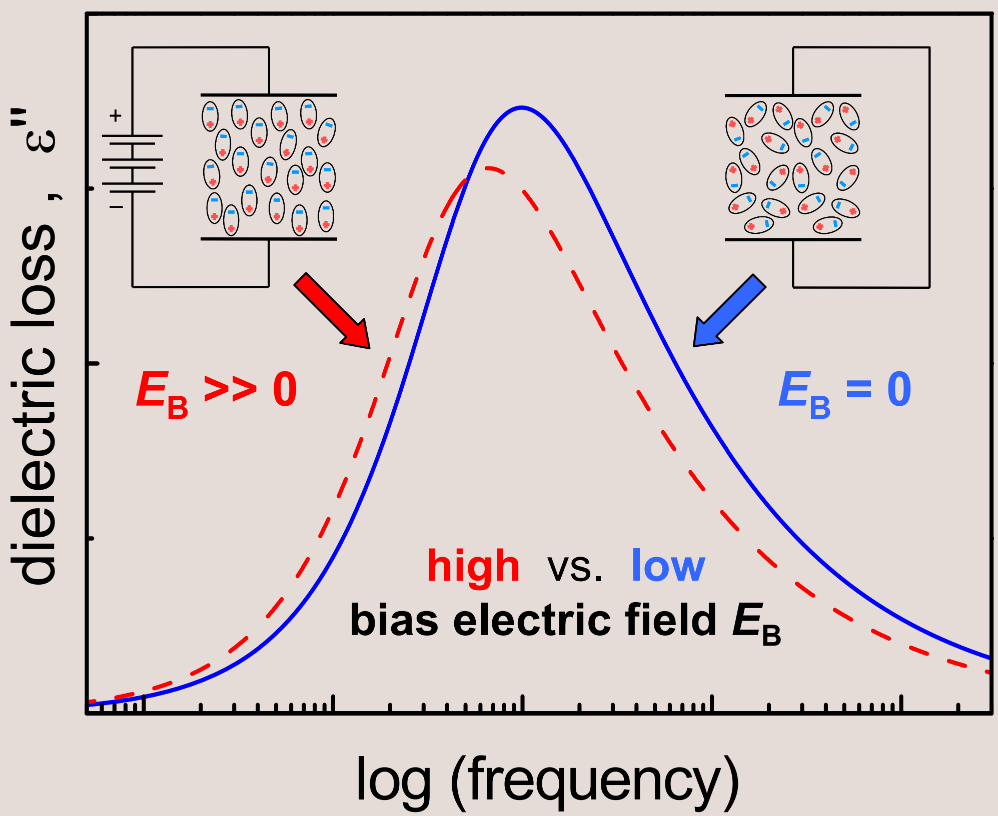
not yet steady state after 30 000 periods

S. Samanta, R. Richert, J. Chem. Phys. 140 (2014) 054503

# Entropy Effects



# dc-field induced change of entropy at constant temperature




$$\Delta_E S \propto \left(\frac{\partial \varepsilon_s}{\partial T}\right)_V E^2$$

$$\Delta_E \ln(\tau_\alpha)$$

&

$$\Delta_E \ln(\eta)$$

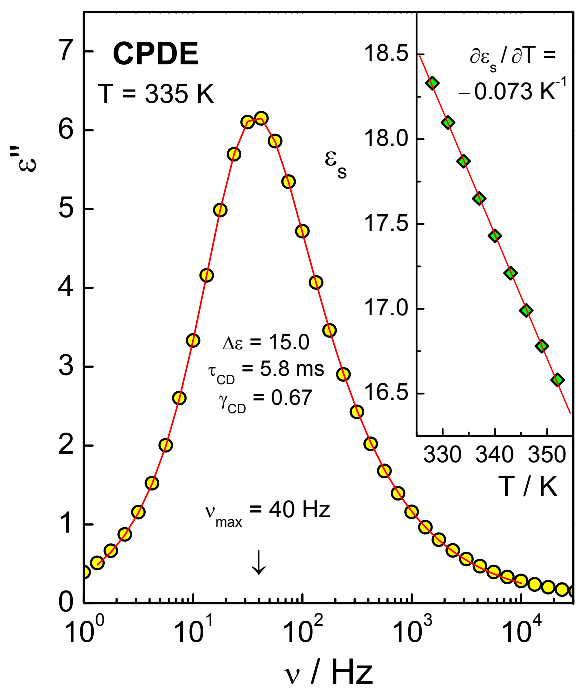
G. P. Johari, J. Chem. Phys. 138 (2013) 154503

