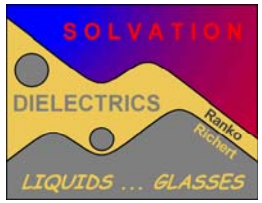
School of Molecular Sciences
ARIZONA STATE UNIVERSITY



Non-linear approach to complex dynamics

Ranko Richert

Tutorial organized by "International Dielectric Society"

Wisła, Poland
23 July 2017

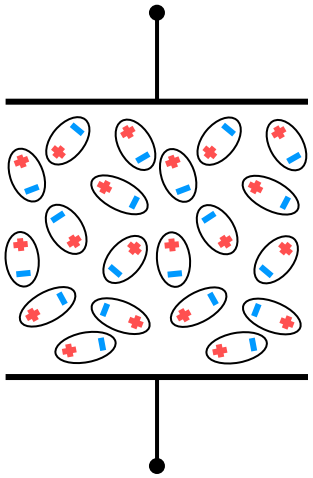
- non-linear basics
- experimental techniques
- summary of effects
- chemical effects
- energy absorption
- electroviscous effects

dielectric relaxation: static permittivity

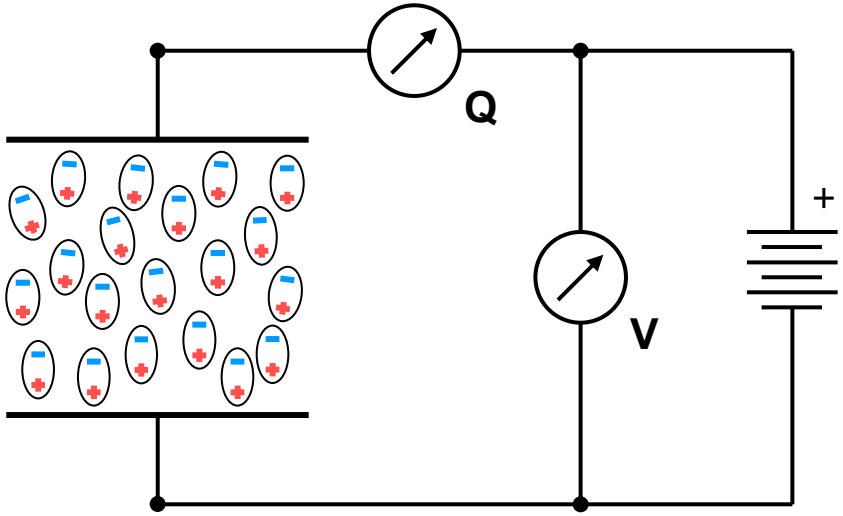
constitutive equation: $\mathbf{D} = \boldsymbol{\varepsilon}\ \boldsymbol{\varepsilon}_0\ \mathbf{E}$

dielectric displacement $D = \frac{Q}{A} = \frac{\int_t I}{A} = \varepsilon\varepsilon_0 \frac{V}{d} = \varepsilon\varepsilon_0 E$ *electric field*

E ≈ 0



E > 0



$\mu E << k_B T$

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

Nonlinear Basics

P. Debye, Polar Molecules, Chemical Catalog Company, 1929:

"Here we see that the mean moment is not a linear function for large values of the argument, and for such values the dielectric constant would not be a true constant but would depend upon the field intensity."

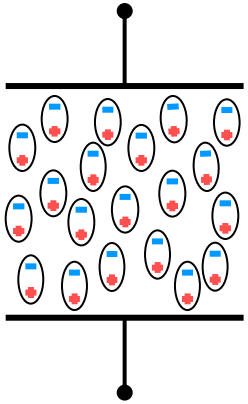
limits to linear dielectric behavior

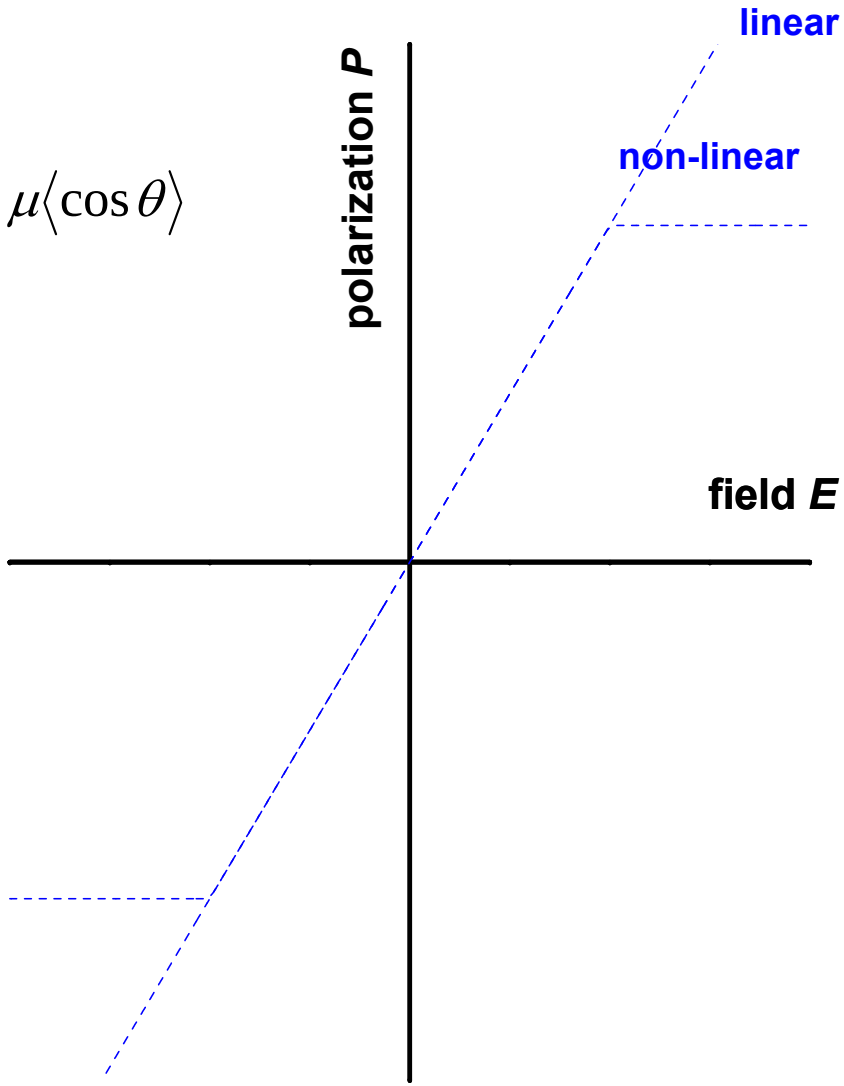
$$P = \frac{\rho N_A}{M}\left(\alpha_{el} + \alpha_{or}\right) E$$

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

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

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





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

dielectric saturation for non-interacting dipoles

Langevin saturation effect
(for dipole gas)

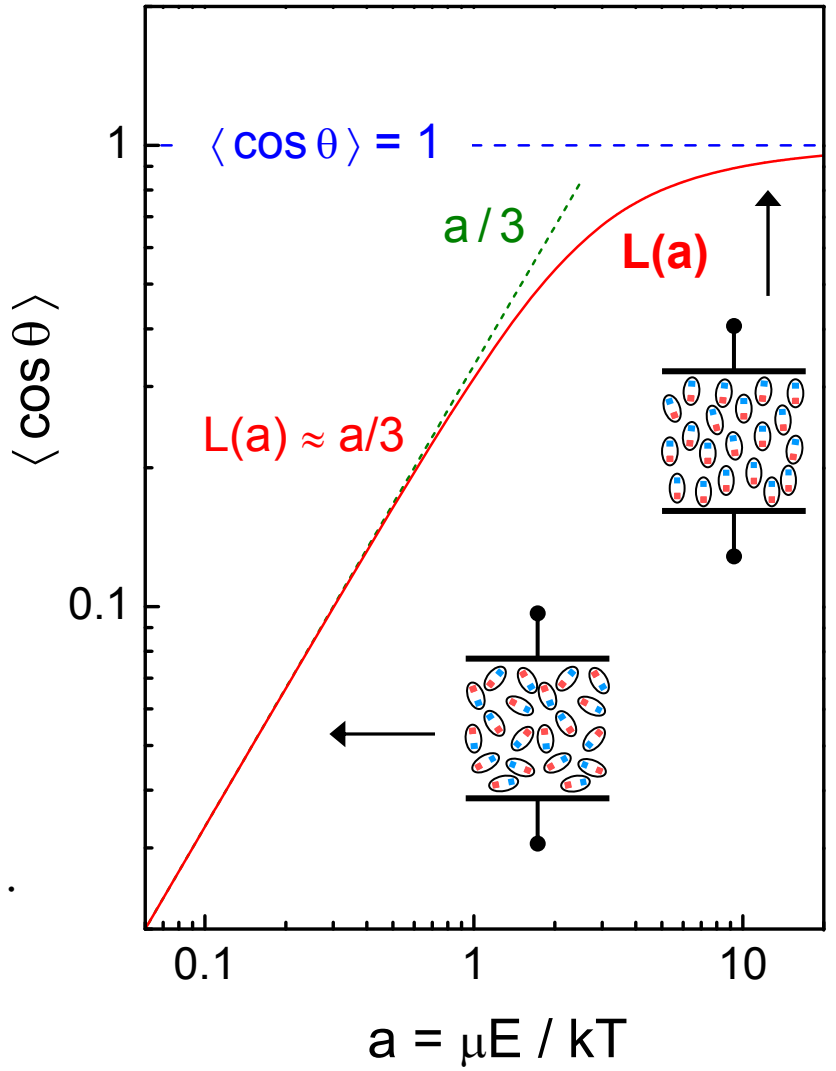
$$\langle \cos\theta \rangle = \frac{\iint_{4\pi} \cos\theta \, e^{\mu E \cos\theta / kT} \, d\Omega}{\iint_{4\pi} e^{\mu E \cos\theta / kT} \, d\Omega}$$

$\Rightarrow$

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

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

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

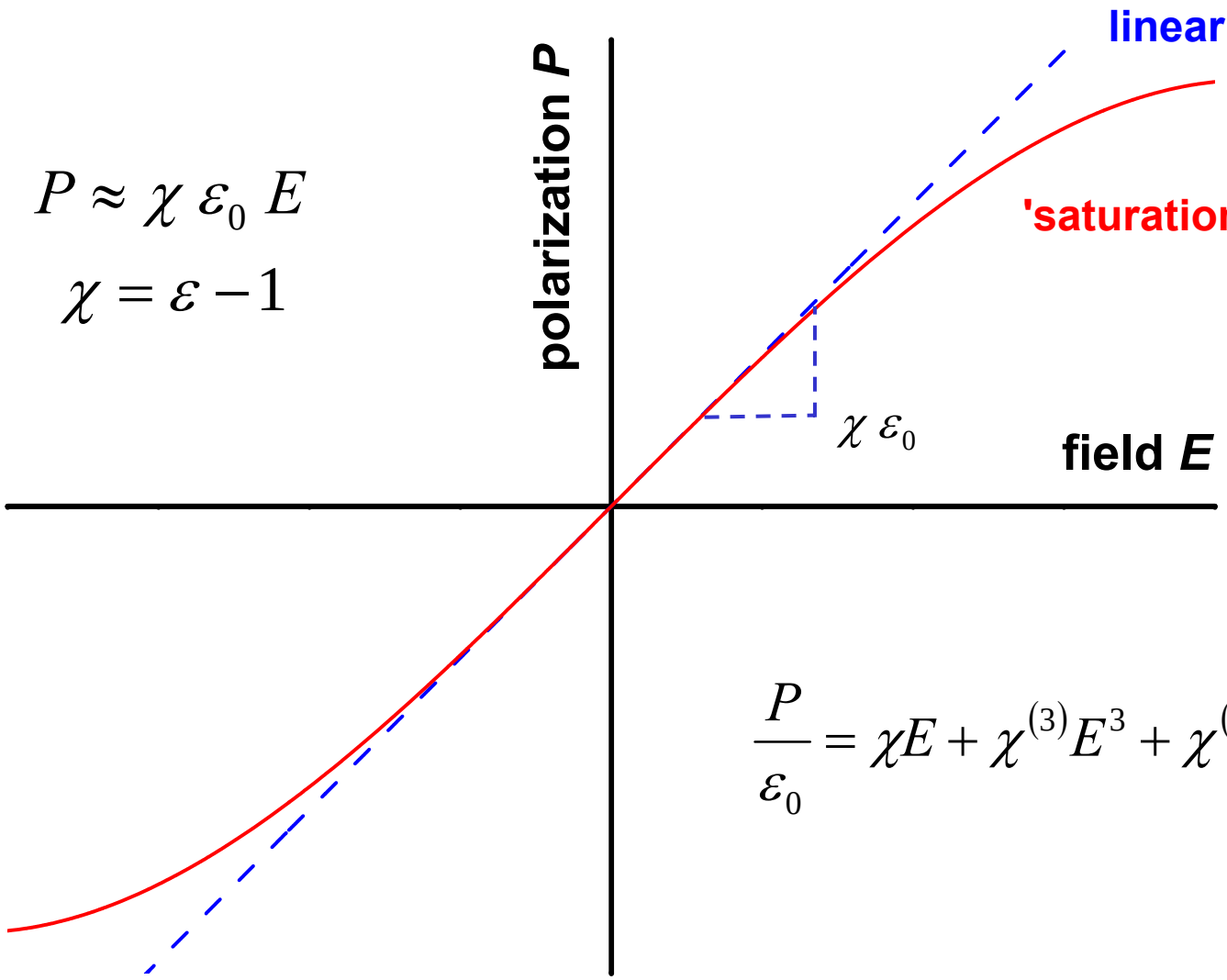


P. Debye, Polar Molecules (Chemical Catalog Company, 1929)

non-linear dielectric effects: static limit

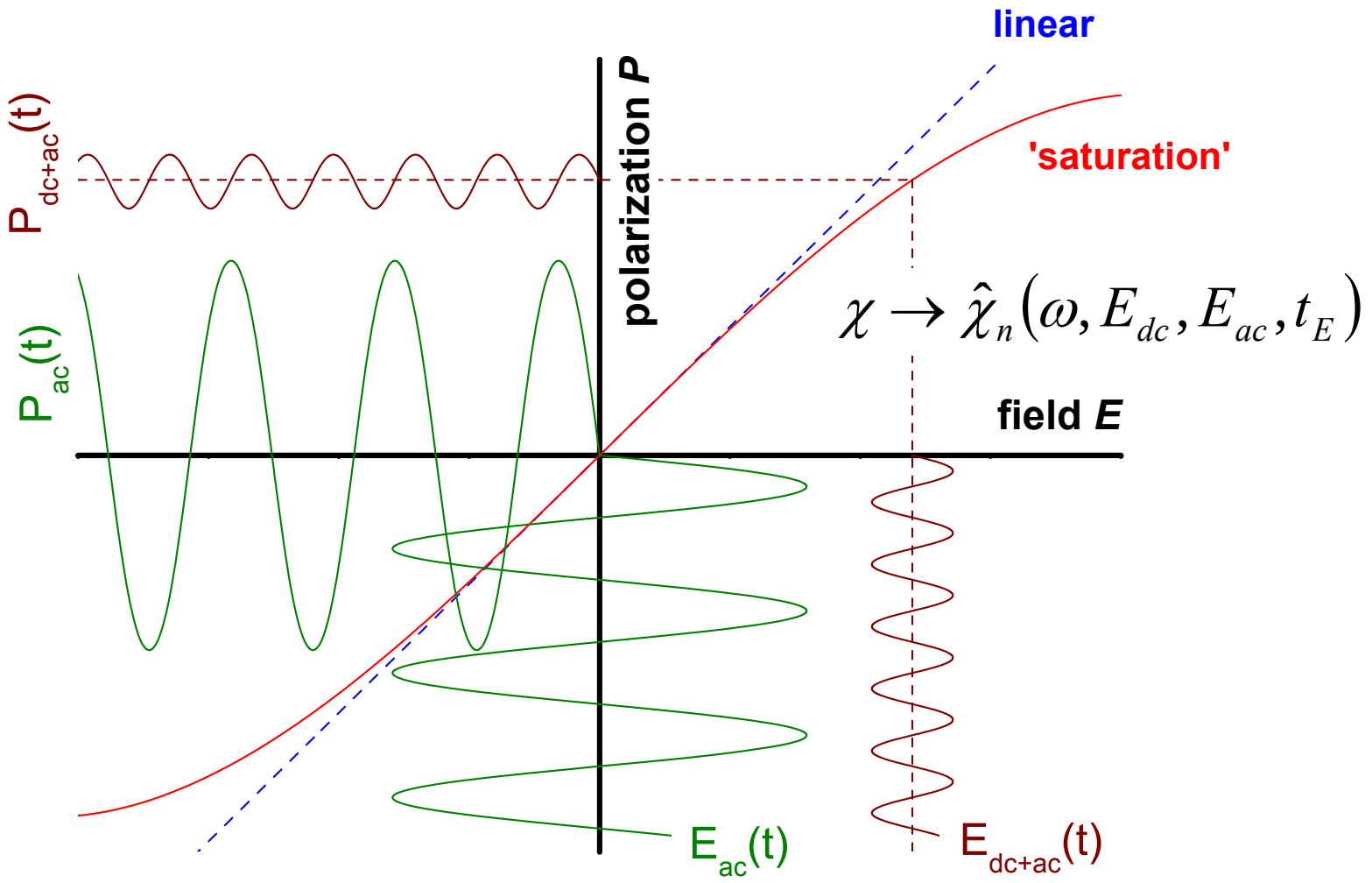
$$P \approx \chi \, \varepsilon_0 \, E$$

