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BROADBAND DIELECTRIC SPECTROSCOPY - BASICS AND SELECTED APPLICATIONS

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Table of Content

Dielectric Spectroscopy

Maxwell´s Equations:

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

Electric field

Magnetic induction

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

Density of charges

Magnetic field

Dielectric displacement

Current density

Material Equation:

Small electrical field strengths:

$$\vec{D} = \varepsilon^* \varepsilon_0 \vec{E} \longrightarrow \vec{P} = \vec{D} - \vec{D}_0 = (\varepsilon^* - 1)\,\varepsilon_0 \vec{E}$$

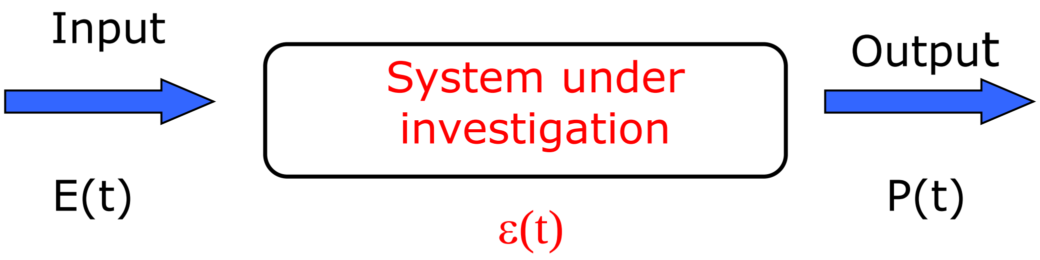
Polarization

Complex Dielectric Function →

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

ε_0 – permittivity of vacuum

Dielectric Spectroscopy



Input

E(t)

System under investigation

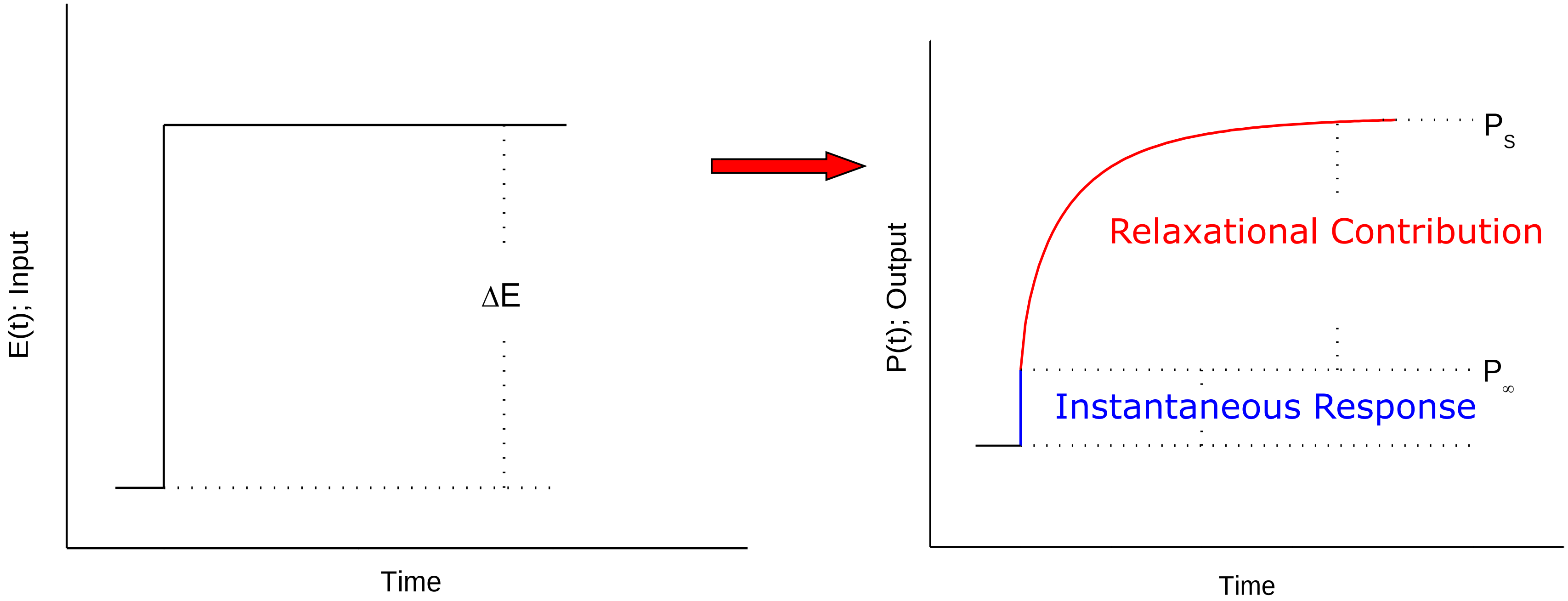
ε(t)