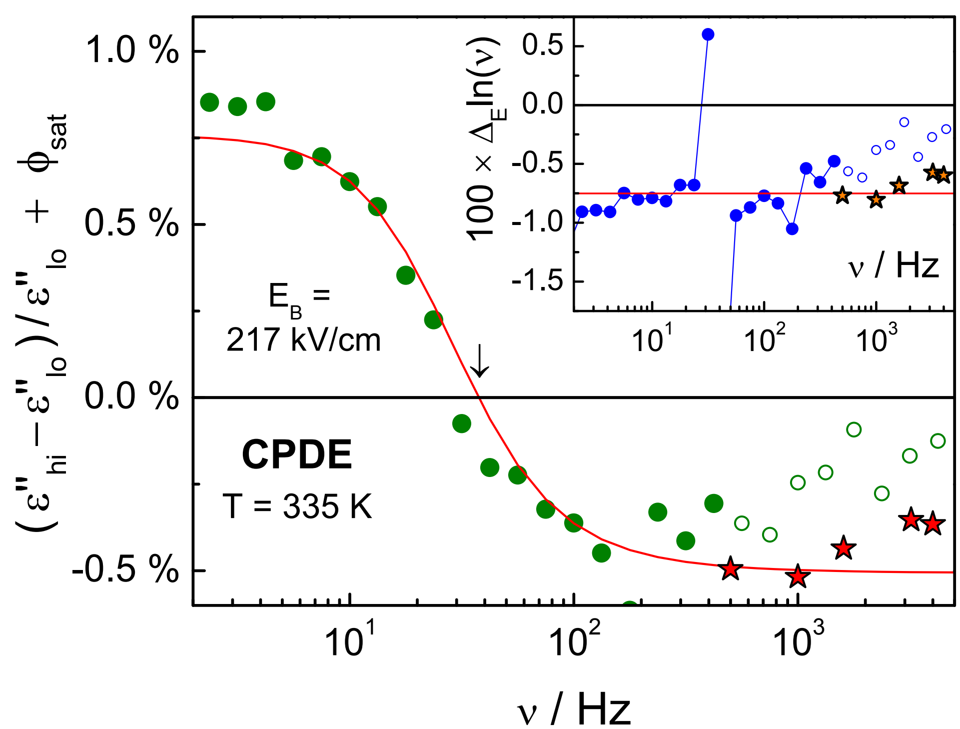
G. Adam and J. H. Gibbs,
J. Chem. Phys. 43 (1965) 139

$$\tau_{AG} \propto \exp\left[\frac{s_c^* \Delta\mu^E}{k_B T S_{cfg}(T)}\right]$$

# field induced change of entropy

cresolphthalein-dimethylether (CPDE)



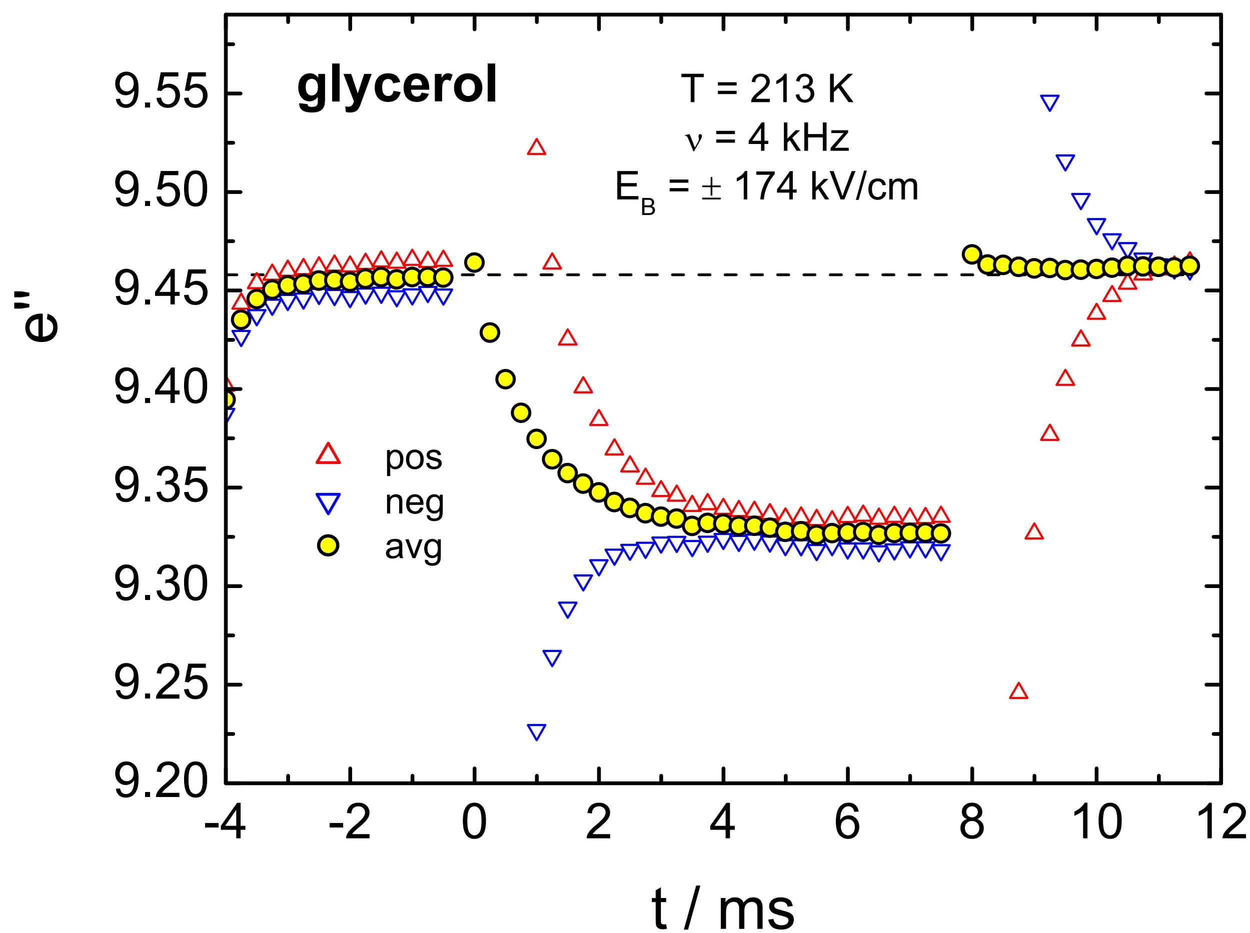

$$\Delta_E S = \frac{\varepsilon_0}{2}\left(\frac{\partial \varepsilon_s}{\partial T}\right)E^2$$

