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Dynamics slower than structural relaxation in viscous liquids

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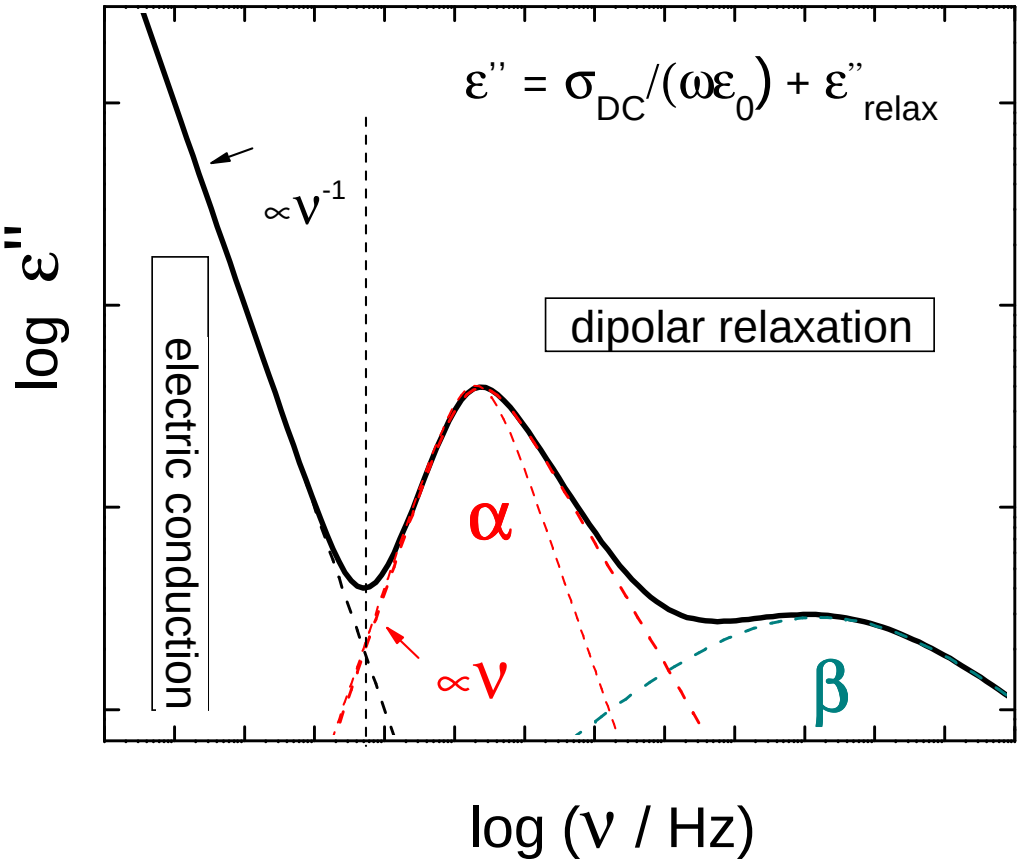
1. Introduction
   Dielectric response of supercooled molecular liquids;
   Reorientation slower than α-process in type A polymers and monoalcohols;

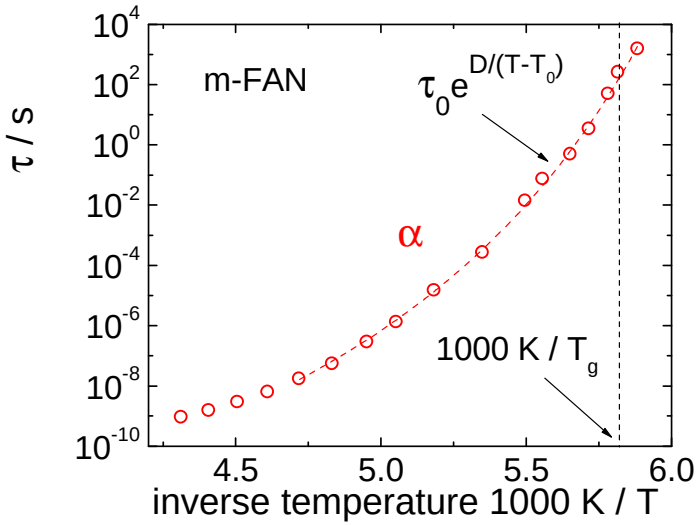
2. Monohydroxy alcohol 2-ethyl-1-hexanol; new findings

