Dielectric spectroscopy in relation to other experimental techniques

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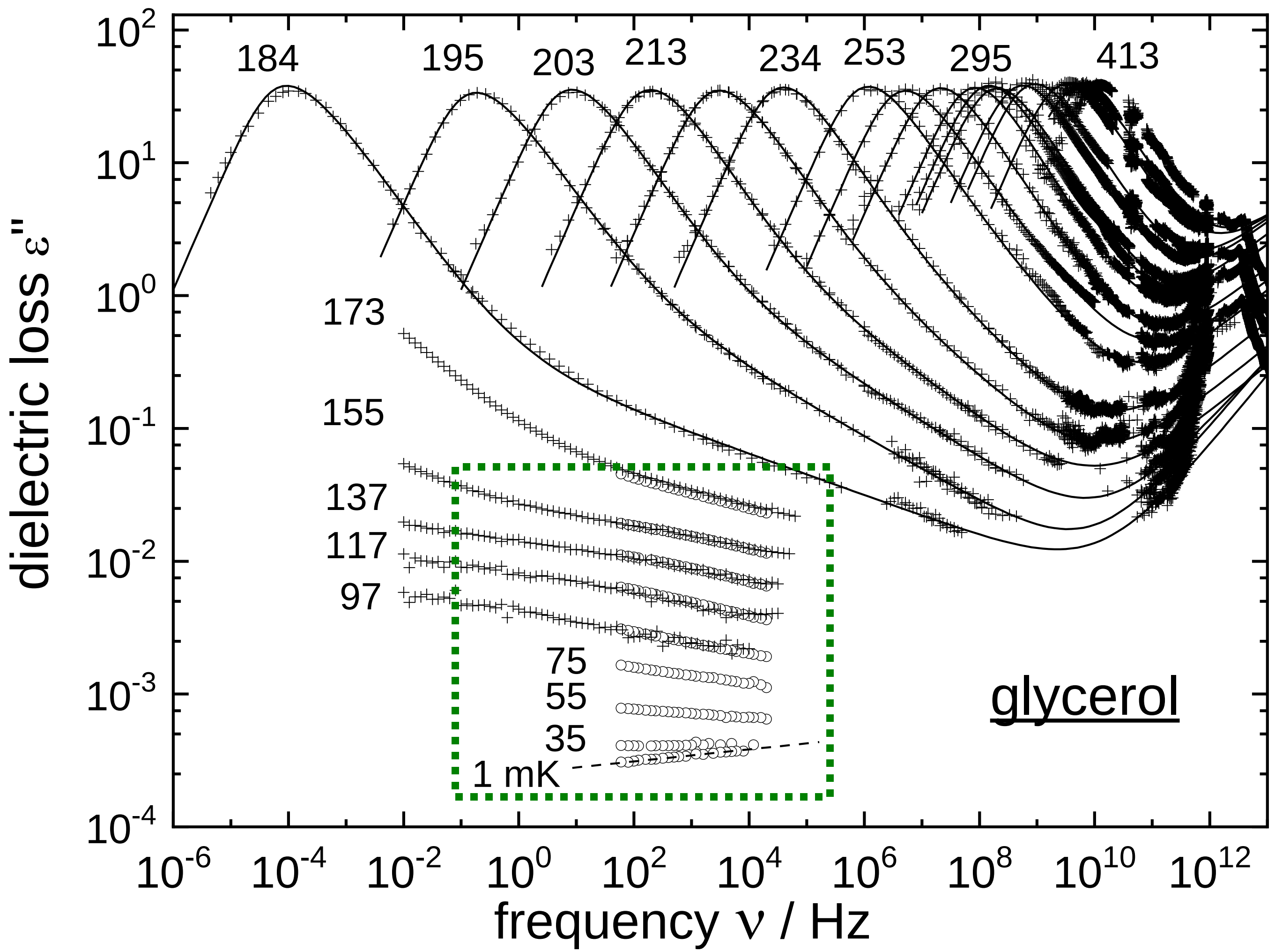
1. **Basics of molecular dynamics**
2. **Reorientational dynamics**

   connection with NMR, light scattering, and rheology

3. **Specificity of dielectric response: collective dynamics**
4. **Conclusions**

BDS2024

Why dielectric spectroscopy ?



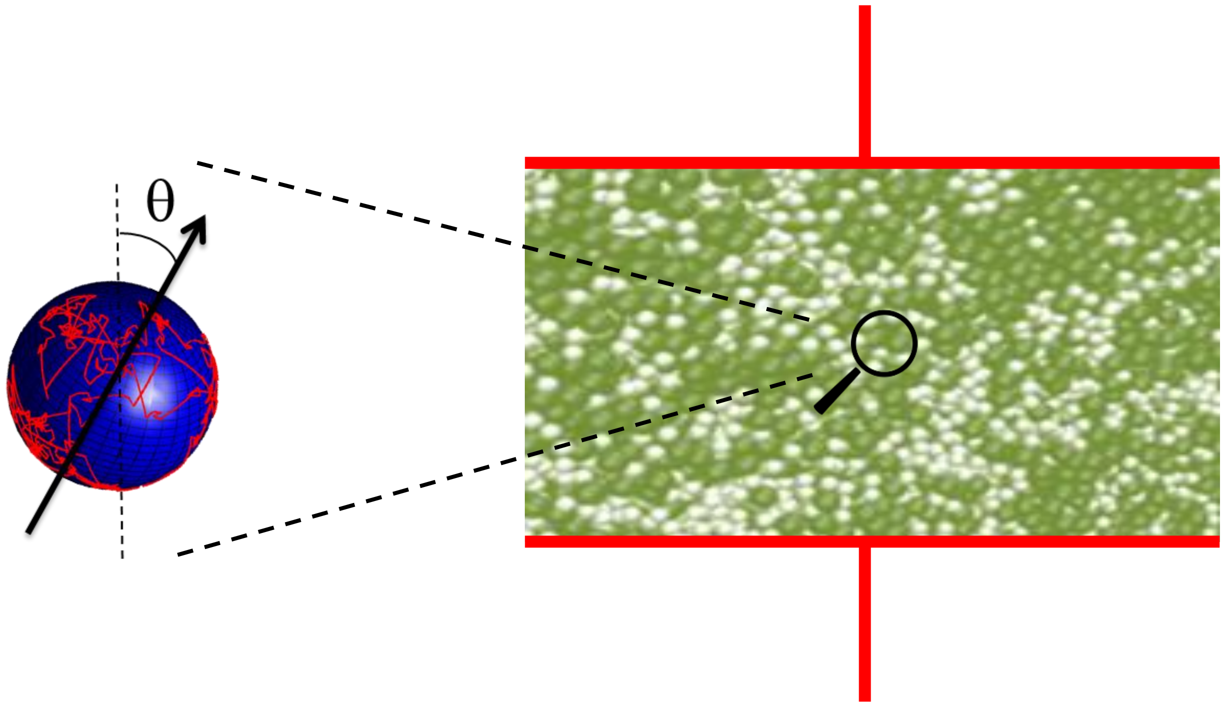
Lunkenheimer, Schneider, Brand, Loidl, Contemp. Phys. **41**, 15 (2000)

Gainaru, Rivera, Putselyk, Eska, Rössler, Phys. Rev. B **72**, 174203 (2005)

It can access the entire relaxation map (0-1 THz), from boiling point down to the cryogenic regime

Why not only dielectric spectroscopy ?