$$\Delta_E \ln \Delta\varepsilon = -0.72\%$$

$$\Delta_E \ln \tau = +0.75\%$$

S. Samanta, O. Yamamuro, R. Richert, Thermochim. Acta 636 (2016) 57

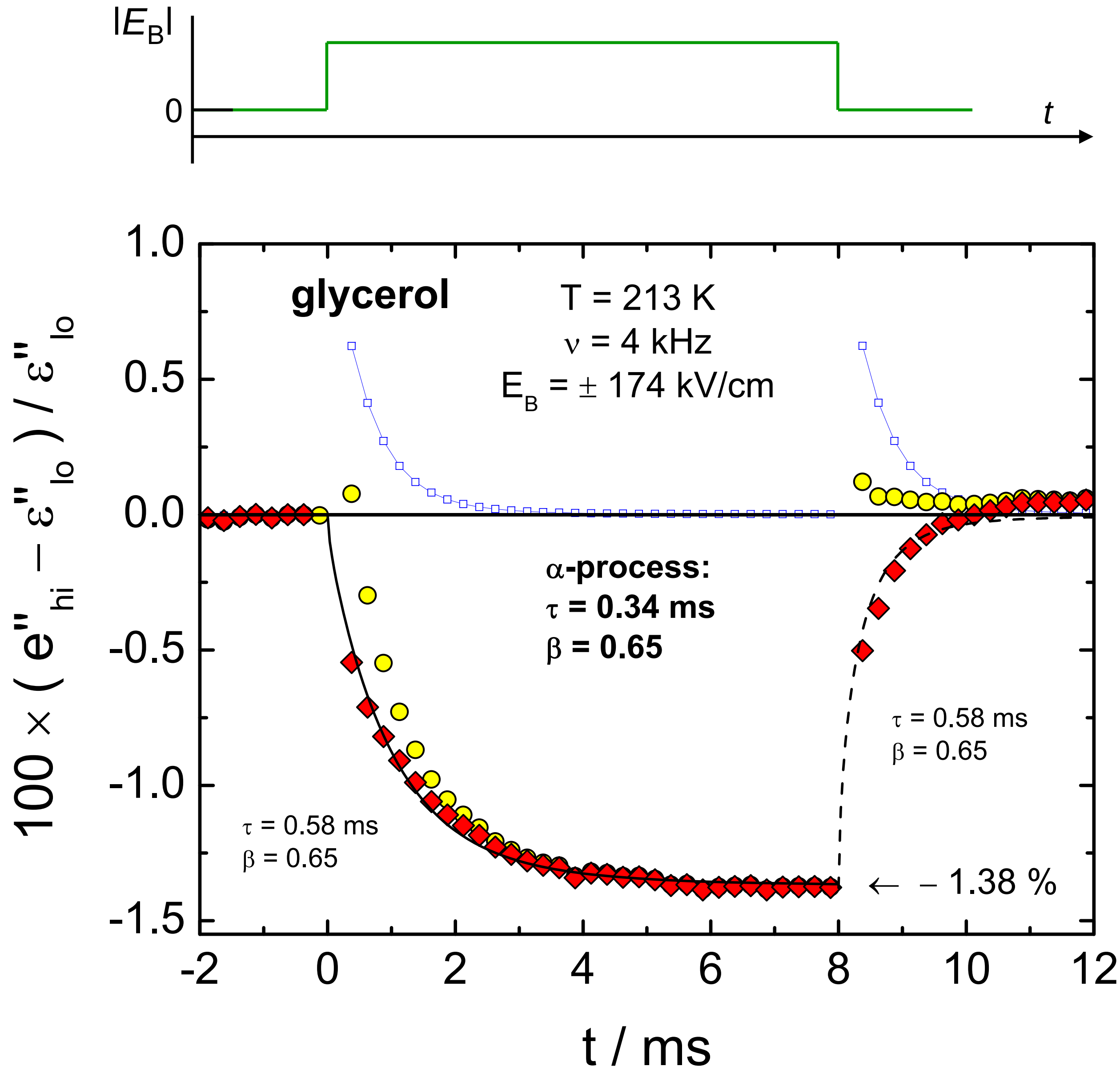
# field induced change: entropy effect




$$e'' = \left| \frac{A_I \cos(\varphi_I - \varphi_V)}{\omega A_V C_0} \right|$$

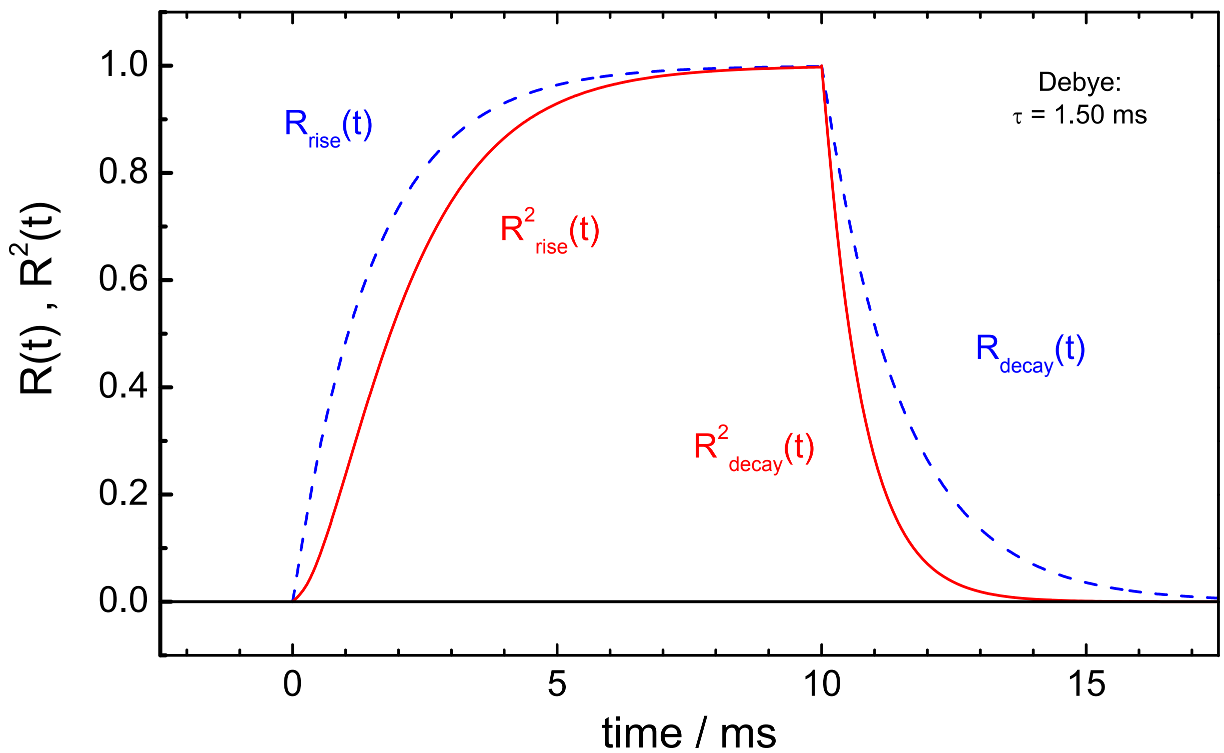
S. Samanta, R. Richert, J. Chem. Phys. 142 (2015) 044504