3. Debye process vs. normal modes (BuBr and PPG)

4. Summary

Dielectric response of a supercooled molecular liquid



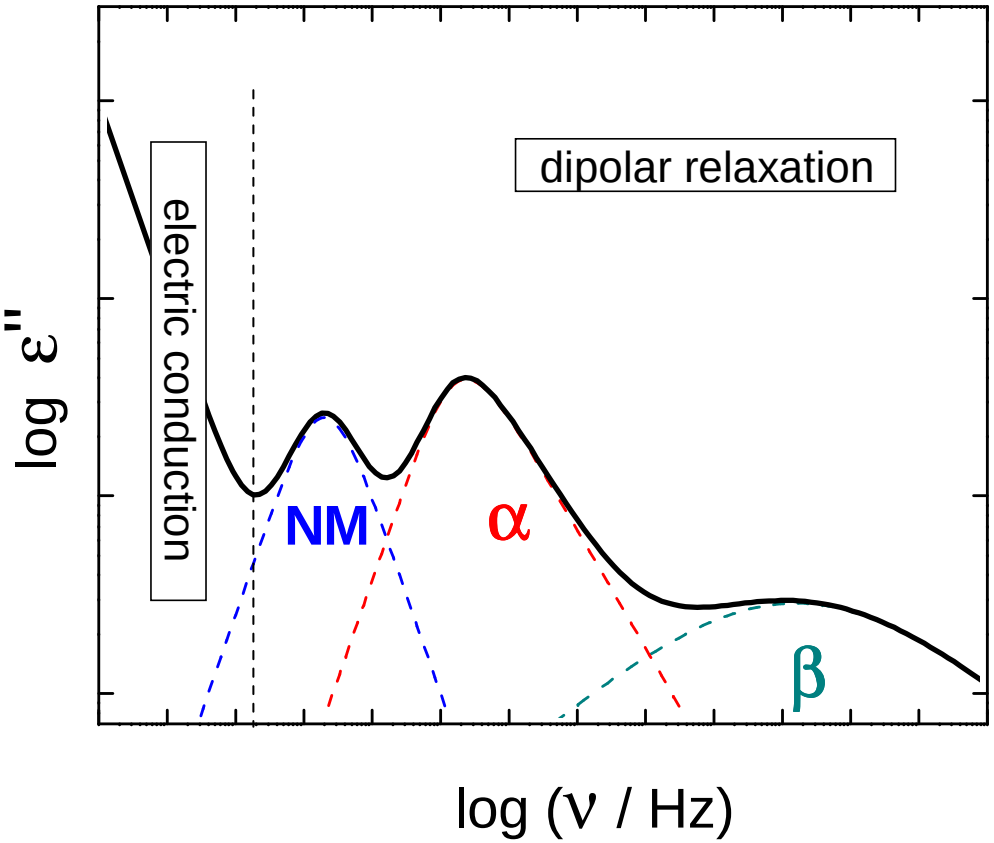


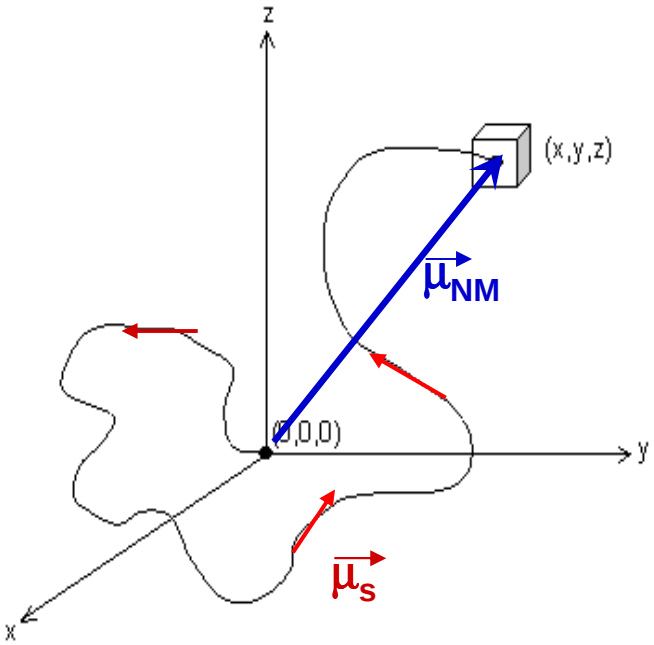
Slowest orientational process (α):

- dispersive, non-Arrhenius

- strong manifestation in mechanical and thermodynamical quantities

Reorientation slower than α-process: type A polymers





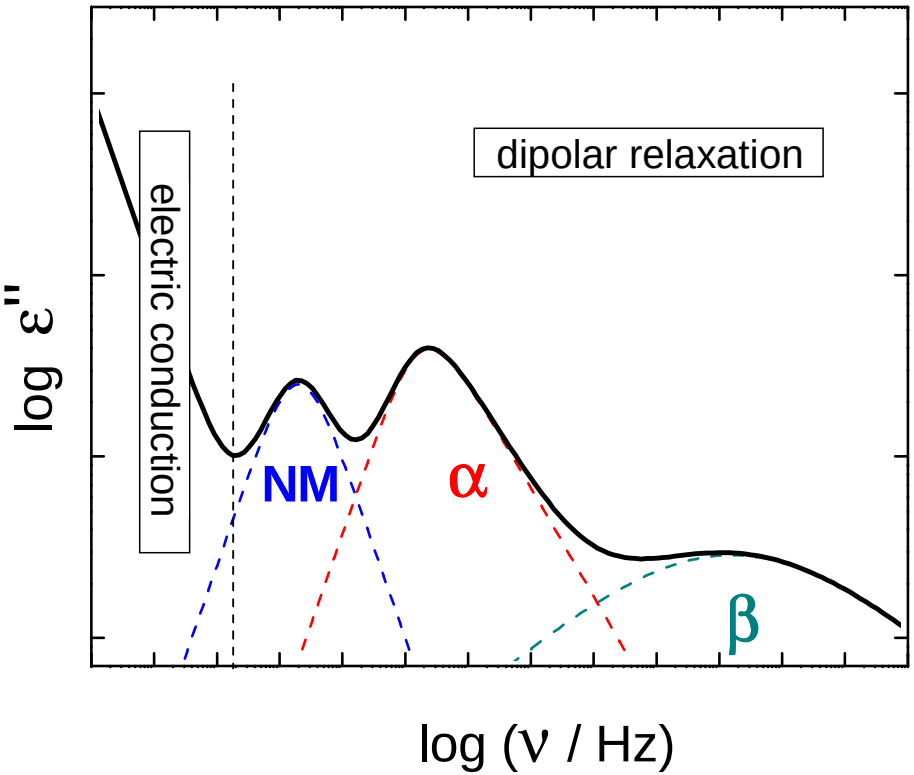
Slowest orientational process (NM):