$$\chi = \varepsilon - 1$$



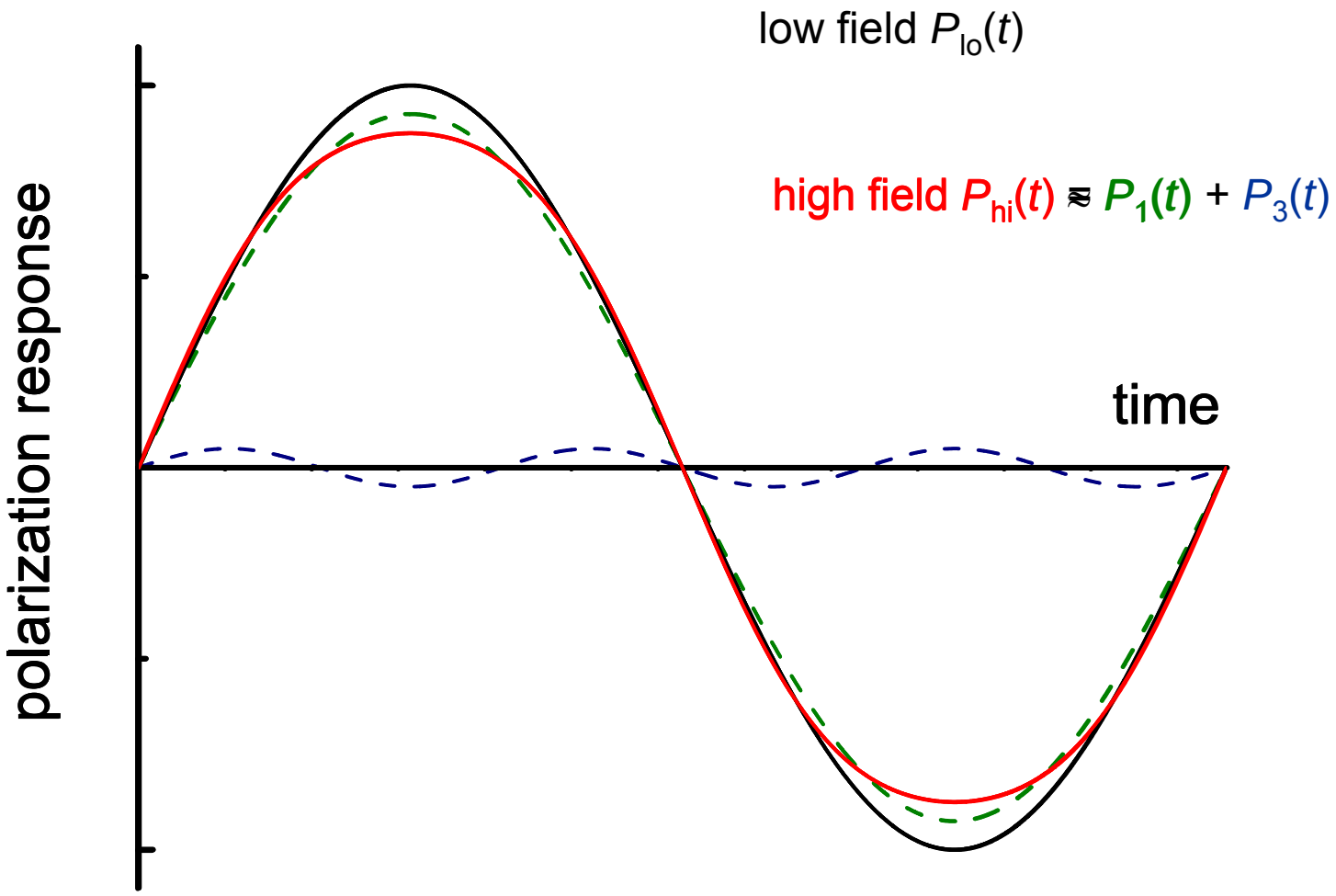
$$\frac{P}{\varepsilon_0} = \chi E + \chi^{(3)} E^3 + \chi^{(5)} E^5 + \ldots$$

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



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

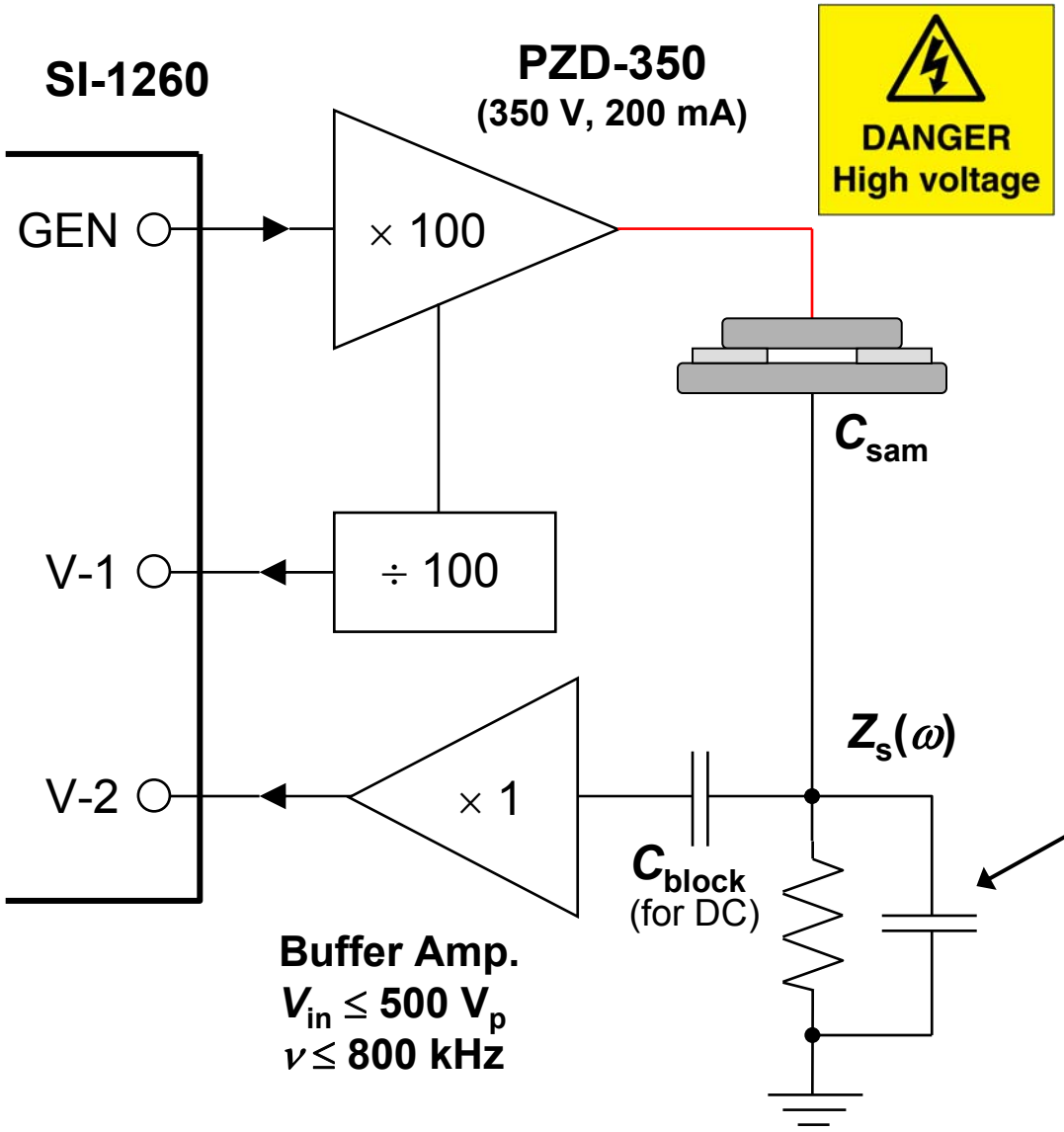
gauging deviation from linear dielectric response



Experimental Techniques

(polar viscous liquids)

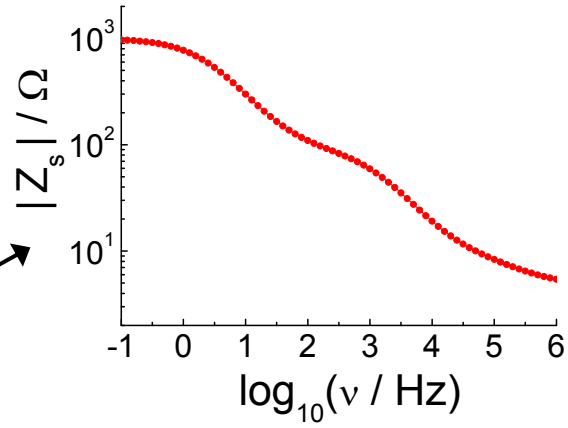
experimental techniques: high field impedance



$E_0 \leq 650$ kV/cm

$\mu E \leq 0.1\ kT$

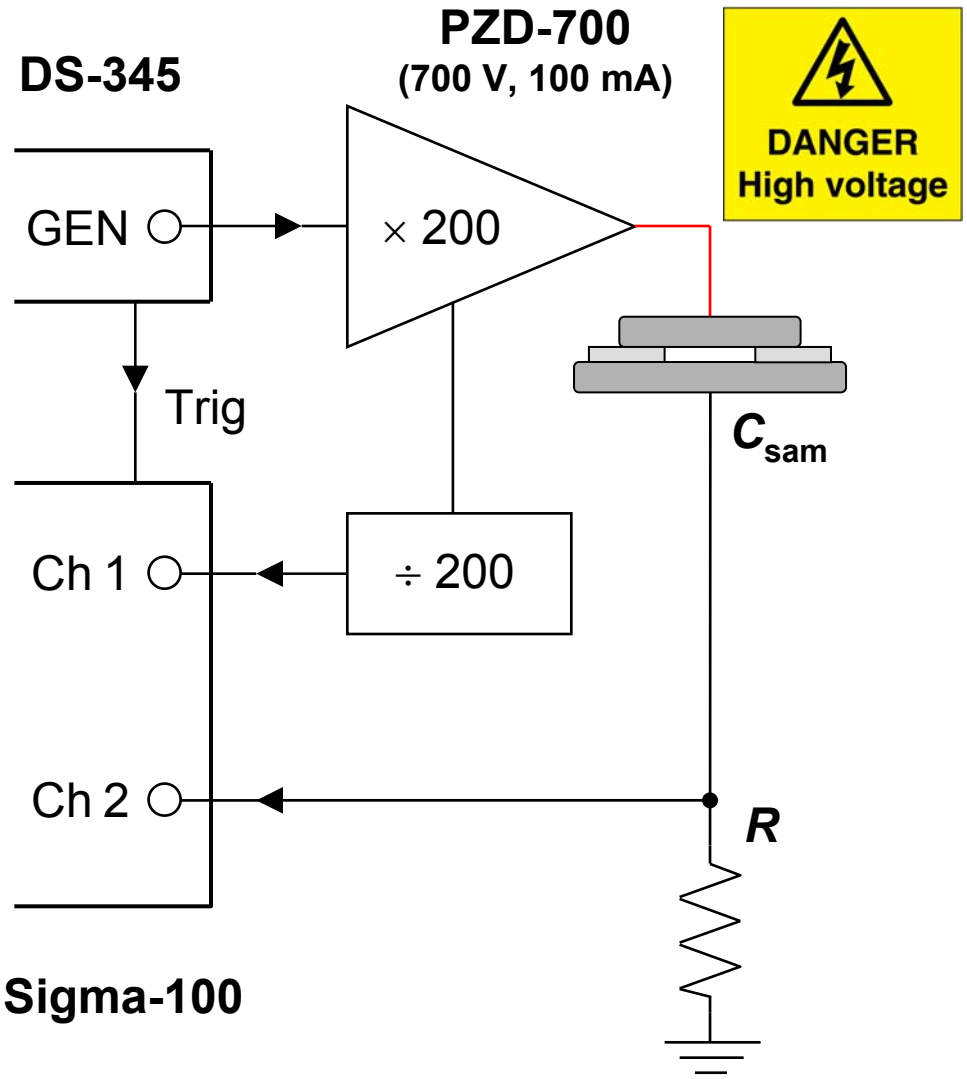
$\nu = 0.1$ Hz ... 350 kHz



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

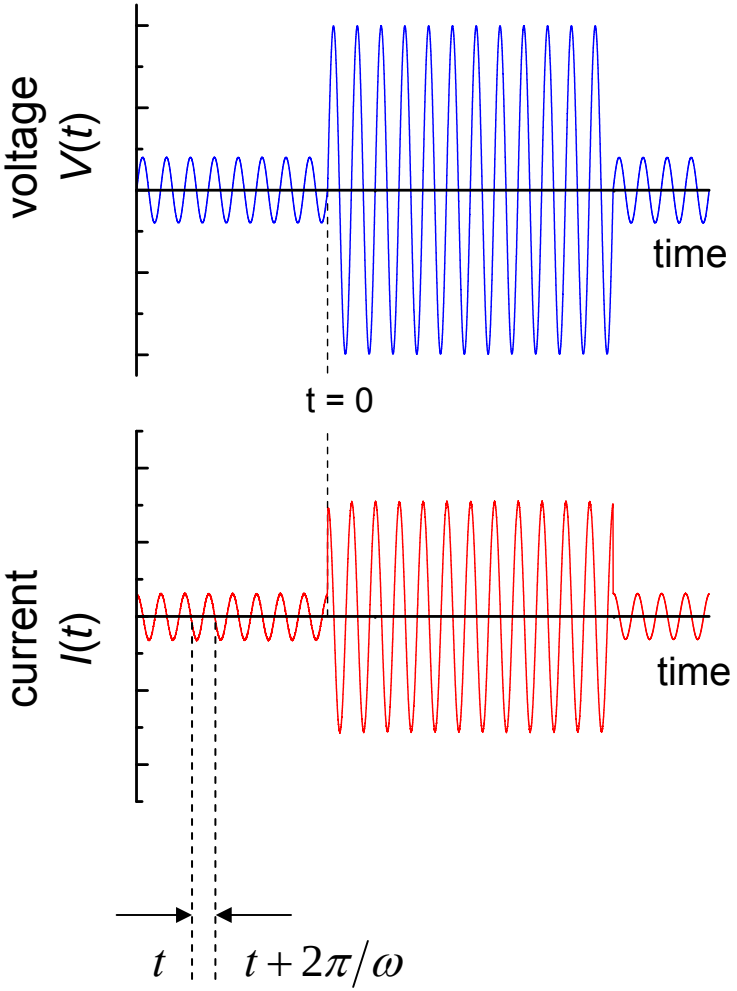
SRS DS-345:
Arbitrary Waveform Signal Generator
(16300 points, 12 bit)
10 μHz ≤ ν ≤ 30 MHz