# 'heat'-corrected results: glycerol




A. R. Young-Gonzales, S. Samanta, R. Richert, J. Chem. Phys. 143 (2015) 104504

# explaining the rise/decay asymmetry




$$R_{rise}(t) = \left(1 - e^{-t/\tau_D}\right)$$

$$R_{decay}(t) = \left(e^{-t/\tau_D}\right)$$

$$R^2_{rise}(t) = \left(1 - e^{-t/\tau_D}\right)^2$$

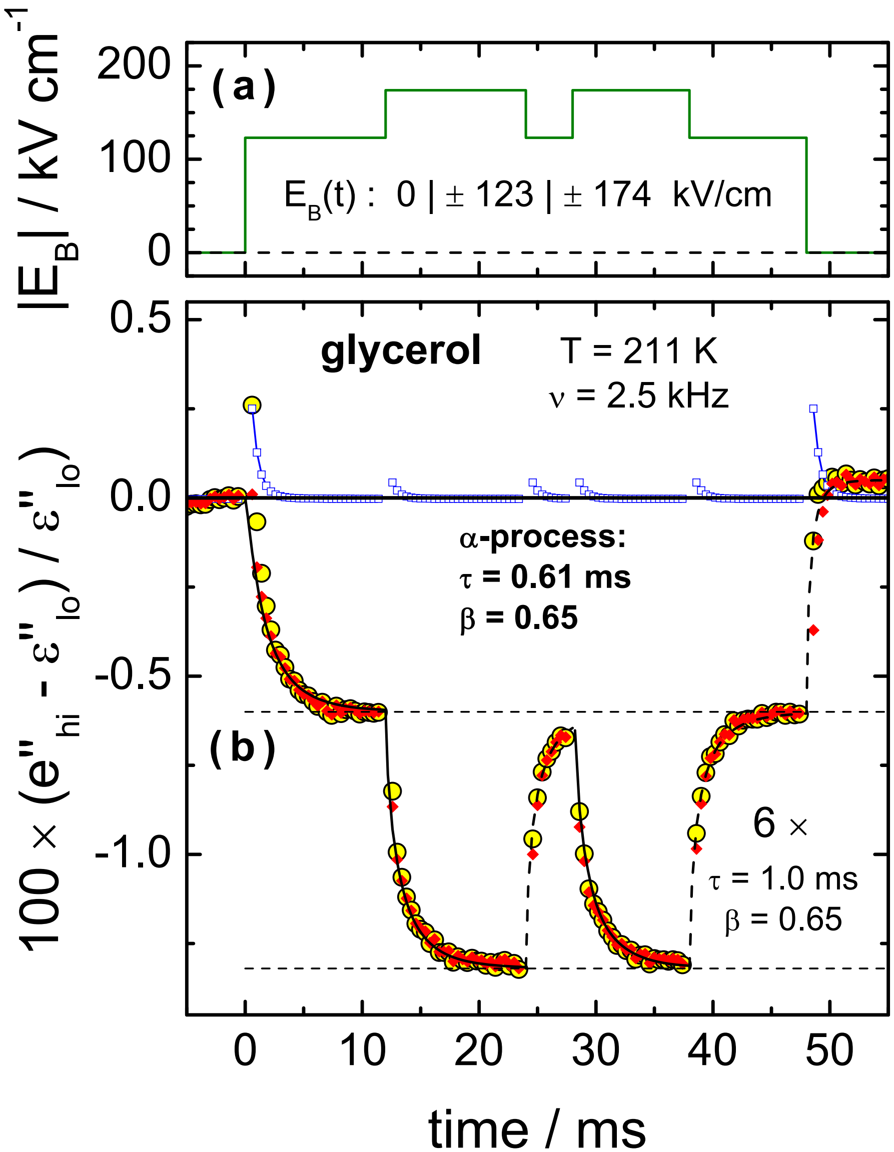
$$R^2_{decay}(t) = \left(e^{-t/\tau_D}\right)^2$$