Output

P(t)

Simplest Case : Step-like Input →

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



Dielectric Spectroscopy

Input → System under investigation → Output

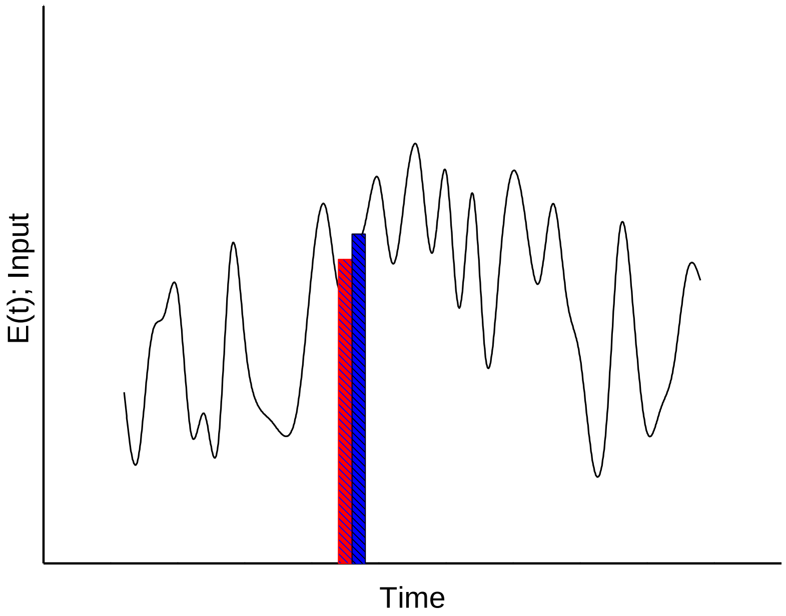
E(t) $\varepsilon(t)$ P(t)