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: $t \ldots t + 2\pi/\omega$

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

$$A_V = \sqrt{V'^2 + V''^2} \qquad \varphi_V = \arctan(V''/V')$$

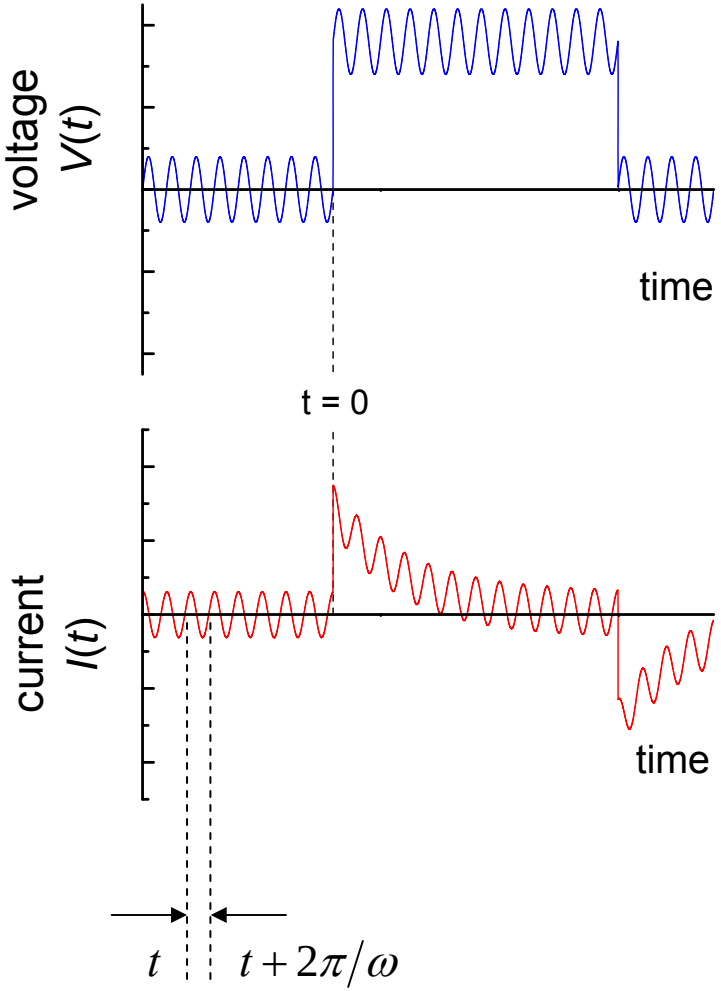
$$I' = \frac{\omega}{\pi}\int_{t}^{t+2\pi/\omega} \sin(\omega t')I(t')dt' \qquad I'' = \frac{\omega}{\pi}\int_{t}^{t+2\pi/\omega} \cos(\omega t')I(t')dt'$$

$$A_I = \sqrt{I'^2 + I''^2} \qquad \varphi_I = \arctan(I''/I')$$

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

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: $t \ldots t + 2\pi/\omega$

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

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

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

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

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

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

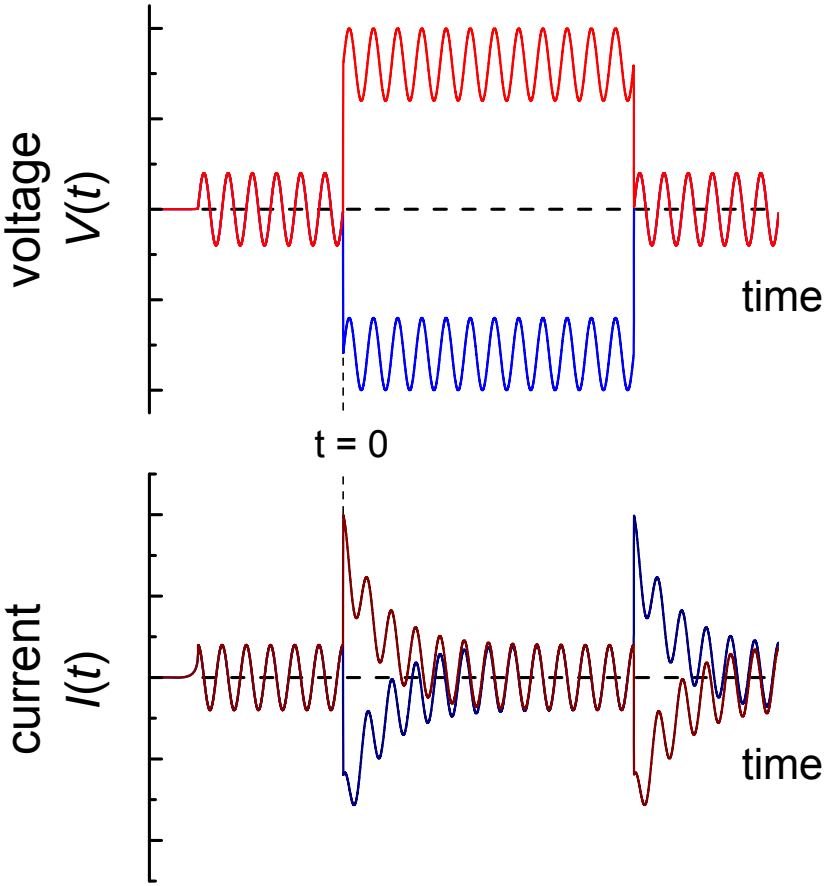
$$A_I = \sqrt{I'^2 + I''^2}$$

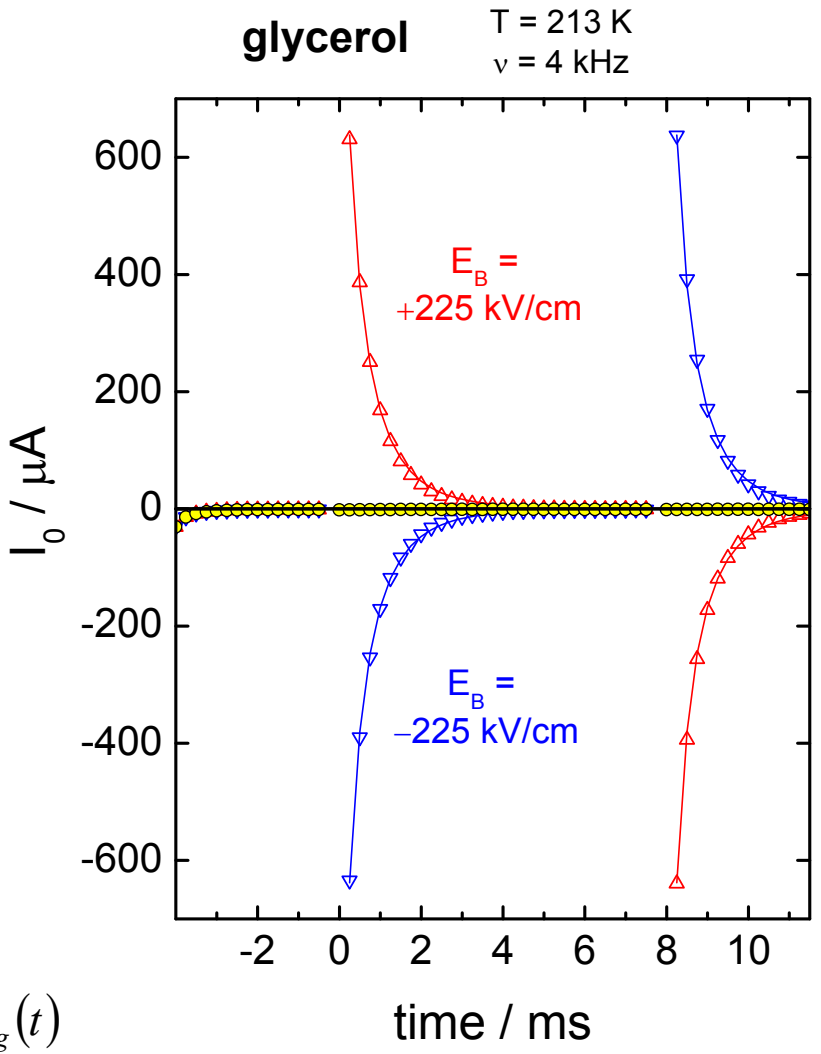
$$\varphi_I = \arctan(I''/I')$$

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

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

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





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

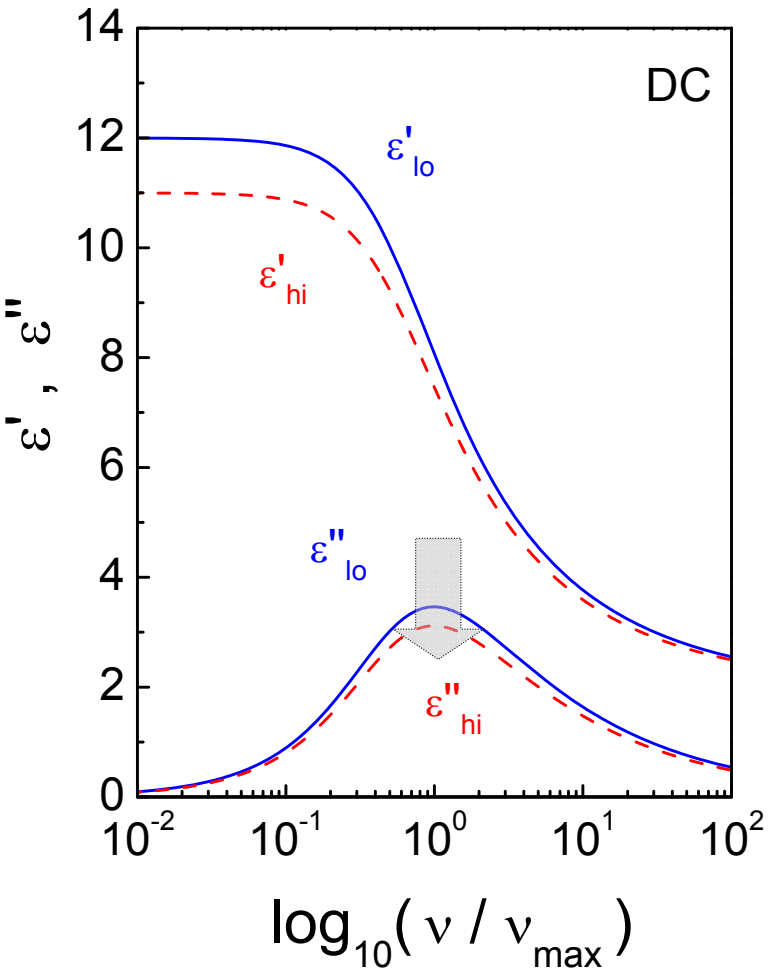
(eliminates all even Fourier components)

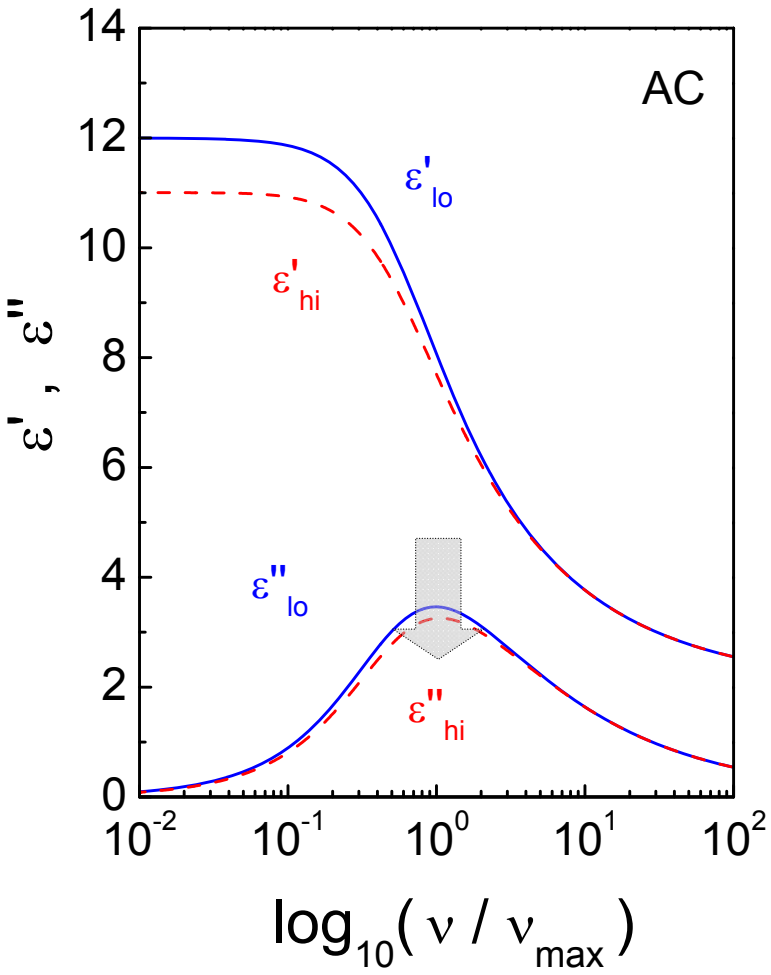
S. Samanta, R. Richert, J. Chem. Phys. 142 (2015) 044504

NDE Summary

(AC / DC)