$$\Delta_E S = \frac{\varepsilon_0 M}{2\rho}\left(\frac{\partial \varepsilon_s}{\partial T}\right) \times E_B^2 \quad \Rightarrow \quad "\Delta_E S(t)" = \frac{\varepsilon_0 M}{2\rho}\left(\frac{\partial \varepsilon_s}{\partial T}\right) \times \left(\frac{\Delta P(t)}{\varepsilon_0 \Delta \varepsilon}\right)^2$$

$$\Delta P = \varepsilon_0 \Delta \varepsilon \times E_B$$

A. R. Young-Gonzales, S. Samanta, R. Richert, J. Chem. Phys. 143 (2015) 104504

# more complicated field patters




Effect is quadratic in field.

Two step field pattern practically eliminates need for 'heating' correction.

All six transitions are represented by one common set of parameters (β,τ).

$$R^2_{rise}(t) \approx \left(1 - e^{-(t/\tau)^\beta}\right)^2$$

$$R^2_{decay}(t) \approx \left(e^{-(t/\tau)^\beta}\right)^2$$

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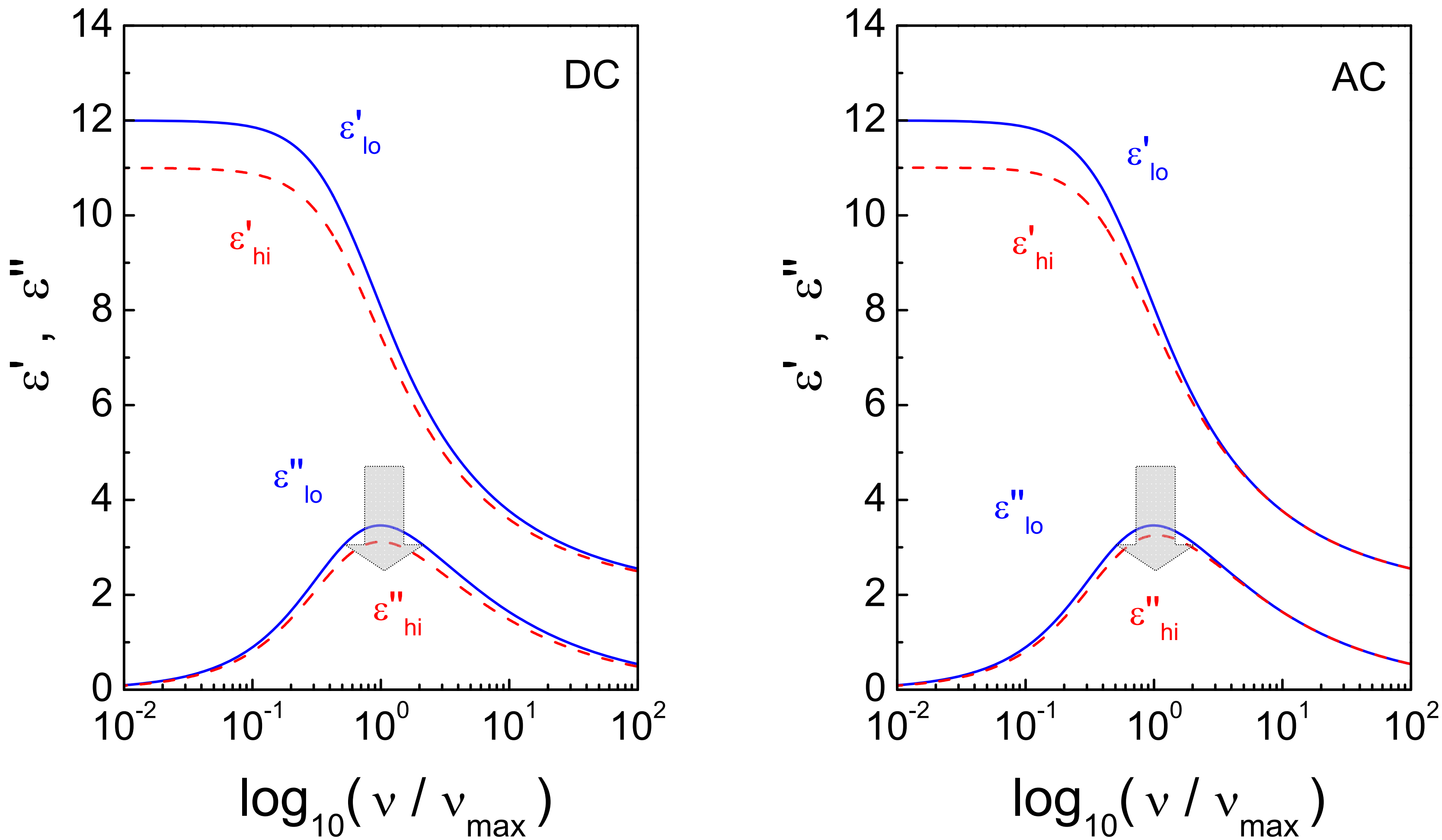
## NDE Summary

