Broadband Dielectric Spectroscopy and its Relationship to Other Spectroscopic Techniques

A. Schönhals

BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin

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Content

- Introduction, Dielectric Spectroscopy
- Basics of Relaxation Spectroscopy
- Examples of Relaxation Spectroscopy

  Thermal spectroscopy

  Neutron spectroscopy (Scattering)

- Application of Relaxation Spectroscopy

Dielectric Relaxation Spectroscopy

Maxwell´s Equations:

$$\mathrm{rot}\,\vec{E} = -\frac{\partial}{\partial t}\vec{B} \qquad \mathrm{div}\,\vec{B} = 0$$

Electric field — Magnetic induction

$$\mathrm{rot}\,\vec{H} = \vec{j} + \frac{\partial}{\partial t}\vec{D} \qquad \mathrm{div}\,\vec{D} = \rho$$

Density of charges

Magnetic field — Current density — Dielectric displacement

Material Equation:

Small electrical field strengths: $\vec{D} = \varepsilon^* \varepsilon_0 \vec{E} \rightarrow \vec{P} = \vec{D} - \vec{D}_0 = (\varepsilon^* - 1)\varepsilon_0 \vec{E}$ Polarization

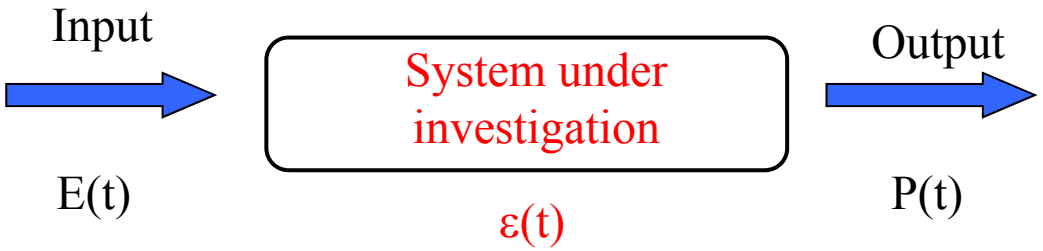
ε_0 – permittivity of vacuum

Complex Dielectric Function →

ε^* is time dependent if time dependent processes taking place within the sample

Dielectric Relaxation Spectroscopy

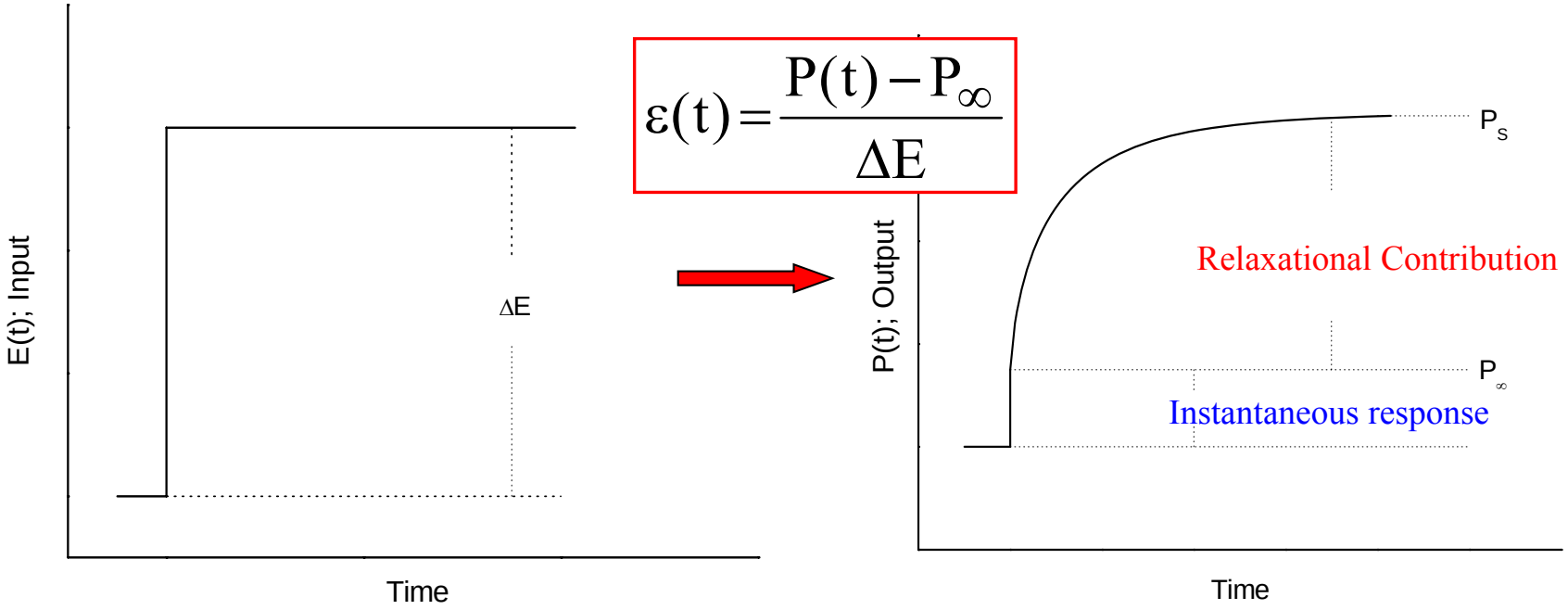
A Special Case of Linear Response Theory



Simplest Case : Step-like Input

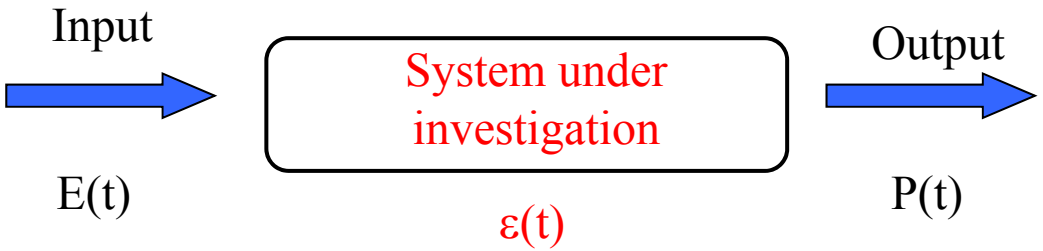
The polarization measured as response to a step-like disturbance

$$\varepsilon(t) = \frac{P(t) - P_\infty}{\Delta E}$$

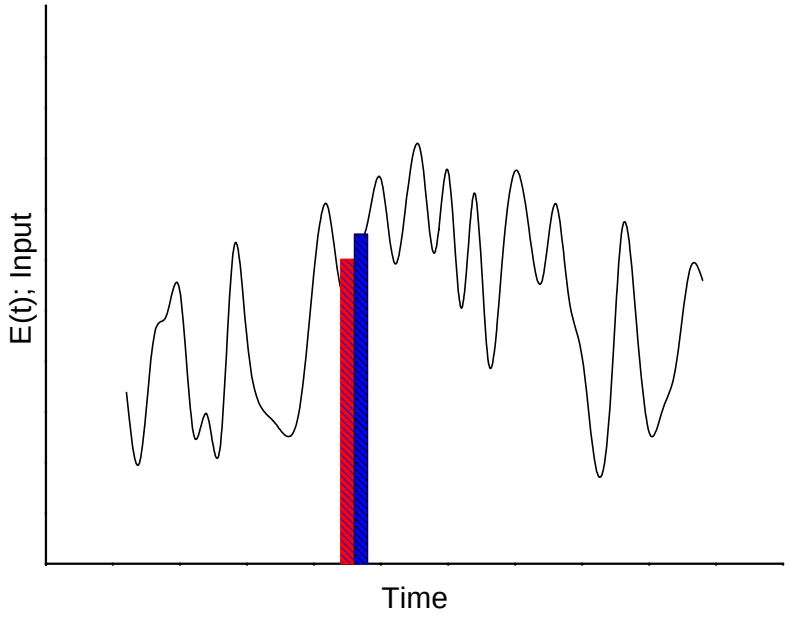


Dielectric Relaxation Spectroscopy

A Special Case of Linear Response Theory



Arbitrary input → Approximation of the Input by step-like changes → $\frac{\Delta E}{\Delta t} * \Delta t$



$$E(t) \approx E(0) + \sum \frac{\Delta E}{\Delta t} * \Delta t$$

$$\frac{dx}{dt} * dt$$

$$P(t) = P_\infty + \varepsilon_0 \int_{-\infty}^{t} \varepsilon(t - t') \frac{d\,E(t')}{dt'} dt'$$

→ Linearity

→ Causality

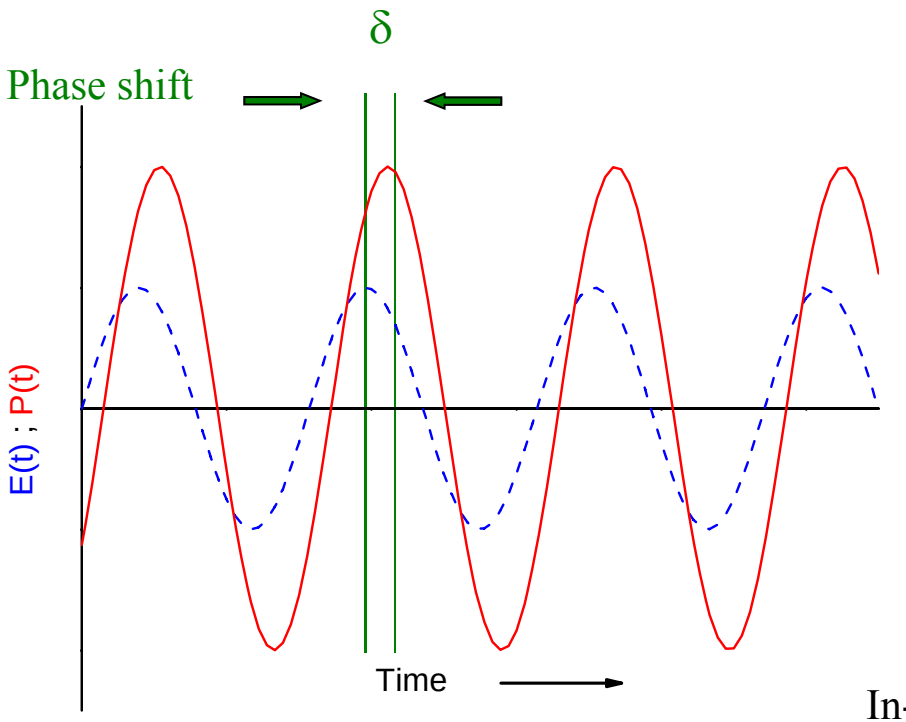
Basics of Linear Response Theory

Dielectric Relaxation Spectroscopy

A Special Case of Linear Response Theory

Special input → Periodical input → $E(t) = E_0 \exp(-i\omega t) = E_0 \sin(\omega t)$

ω - angular frequency



$P(t) = P_0 \sin(\omega t + \delta)$

Complex Numbers

$P(\omega) = \varepsilon_0[(\varepsilon' - i\varepsilon'') - 1]E(\omega)$

In-Phase with E(t)

90°-shifted to E(t)

Complex Dielectric Function $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$

Complex Compliance

Dielectric Relaxation Spectroscopy

A Special Case of Linear Response Theory

Complex Compliance

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

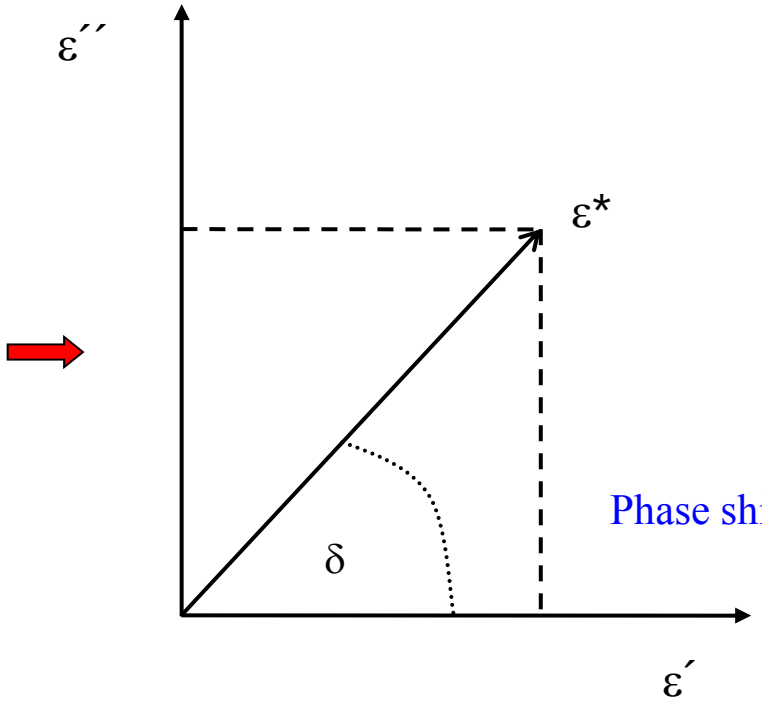
Real Part

Related to the energy stored reversibly during one cycle

Imaginary or Loss Part

Related to the energy dissipated during one cycle

Complex Plane



$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Dielectric Relaxation Spectroscopy

A Special Case of Linear Response Theory

Real Part → Related to the energy stored reversibly during one cycle

Loss Part → Related to the energy dissipated during one cycle

→ Law of energy conservation

↓

Relationship between both quantities

Kramers – Kronig Relationships

$$\varepsilon'(\omega) - \varepsilon_\infty = \frac{1}{\pi} \oint \frac{\varepsilon''(\xi)}{\xi - \omega} d\xi$$

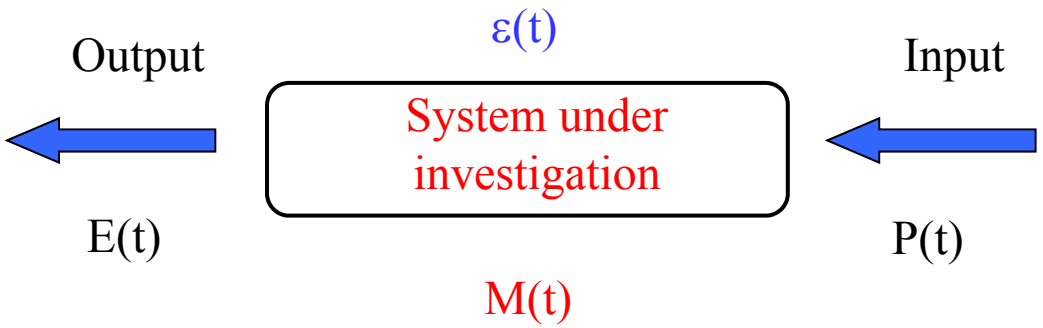
$$\varepsilon''(\omega) = \frac{1}{\pi} \oint \frac{\varepsilon'(\xi) - \varepsilon_\infty}{\xi - \omega} d\xi$$

Dielectric Relaxation Spectroscopy

A Special Case of Linear Response Theory

$$P(t) = P_\infty + \varepsilon_0 \int_{-\infty}^{t} \varepsilon(t-t') \frac{dE(t')}{dt'} dt'$$

→ Linear Equation → Can be inverted



Electrical Modulus

↔ Relationship between ε(t) and M(t)

$$\int_{-\infty}^{-\infty} \varepsilon(t-t') M(t') dt' = \delta(t)$$

δ(t) – Dirac function

Fourier Transformation

$$M^*(\omega)\varepsilon^*(\omega) = 1$$

Dielectric Relaxation Spectroscopy

A Special Case of Linear Response Theory

Thermodynamic quantities are average values. Because of the thermal movement of the molecules these quantities fluctuate around their mean values