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

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

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

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

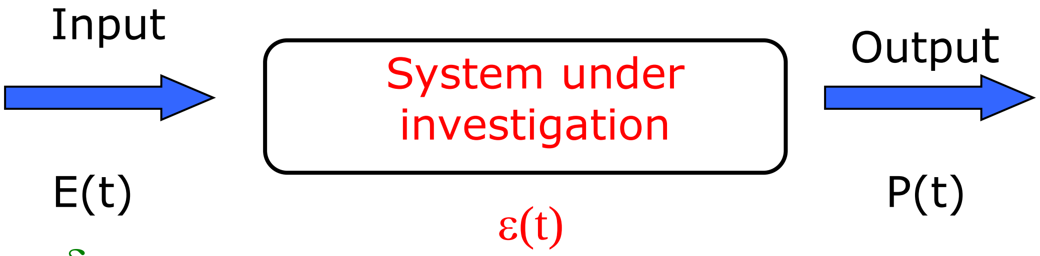


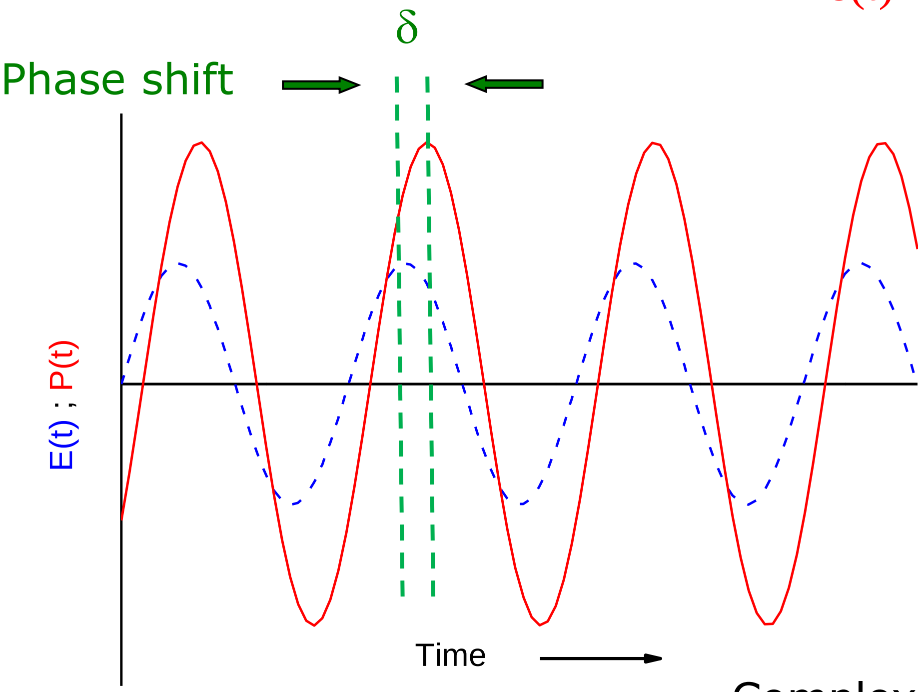
Basics of Linear Response Theory

→ Linearity

→ Causality

Dielectric Spectroscopy





$$E(t) = E_0 \, exp(-i\omega t) = E_0 \, sin(\omega t)$$

ω - Angular Frequency

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

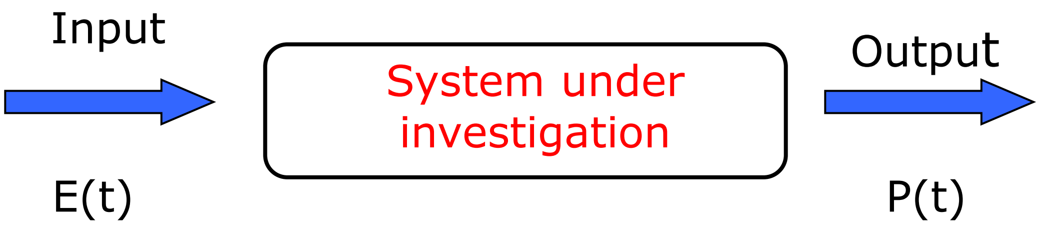
Complex Numbers

Complex Dielectric Function

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

Dielectric Spectroscopy

Phase angle



Input

System under investigation

Output

E(t)

P(t)

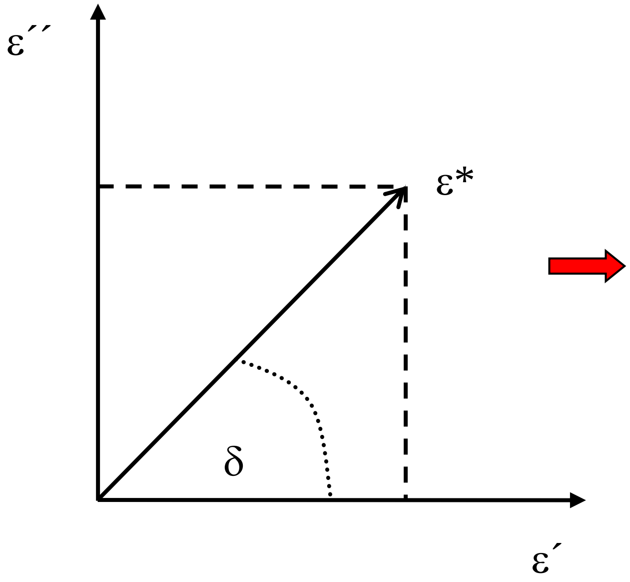
Complex Dielectric Function $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\,\varepsilon''(\omega)$