( AC / DC )

# NDE summary: dielectric saturation

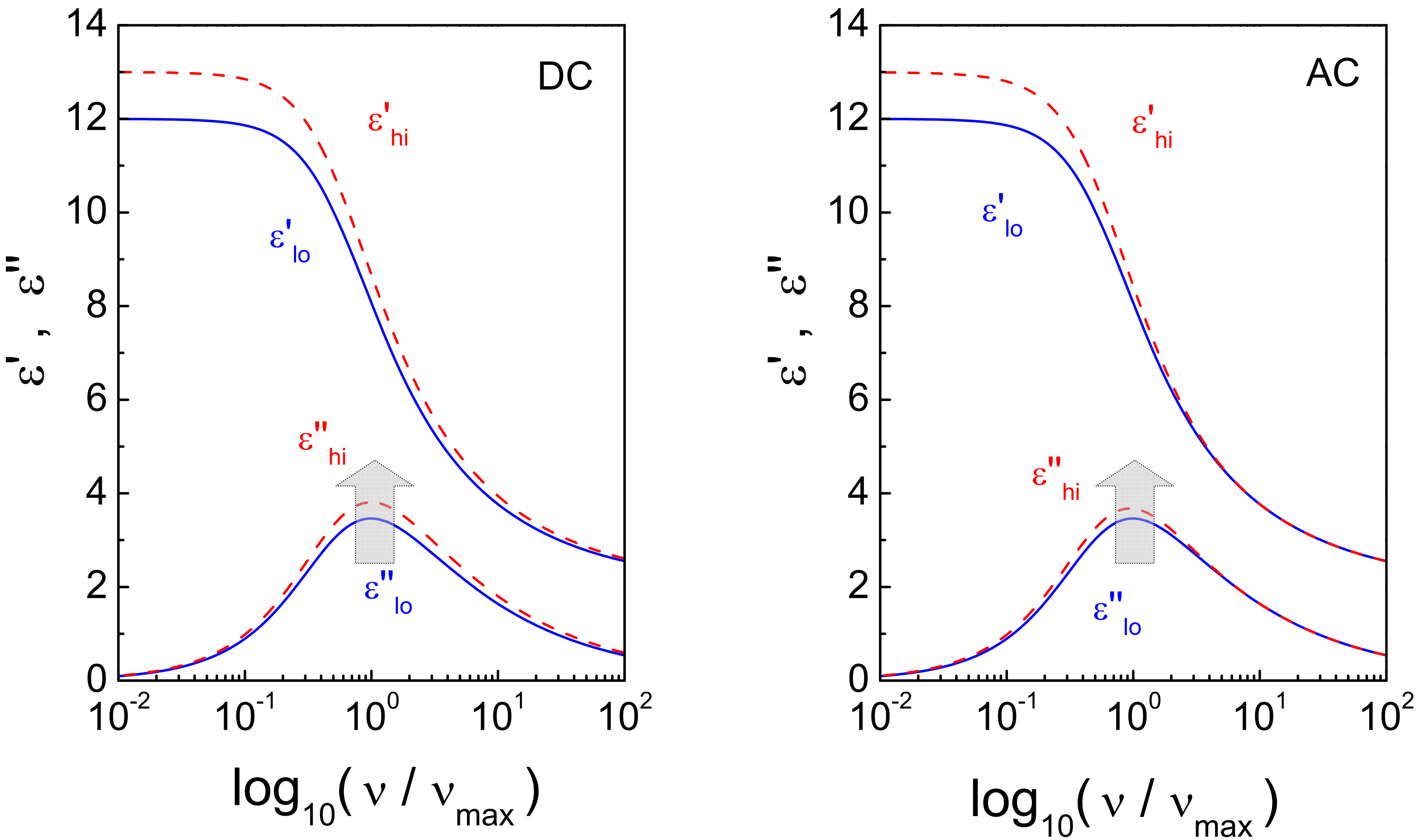



DC: amplitude reduction at all frequencies

AC: amplitude reduction fades for $\nu > \nu_{max}$

(depending on number of $T_{fic}$ for structural recovery)