Correlation function of Polarization Fluctuations

$$\Phi(\tau) = \frac{<\Delta P(\tau)\,\Delta P(0)>}{<\Delta P^2>} \longrightarrow \vec{P} = \frac{1}{V}\sum \vec{\mu}_i \longrightarrow \Phi(\tau) = \frac{\sum_i <\mu_i(0)\mu_i(\tau)> + 2\sum_i \sum_{i<j} <\mu_i(0)\mu_j(\tau)>}{<(\sum_i \mu_i)^2>}$$

Spectral Density

$$(\Delta P^2)_\omega = \frac{<\Delta P^2>}{2\pi} \int_{-\infty}^{\infty} \Phi(\tau)\exp(i\omega\tau)\,d\tau$$

Measure for the frequency distribution of the fluctuations

Fluctuation Dissipation Theorem

$$\Phi(\tau) = -\frac{1}{kT}\frac{\varepsilon(\tau)-1}{\Delta\varepsilon}$$

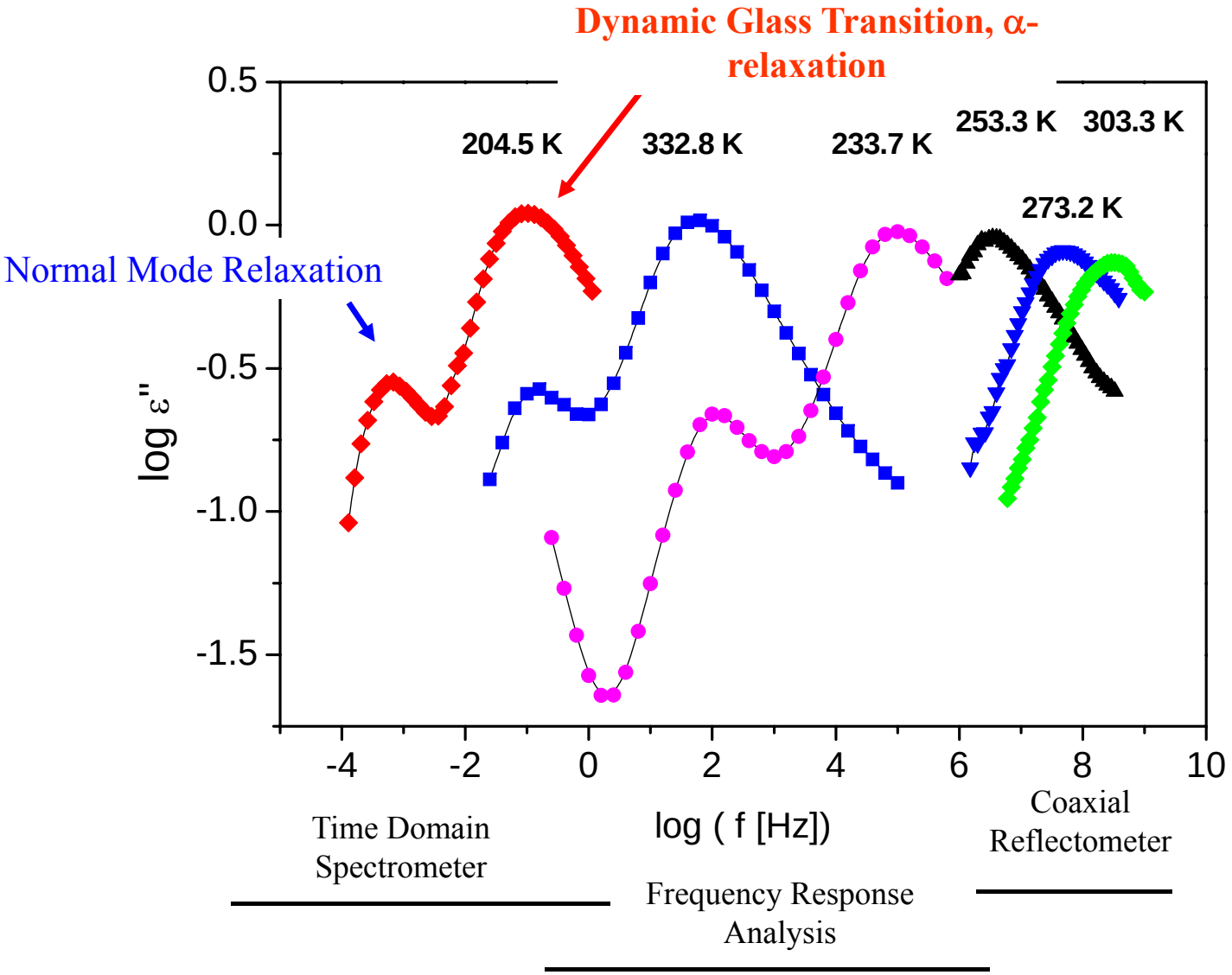
$$(\Delta P^2)_\omega = \frac{1}{kT}\frac{\varepsilon''(\omega)-1}{\pi\omega}$$

Links microscopic fluctuations and macroscopic reactions

For a small (linear) disturbance a system reacts only in the way as it fluctuates

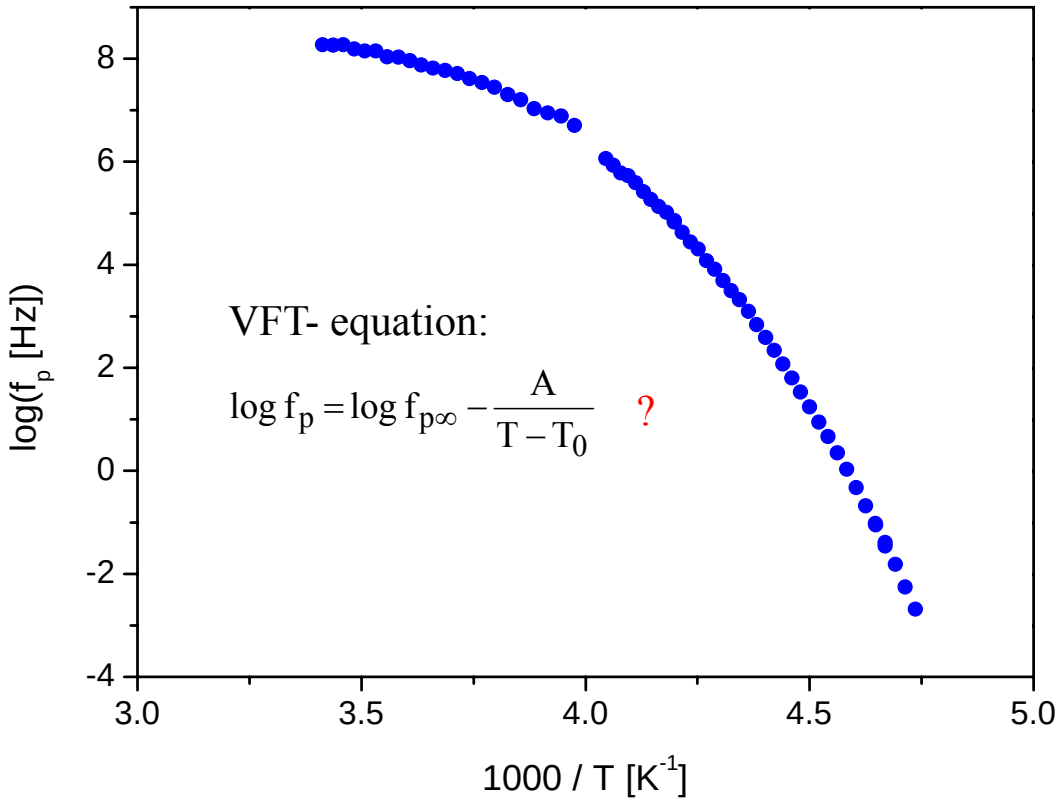
Dielectric Spectroscopy…..

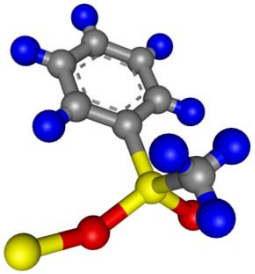
…PPG, M_w= 4000 g/mol



Dielectric Spectroscopy …..

…PMPS, M_w= 1000 g/mol

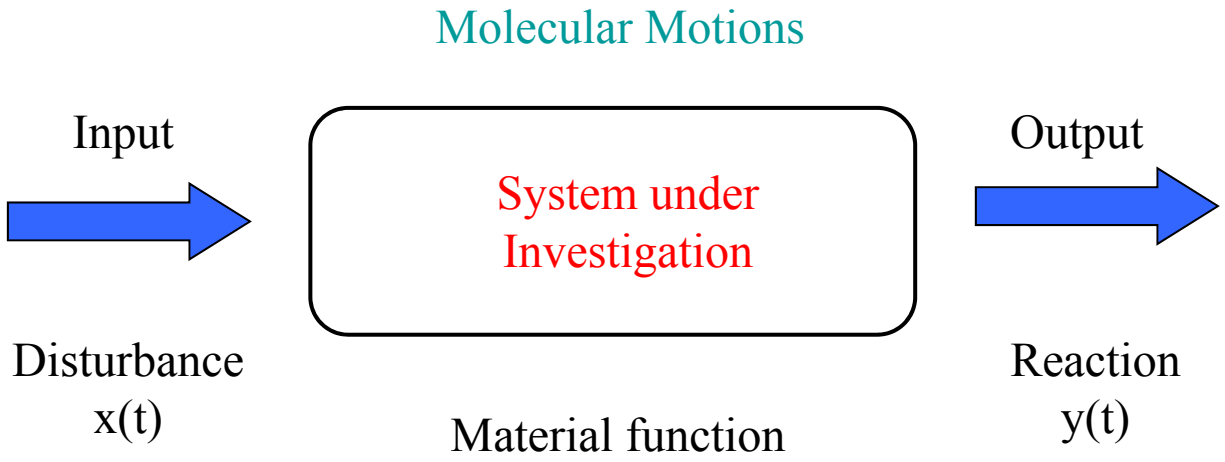




Mean Relaxation Rate f_p

Dielectric Strength Δε

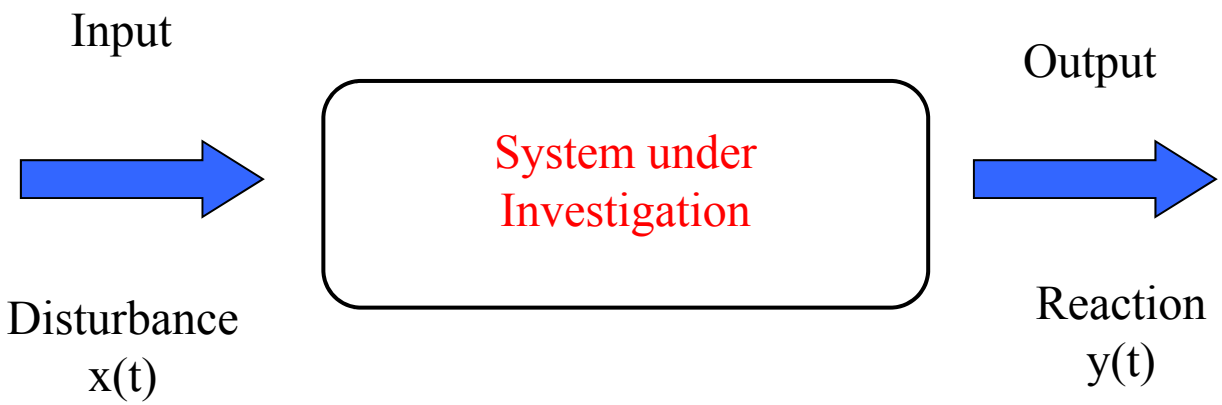
Linear Response Theory



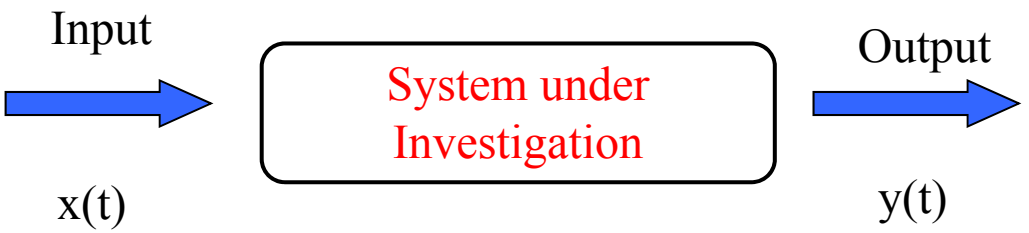
Electric field E	Polarization P
Shear tension σ	Shear angle γ
Magnetic field H	Magnetization M
Temperature T	Entropy S

Basics of Relaxation Spectroscopy

Molecular Motions



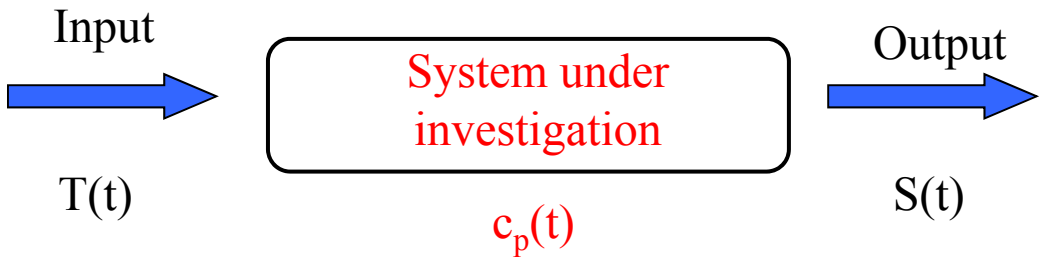
Disturbance	Reaction	Material function
Intensive - independent of V	**Extensive** ~ V	**Generalized Modulus G(t)**
		Relaxation
Tensile Strain	Strain	Elastic Modulus
Extensive ~ V	**Intensive** - independent of V	**Generalized Compliance J(t)**
		Retardation
Strain	Tensile Strain	Elastic Compliance



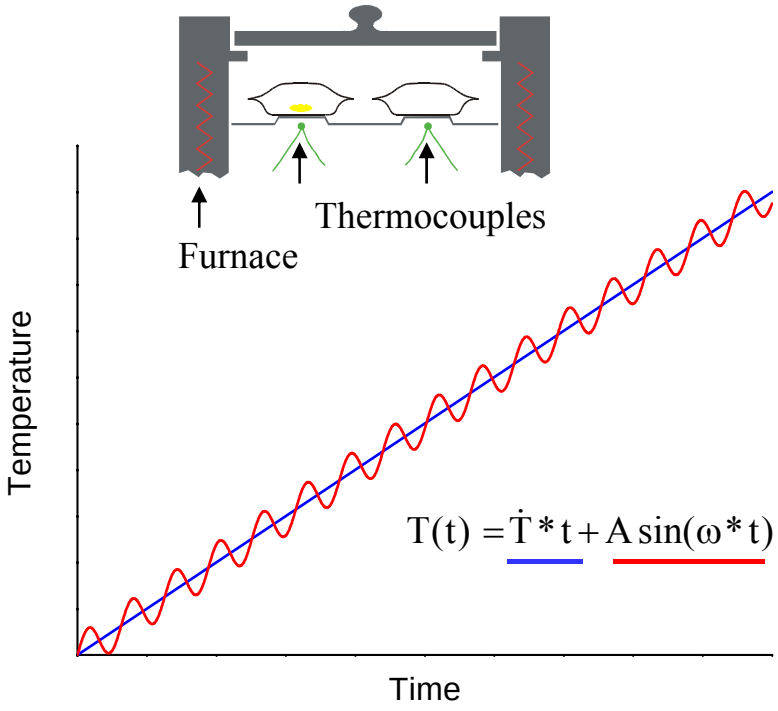
Type of Experiment	**Disturbance x(t)**	**Response y(t)**	**Compliance J(t) or J*(ω)**	**Modulus G(t) or G*(ω)**
Dielectric	Electric field E	Polarization P	Dielectric Susceptibility $\chi^*(\omega)=(\varepsilon^*(\omega)-1)$	Dielectric Modulus
Mechanical Shear	Shear tension σ	Shear angel γ	Shear compliance J(t)	Shear Modulus G(t)
Isotropic Compression	Pressure p	Volume V	Volume compliance B(t) V	Compression Modulus K(t)
Magnetic	Magnetic field H	Magnetization M	Magnetic susceptibility $\alpha^*(\omega)=(\mu^*(\omega)-1)$	-
Heat	Temperature T	Entropy S	Heat capacity $c_p(t)$	Temperature Modulus $G_T(t)$