NDE summary: dielectric saturation

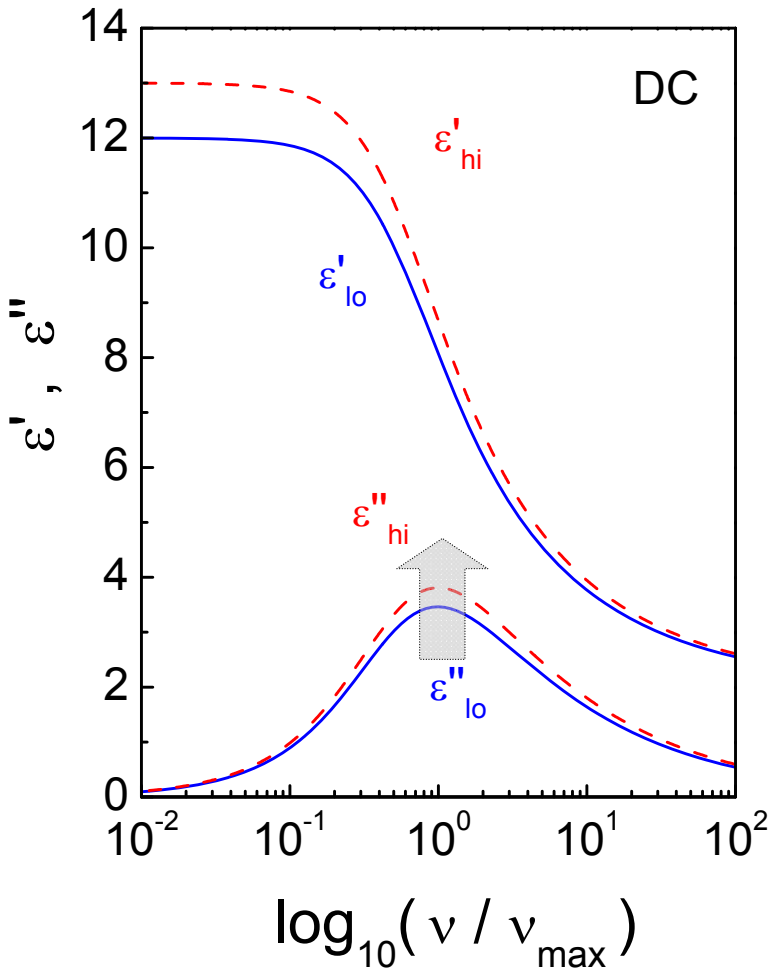


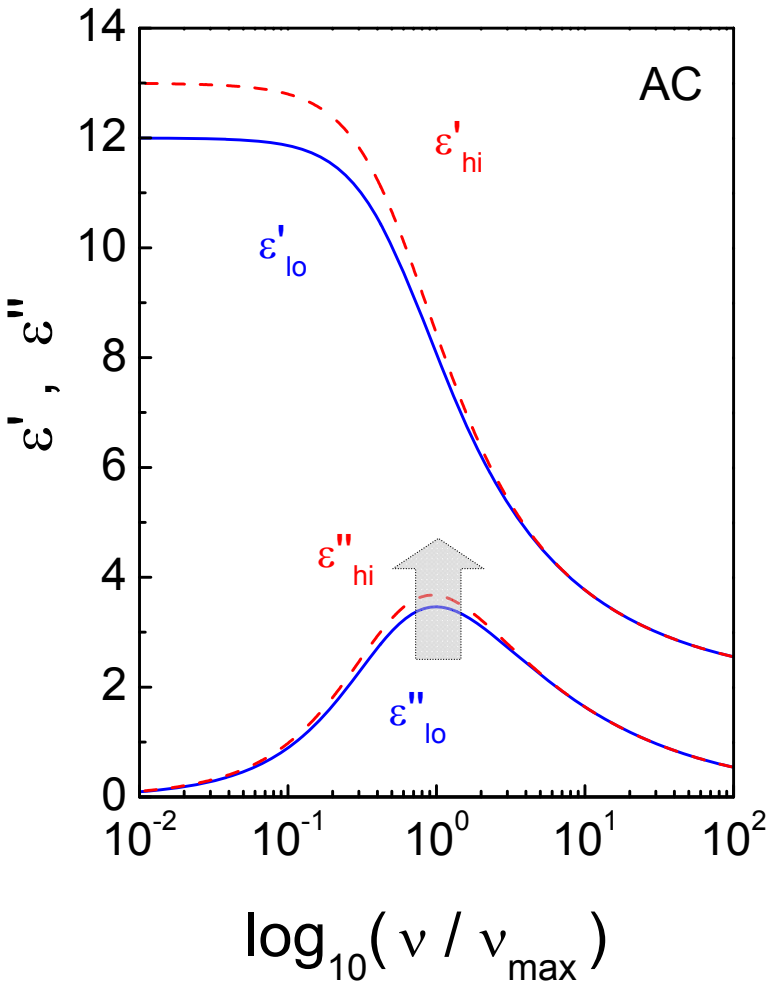


DC: amplitude reduction at all frequencies
AC: amplitude reduction fades for $\nu > \nu_{max}$
(depending on number of T_{fic} for structural recovery)

R. Richert, J. Phys.: Condens. Matter (in press)

NDE summary: chemical effect

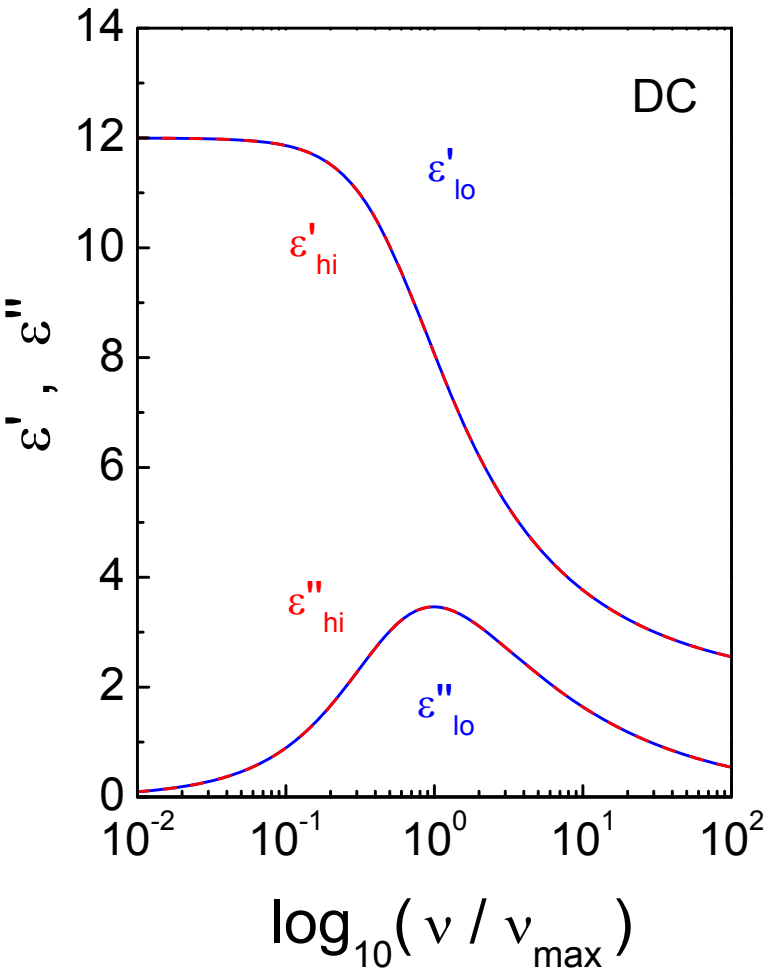


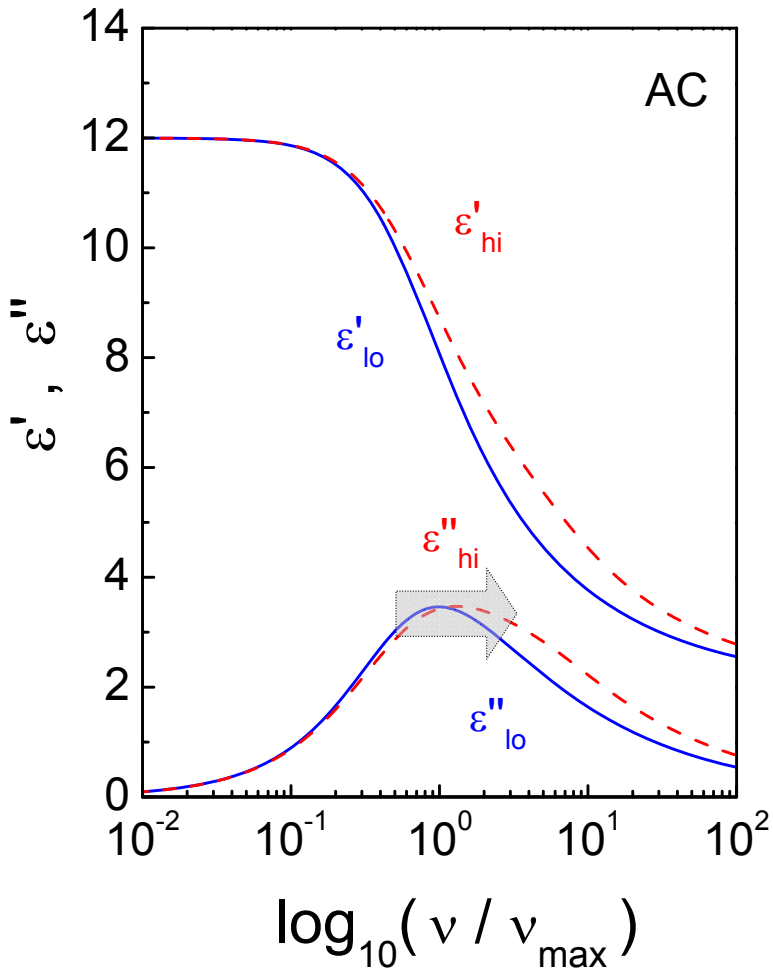


DC: amplitude enhancement at all frequencies
AC: amplitude enhancement can fade for $\nu > \nu_{max}$
(depends on nature of chemical effect)

R. Richert, J. Phys.: Condens. Matter (in press)

NDE summary: energy absorption



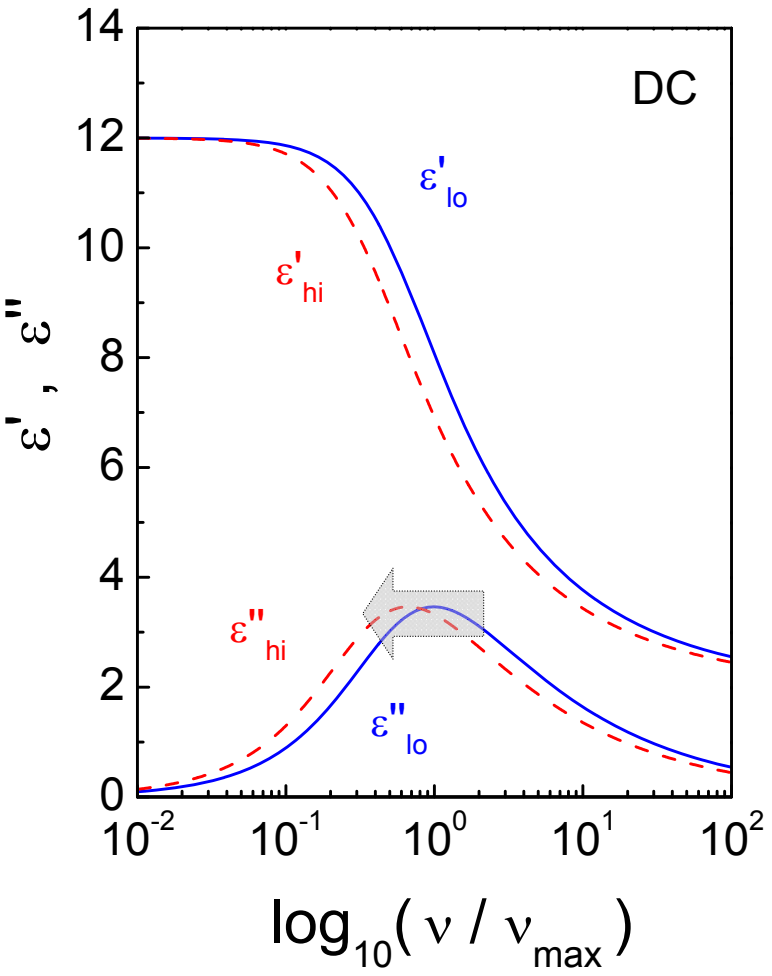


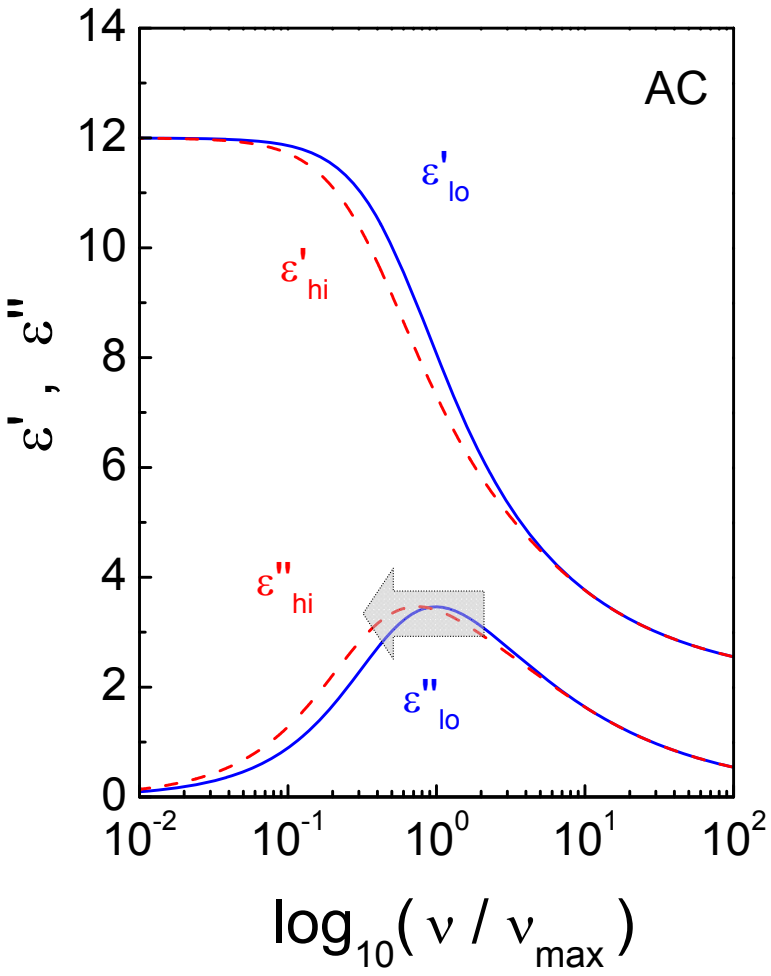
DC: no energy absorbed from static field

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

R. Richert, J. Phys.: Condens. Matter (in press)

NDE summary: electroviscous effect (entropy reduction)