- close to monodispersive, non-Arrhenius

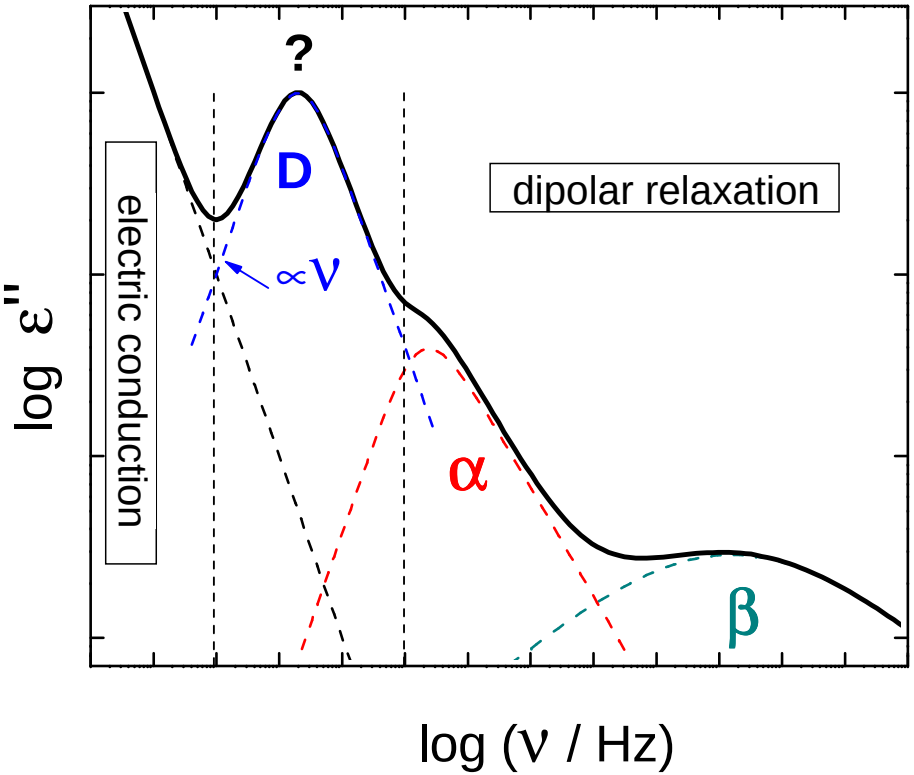
- no manifestation in thermodynamical quantities

- controls the mechanical behavior (e.g. the flow)

type A polymers



monohydroxy alcohols



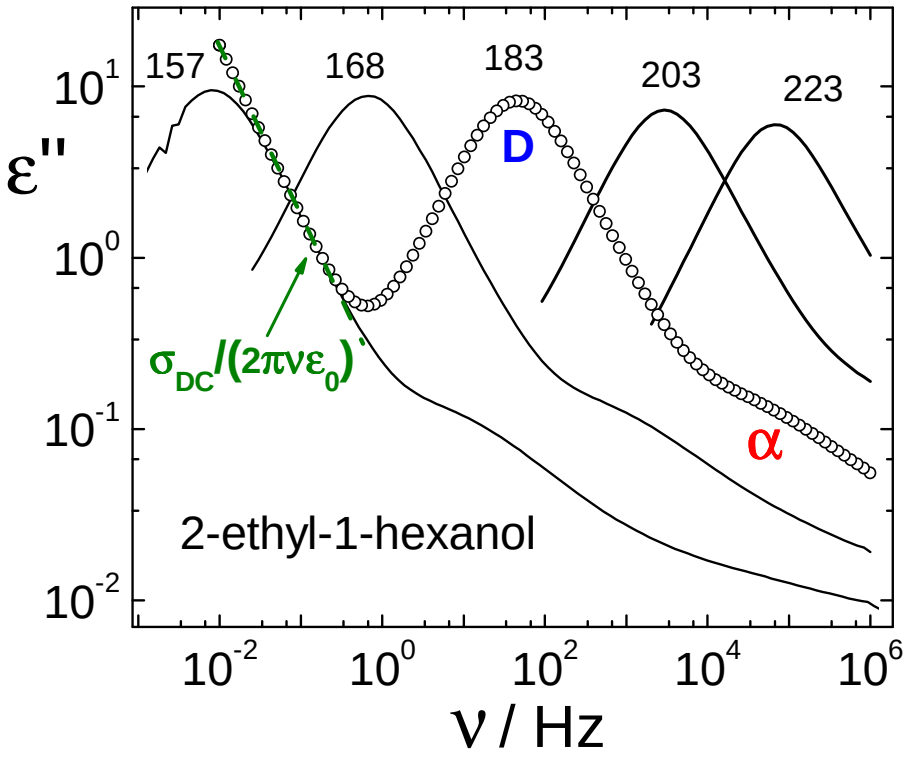
Debye process:

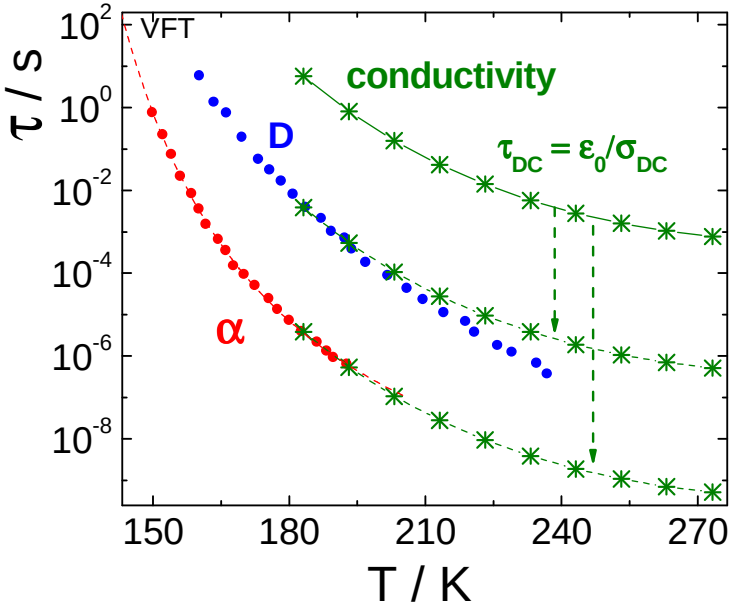
- monodispersive, non-Arrhenius

- no manifestation in mechanical and thermodynamical quantities

Monohydroxy alcohol 2-ethyl-1-hexanol; new findings

Debye process - Charge fluctuations?