Real Part (in Phase)

Imaginary or Loss Part

(90 ° Phase shifted)

Complex Plane



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

Dielectric Spectroscopy

Kramers-Kronig relationship

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

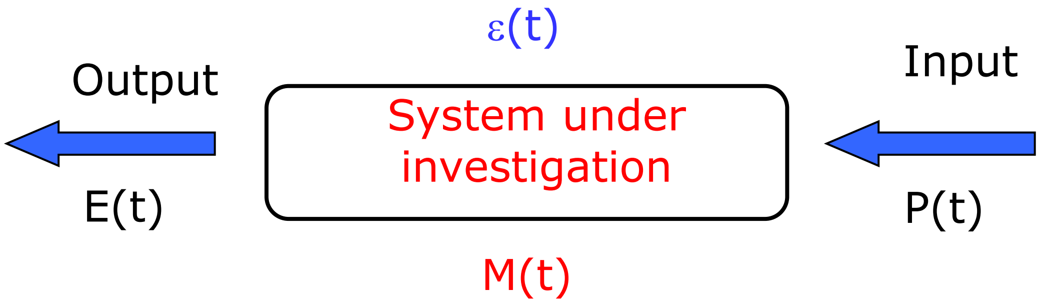
$$\varepsilon'(\omega)-\varepsilon_\infty = \frac{1}{\pi}\oint\frac{\varepsilon''(\xi)}{\xi-\omega}\,d\xi$$

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

Dielectric Spectroscopy

Modulus

$$P(t) = P_{\infty} + \varepsilon_0 \int_{-\infty}^{t} \varepsilon(t-t')\frac{dE(t')}{dt'}dt'$$ → Linear Equation → Can be inverted



ε(t)

Output

E(t)

System under investigation

Input

P(t)

M(t)