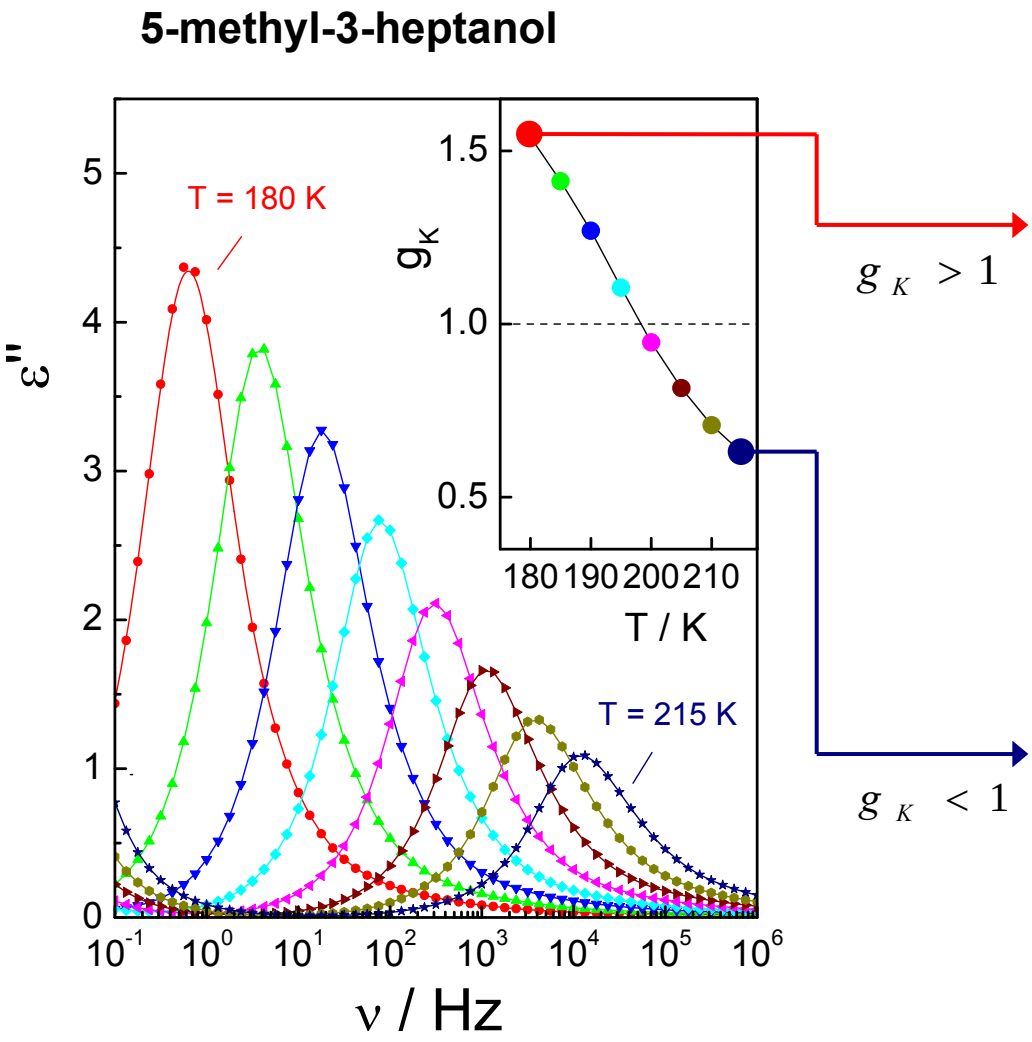


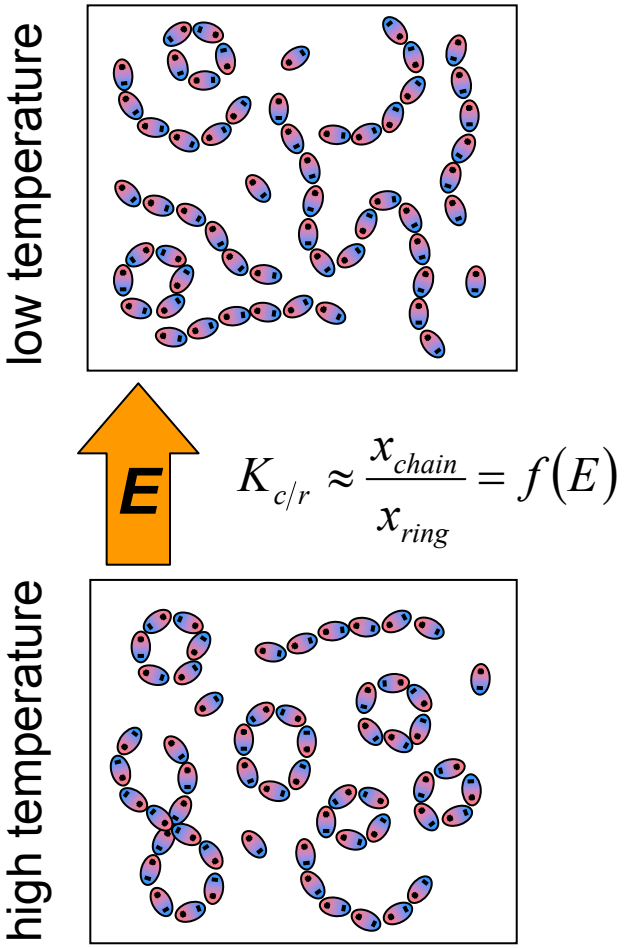
DC: increased relaxation times for all frequencies
AC: increased relaxation times only for $\nu < \nu_{max}$
(always combined with dielectric saturation)

R. Richert, J. Phys.: Condens. Matter (in press)

Chemical Effect
(Monohydroxy Alcohols)

special case of 5-methyl-3-heptanol





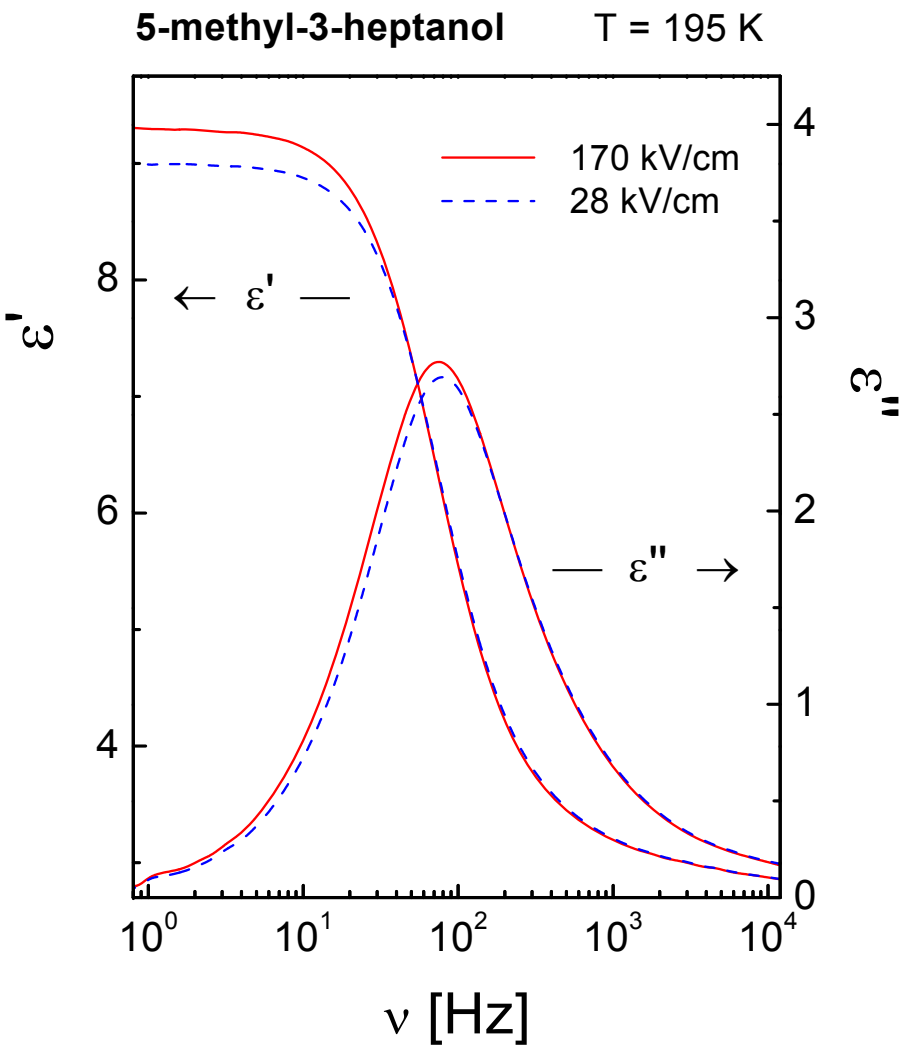
$$K_{c/r} \approx \frac{x_{chain}}{x_{ring}} = f(E)$$

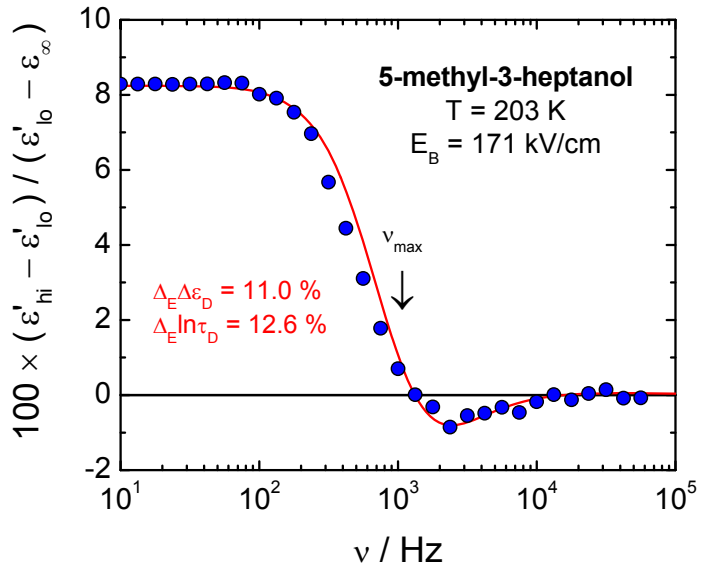
$$g_K = 1 + z\langle \cos\theta \rangle$$

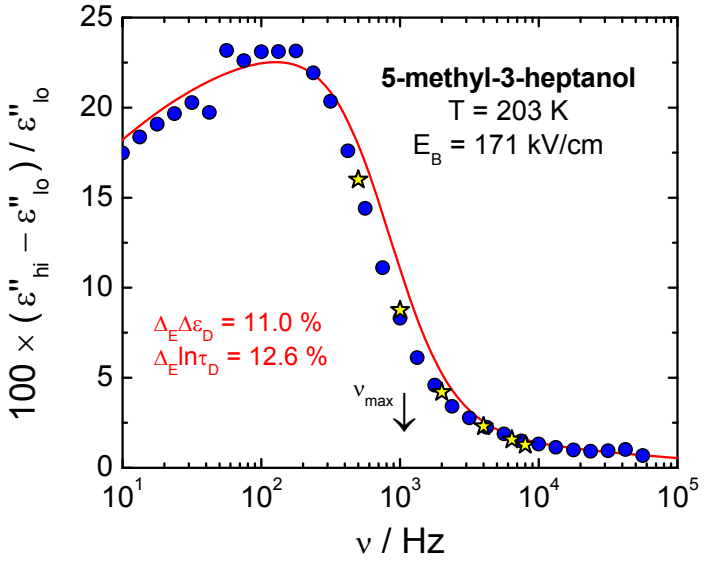
W. Dannhauser, J. Chem. Phys. 48 (1968) 1911

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

special case of 5-methyl-3-heptanol



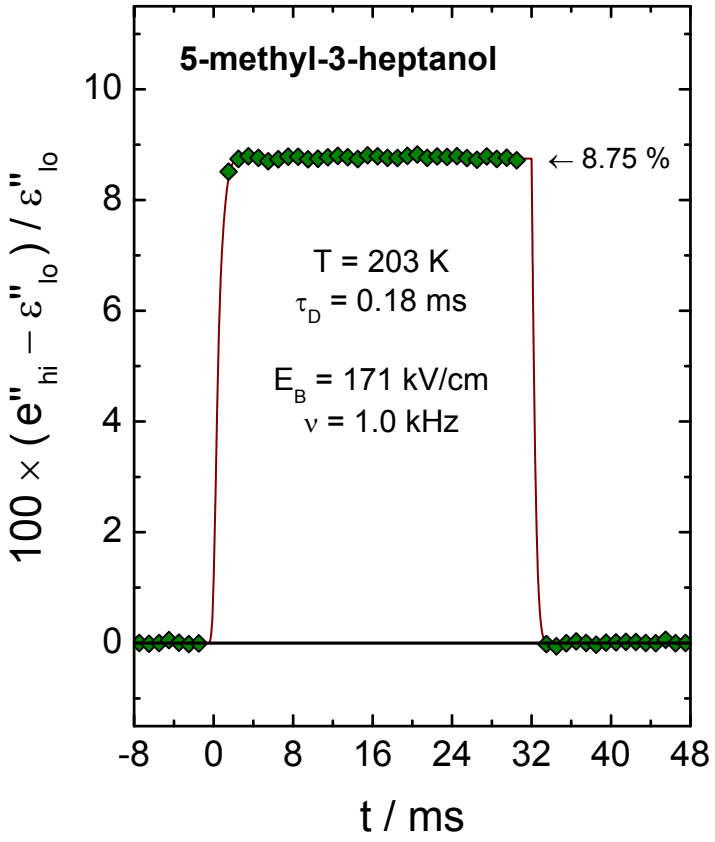


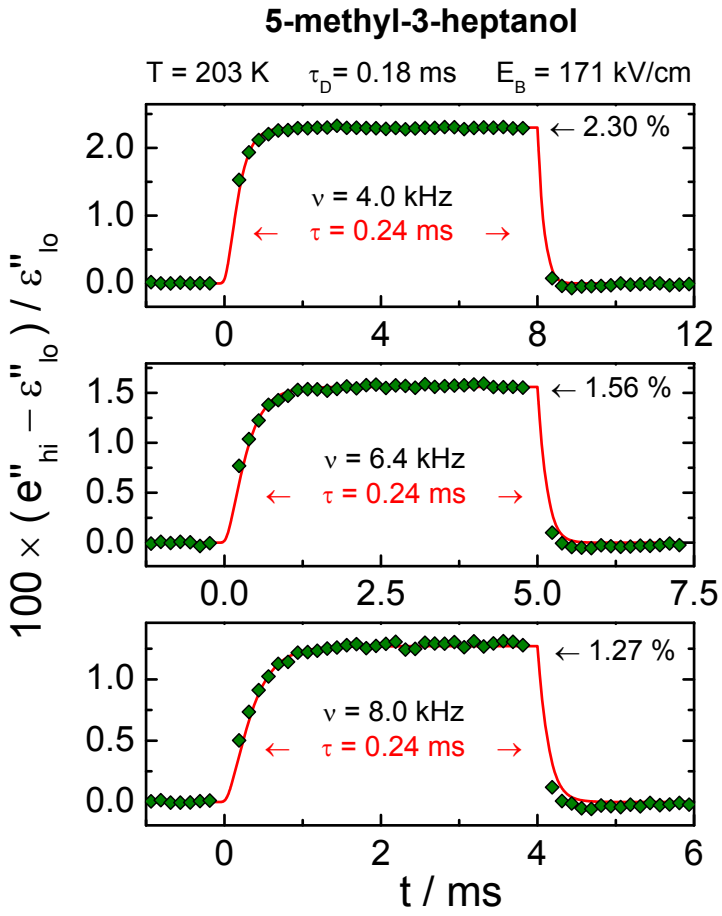


L.P. Singh, R. Richert, Phys. Rev. Lett. 1009 (2012) 167802

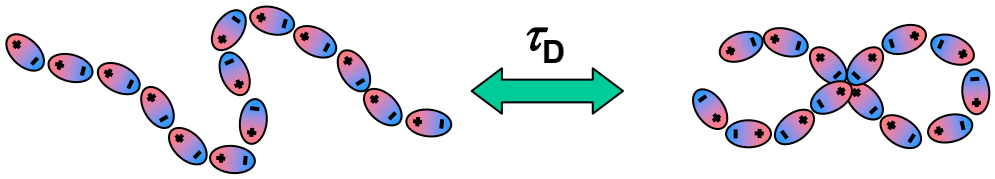
A. R. Young-Gonzales, R. Richert, J. Chem. Phys. 145 (2016) 074503