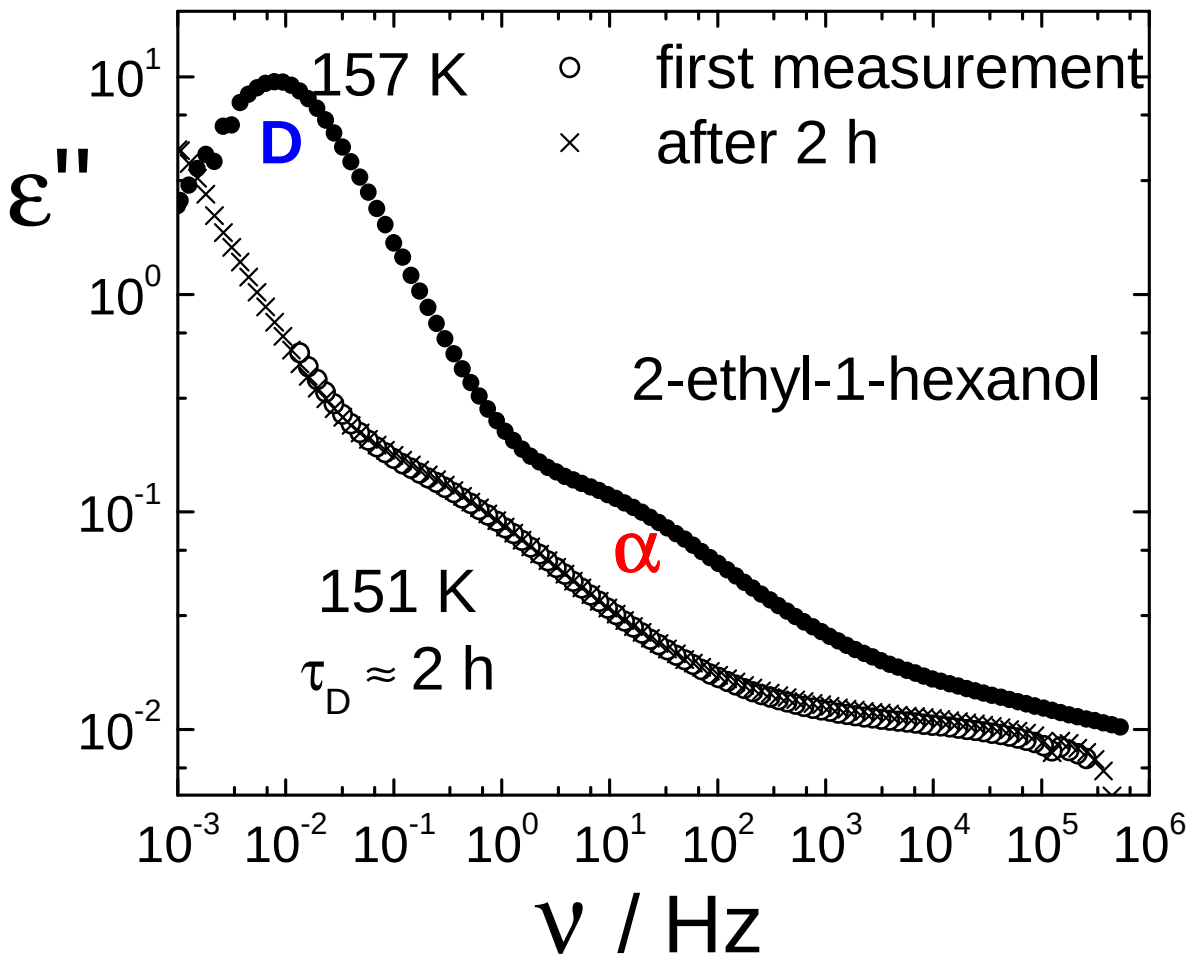




Conductivity scales with α-process

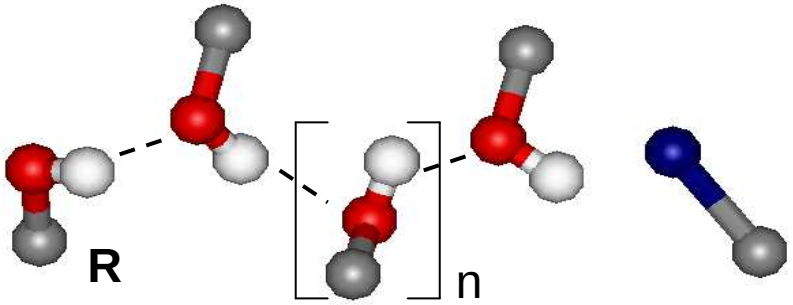
$$\tau_\alpha \propto \eta \propto 1/D \propto 1/\sigma_{DC}$$