- probes a macroscopic, cumulative response

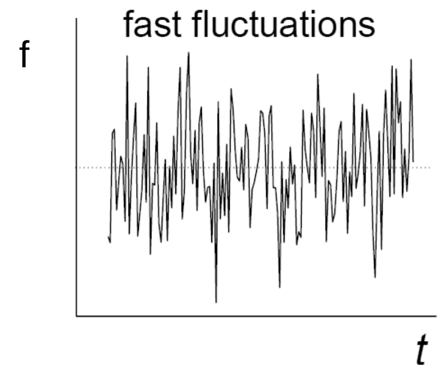


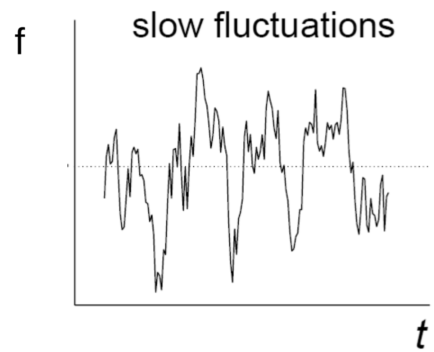
- not able to provide microscopic details

complementary methods and common “language” required

1. Basics of molecular dynamics

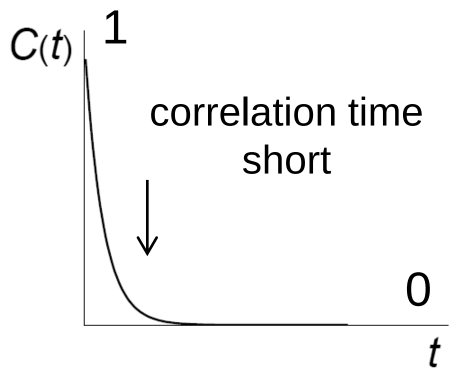
molecular properties – orientation, position, velocity, etc. fluctuate in time: *f*(*t*)

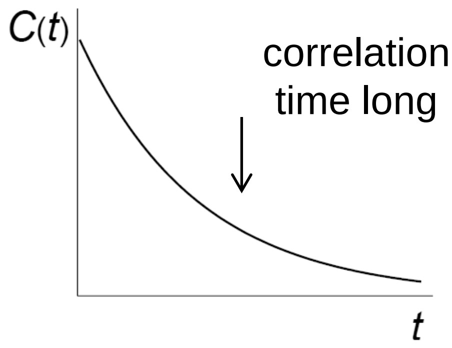




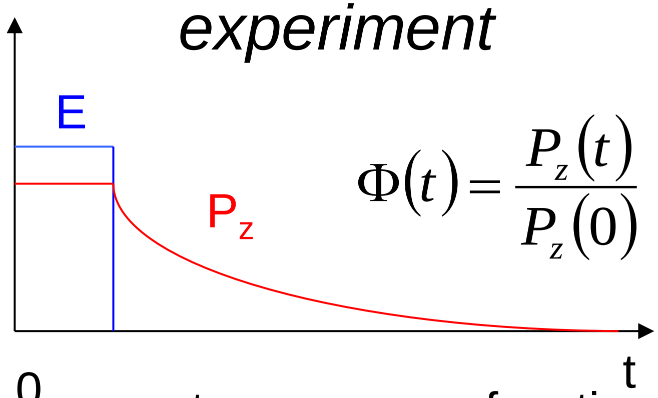
correlation function

$$C(t) = \frac{\langle f(0)\, f(t) \rangle}{\langle f(0)\, f(0) \rangle} \qquad \tau = \int_0^\infty C(\mathrm{t})\, \mathrm{dt}$$





experiment



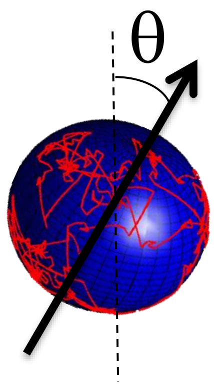
$$\Phi(t) = \frac{P_z(t)}{P_z(0)}$$

step-response function

fluctuation-dissipation theorem: Φ(t) = C(t)

2. Reorientional dynamics

- Dielectric Spectroscopy
- NMR
- Light Scattering



reorientational correlation function

$$\boxed{C_l(\mathrm{t}) = \langle P_l[\cos\theta(0)]P_l[\cos\theta(\mathrm{t})]\rangle / \langle P_l^2[\cos\theta(0)]\rangle}$$

l – rank of Legendre polynomial

Dielectric Spectroscopy: vector (dipole moment) reorientations ***l* = 1**

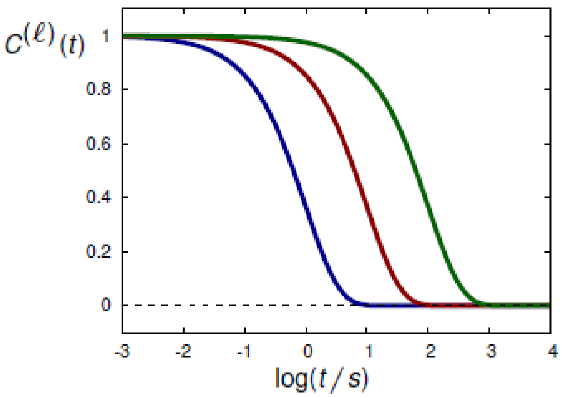
$$P_1(x) = x \longrightarrow C_1(\mathrm{t}) = \langle \cos\theta(0)\cos\theta(\mathrm{t})\rangle / \langle \cos^2\theta(0)\rangle$$

classical example: Debye model $C_1(t) = \exp(-\mathrm{t}/\tau)$

relation with frequency domain data

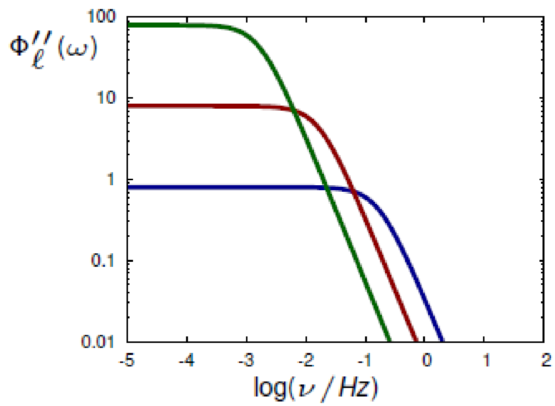
Correlation Function:

$$C^{(\ell)}(t) = \langle P_\ell(\cos\theta)\rangle$$



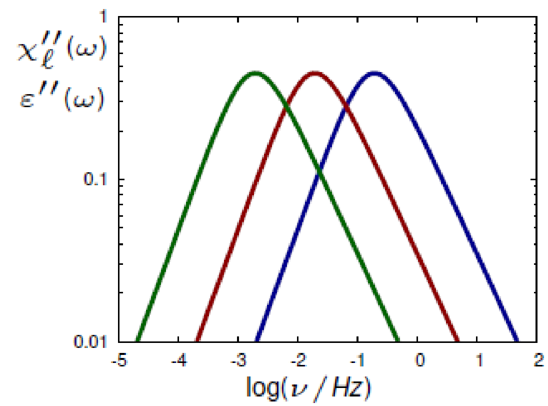
Spectral Density:

$$\Phi''_\ell(\omega) = \int_0^\infty C^{(\ell)}(t)\ \cos(\omega t)\,dt$$



Susceptibility:

$$\chi''_\ell(\omega) = \frac{\omega}{k_B T}\cdot\Phi''_\ell(\omega)$$



$$C(t) = \exp(-t/\tau)$$

$$\frac{\chi^*(\omega)-\chi_\infty}{\Delta\chi} = 1 - i\omega\int_0^\infty C(t)\exp(-i\omega t)\,dt$$

$$\chi^*(\omega) = \chi'(\omega) - i\chi''(\omega)$$

Debye model

$$\boxed{\chi''(\omega) = \frac{\Delta\chi\omega\tau}{(1+\omega^2\tau^2)}}$$

Reoriențional dynamics

- Dielectric Spectroscopy
- **NMR**
- **Light Scattering**

reorientational correlation function

$$\boxed{C_l(\mathrm{t}) = \left\langle P_l[\cos\theta(0)]P_l[\cos\theta(\mathrm{t})]\right\rangle / \left\langle P_l^2[\cos\theta(0)]\right\rangle}$$

l – rank of Legendre polynomial

NMR and **LS:** tensor (nuclear dipole and quadrupole interaction, optical anisotropy) reorientations ***l* = 2**

$$P_2(x) = \frac{1}{2}\left(3x^2 - 1\right) \longrightarrow P_2(\cos\theta) = \frac{1}{2}\left(3\cos^2\theta - 1\right)$$