time resolved changes: structural recovery



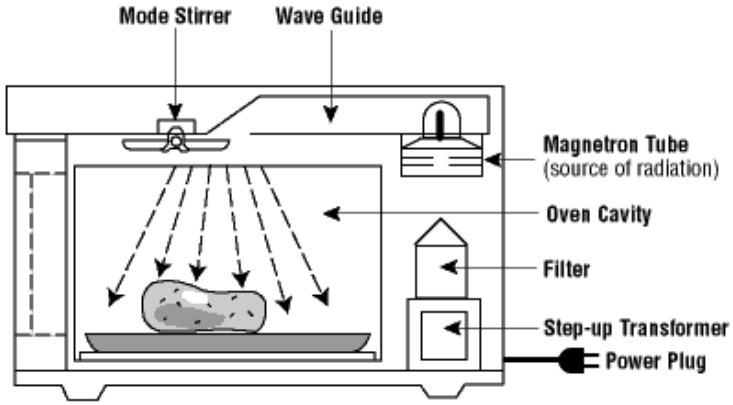


Origin of Debye peak



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

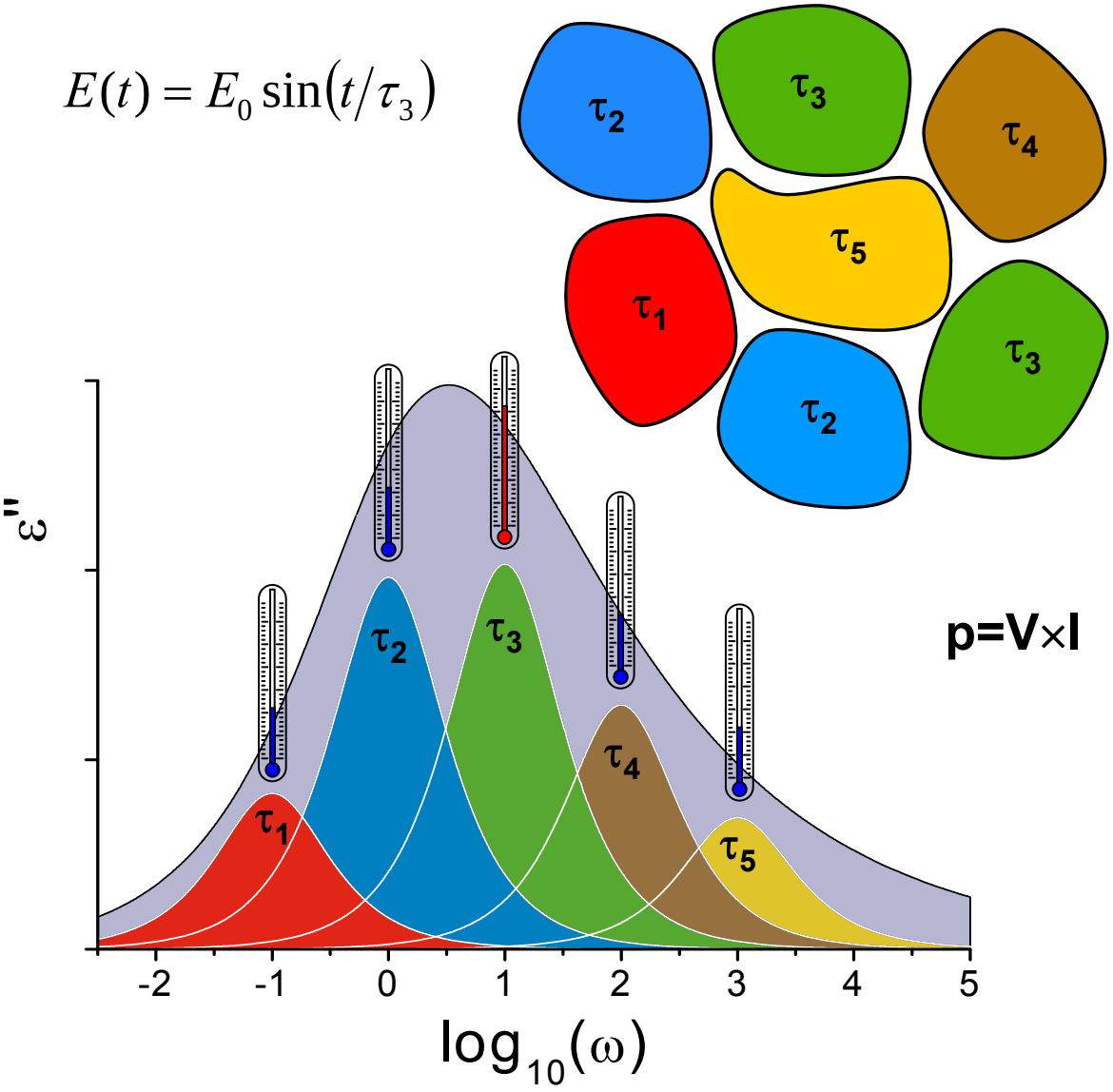
Energy Absorption



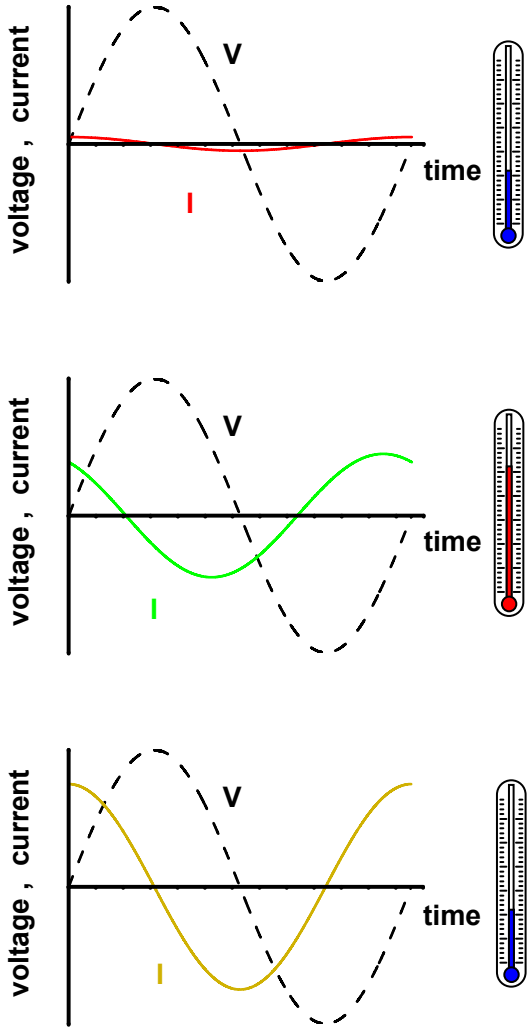
energy absorption with heterogeneous dynamics

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

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



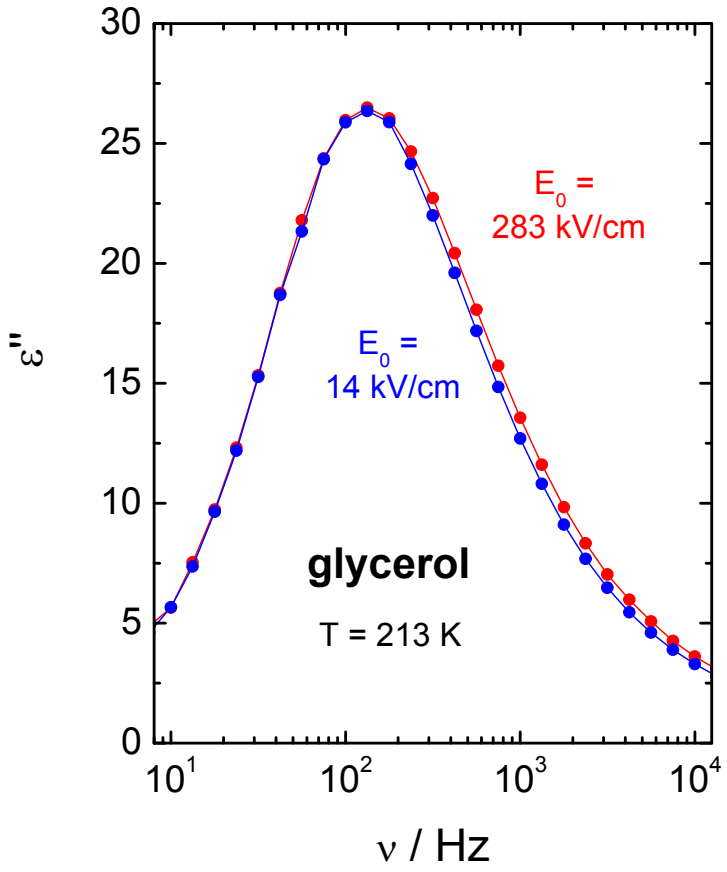
p=V×I



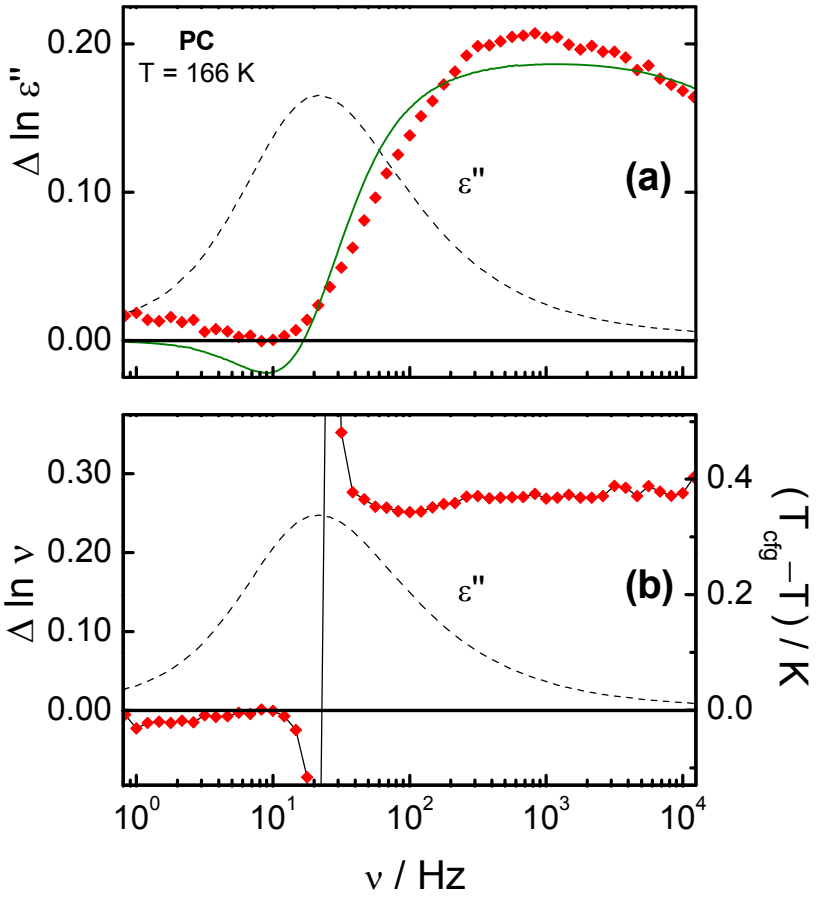
R. Richert, Eur. Phys. J. Special Topics 189 (2010) 223

high field impedance of glycerol and propylene carbonate

glycerol
(E_0 = 283 kV/cm)

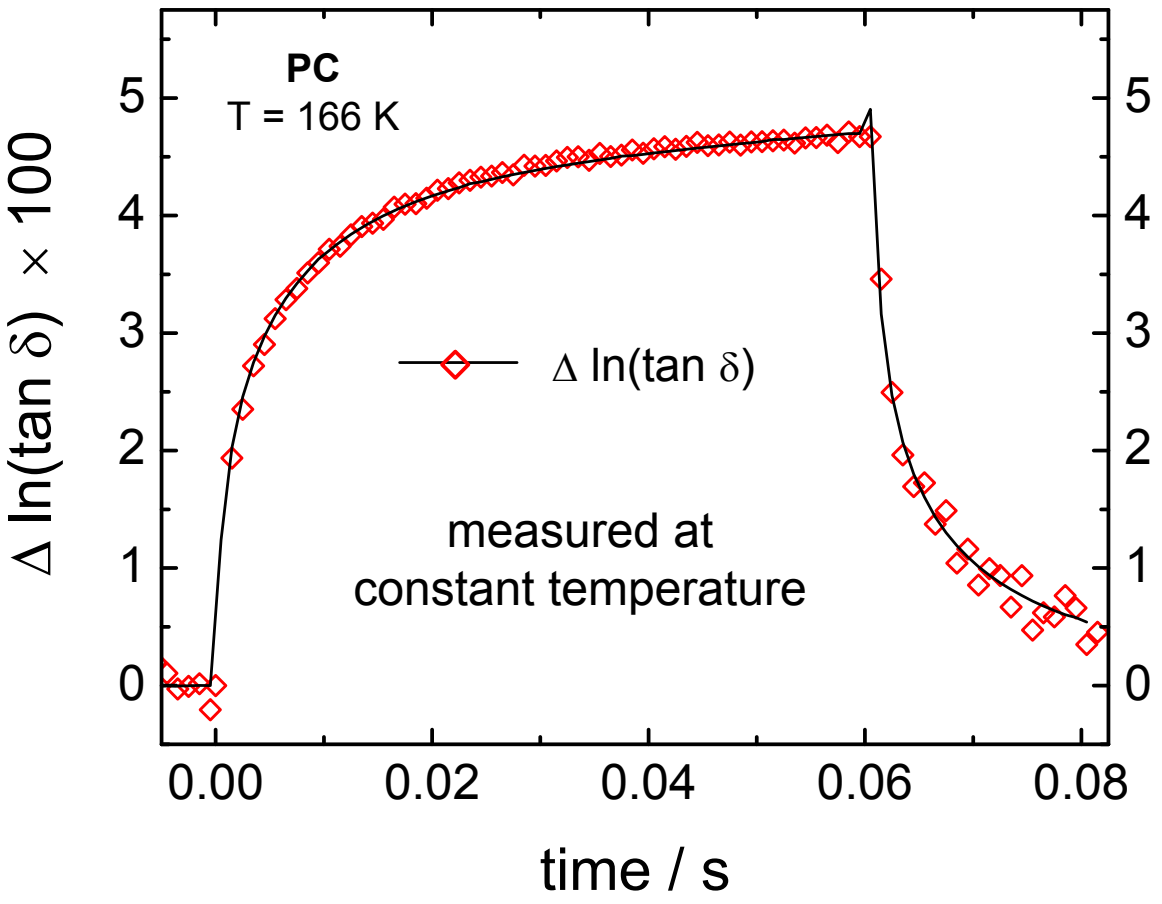


propylene carbonate
(E_0 = 177 kV/cm)



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)

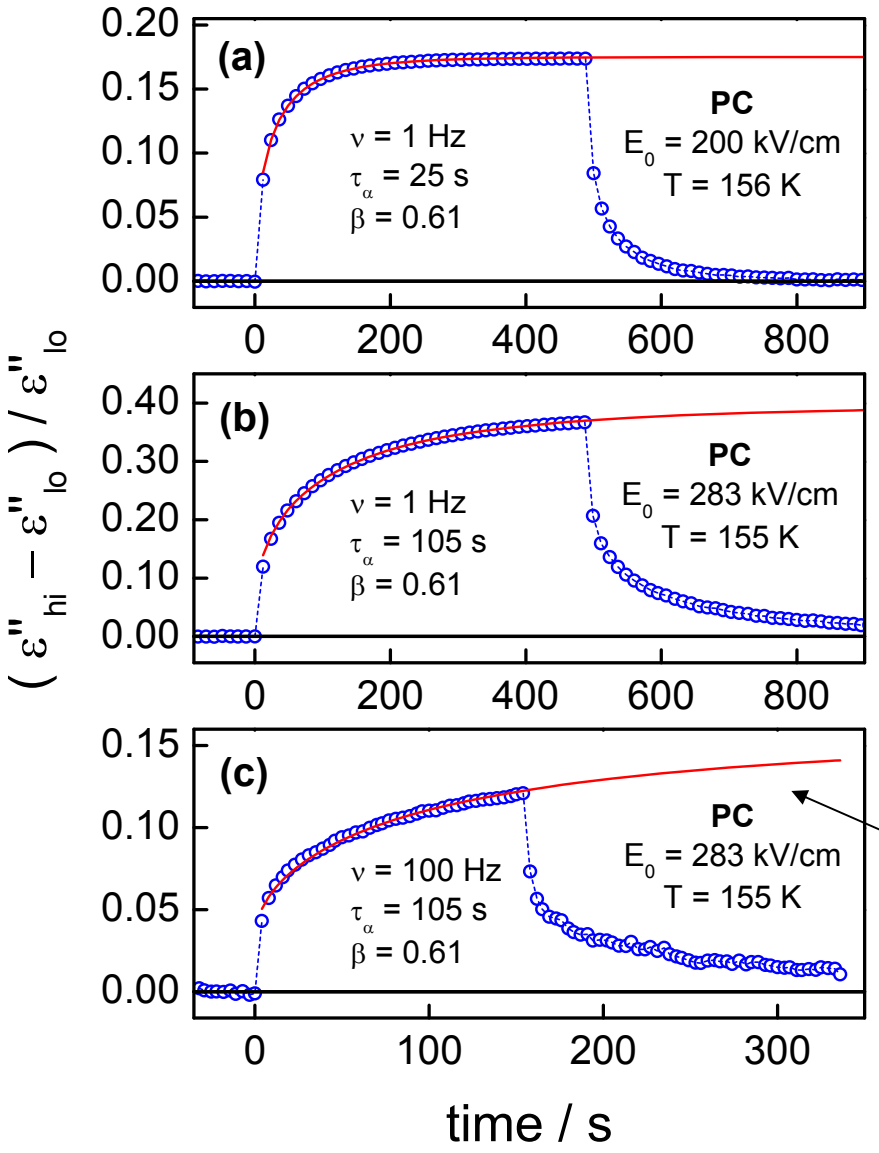
time resolved increase of fictive temperature,

at isothermal conditions

ν = 1000 Hz

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

observations at high frequencies



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

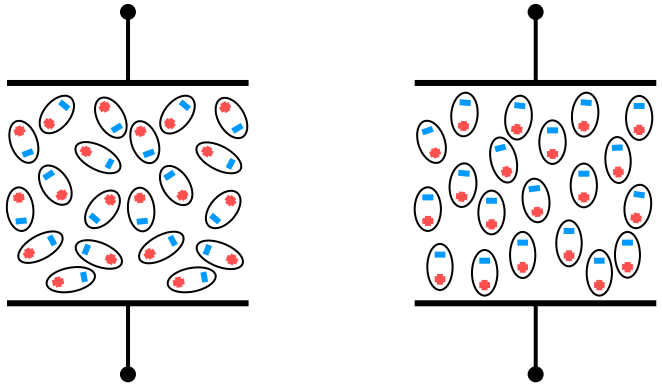
time correlation function of τ's is structural recovery :