Specific Heat Spectroscopy

A Special Case of Linear Response Theory



Temperature Modulated DSC



The modulated temperature results in a modulated heat flow

The heat flow is phase shifted if time dependent processes take place in the sample

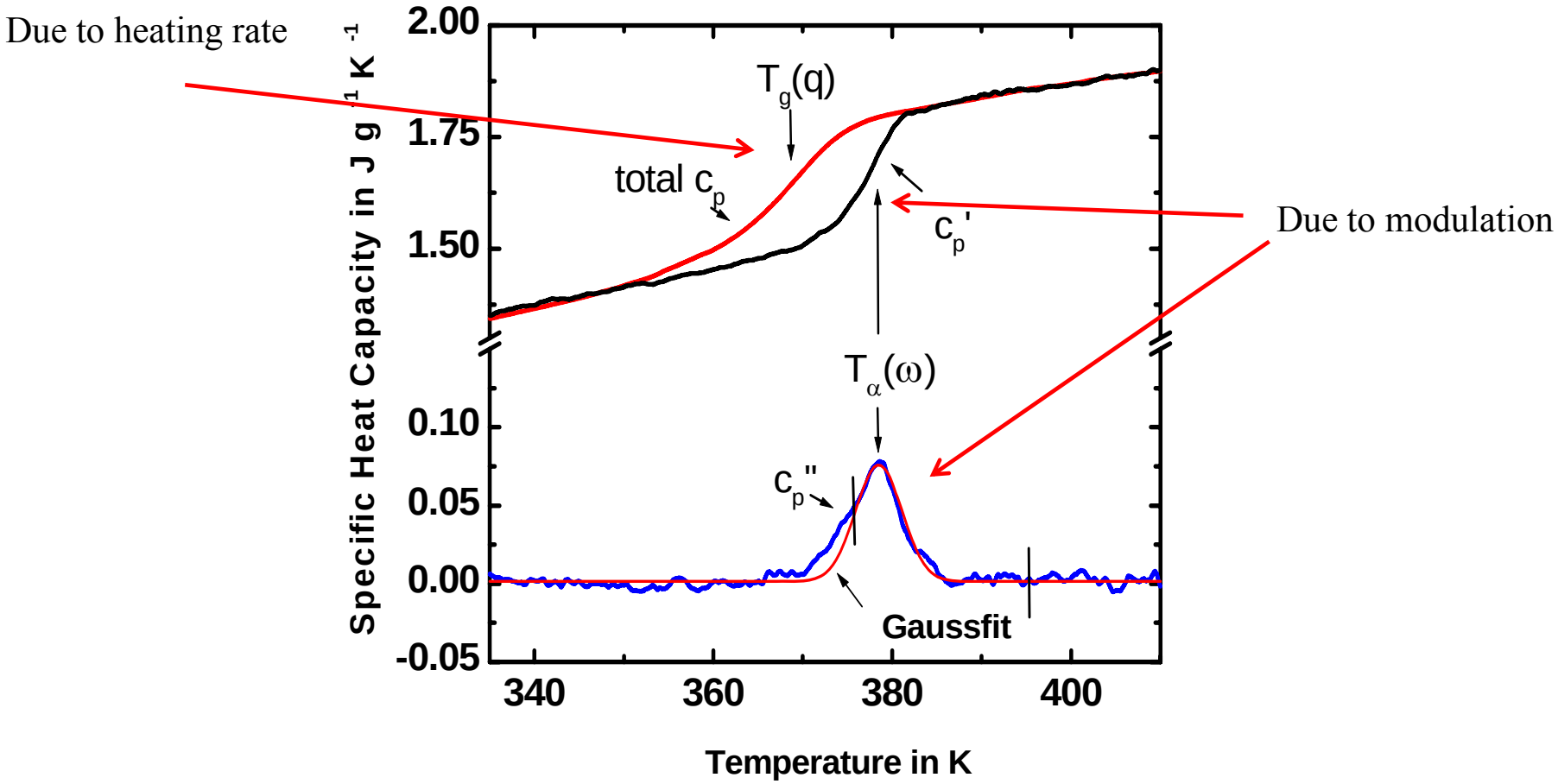
$$C^*_p(\omega) = C'_p(\omega) - i\, C''_p(\omega)$$

Ch. Schick, Temperature Modulated Differential Scanning Calorimetry - Basics and Applications to Polymers in Handbook of Thermal Analysis and Calorimetry edited by S. Cheng (Elsevier, p 713. Vol. 3, 2002).

Specific Heat Spectroscopy

A Special Case of Linear Response Theory

Example Temperature Modulated DSC → Polystyrene



Hensel, A., and Schick, C.: J. Non-Cryst. Solids, 235-237 (1998) 510-516.

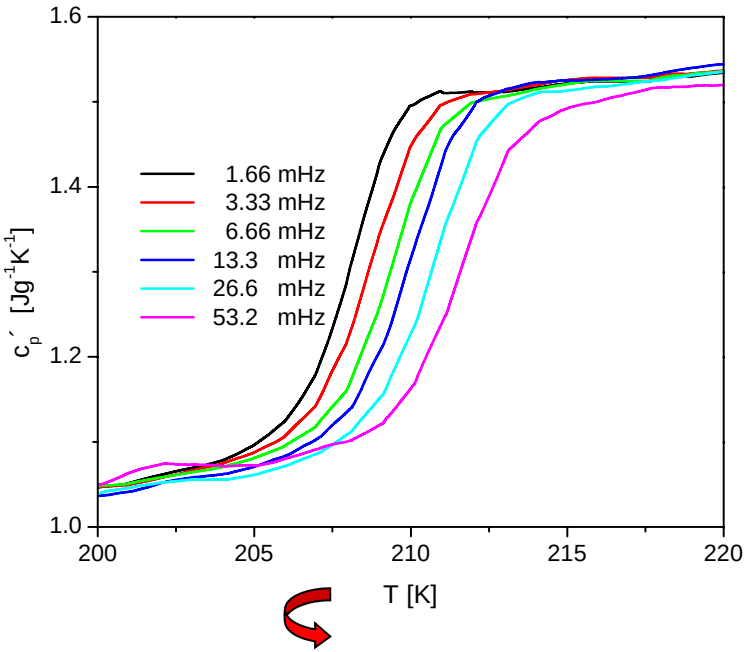
Specific Heat Spectroscopy

A Special Case of Linear Response Theory

Example Temperature Modulated DSC → Glass forming liquid crystal E7

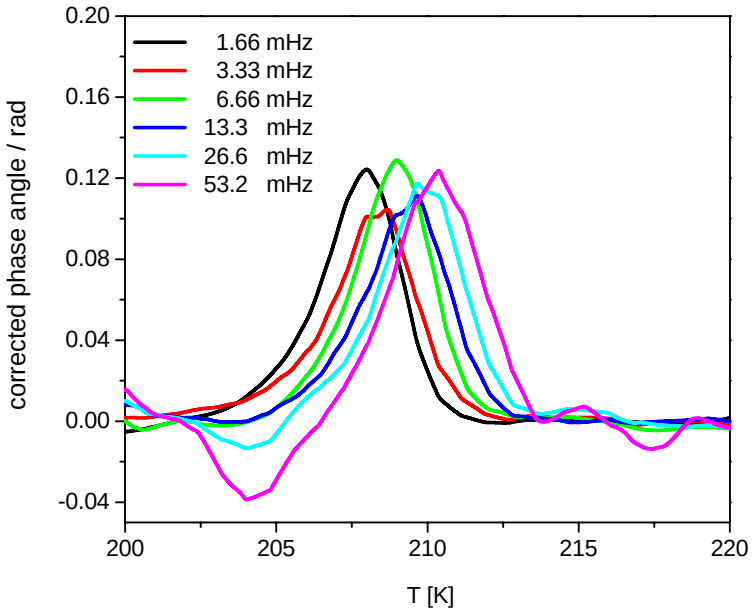
Real Part

Frequency →



Loss factor

Frequency →

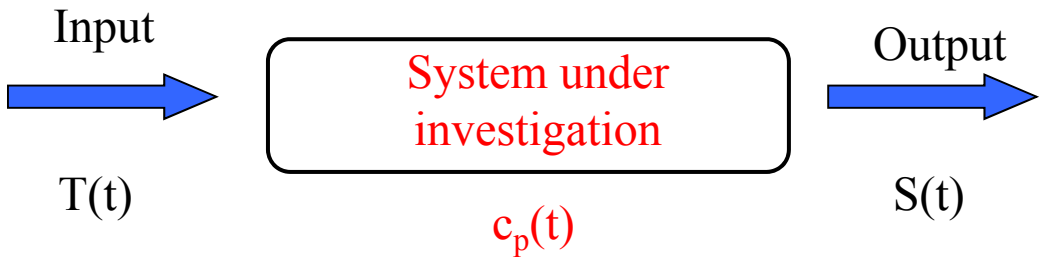


Frequency range : 10^{-3} Hz …. 5 *10^{-2} Hz

Heating and cooling rates must be adjusted to meet stationary conditions !

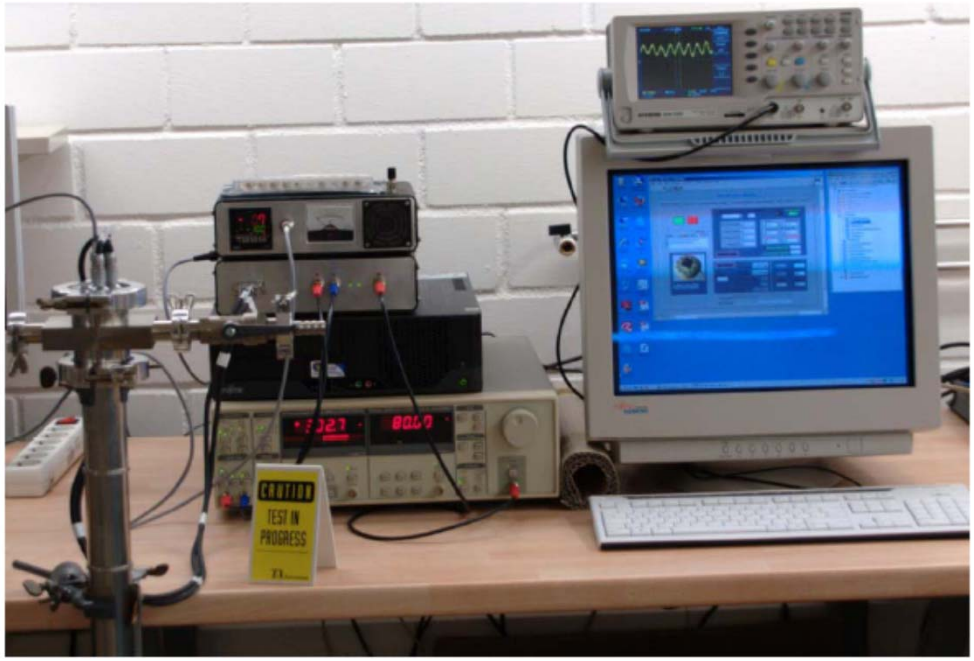
Specific Heat Spectroscopy

A Special Case of Linear Response Theory



AC Chip calorimetry → Pressure gauge, Xsensor Integration

Differential setup



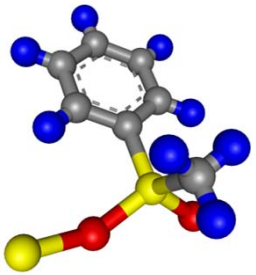
H. Huth, A. Minakov, Ch. Schick, Polym. Sci. B Polym. Phys. **44**, 2996 (2006).

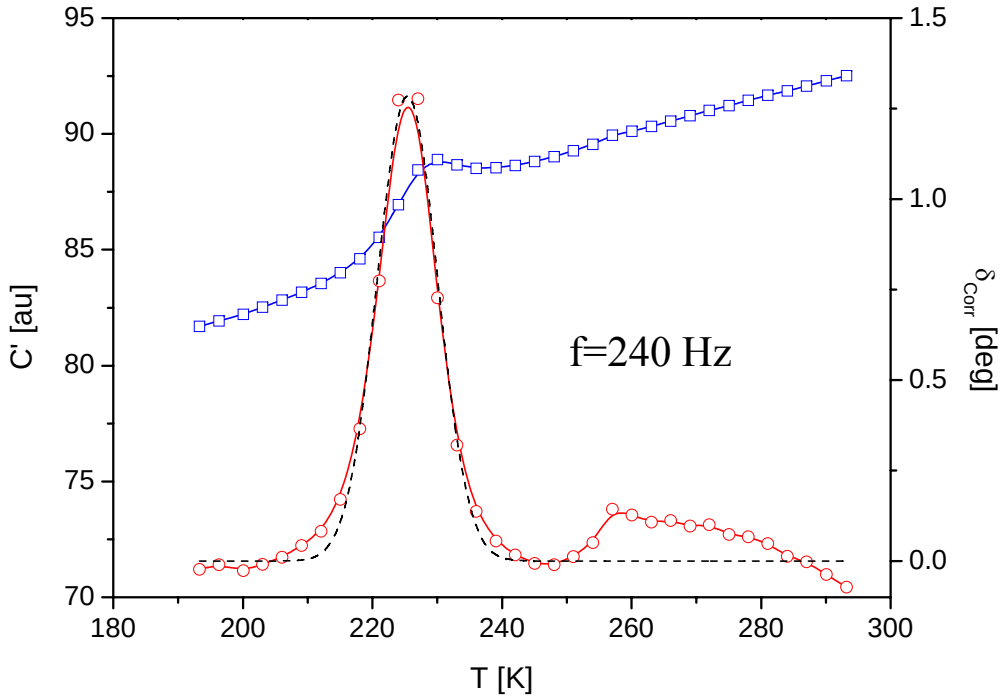
Specific Heat Spectroscopy

A Special Case of Linear Response Theory

Example AC calorimetry

PMPS, M_w= 1000 g/mol





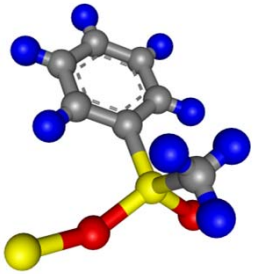
Frequency range : 10 Hz …. 5000 Hz

A. Schönhals et al. J. Non-Cryst. Solids 353 (2007) 3853

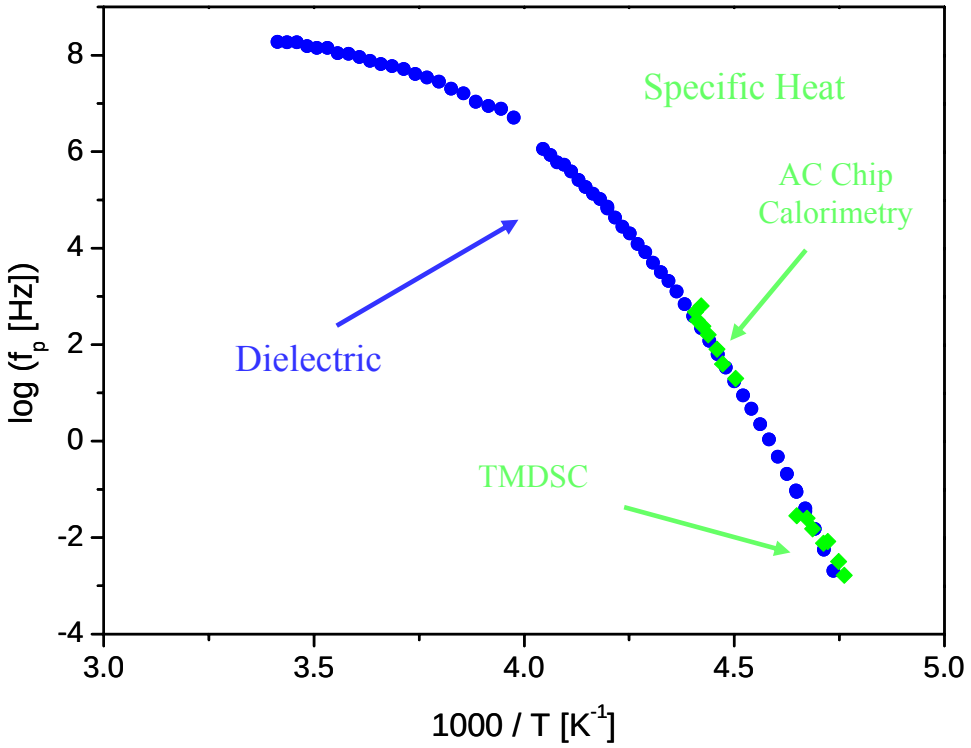
Combination of

Dielectric Spectroscopy …..