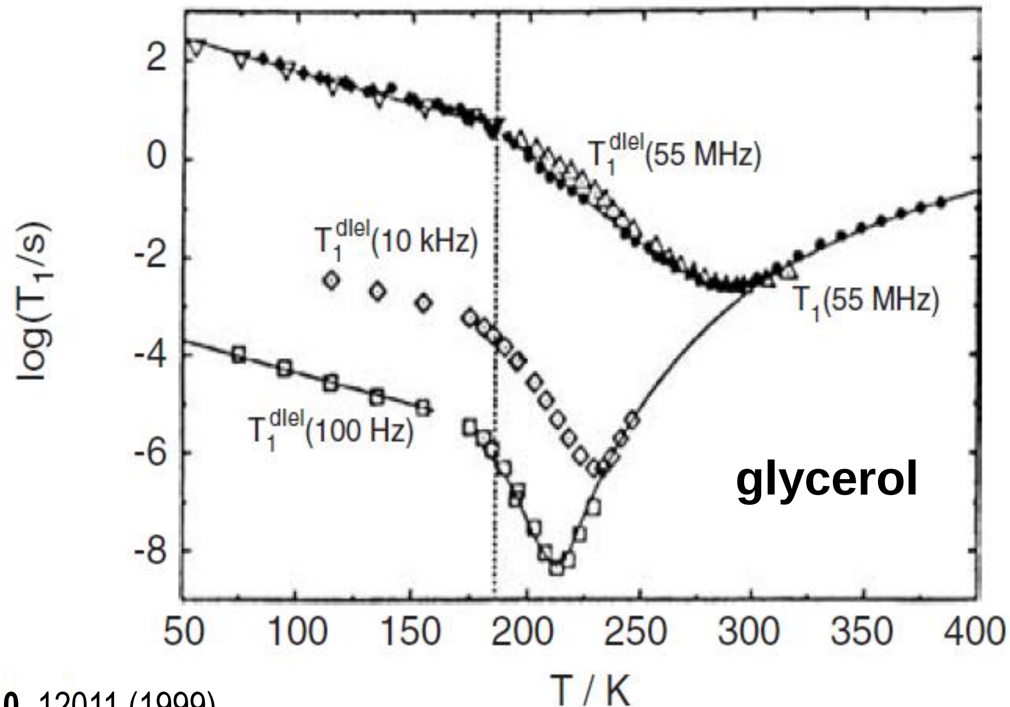
NMR

$$C_2(t) = \exp(-t/\tau) \longrightarrow J(\omega) = \frac{\tau}{1+(\omega\tau)^2}$$

$$\frac{1}{T_1} = \frac{2}{15}\delta^2 \cdot [J(\omega_L) + 4J(2\omega_L)] \longrightarrow \frac{\omega}{T_1} \approx \frac{\omega\tau}{1+(\omega\tau)^2} + \ldots \propto \chi''(\omega)$$

measured spin-lattice relaxation time

$$\boxed{\frac{\omega}{T_1(\omega)} \cong \frac{\chi''(\omega)}{\Delta\chi}}$$

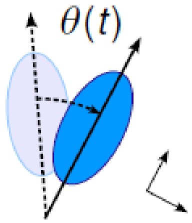


Blochowicz et al., JCP **110**, 12011 (1999)

filled symbols: from NMR
open symbols: from dielectric response

Light scattering

$$\chi''_{LS}(\omega) = \frac{I(\omega)}{\hbar\left[n(\omega,T)+1\right]}$$



reorientiation:

optical anisotropy

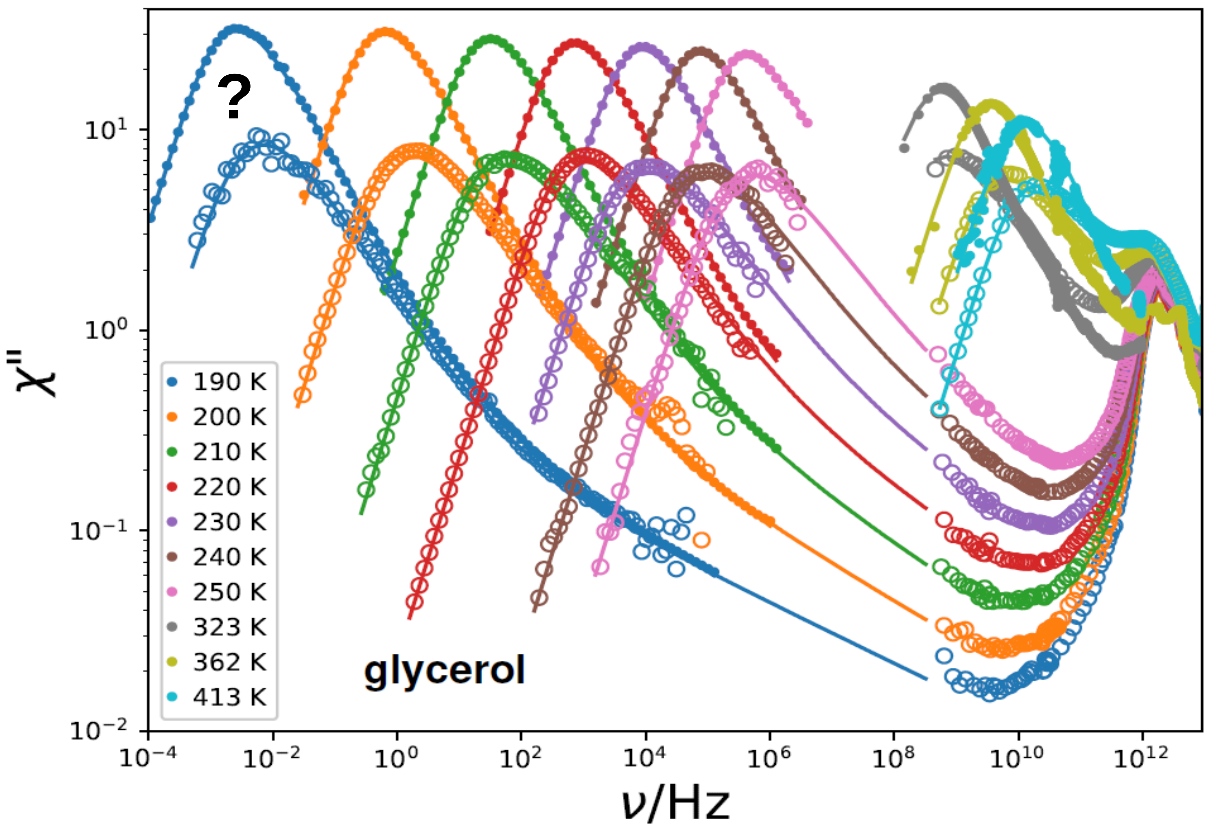
$$n(\omega,T) = \left[\exp(\hbar\omega / k_B T) - 1\right]^{-1}$$