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

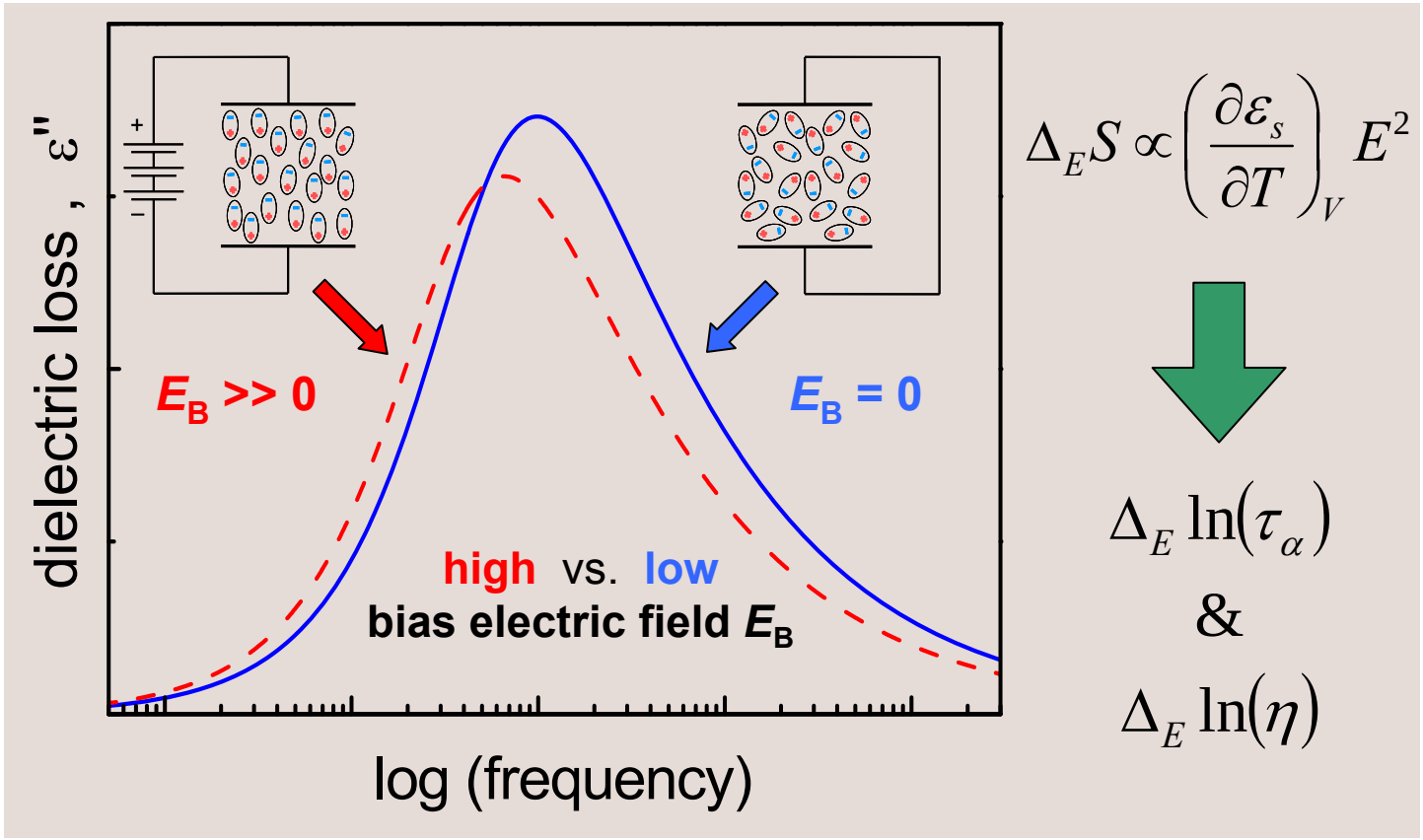
not yet steady state after 30 000 periods

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

Electroviscous Effects



dc-field induced change of entropy at constant temperature



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

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

&

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

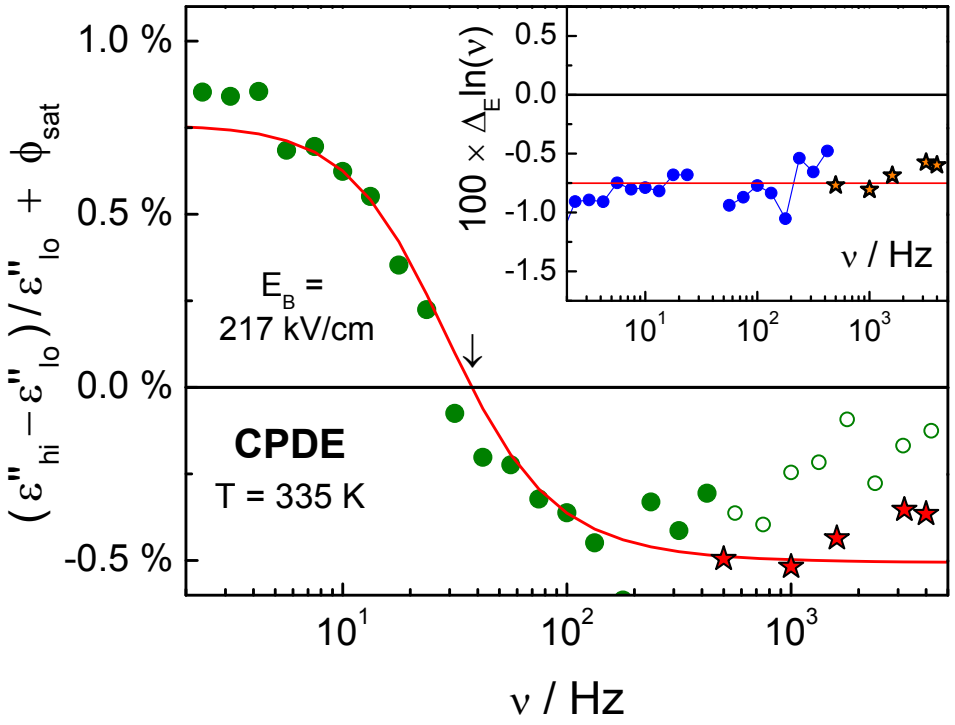
G. Adam and J. H. Gibbs,
J. Chem. Phys. 43 (1965) 139

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

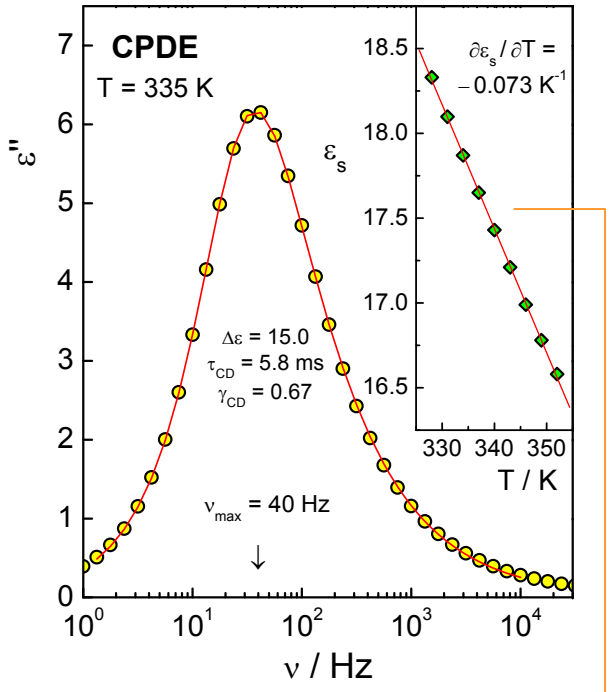
G. P. Johari, J. Chem. Phys. 138 (2013) 154503

field induced 'entropy effect': CPDE

cresolphthalein-dimethylether (CPDE)



$$\left(\frac{\partial \varepsilon_s}{\partial T}\right)_p = -0.073\,\mathrm{K}^{-1}$$



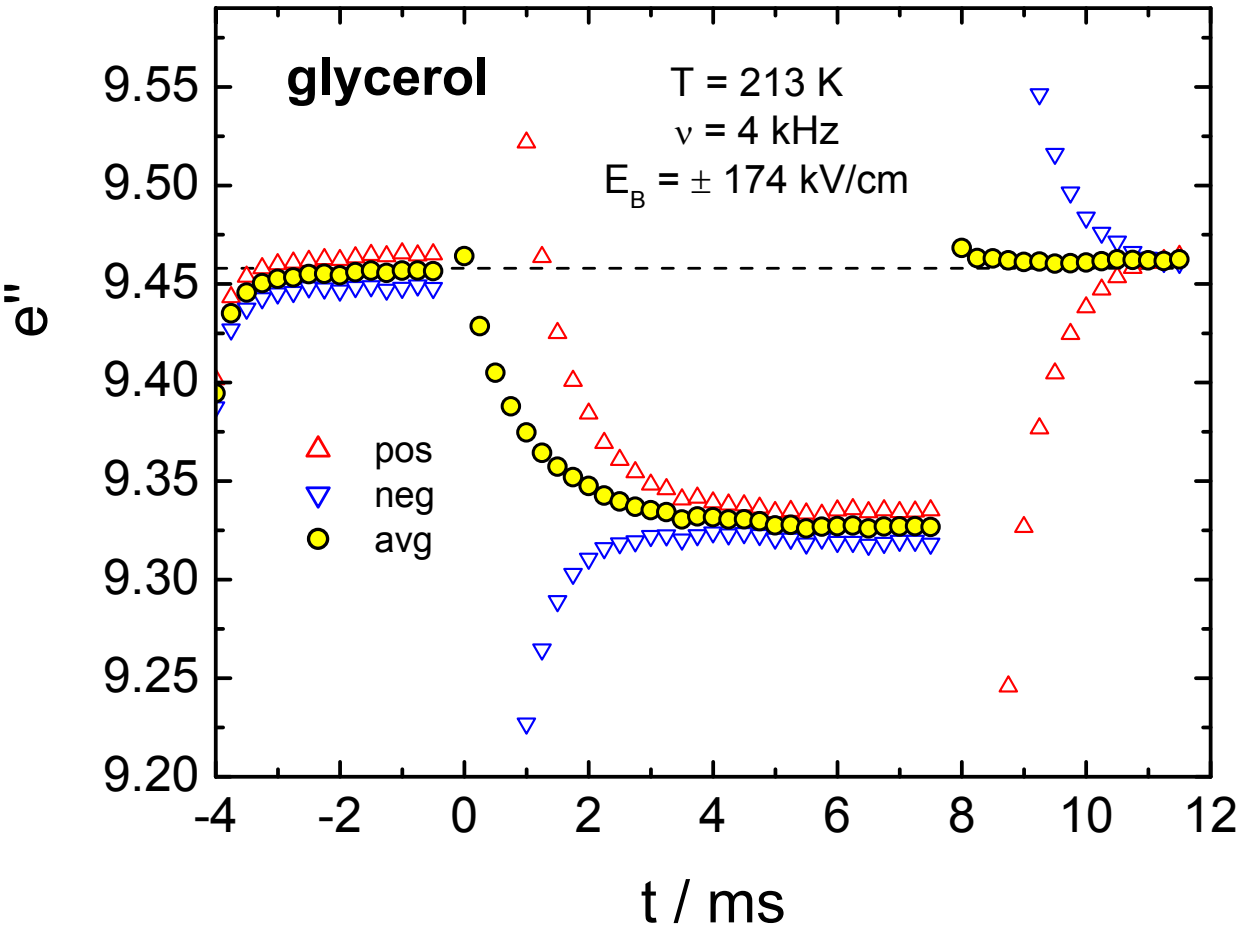
$$\Delta_E \ln \Delta\varepsilon = -0.72\%$$