Debye process not governed by the diffusion of free charges



No aging effects on time scale of τ_D

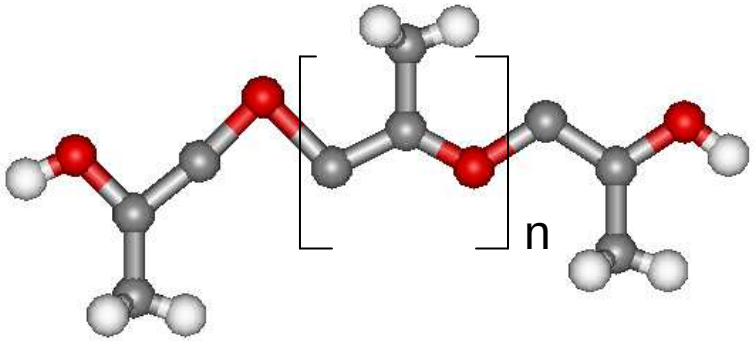
$(BuBr)_{1-x}(BuOH)_x$, $0 < x < 1$



Hydrogen bonds

versus

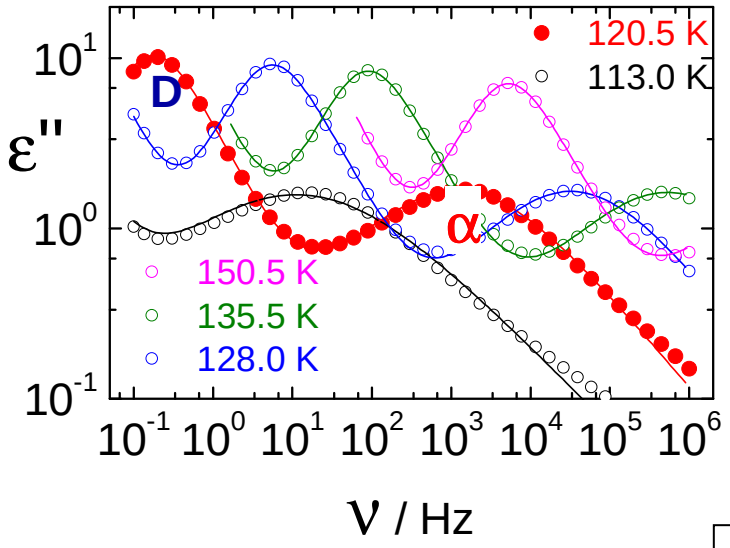
Covalent bonds

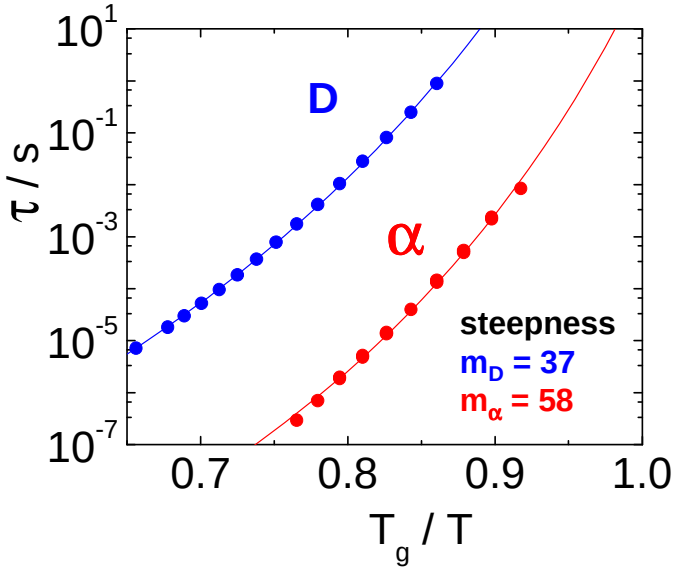


Polypropylene glycol, 76 g/mol < M_w < 18 200 g/mol

Dielectric spectra of $(BuBr)_{1-x}(BuOH)_x$

X = 0.41



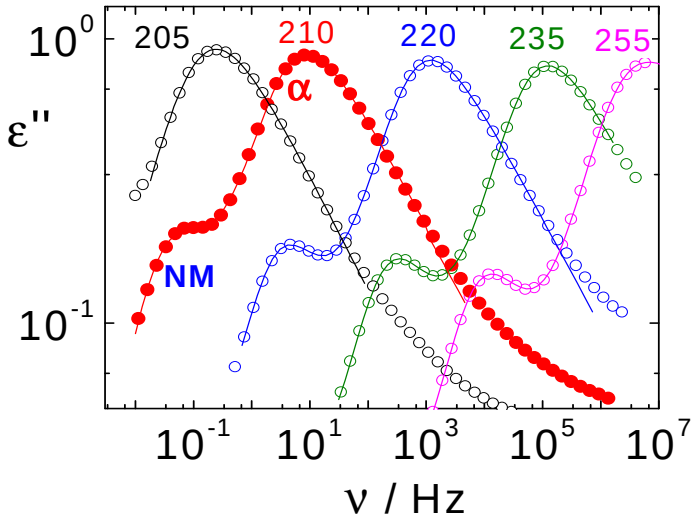


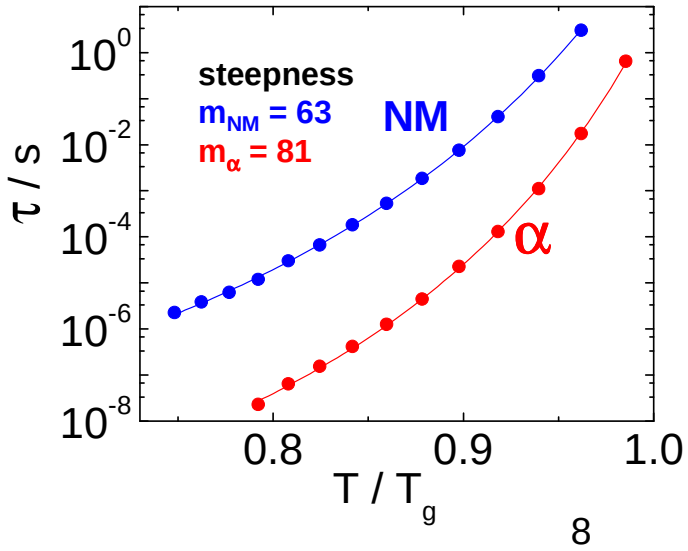
all processes can be described by:

$\tau = \tau_0 \exp[D/(T-T_0)]$

Dielectric spectra of polypropylene glycol

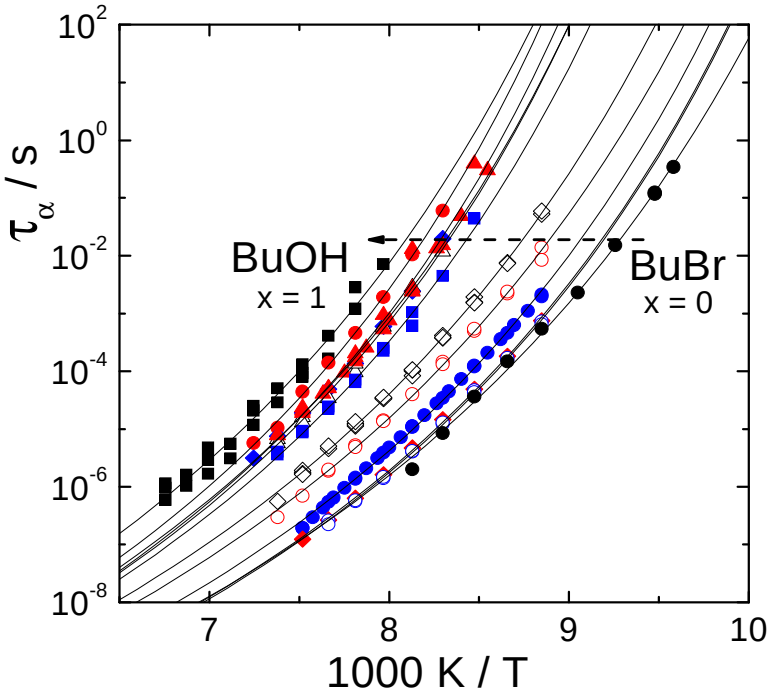
M_w = 3080 g/mol

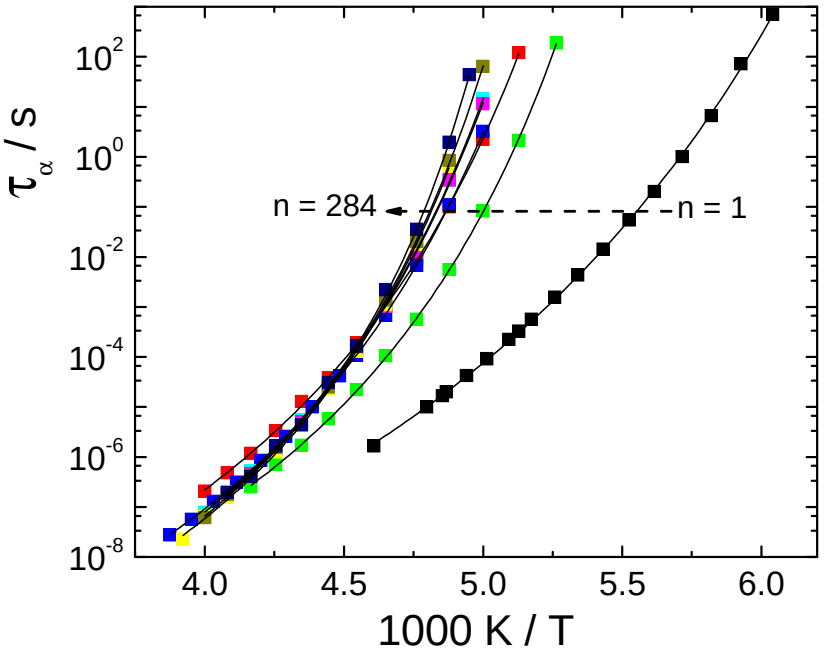


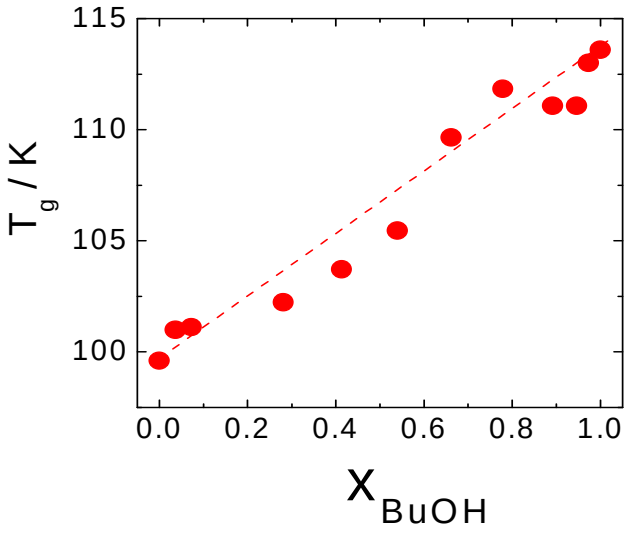


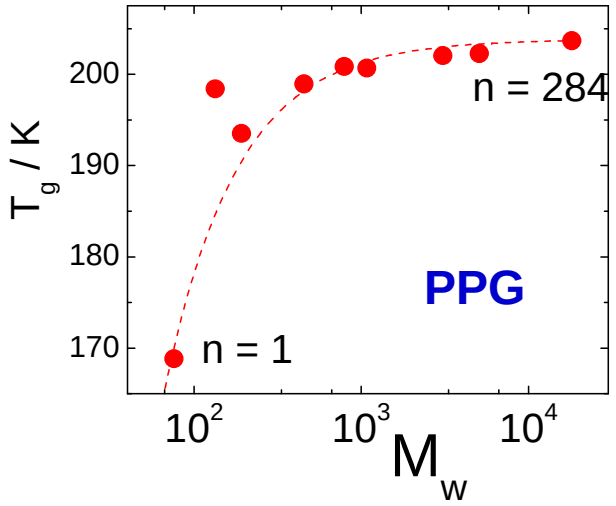
Structural relaxation (α-process)