Bose factor

$$\hbar\omega / k_B T << 1$$

$$\boxed{\chi''_{LS}(\omega) \approx \frac{\omega}{kT} I(\omega)}$$

BDS vs. DDLS



Gabriel, Pabst, Blochowicz,. J. Phys Chem B. 21, 8847 (2017)

Dielectric spectroscopy (l=1)

$$\varepsilon''(\omega) = \omega \Delta\varepsilon J_1(\omega)$$

$$\boxed{\chi''_{DS}(\omega) = \varepsilon''(\omega)}$$

NMR (l=2)

$$1/T_1(\omega) = C[J_2(\omega) + 4J_2(2\omega)]$$

$$\boxed{\chi''_{NMR}(\omega) \propto \frac{\omega}{T_1(\omega)}}$$

Light scattering (l=2)

$$I(\omega) = J_2(\omega)$$

$$\boxed{\chi''_{LS}(\omega) \approx \frac{\omega}{kT} I(\omega)}$$

connection with rheology

i) $$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+i\omega\tau_{rot}}$$ P. Debye

ii) $$\tau_{rot} = \frac{4\pi R_H^3}{k_B T}\eta$$ Debye-Stokes relation

iii) $$i\omega\eta = G$$

$$\boxed{\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+\frac{4\pi R_H^3}{k_B T}G^*}}$$

DiMarzio – Bishop model

generalization proposed in J. Chem. Phys. 137, 064508 (2012)

$$\boxed{\varepsilon^*(\omega) = A + \frac{B}{1+\lambda G^*(\omega)}}$$

(a) $\varepsilon'(\omega \to 0) = \varepsilon_\infty + \Delta\varepsilon = A + B$

(b) $\varepsilon'(\omega \to \infty) = \varepsilon_\infty = A + \frac{B}{1+\lambda B G_\infty}$

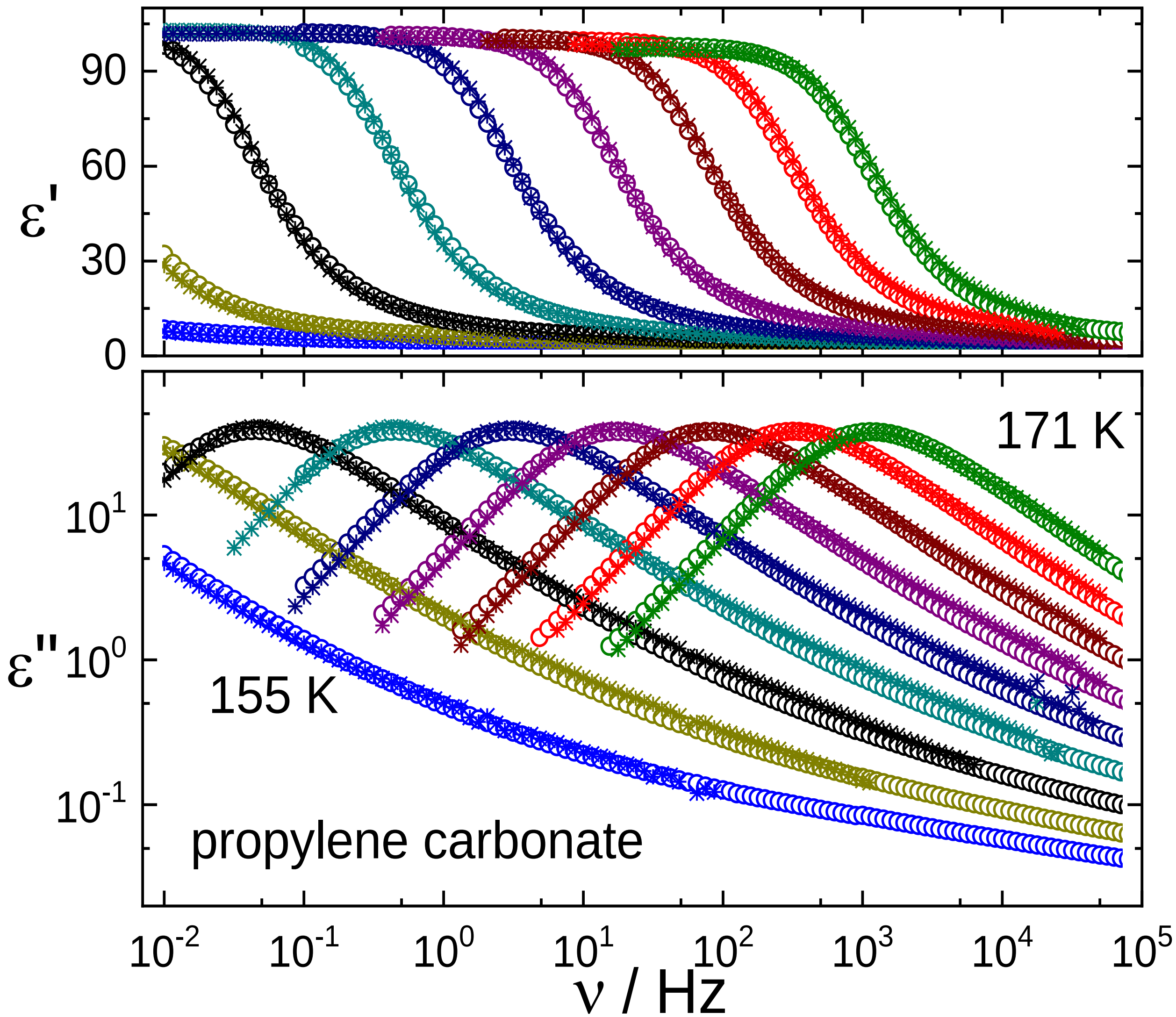
$$A = \varepsilon_\infty + \frac{1}{2}\left(\Delta\varepsilon - \sqrt{\Delta\varepsilon^2 + \frac{4\Delta\varepsilon}{\lambda G_\infty}}\right)$$

$$B = \frac{1}{2}\left(\Delta\varepsilon + \sqrt{\Delta\varepsilon^2 + \frac{4\Delta\varepsilon}{\lambda G_\infty}}\right)$$

$$\boxed{\begin{aligned} G' &= \frac{1}{\lambda}\left\{\frac{\varepsilon' - A}{[\varepsilon' - A]^2 + (\varepsilon'')^2} - \frac{1}{B}\right\} \\ G''(\omega) &= \frac{1}{\lambda}\frac{\varepsilon''}{[\varepsilon' - A]^2 + (\varepsilon'')^2} \end{aligned}}$$

one parameter (λ) needed for each material!