PMPS, M_w= 1000 g/mol



and Specific Heat Spectroscopy



Both methods measure the same process….

… Glassy dynamics of PMPS

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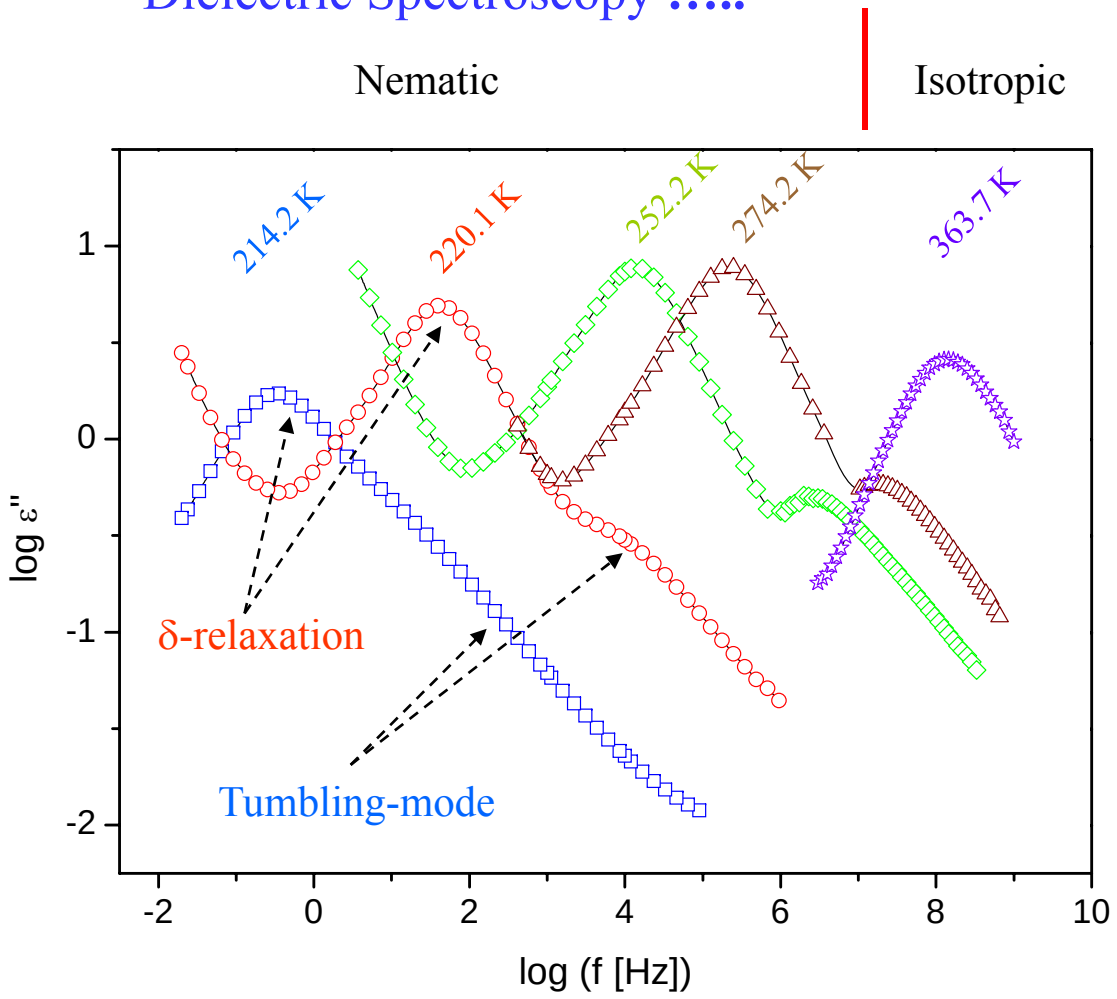
Combination of

Dielectric Spectroscopy .....

Glass forming liquid crystal E7



Questions:

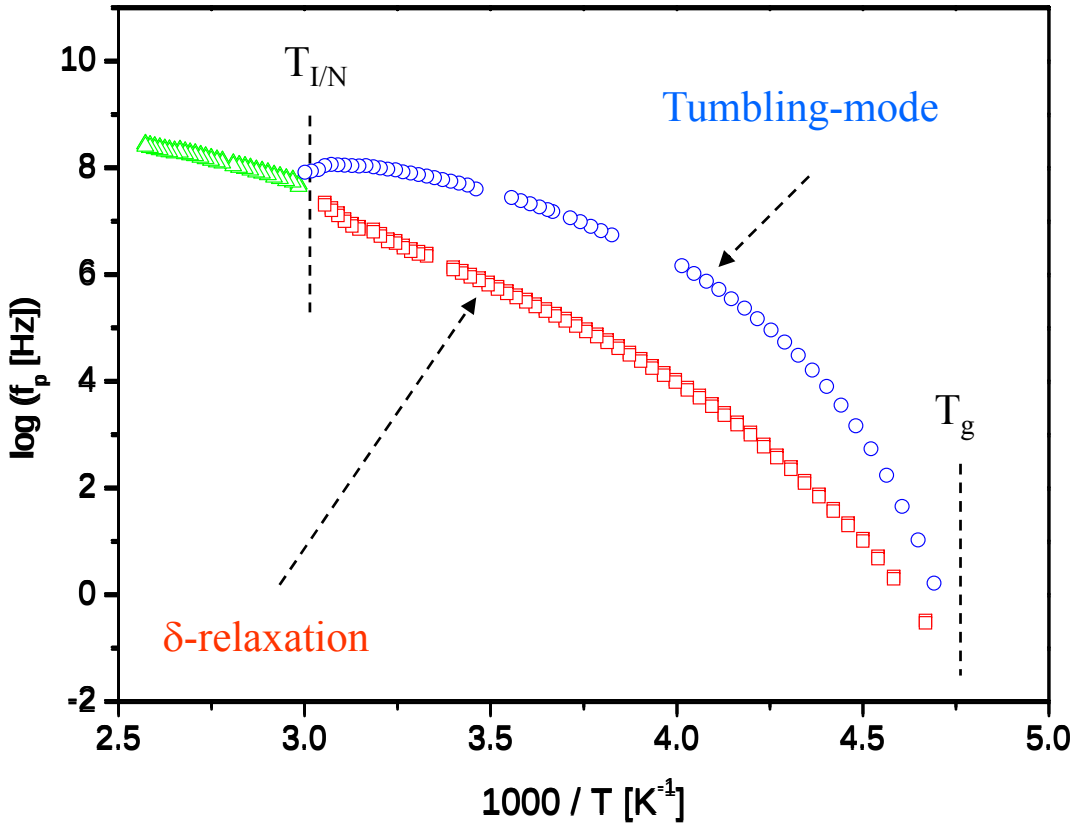
- Temperature dependence of both modes?
- Which mode corresponds to glassy dynamics?

A.R. Bras et al. Phys Rev. E 75 (2007) 61708

Combination of

Dielectric Spectroscopy .....

Glass forming liquid crystal E7



- The temperature dependence of the relaxation rates of both the δ- and the tumbling mode is curved vs. 1/T.
- Close to T_g the temperature dependencies of both mode seems to collapse.

Derivative analysis

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Combination of

Dielectric Spectroscopy .....

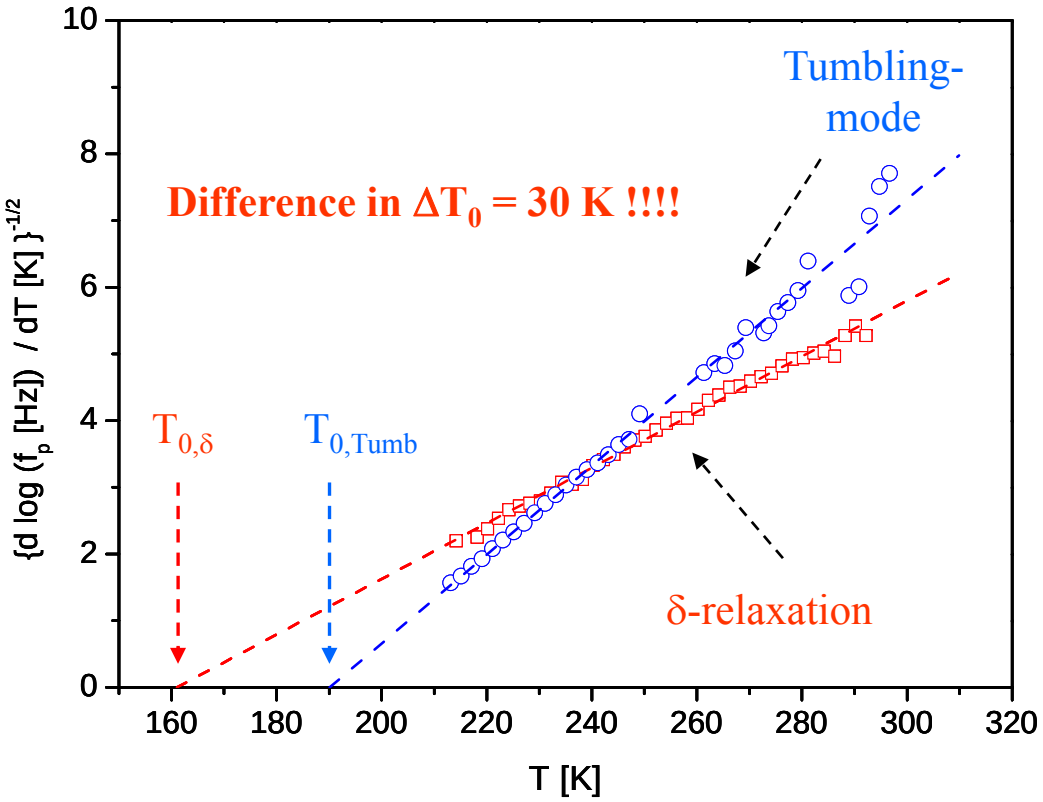
Glass forming liquid crystal E7

- Similar to the decoupling of rotational and translation diffusion in glass-forming liquids
- Similar to the decoupling of segmental and chain dynamics in polymers

Can be explained by different averaging of modes with different length scales

Which mode is responsible for glassy dynamics?

The temperature dependence of the relaxation rates of both the δ- and the tumbling mode follow the VFT-equation.



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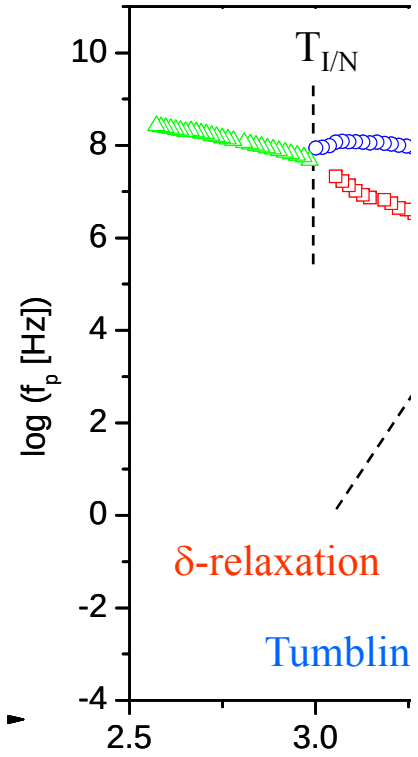
Combination of
Dielectric Spectroscopy .....

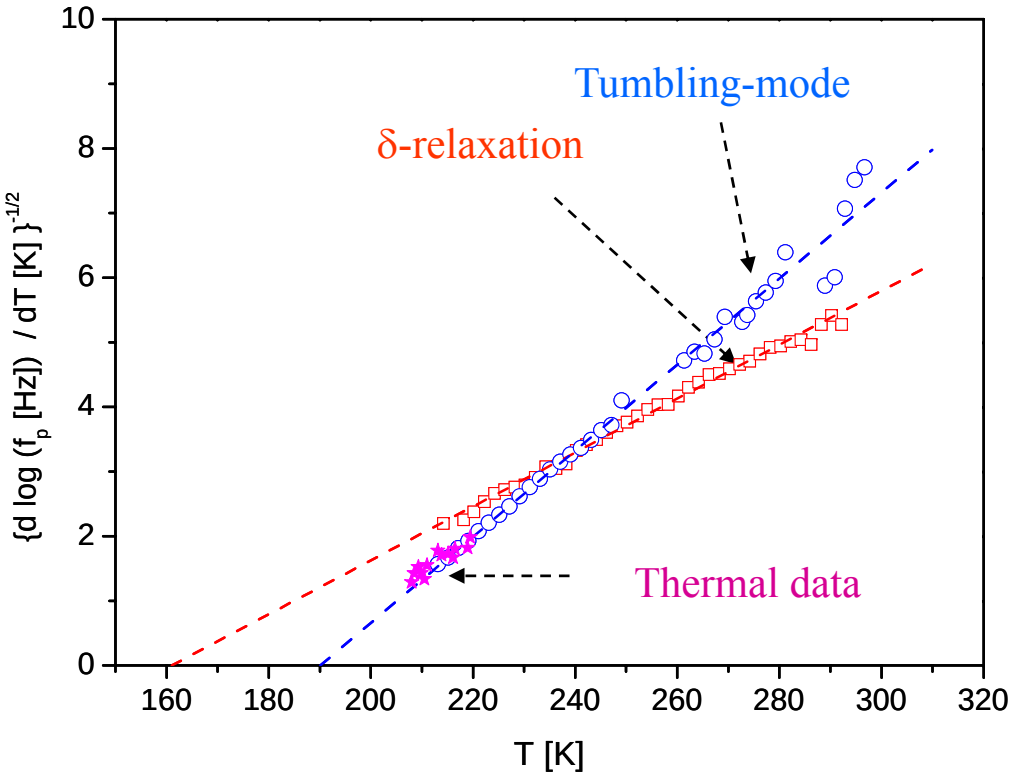
Glass forming liquid crystal E7

and Specific Heat Spectroscopy

Relaxation Map



Derivative Plot



The thermal data agree perfectly with that of the tumbling with regard to the absolute values and its temperature dependence

Tumbling mode is responsible for glassy dynamics!

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Neutron Scattering

➡ Neutrons are parts of the atomic nuclei

Isotopes: Elements with the same number of protone but with a different number of neutrons.