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 Spectroscopy

Molecular quantities

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

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

Spectral Density

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

Measure for the frequency distribution of the fluctuations

Fluctuation Dissipation Theorem

→ Links microscopic fluctuations and macroscopic reactions

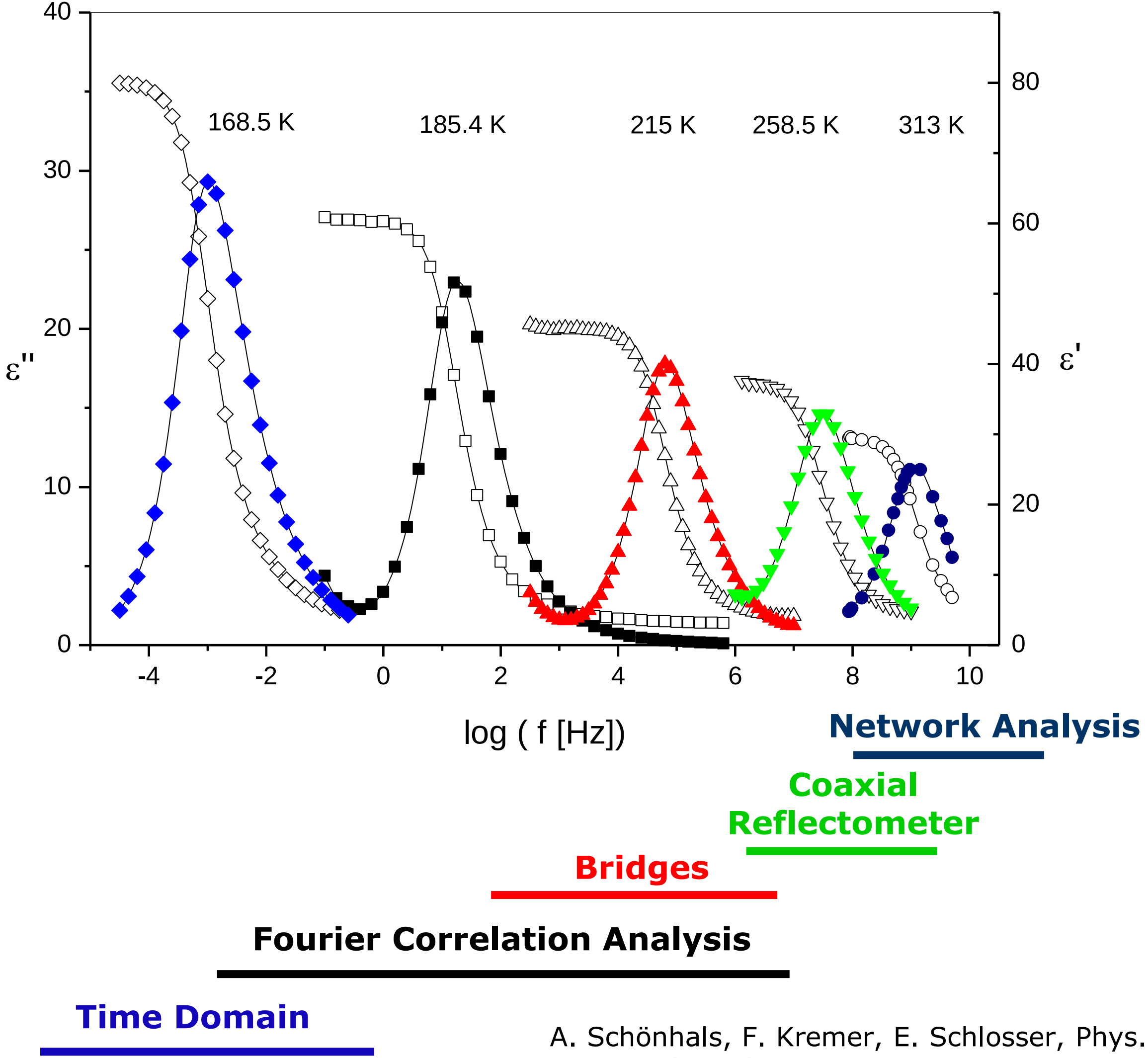
$$\Phi(\tau)=-\frac{1}{kT}\frac{\varepsilon(\tau)-1}{\Delta\varepsilon}$$

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

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

Dielectric Spectroscopy

Propylene glycol



Network Analysis

Coaxial Reflectometer

Bridges

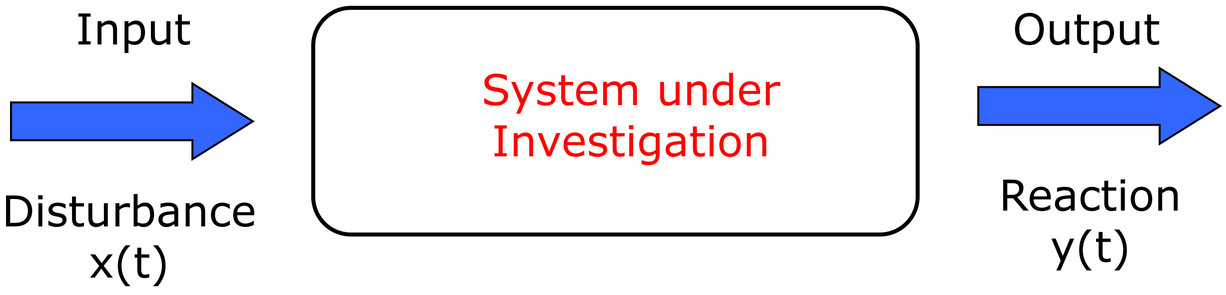
Fourier Correlation Analysis

Time Domain

A. Schönhals, F. Kremer, E. Schlosser, Phys. Rev. Lett. **67**, 999 (1991)

Linear Response Theory

Molecular Motions



Input

Disturbance
x(t)