Tests of mechanical-dielectric transformation

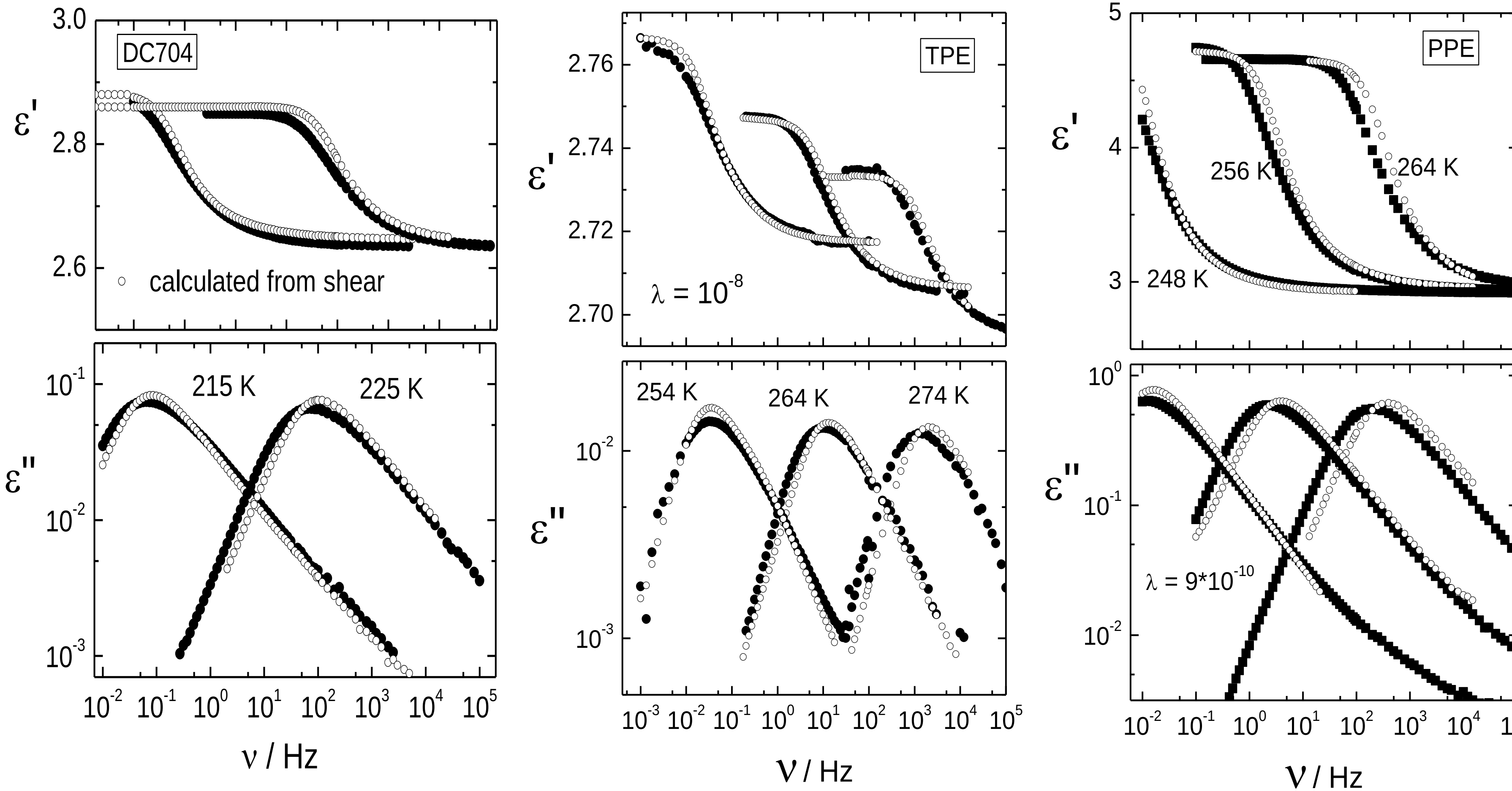


open symbols: dielectric data

stars: mechanical data converted to permittivity

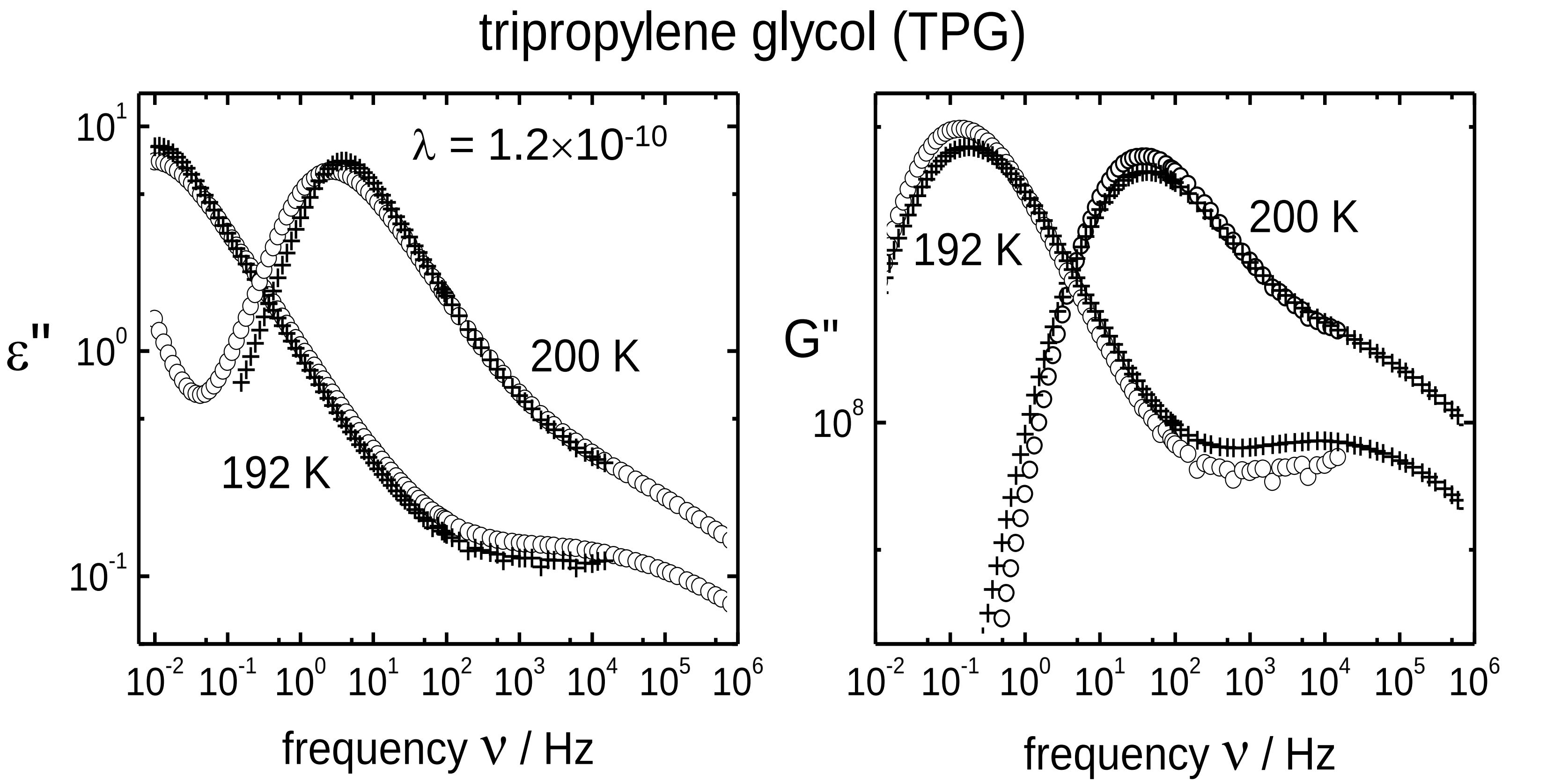
C. Gainaru et al., J. Chem. Phys. 137, 064508 (2012)

Tests of mechanical-dielectric transformation



data from B. Jakobsen et al., J. Chem. Phys. **129**, 184502 (2008); B. Jakobsen et al., J. Chem. Phys. **123**, 234511 (2005); C. Maggi et al., J. Phys. Chem. B **112**, 16320 (2008). K. Niss et al., J. Chem. Phys. 123, 234510 (2005).