Examples: Hydrogen, Deuterium, Tritium

➡ Neutrons

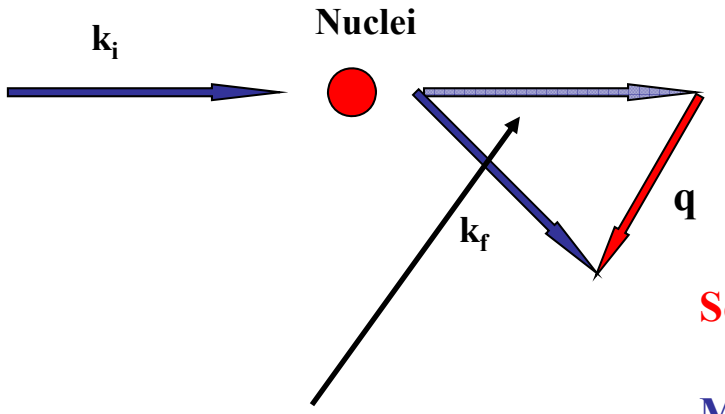
- Have the same mass than protons
- Electrically neutral
- Have a spin

➡ Neutrons can be obtained by nuclear fission processes

Atomic reactor, Neutron spallation source

Neutron Scattering

Theoretical Consideration – Neutron Cross Sections, Correlation Functions



2θ - scattering angle

k_i – wave vector of the incoming neutron

k_f – wave vector of the scattered neutron

Scattering vector: $\mathbf{q = k_f - k_i}$

Momentum transfer: $\hbar\mathbf{q} = \hbar(\mathbf{k_f} - \mathbf{k_i})$

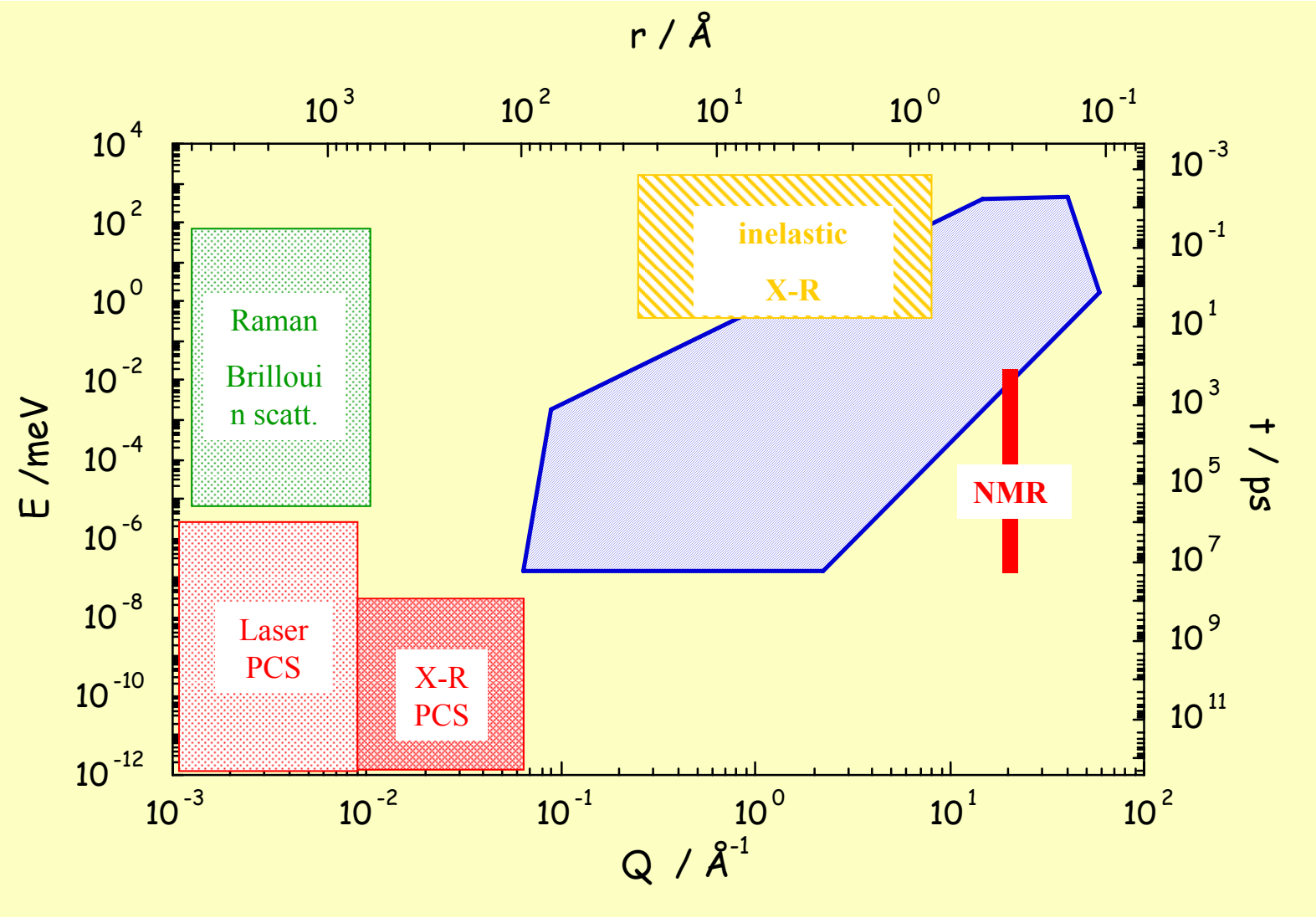
Energy transfer: $\hbar\omega = \hbar^2(k_f^2 - k_i^2)$

Elastic scattering: $|k_f| \approx |k_i| \Longrightarrow q = |\vec{q}| = \frac{4\pi}{\lambda_0}\sin\theta$

Inelastic scattering: $|k_f| \neq |k_i| \Longrightarrow$ **Time dependence**

Time and spatial information

Comparison of Scattering Vector and Energy Ranges of Different Inelastic Scattering Methods



Neutron Scattering

Theoretical Consideration – Neutron Cross Sections, Correlation Functions

The intensity of the scattered neutrons is described by a double differential cross section:

$$\frac{\partial^2\sigma}{\partial\Omega\partial\hbar\omega} = \frac{1}{2\pi\hbar}\frac{k_f}{k_i}\int_{-\infty}^{\infty} dt \exp(-i\omega t)\left\langle \sum_{j,k}^{N} b_j b_k \exp\left\{i\vec{q}\left[\vec{r}_j(t) - \vec{r}_k(0)\right]\right\}\right\rangle$$

Solid angle — **Energy change** — **Scattering lengths** — **Position of atom j at time t** — **Position of atom k at time t =0**

$$\frac{\partial^2\sigma}{\partial\Omega\partial\hbar\omega} = \frac{k_f}{\hbar k_i} N\left\{\left[\left\langle b^2\right\rangle - \left\langle b\right\rangle^2\right] S_{inc}(\vec{q},\omega) + \left\langle b\right\rangle^2 S(\vec{q},\omega)\right\}$$

Scattering lenght:

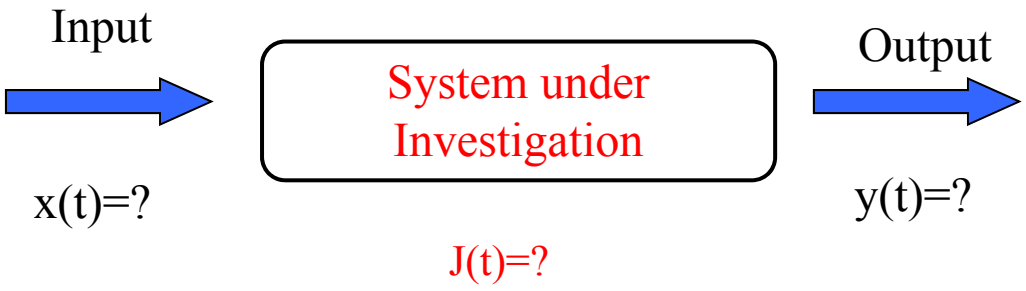
Self Correlation — **Hydrogen $b_H = -0.374 * 10^{-12}$ cm**

Pair Correlation — **Deuterium $b_D = 0.667 * 10^{-12}$ cm**

Time Domain, Incoherent scattering → $$S_{inc}(\vec{q},t) = \frac{1}{N}\sum_{j}^{N}\exp\left\{-\frac{\vec{q}}{6}\left\langle\left[r_j(t) - r_j(0)\right]^2\right\rangle\right\}$$

Neutron Scattering

A Special Case of Linear Response Theory ?



$$S_{inc}(\vec{q},t) = \frac{1}{N}\sum_{j}^{N} \exp\left\{-\frac{\vec{q}}{6}\left\langle\left[r_j(t)-r_j(0)\right]^2\right\rangle\right\} \longrightarrow S_{inc}(\vec{q},t) =< \rho(\vec{q},t)\rho(\vec{q}) >$$

van Hove Correlation function — Density correlation function

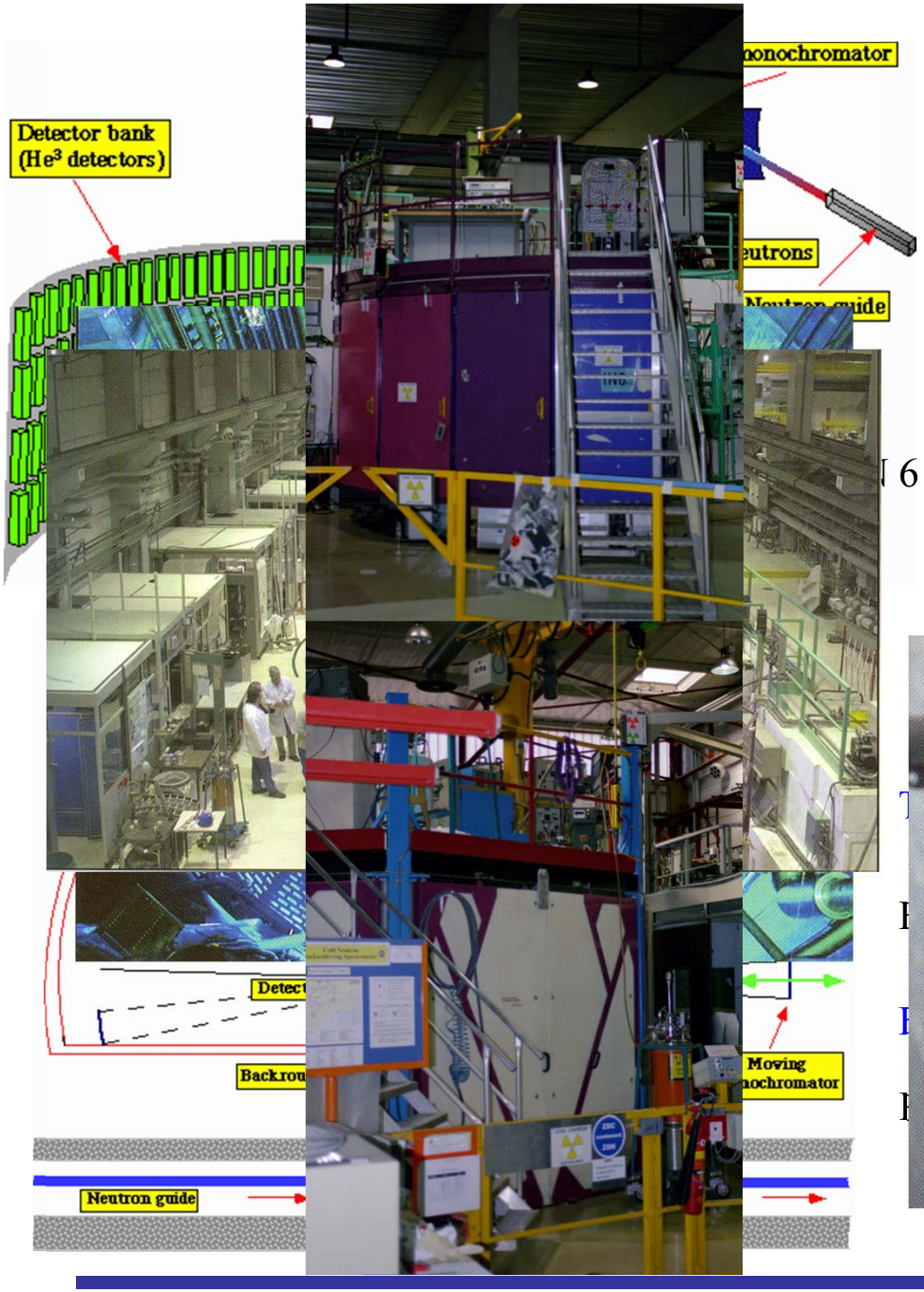
Correlation function → Fluctuation Dissipation Theorem → Modulus, Compliance ?

Thermodynamics (t=0): → $\kappa(q) = \frac{S(q)}{k\,T\,N}$ → Isothermal compressibility

S(q,t) is related to a q-dependent Compression Modulus

W. Götze in Hansen et al. "Liquids, Freezing and the Glass Transition", North Holland 1990

Neutron Scattering



.. 20 ps

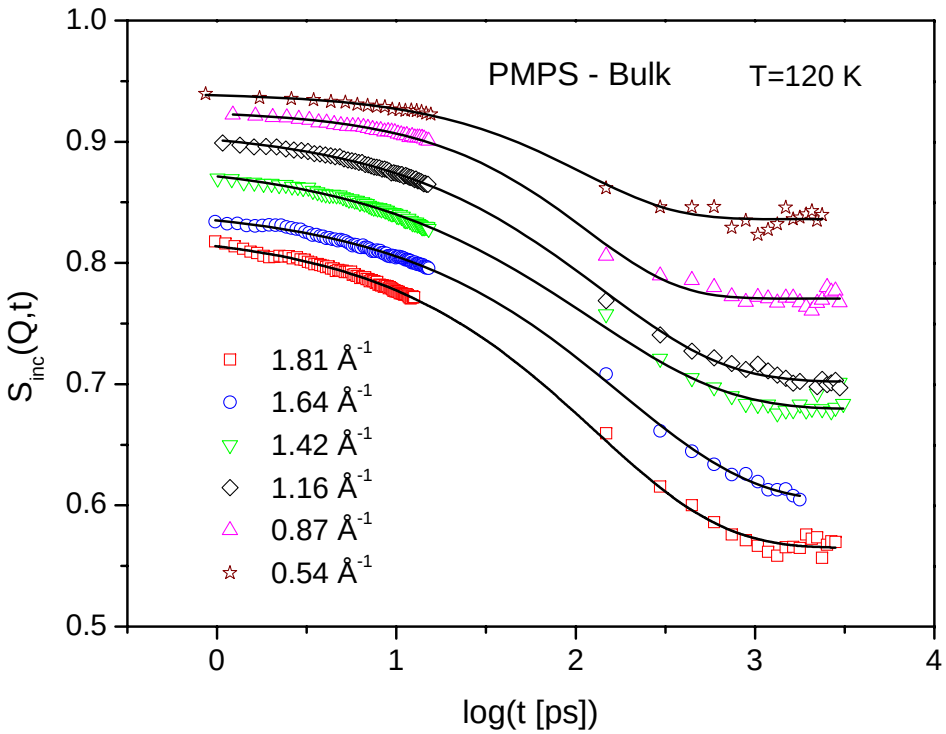
.. 4 ns

BAM

Neutron Scattering…..

… Examples

IN 6 IN 16



Broadband Neutron Spectroscopy

$S_{inc}(Q,t)$

incoherent intermediate scattering function

Spectral Shape of **IN16** data
similar but **energy resolution µeV**

→ **Fourier Transformation of each data set**

→ **Comparison in time domain**

Overview of the molecular Dynamics of PMPS…

… by elastics Scans

Elastic scans on a backscattering instrument give an efficient overview over the temperature dependent dynamics.