# NDE summary: chemical effect

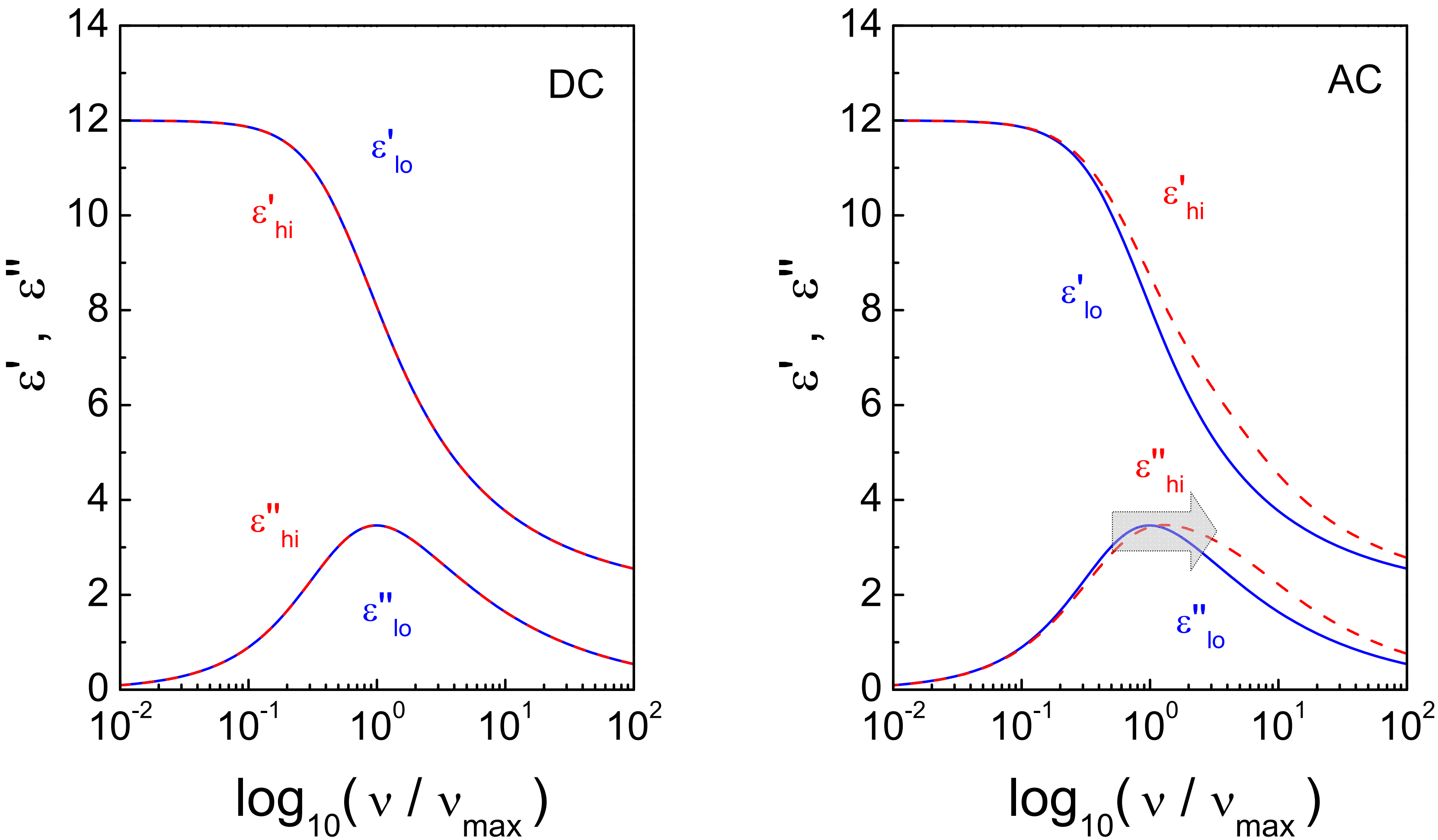



DC: amplitude enhancement at all frequencies

AC: amplitude enhancement can fade for $\nu > \nu_{max}$

(depends on nature of chemical effect)