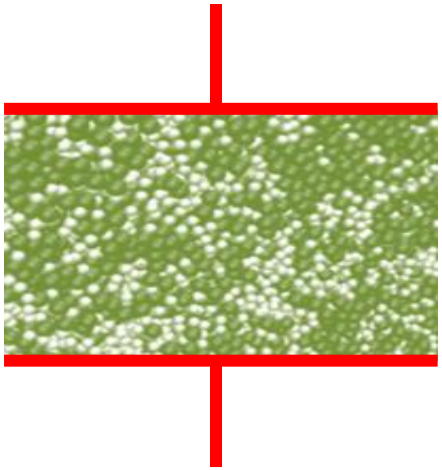
Tests of mechanical-dielectric transformation



data from B. Jakobsen et al., J. Chem. Phys. **123**, 234511 (2005)

a single parameter convert the spectra including structural *and* secondary relaxation processes!

specificity of dielectric response: cross-correlations



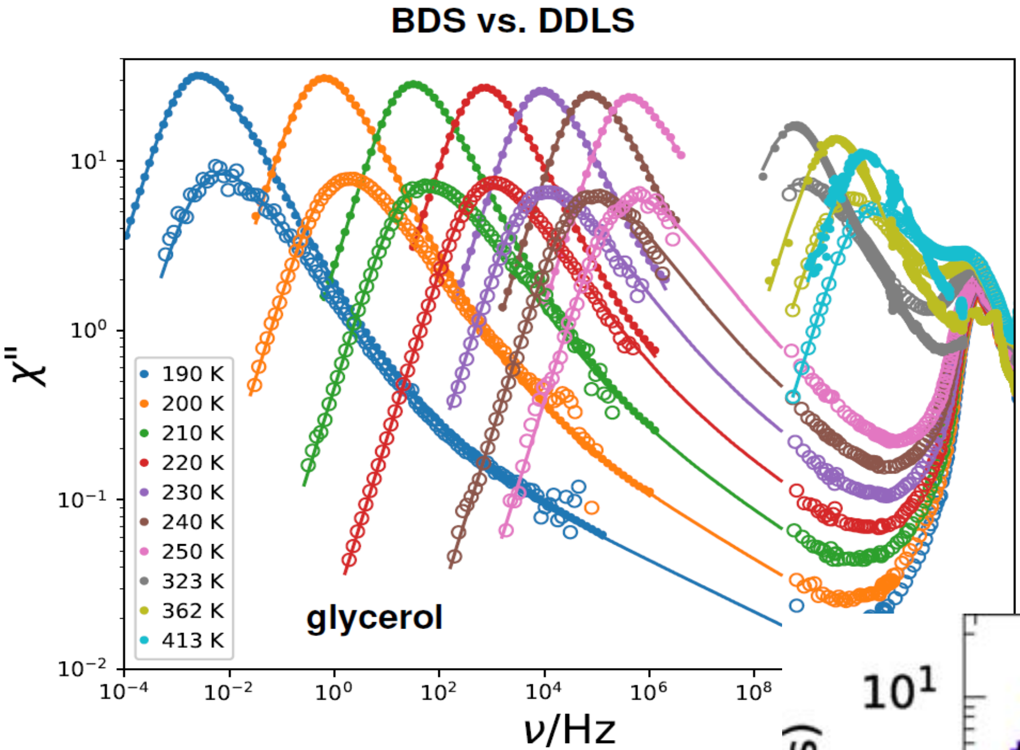
probed quantity: orientational (macroscopic) polarization

$$P_0 = \frac{\sum_{i=1}^{N} \vec{\mu}_i}{V} \cdot \vec{z} \qquad \phi_P(t) \equiv \frac{\left\langle \vec{P}_o(0) \cdot \vec{P}_o(t) \right\rangle}{\left\langle \vec{P}_o(0) \cdot \vec{P}_o(0) \right\rangle}$$

self-correlations cross-correlations

$$\phi(t) = \frac{\left\langle \sum_i^N \vec{\mu}_i(0) \cdot \sum_j^N \vec{\mu}_j(t) \right\rangle}{\left\langle \sum_i^N \vec{\mu}_i(0) \cdot \sum_j^N \vec{\mu}_j(0) \right\rangle} = \frac{\sum_i^N \left\langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(t) \right\rangle + \sum_{i \neq j}^N \left\langle \vec{\mu}_i(0) \cdot \vec{\mu}_j(t) \right\rangle}{N\mu^2 + \sum_{i \neq j}^N \left\langle \vec{\mu}_i(0) \cdot \vec{\mu}_j(0) \right\rangle}$$

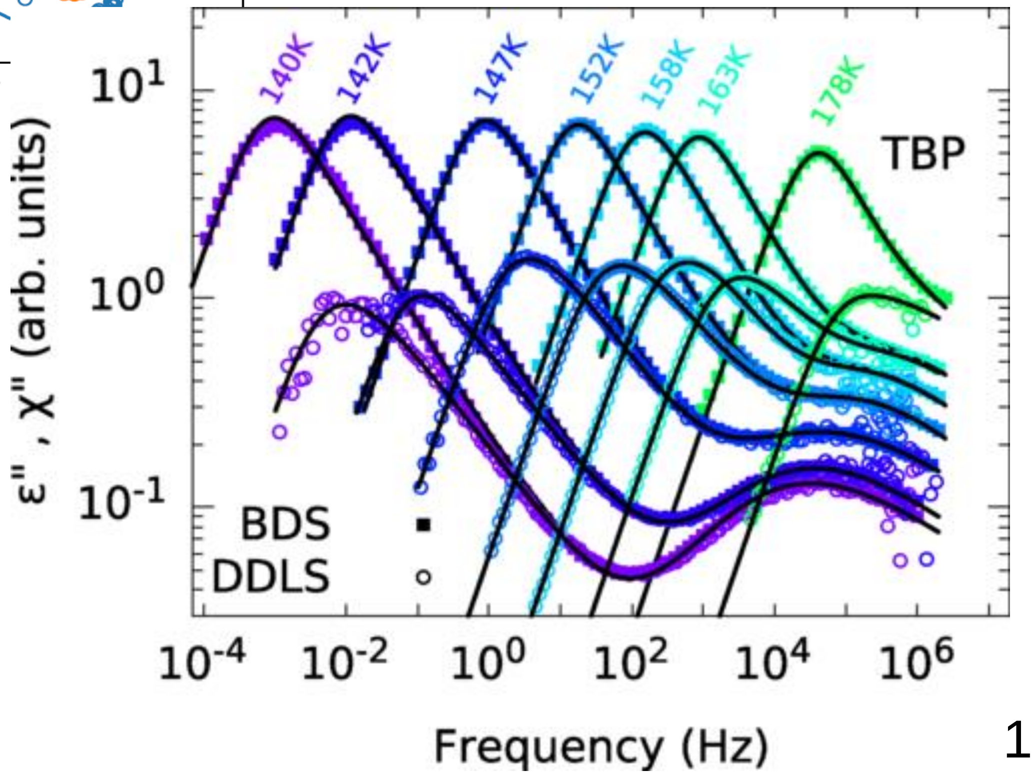
can one disentangle the two contributions?



self- and cross-correlation dynamics identified based on DS and LS comparison

Pabst, Helbling, Gabriel, Weigl, Blochowicz
Phys. Rev. E 102, 010606 (2020)