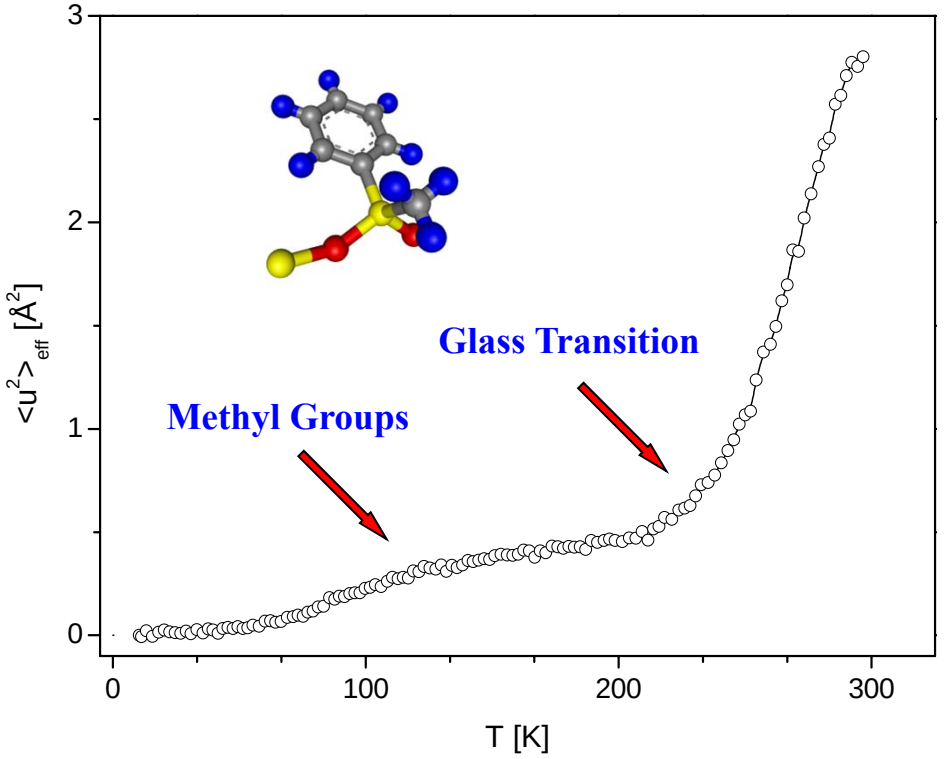
Mean square displacement u_{eff}:

$$I_{el} / I_0 = \exp\left[-\frac{Q^2 < u^2 >_{eff}}{3}\right]$$

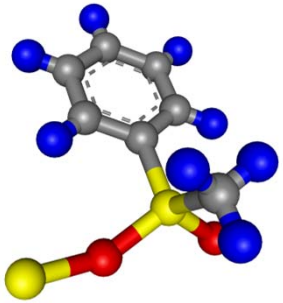
I_{el} – elastically scattered intensity

I_0 – totally scattered intensity

- Analysis Methyl group rotation
- Analysis Glass transition



Data Analysis Methyl Groups PMPS



8 protons

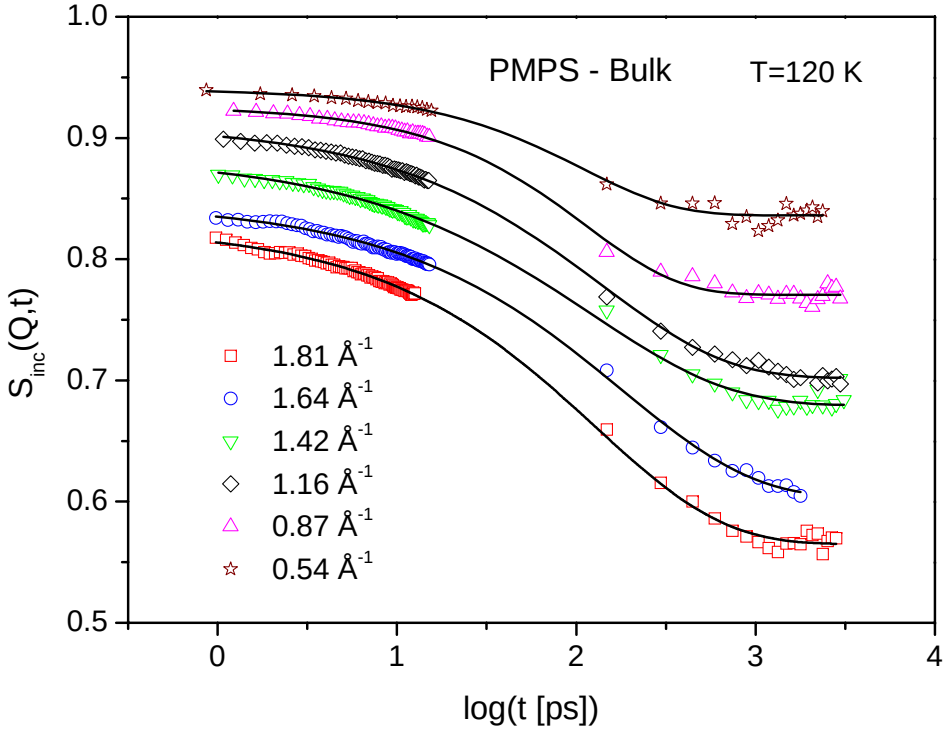
3 protons in the CH_3 -group

5 protons in the phenyl ring

3/8 of the scattering is due to localized rotation of the CH_3 -group

Analysis of the CH_3 – group rotation !

IN 6 IN 16



Debye-Waller-factor

Elastic incoherent structure factor (EISF)

$$S_{Inc}(Q,t) = DWF * \left((1-A)\exp\left(-\left(\frac{t}{\tau_{CH_3}} \right)^{\beta_{CH_3}} \right) + A \right)$$

KWW-function

β=0.7 !

Data Analysis Segmental Relaxation PMPS

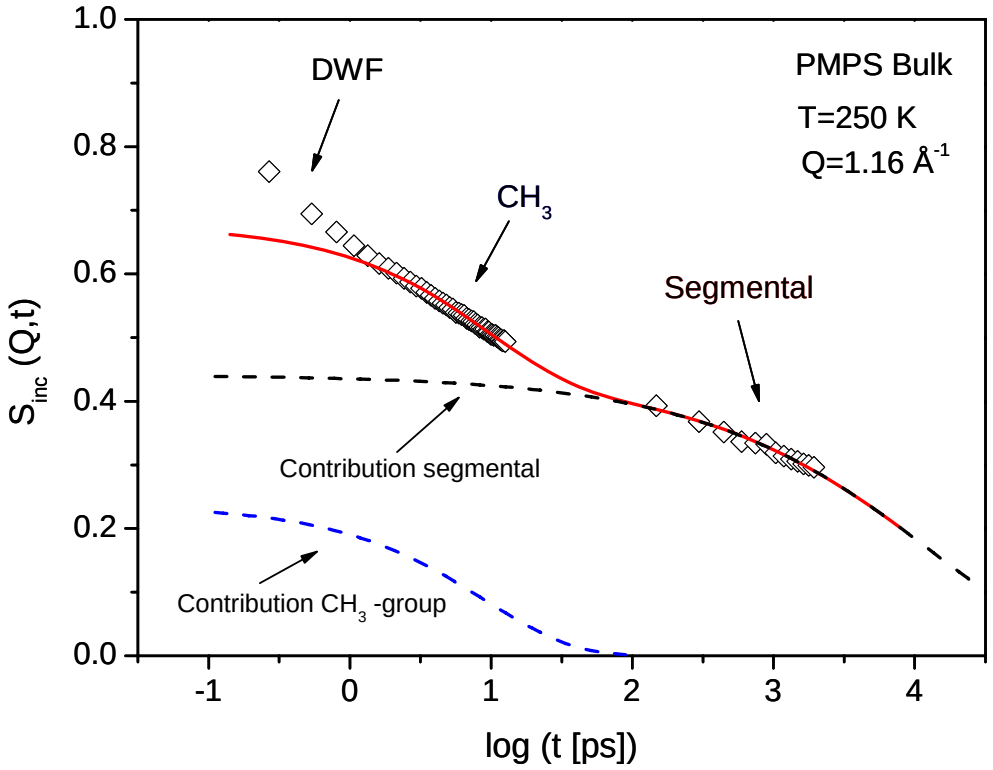
Above **From CH_3-Analysis** **t- from the** **From Dielectric**

Fast Processes (DWF)

$$S_{Inc}(Q,t) = DWF * \left((1-A)\exp\left(-\left(\frac{t}{\tau_{CH_3}} \right)^{\beta_{CH_3}} \right) + A\exp\left(-\left(\frac{t}{\tau_{seg}} \right)^{\beta_{seg}} \right) \right)$$

CH_3 –group rotation

Segmental relaxation



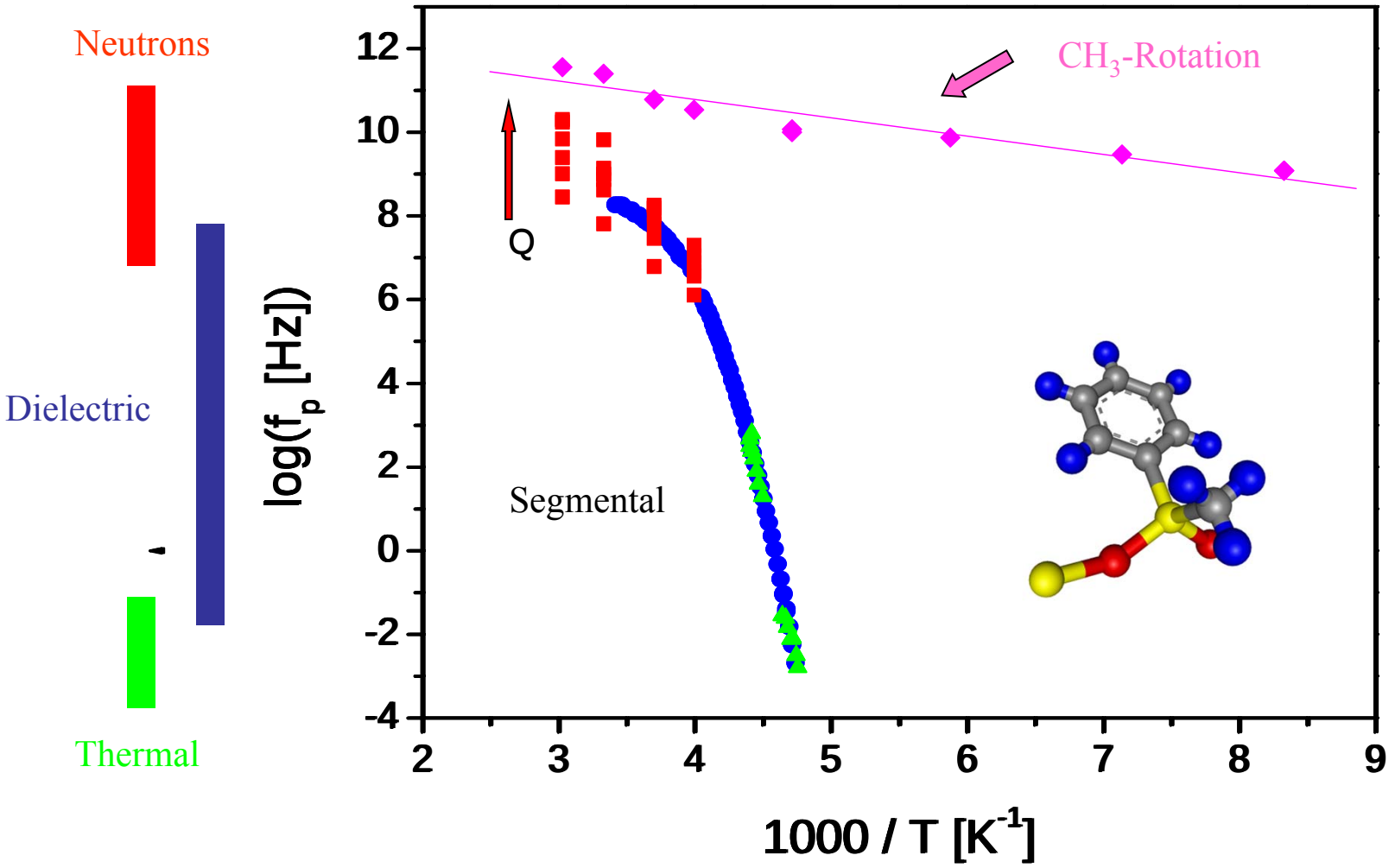
$$\langle \tau \rangle = \frac{\tau_{KWW}}{\beta} \Gamma\left(\frac{1}{\beta} \right)$$

Comparison with other experiments

BAM

Overall Molecular Dynamics PMPS

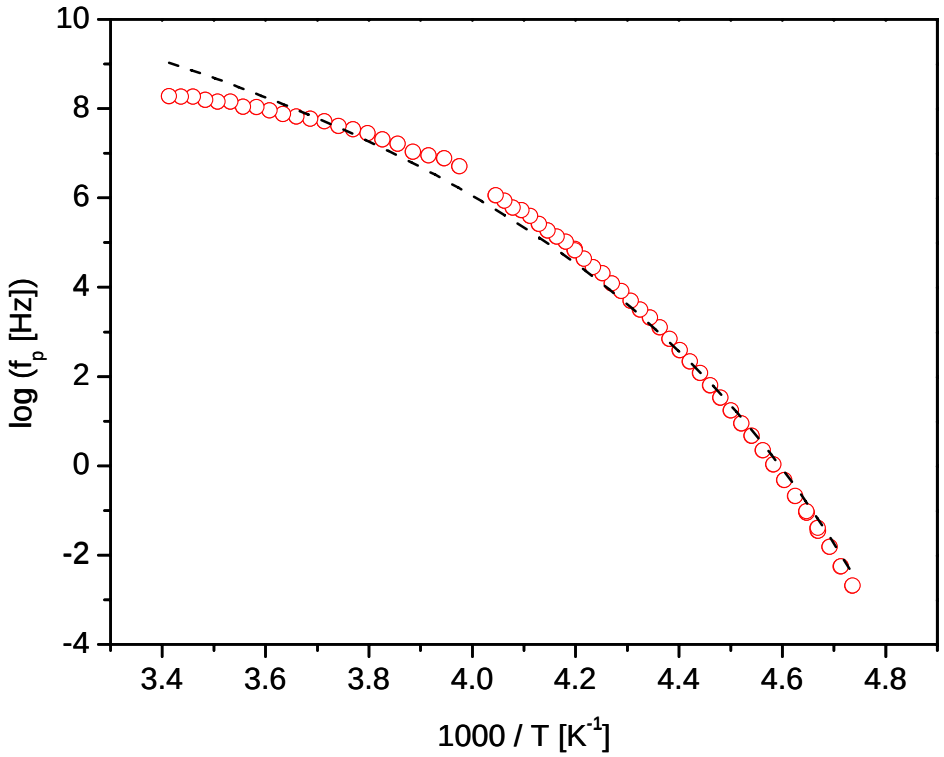
Precise determination of glassy dynamics in a wide temperature range using different probes