$(BuBr)_{1-x}(BuOH)_x$

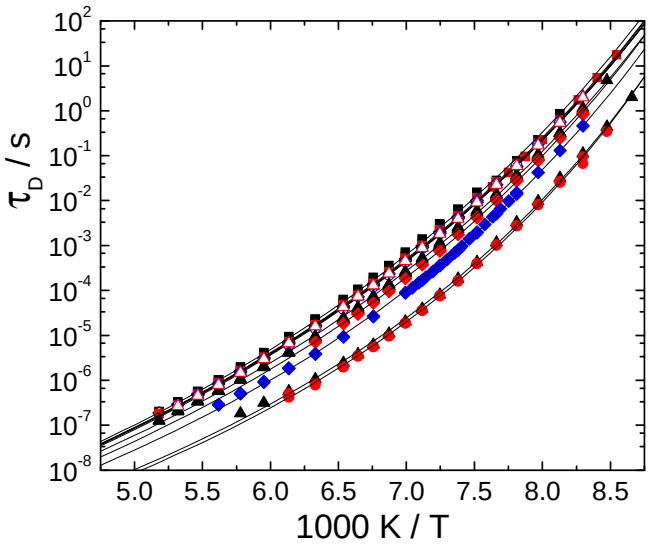


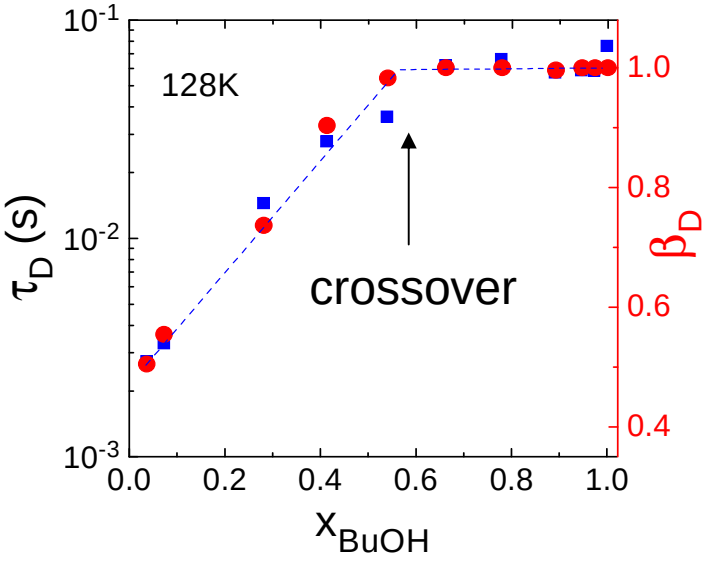




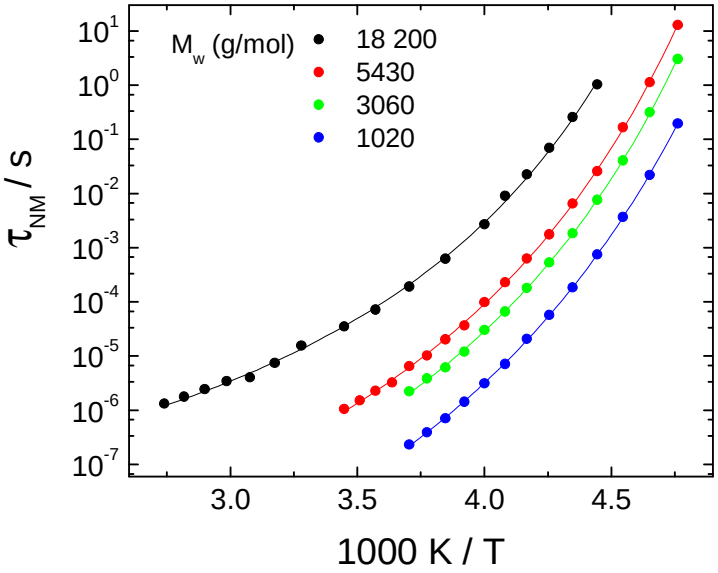


Debye process





Normal modes



$$\Delta\varepsilon_{NM} = \frac{n_{NM}\mu_{NM}^{\ 2}}{3\varepsilon_0 k_B T}$$

Curie-law

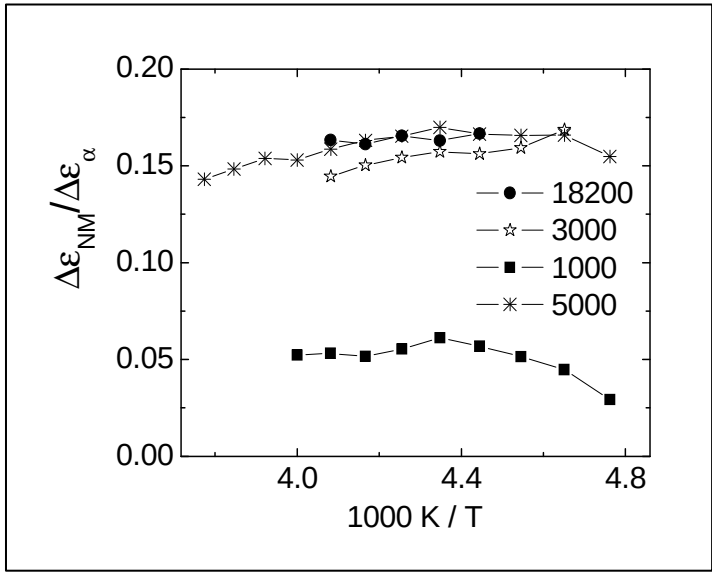
Gaussian chain:

$$\mu_{NM}^{\ 2} = q^2 l_{NM}^{\ 2} \propto N_S$$

$$N_S \cdot n_{NM} = cst$$

$$\Delta\varepsilon_{NM} / \Delta\varepsilon_\alpha$$

Independent of M_w



Summary

Debye process

- not scaling with conductivity

- not aging during its time scale

Normal modes vs. Debye process

Difference of their mechanical signature

High similariries between their dielectric response

Crossover „chain-length“ relevant for the slow dynamics (statics ?)

Polymer theory: starting point for description of the Debye process

Crossover oligmer / polymer dynamics