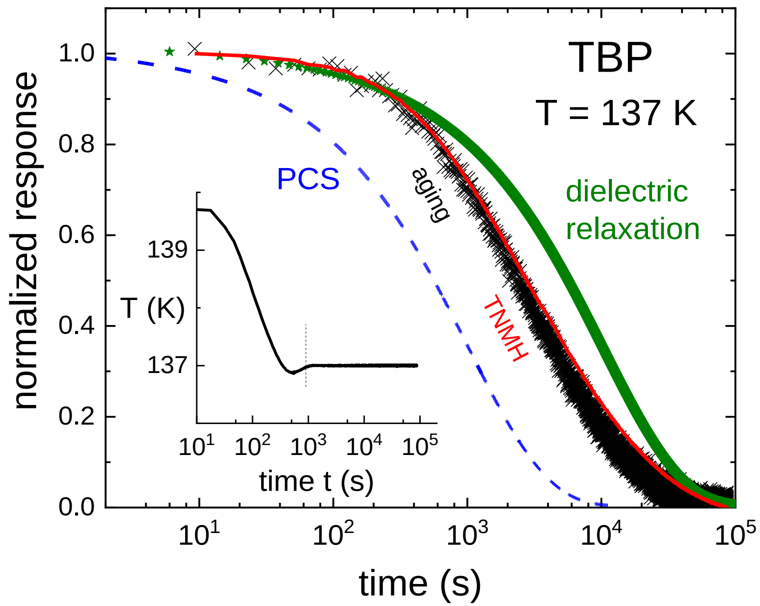
Gabriel J, Pabst F, Blochowicz T,. J. Phys Chem B. 21 8847 (2017)

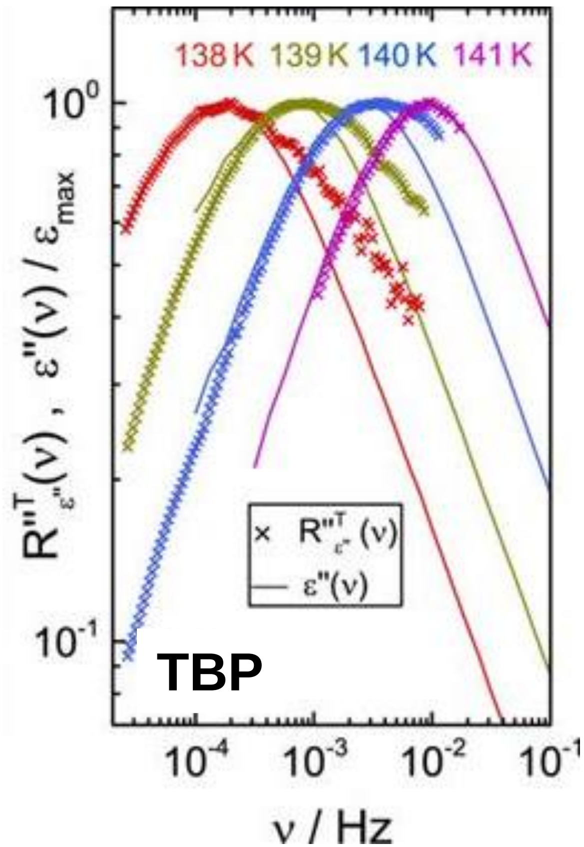


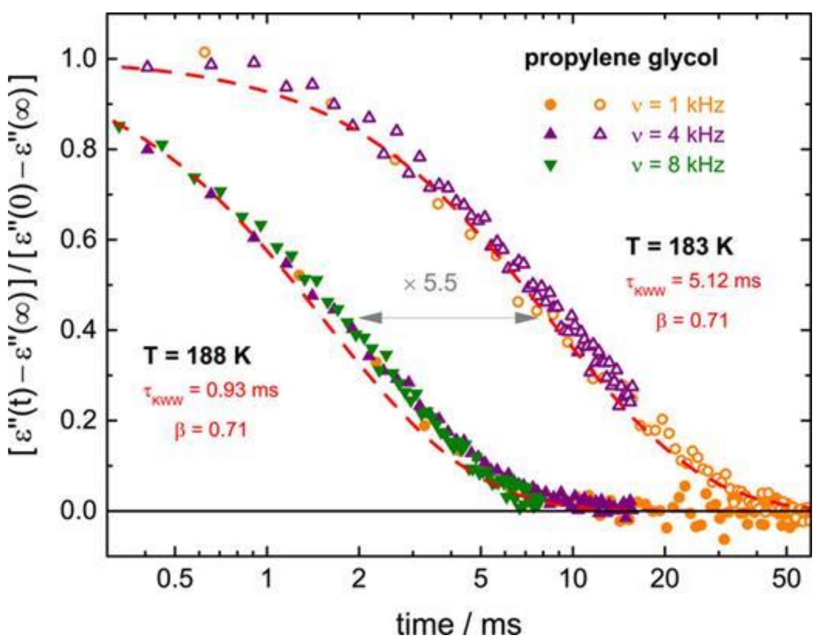
which one better reflects "structural relaxation"?

Moch, Münzner, Böhmer, Gainaru, Phys. Rev. Lett. 128, 228001 (2022)

Gabriel, Richert, J. Chem. Phys. 159, 164502.(2023)