Analysis of the Temperature dependence…

Dielectric data…

… cannot be described by the VFT-equation in the whole temperature range



VFT- equation:

$$\log f_p = \log f_{p\infty} - \frac{A}{T - T_0}$$

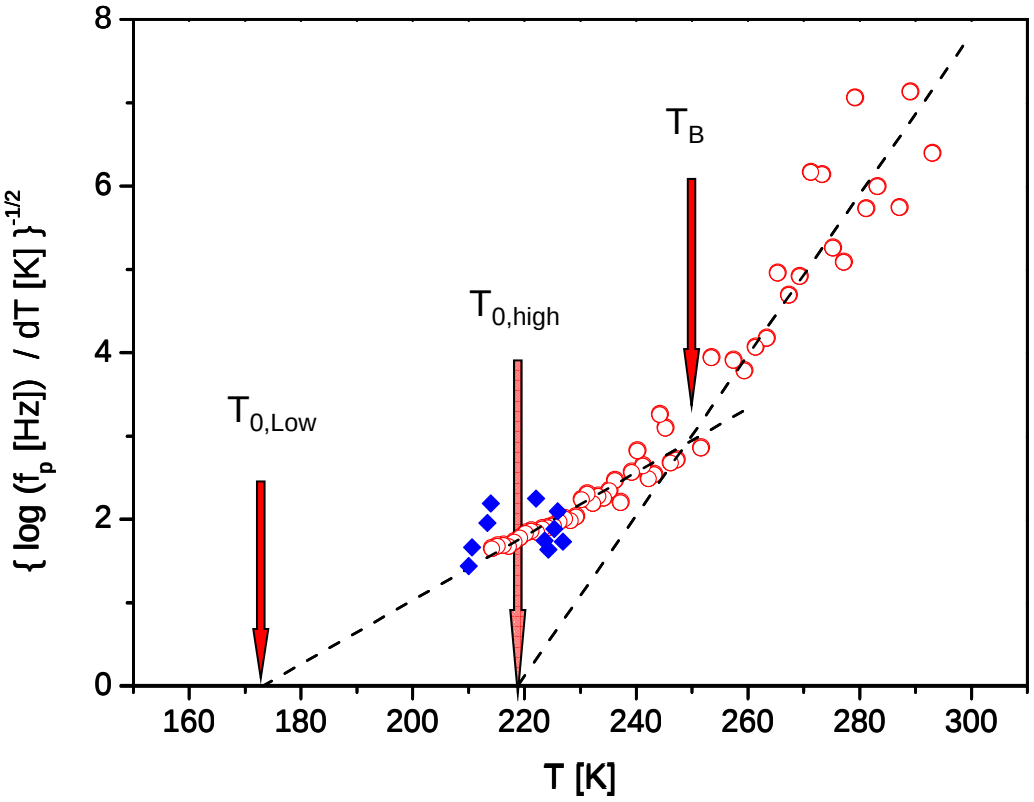
Derivative

$$\left[\frac{d \log f_p}{d T}\right]^{-1/2} = \frac{1}{A^{1/2}}(T - T_0)$$

Straight Line, $T_0 > 0$

Analysis of the Temperature dependence…

Derivative-Plot



red : dielectric data

blue: thermal data

- low and high temperature regime
- two VFT - dependencies
- Crossover temperature

  $T_B = 250$ K
- Thermal and dielectric data have the same temperature dependence

Temperature dependence…

…of the dielectric relaxation strength

Dipole moment

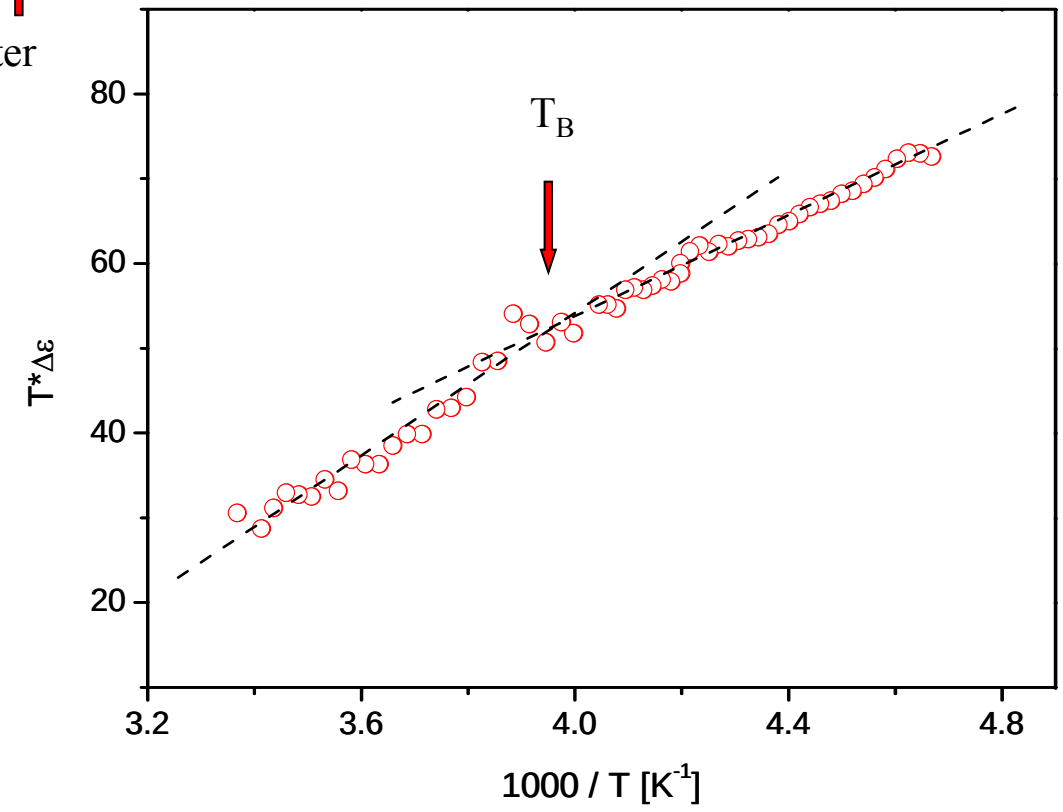
Debye Theory → $\Delta\varepsilon = \frac{1}{3\varepsilon_0}\, g\, \frac{\mu^2}{k_B T}\, \frac{N}{V}$

Interaction parameter

- Temperature dependence of $\Delta\varepsilon$ is much stronger than predicted

  → Cooperative effects

- Change of the temperature dependence of $\Delta\varepsilon$ at T_B



Temperature dependence…

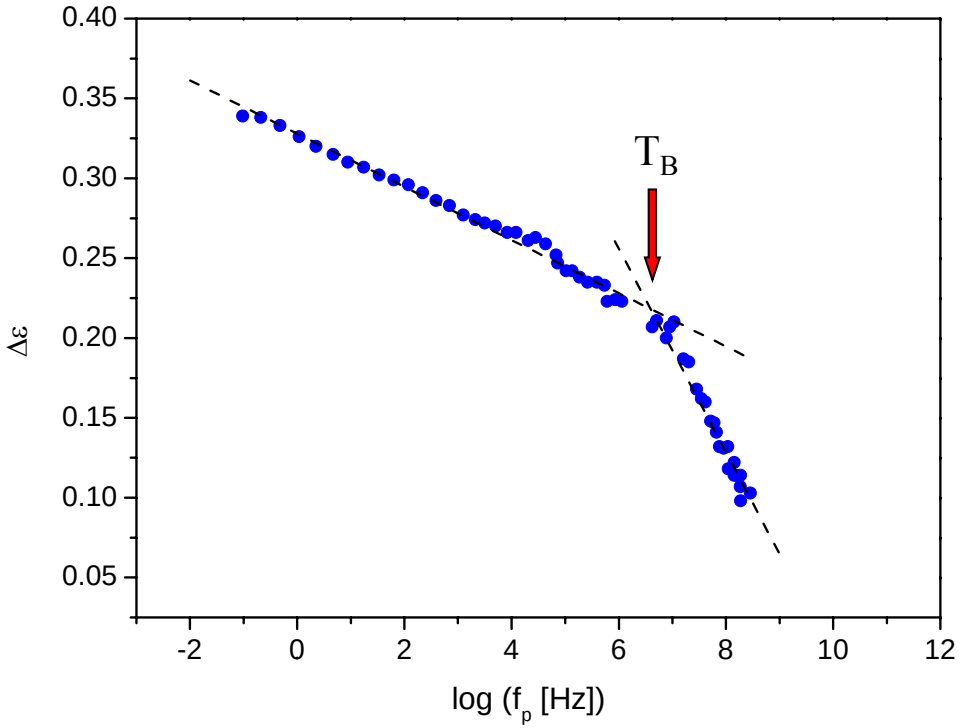
…of the dielectric relaxation strength

The change in the temperature dependence of $\triangle\varepsilon$ is not much pronounced

Plot of $\triangle\varepsilon$ vs. log f_p

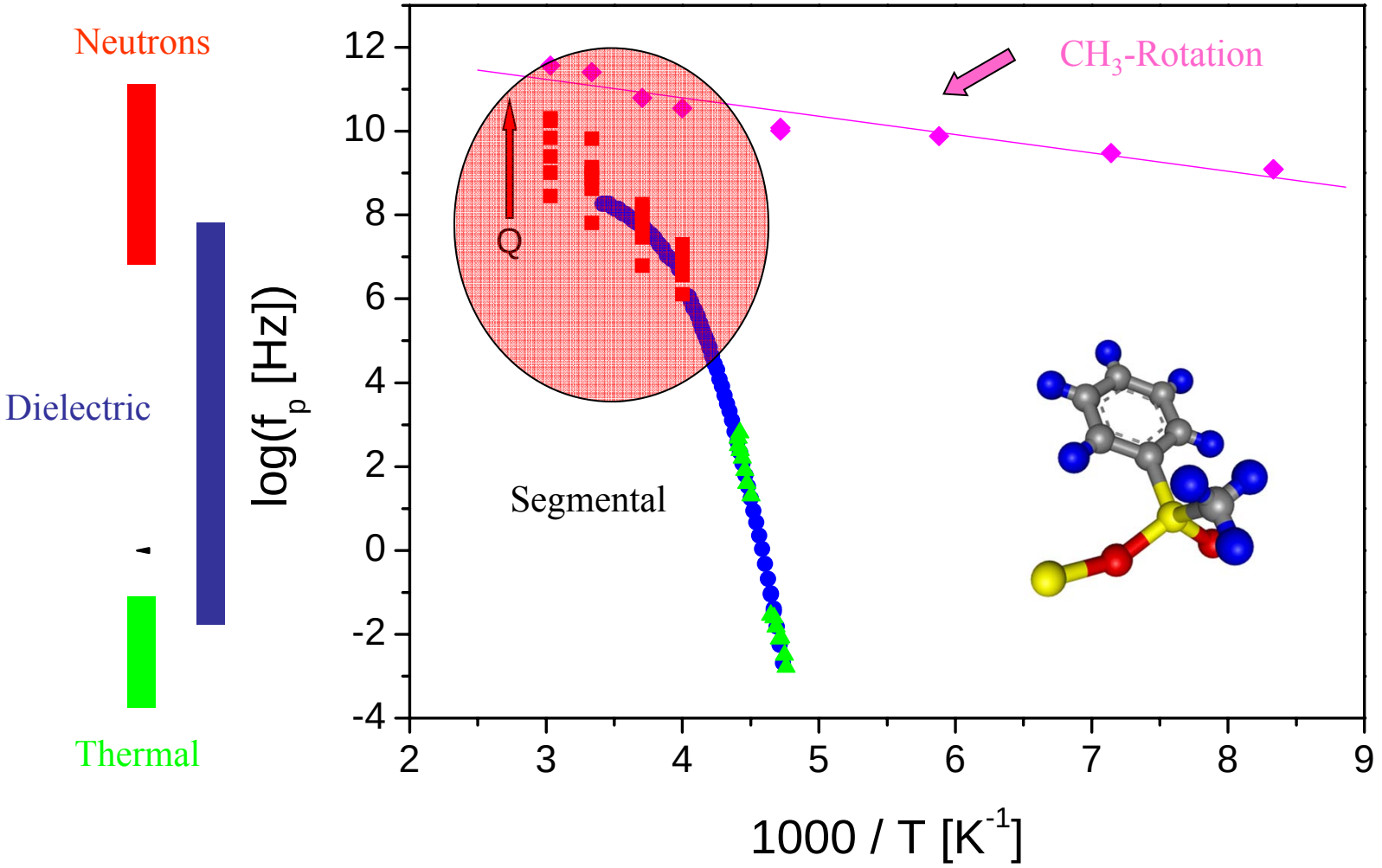
Sharp transition fro a low temperature to a high temperature branch

The crossover frequency coresponds to T_B

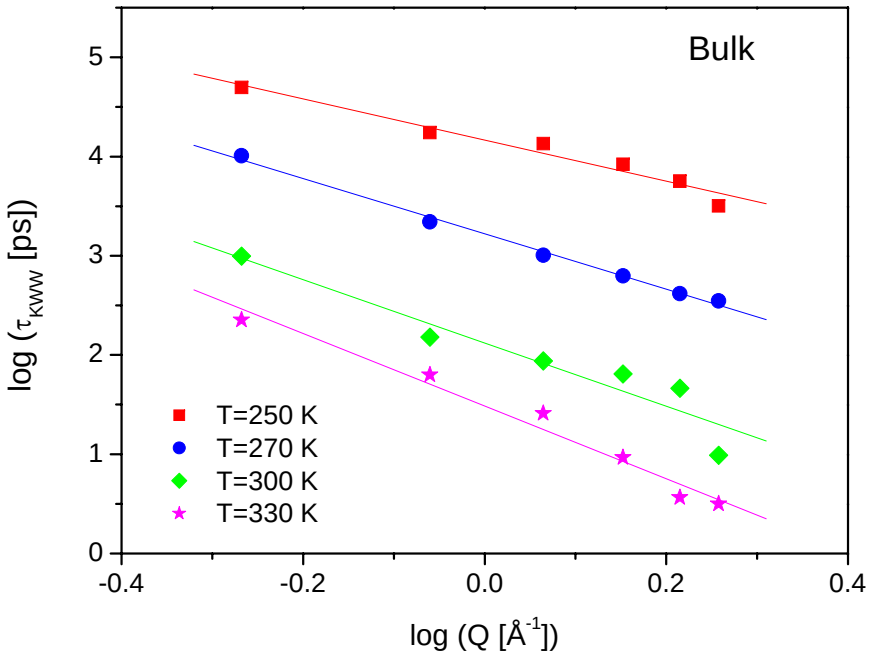


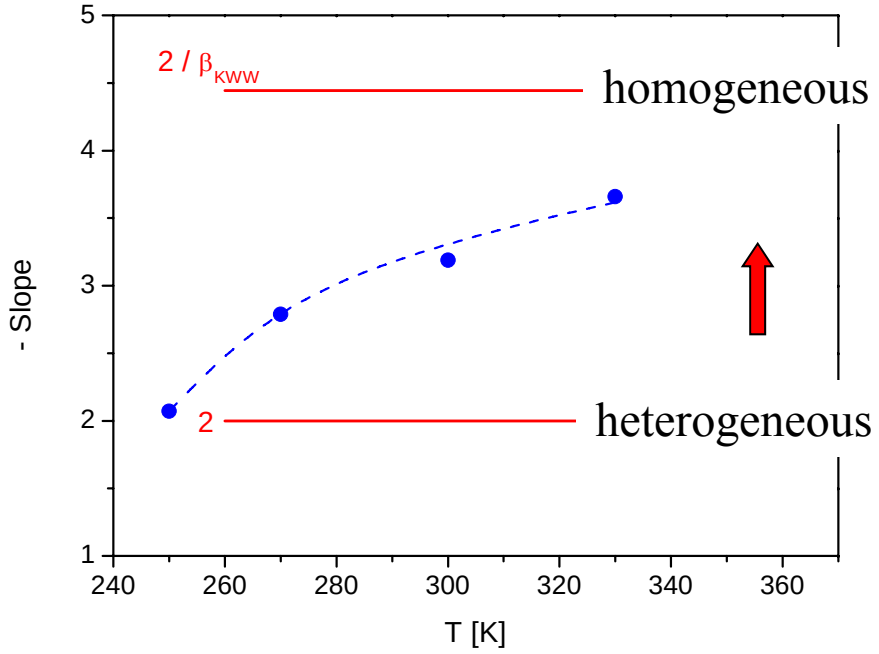
A. Schönhals Euro. Phys. Lett. **56** (2001) 815