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

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

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

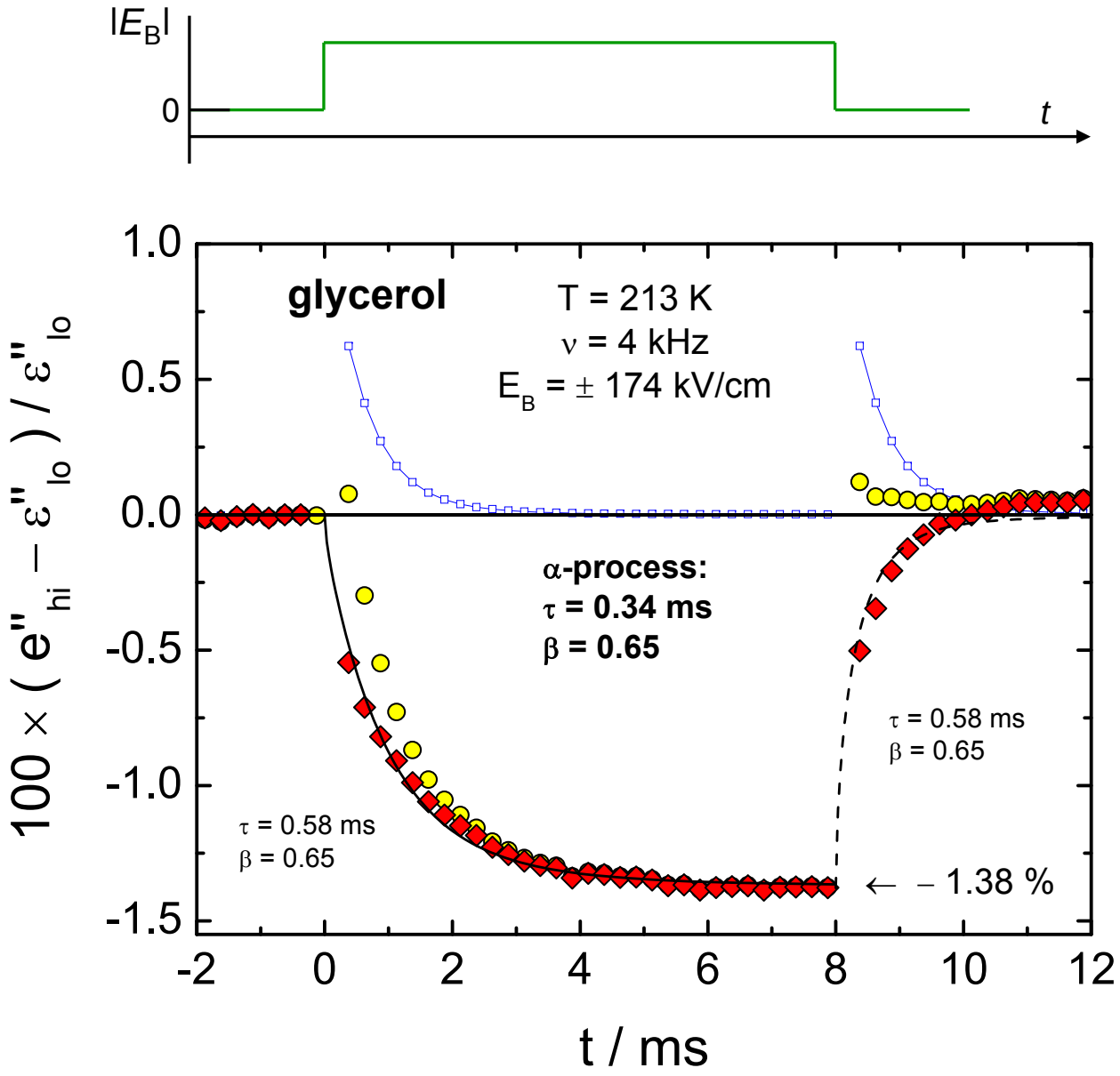
field induced change: entropy effect



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

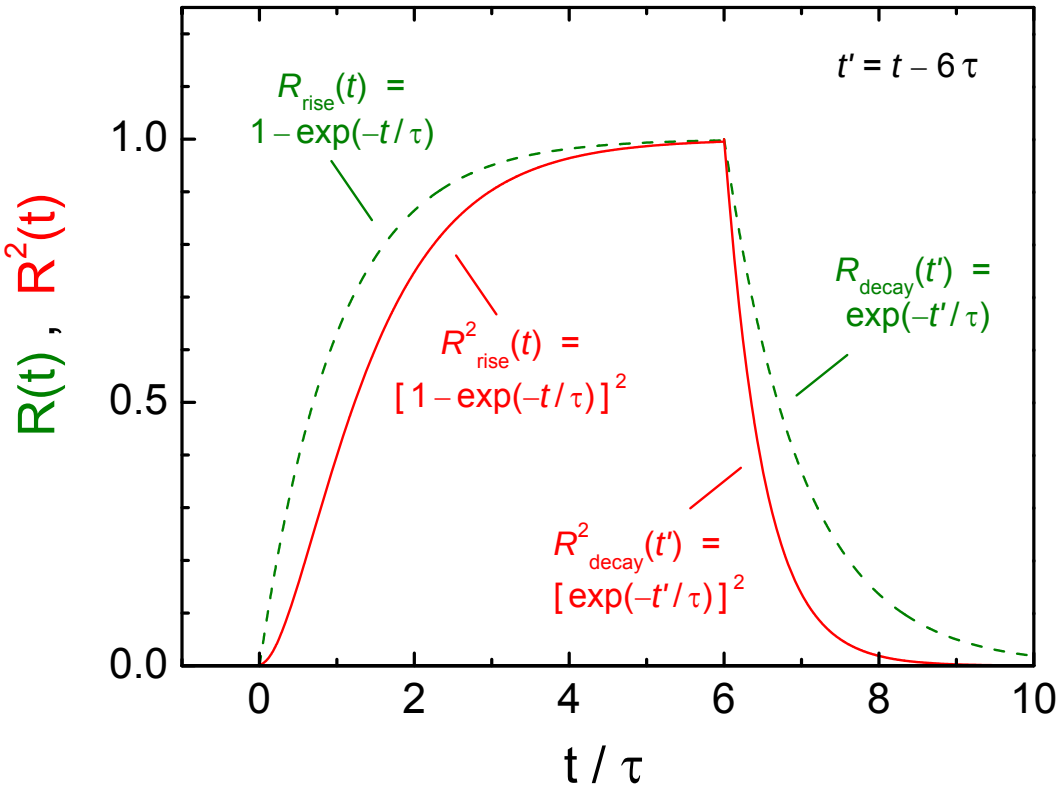
S. Samanta, R. Richert, J. Chem. Phys. 142 (2015) 044504

'heat'-corrected results: glycerol



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

explaining the rise/decay asymmetry



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

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

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

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

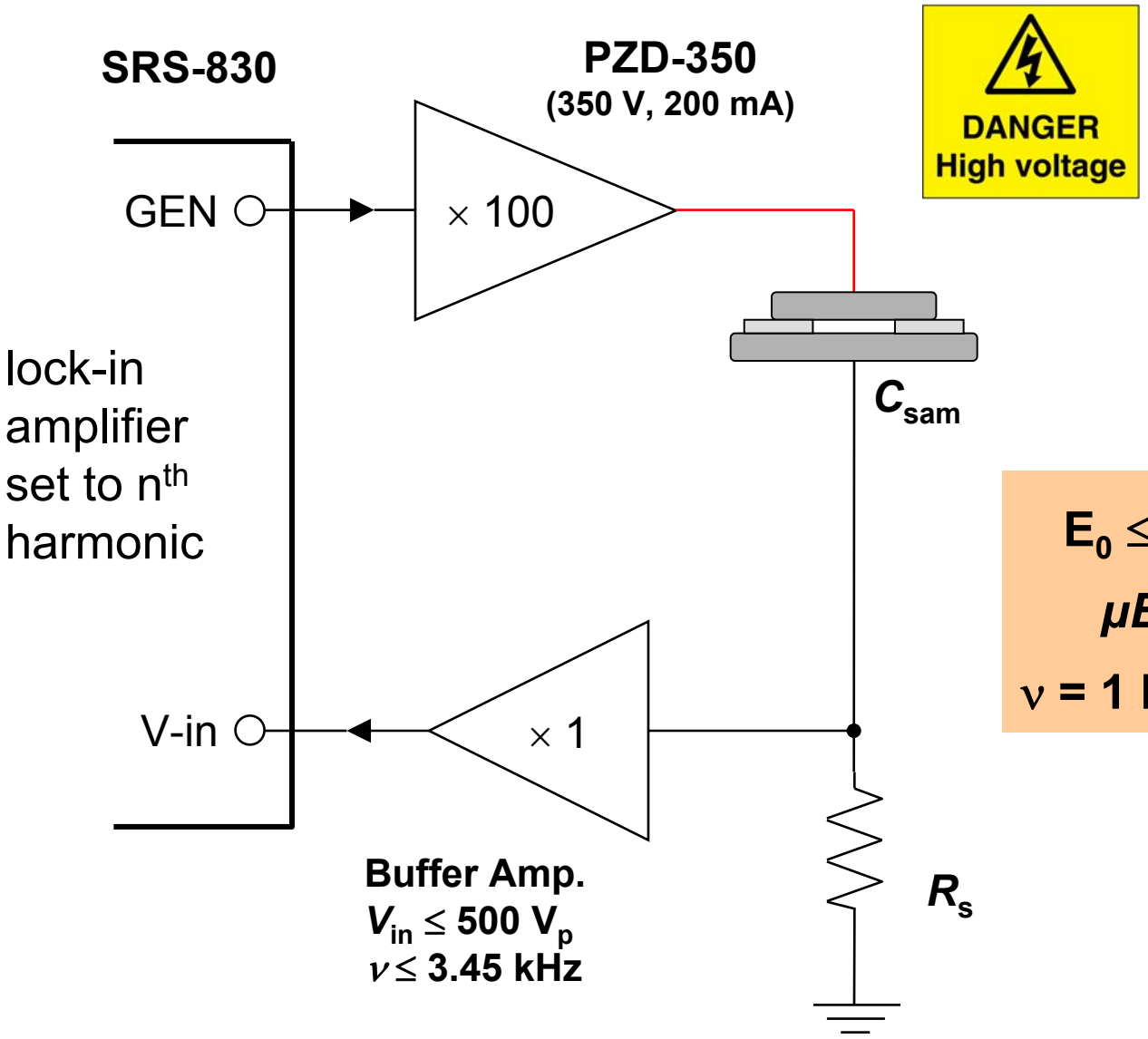
$$\Delta_E S = \frac{\varepsilon_0 M}{2\rho}\left(\frac{\partial \varepsilon_s}{\partial T}\right) \times E_B^2 \quad \Rightarrow \quad "\Delta_E S(t)" = \frac{\varepsilon_0 M}{2\rho}\left(\frac{\partial \varepsilon_s}{\partial T}\right) \times \left(\frac{\Delta P(t)}{\varepsilon_0 \Delta\varepsilon}\right)^2$$

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

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

Higher Harmonics

experimental techniques: higher harmonics



$E_0 \leq$ 650 kV/cm

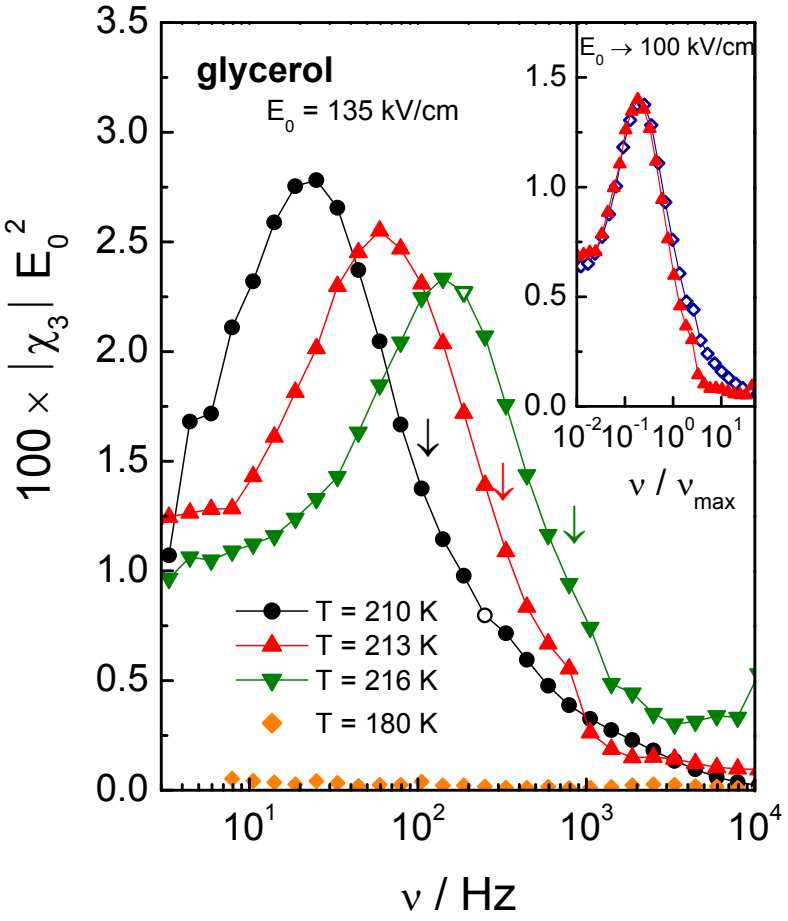
$\mu E \leq 0.1\ kT$

ν = 1 Hz ... 102 kHz

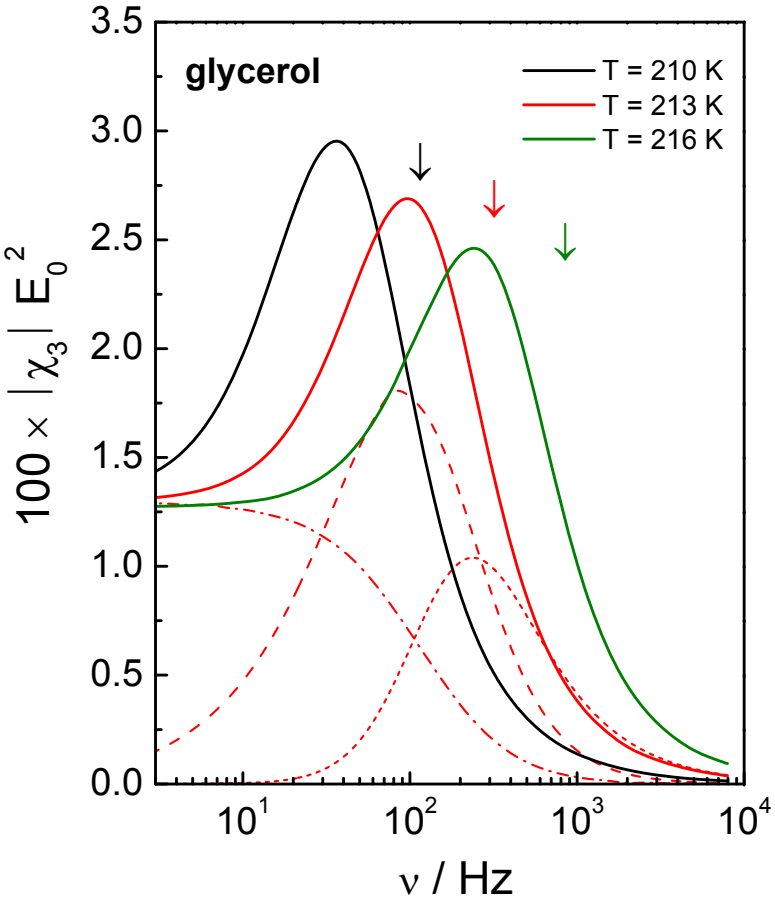
P. Kim, A. R. Young-Gonzales, R. Richert, J. Chem. Phys. 145 (2016) 064510

third harmonic susceptibility χ_3 : glycerol

experiment



model



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

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Topical Review

Nonlinear dielectric effects in liquids: a guided tour

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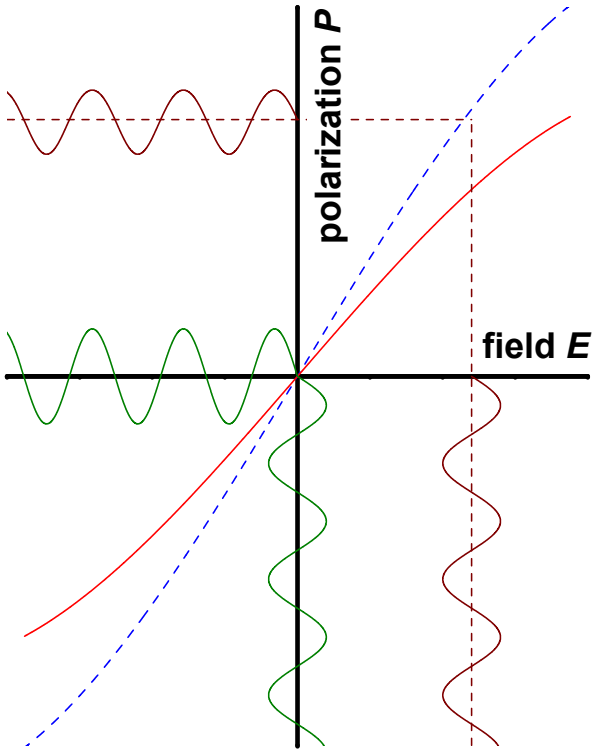
Abstract

Dielectric relaxation measurements probe how the polarization of a material responds to the application of an external electric field, providing information on structure and dynamics of the sample. In the limit of small fields and thus linear response, such experiments reveal the properties of the material in the same thermodynamic state it would have in the absence of the external field. At sufficiently high fields, reversible changes in enthalpy and entropy of the system occur even at constant temperature, and these will in turn alter the polarization responses. The resulting nonlinear dielectric effects feature field induced suppressions (saturation) and enhancements (chemical effect) of the amplitudes, as well as time constant shifts towards faster (energy absorption) and slower (entropy reduction) dynamics. This review focuses on the effects of high electric fields that are reversible and observed at constant temperature for single component glass-forming liquids. The experimental challenges involved in nonlinear dielectric experiments, the approaches to separating and identifying the different sources of nonlinear behavior, and the current understanding of how high electric fields affect dielectric materials will be discussed. Covering studies from Debye's initial approach to the present state-of-the-art, it will be emphasized what insight can be gained from the nonlinear responses that are not available from dielectric relaxation results obtained in the linear regime.

Keywords: dielectric relaxation, nonlinear responses, glass transition, structural relaxation and recovery

CONCLUSIONS



- **Different sources of non-linear behavior can be separted by ac vs.dc or by frequency.**
- **Time resolved non-linear techniques provide information on dynamics of structural recovery, analogous to physical aging.**
- **Effects that can be studied are:**
  Dielectric saturation;
  Field induced shifts of chemical potentials;
  High resolution structural recovery;
  Electroviscous and electrocaloric effects.
- **Phenomenological models exist, but much of the general theory needed for interpretation is still missing.**

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