System under
Investigation

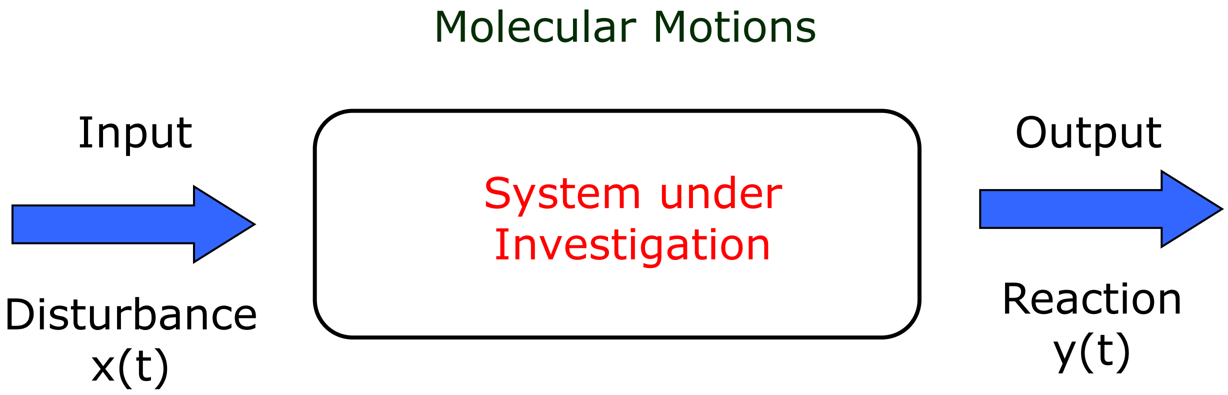
Output

Reaction
y(t)

Material function

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

Linear Response Theory



Molecular Motions

Input

Disturbance
x(t)

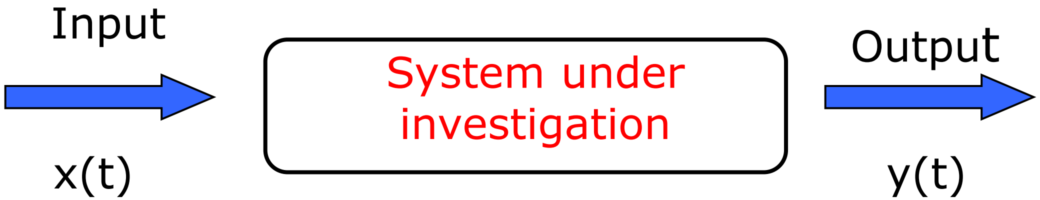
System under
Investigation

Output

Reaction
y(t)