Overall Molecular Dynamics PMPS



Dynamics PMPS: Q-Dependence Segmental Relaxation





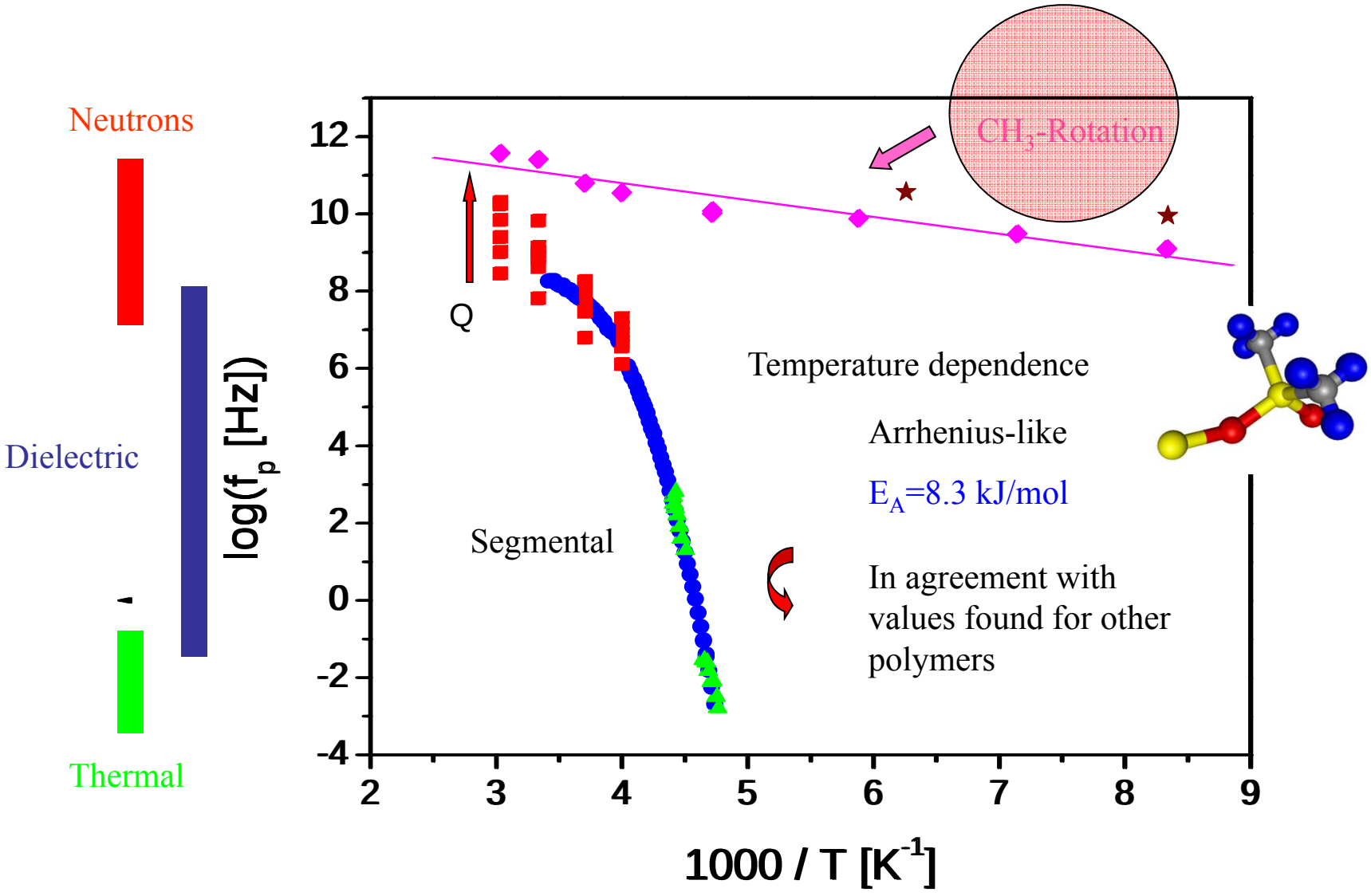
Theory :

$$S_{inc}(Q,t) = \exp(-Q^2 Dt) = \exp\left[-\left(-\frac{t}{\tau}\right)\right] \rightarrow \tau \sim Q^{-2}$$

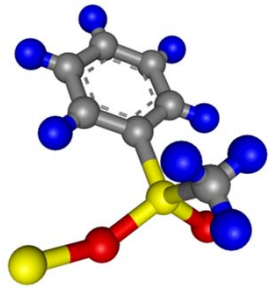
$$S_{inc}(Q,t) = \exp(-Q^2 A t^{\beta}) = \exp\left[-\left(-\frac{t}{\tau}\right)^{\beta}\right] \rightarrow \tau \sim Q^{-2/\beta}$$

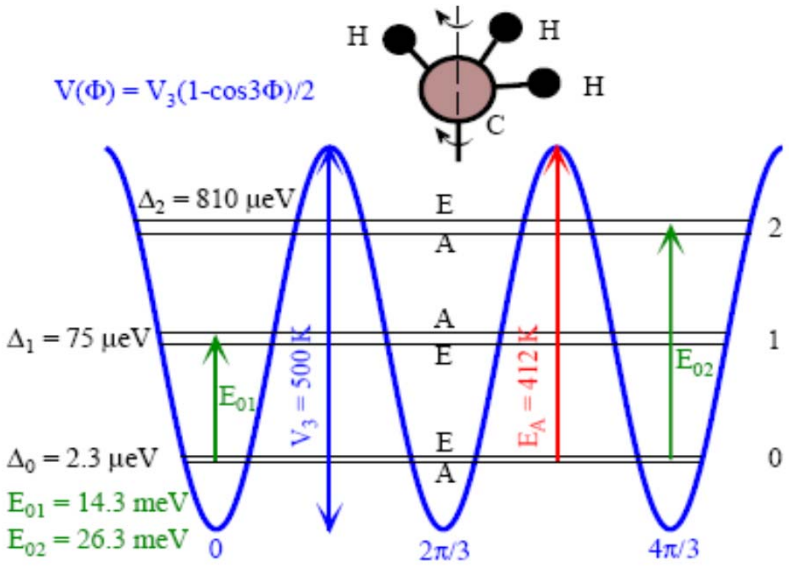
BAM

Overall Molecular Dynamics PMPS



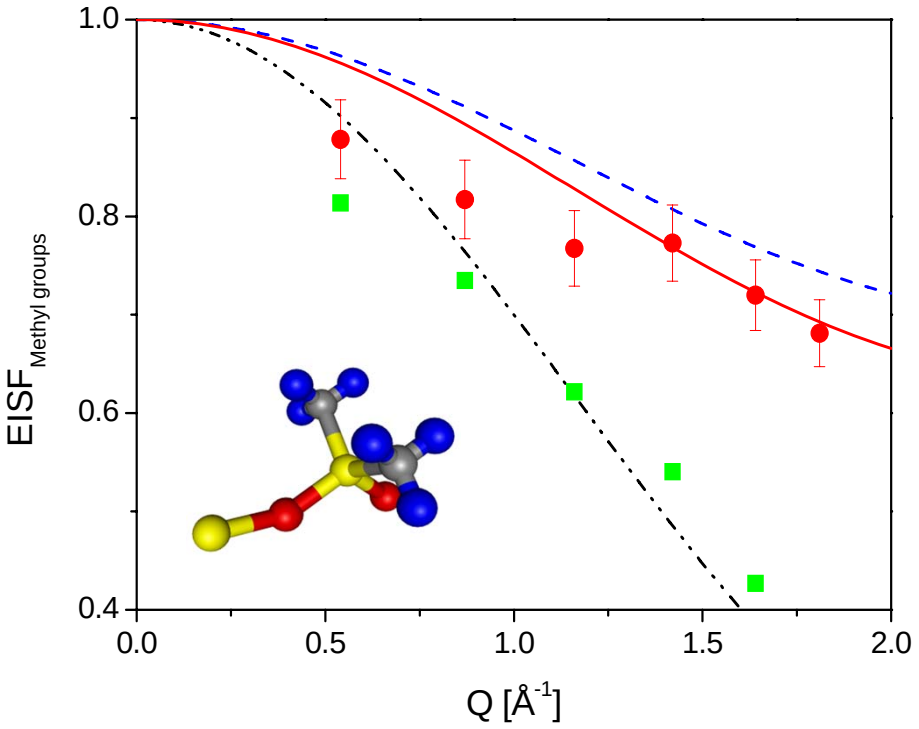
Methyl Group Rotation in PMPS





Threefold Potential

$$A_{3-\mathrm{jump}}(Q)=\frac{1}{3}\left(1+2\frac{\sin(\sqrt{3}\,Q\,r)}{\sqrt{3}\,Q\,r}\right)$$



3/8 of the scattering is due to localized rotation of the CH_3-group

$$A_{\mathrm{App}}(Q)=(1-c_{\mathrm{fix}})\,A(Q)+c_{\mathrm{fix}}$$

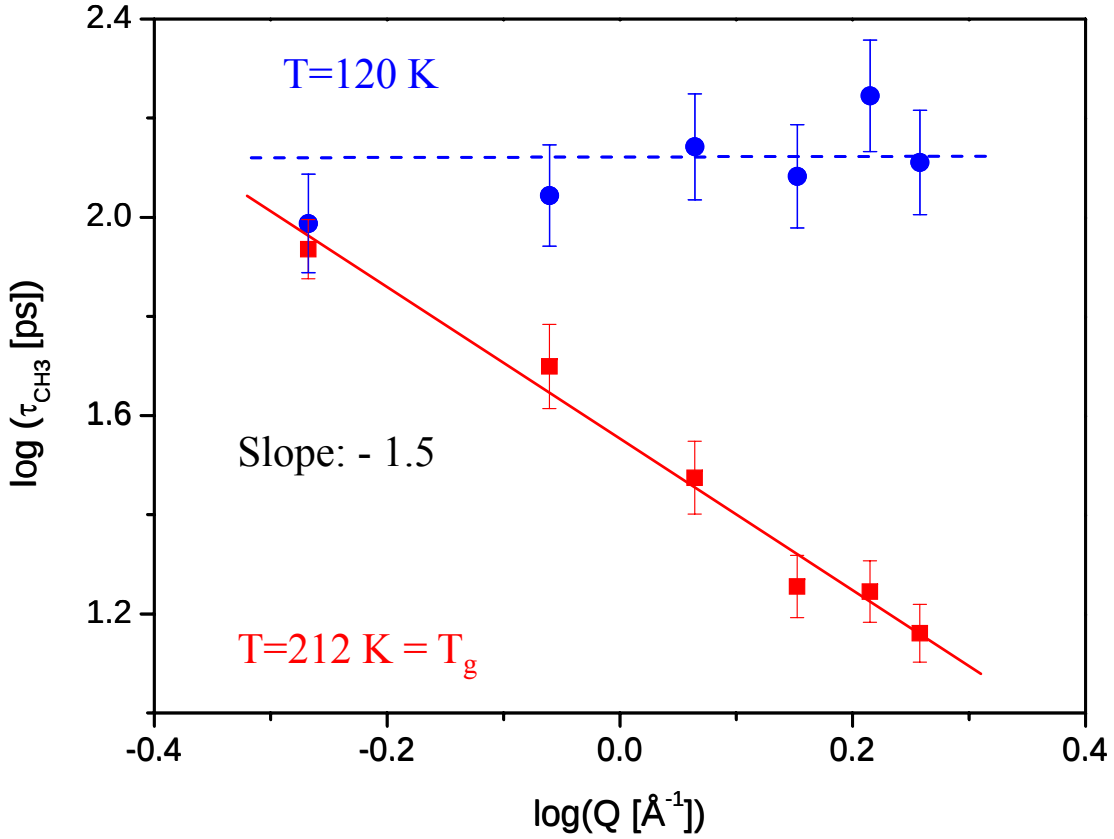
Structure: $c_{fix}=5/8=0.624$

Experiment: $c_{fix}=0.55$

BAM

Methyl Group Rotation in PMPS …

…Q - dependence of the Relaxation **Time**



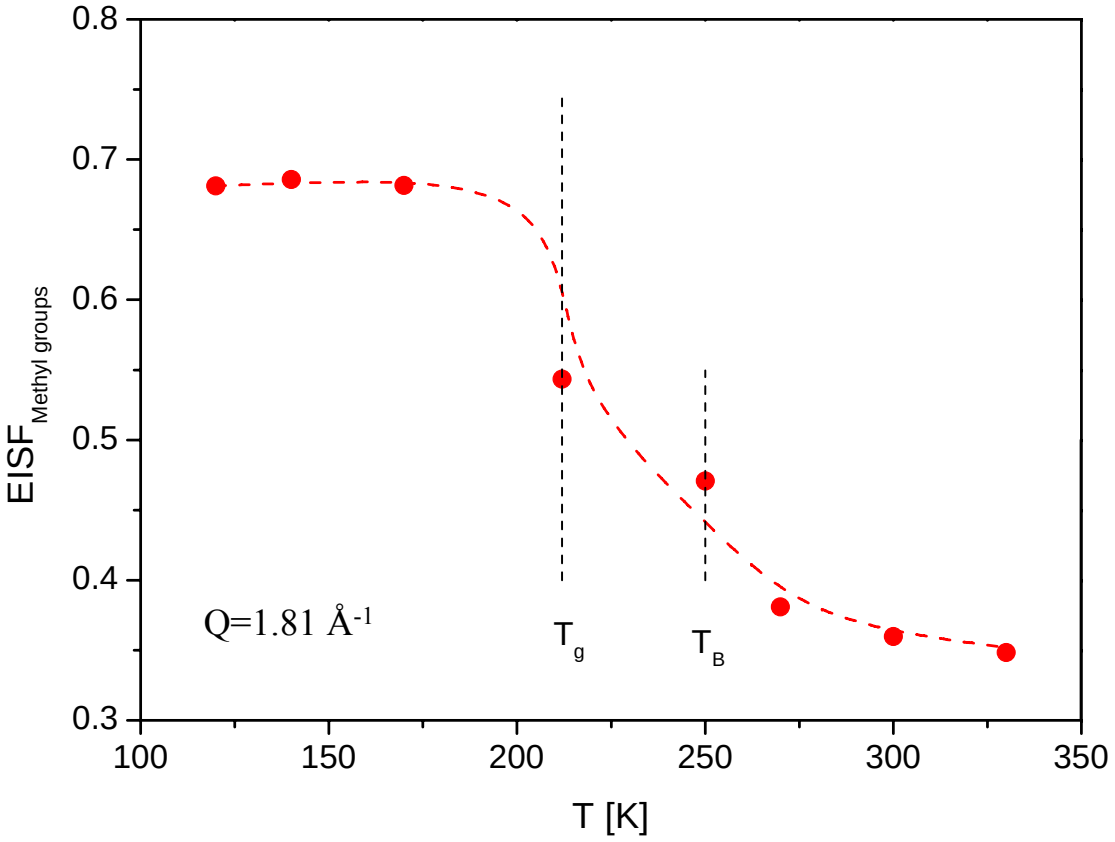
Below T_g the relaxation times are independent of Q

At T_g the relaxation times become Q dependent

… Onset of segmental dynamics

Methyl Group Rotation in PMPS …

…Temperature dependence of the EISF



Additional mobility above T_g

↓

Dynamical Heterogeneities

Islands of Mobility

↓

Higher quasielastic scattering

Phenylring flip ???

Conclusion….

Precise Determination of the molecular dynamics of PMPS over 17 orders of magnitude in time

α-Relaxation (glassy dynamics)

The temperature dependence of the relaxation times shows a crossover from a low to a high temperature range.

Crossover temperature T_B= 250K.

In both ranges the temperature dependence of the relaxation rates is VFT-like with different Vogel temperatures

Also the dielectric strength shows a crossover behavior at the same T_B

The dependence of the relaxation times on the momentum transfer indicates that the molecular dynamics is heterogeneous even above T_B

Methyl group Rotation

The methyl group rotation can be described by jumps in a threefold potential considering the elastic scattering of the frozen chain.

Above T_g the EISF becomes temperature dependent and the relaxation times depends on momentum transfer .

Thanks to the ILL and Research Center Jülich for enabling the neutron experiments.