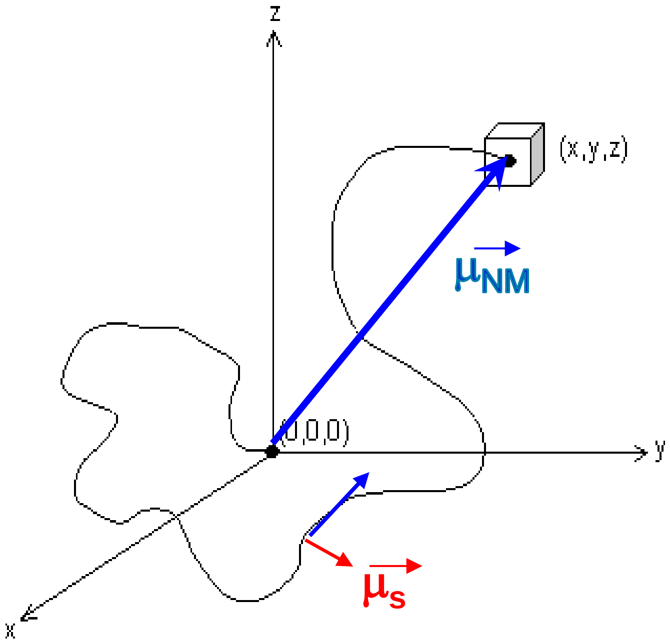


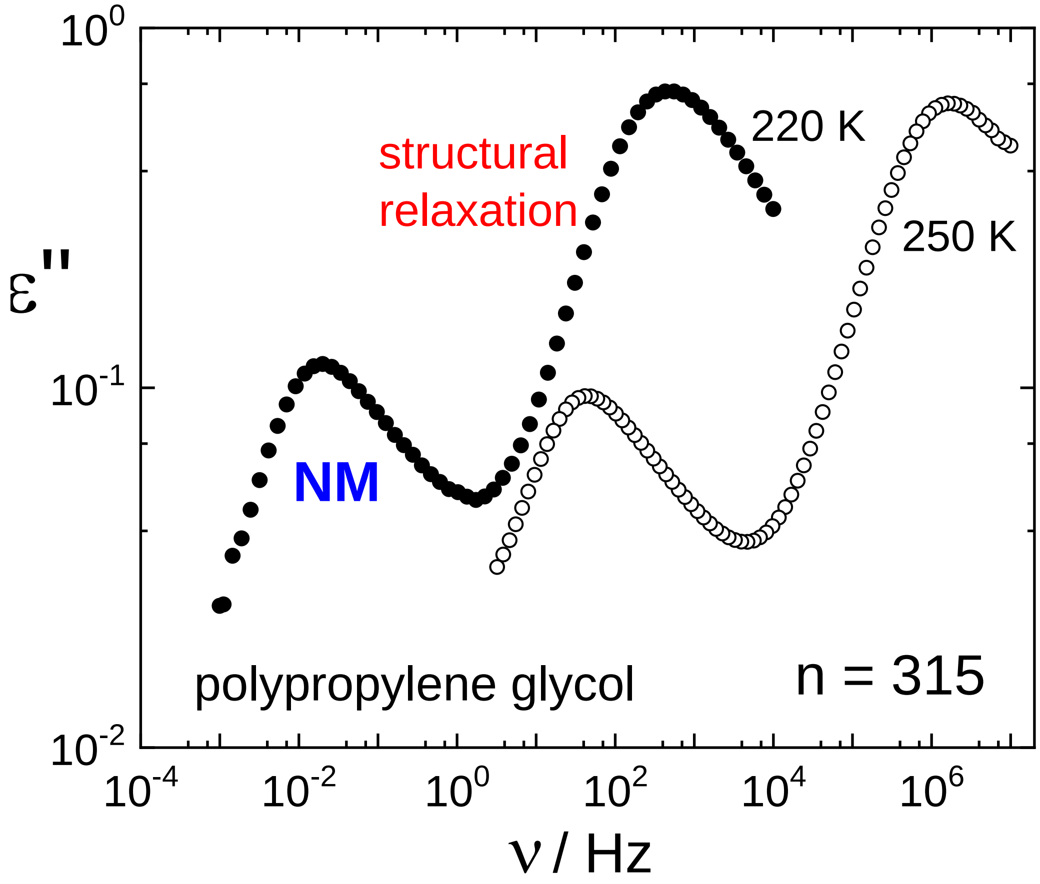
structural rearrangements (probed via T and E-field perturbations) are controlled by cross-correlations (dielectric)

R. Richert, J. Chem. Phys. 157, 224501 (2022)

other advantages of accessing collective dipole dynamics

- probing chain dynamics in type A polymers

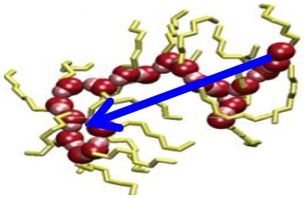


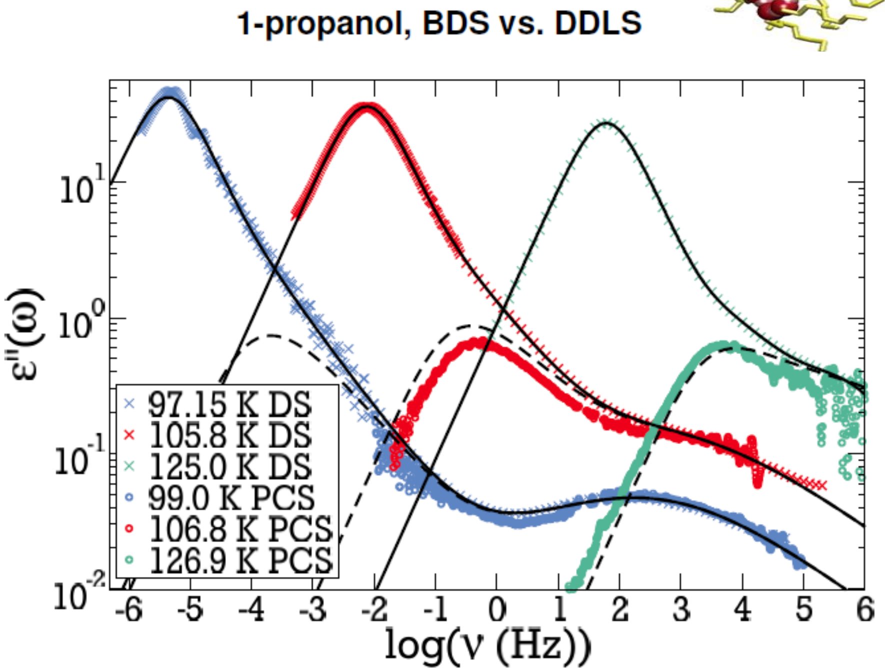


Gainaru, Böhmer, Macromolécules 42, 7616 (2009)

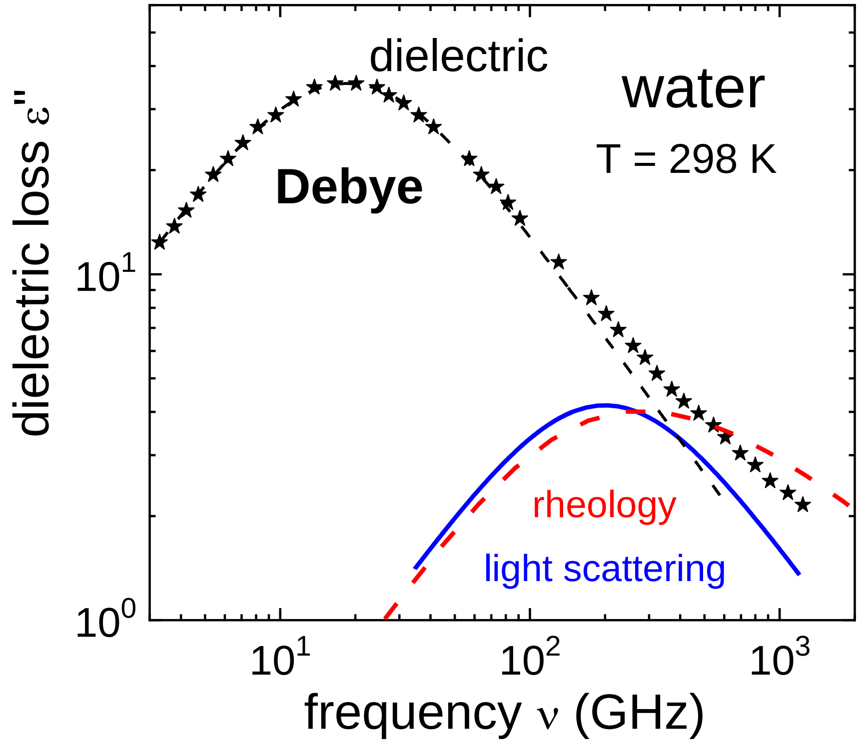
other advantages of accessing collective dipole dynamics

- probing the Debye process in mono-alcohols and water





Gabriel, Pabst, Blochowicz . J. Phys. Chem B. 21 8847 (2017)



Hansen, Kisliuk, Sokolov, Gainaru, Phys. Rev. Lett. 116, 237601 (2016)

Conclusions

Connection between reorientation methods

Dielectric spectroscopy (l=1) $$\chi''_{DS}(\omega) = \varepsilon''(\omega)$$

NMR (l=2) $$\chi''_{NMR}(\omega) \propto \frac{\omega}{T_1(\omega)}$$

Light scattering (l=2) $$\chi''_{LS}(\omega) \approx \frac{\omega}{kT} I(\omega)$$

Connection with rheology

Generalized DiMarzio-Bishop model

Dielectrically-probed collective dynamics provide access to

- structural rearrangements in “simple” liquids
- Debye process in associating liquids
- chain dynamics in type A polymers

Thank you!