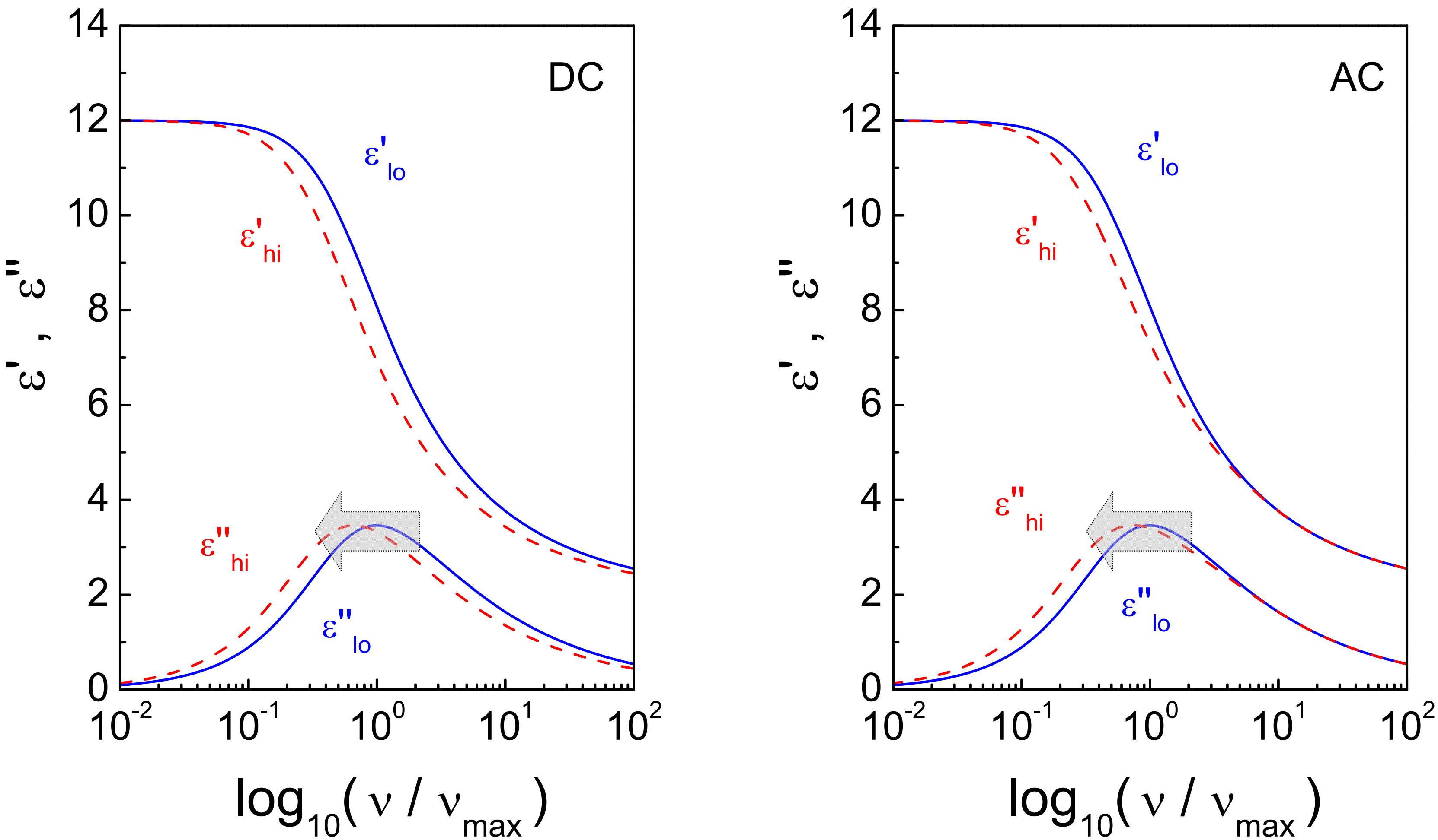
# NDE summary: energy absorption




DC: no energy absorbed from static field

AC: reduction of relaxation times for $\nu > \nu_{max}$

# NDE summary: entropy reduction




DC: increased relaxation times for all frequencies
AC: increased relaxation times only for $\nu < \nu_{max}$
(always combined with dielectric saturation)

# advertisement

## SUPERCOOLED LIQUIDS AND GLASSES BY DIELECTRIC RELAXATION SPECTROSCOPY

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CONTENTS

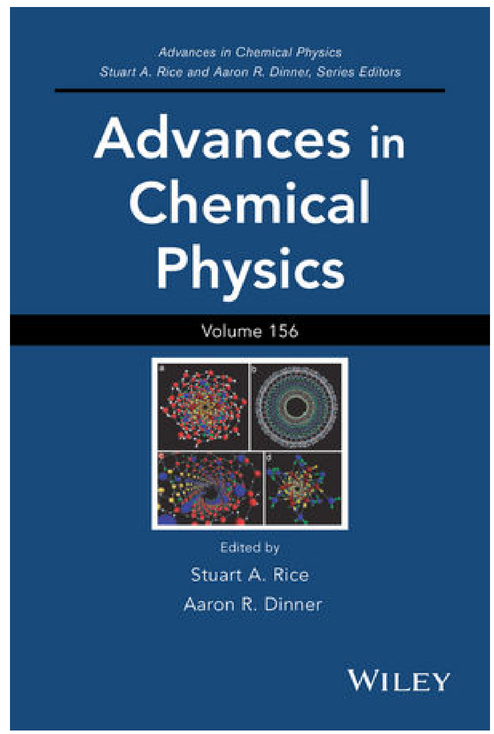


*Advances in Chemical Physics, Volume 156*, First Edition. Edited by Stuart A. Rice and Aaron R. Dinner.



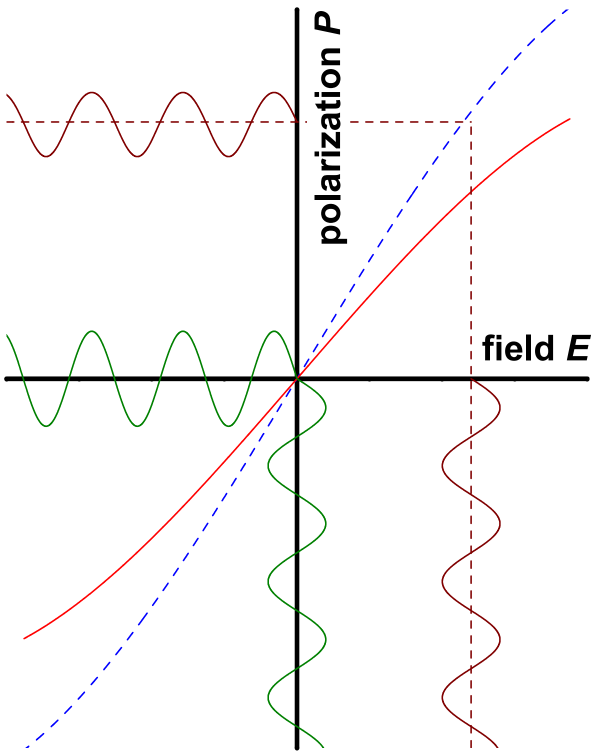





R. Richert, Adv. Chem. Phys. 156 (2015) 101

# CONCLUSIONS




- Time resolved non-linear techniques provide information on dynamics of structural recovery, analogous to physical aging.
- Different sources of non-linear behavior can be separted by ac vs.dc or by frequency.
- Effects that can be studied are:
  - Dielectric saturation;
  - Field induced shifts of chemical potentials;
  - Structural recovery after energy absorption;
  - Electrocaloric effects;
  - Test of Adam-Gibbs model.
- Much of the general theory needed for interpretation is still missing.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NSF