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 Stress	Elastic Compliance

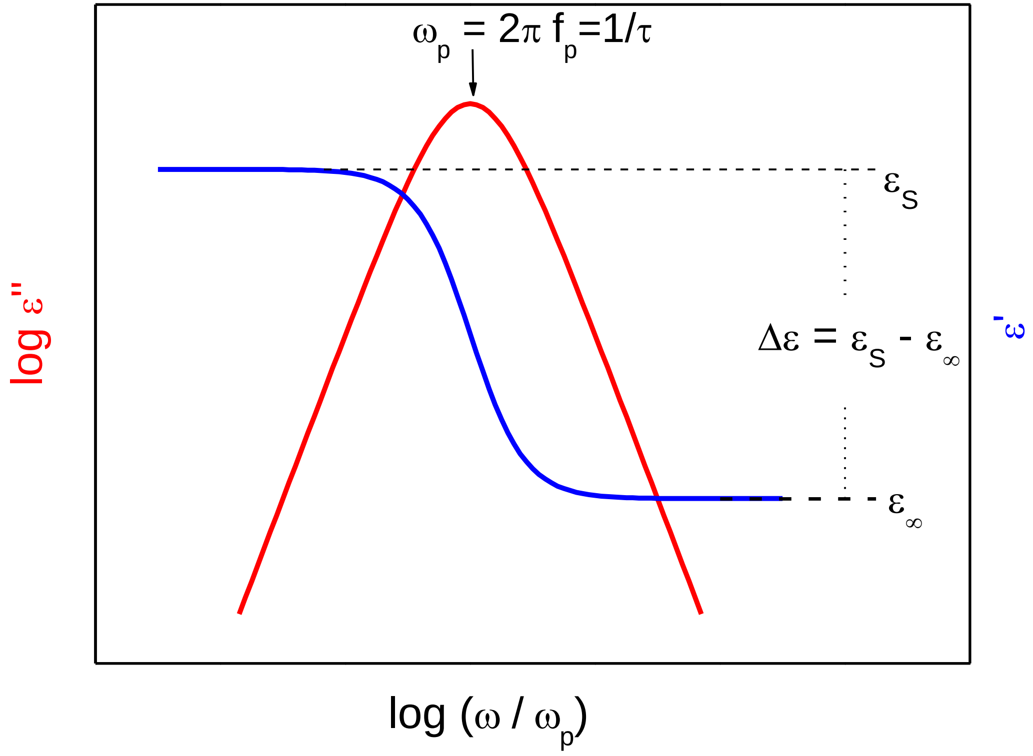
Linear Response Theory



Type of Experiment	**Disturbance $x(t)$**	**Response $y(t)$**	**Compliance $J(t)$ or $J^*(\omega)$**	**Modulus $G(t)$ or $G^*(\omega)$**
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 $G_T(t)$

Dielectric Spectroscopy

Information of a measurement



Three essential measurement information

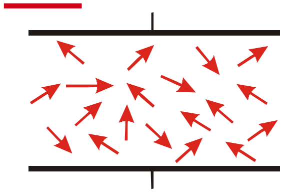
Frequency position f_p

Dielectric relaxation strength $\Delta\varepsilon$

Shape of the relaxation time spectra

Dielectric Spectroscopy

Dielectric relaxation strength

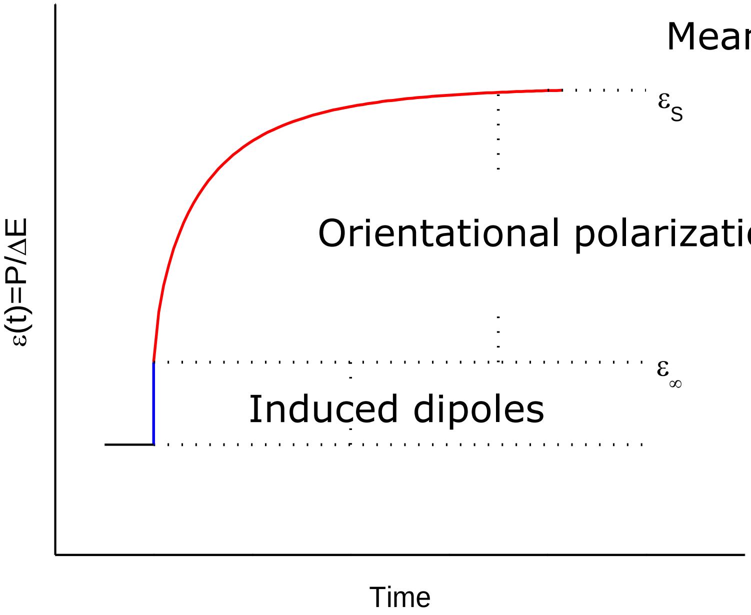


Capacitor with N permanent Dipoles, Dipole Moment μ

Polarization :

$$\vec{P} = \frac{1}{V}\sum \vec{\mu}_i + \vec{P}_\infty = \frac{N}{V}\langle\vec{\mu}\rangle + \vec{P}_\infty$$

Mean Dipole Moment



Mean Dipole Moment:

Counterbalance

$$W_{th} = kT \qquad W_{el} = -\vec{\mu}\cdot\vec{E}$$

Thermal Energy

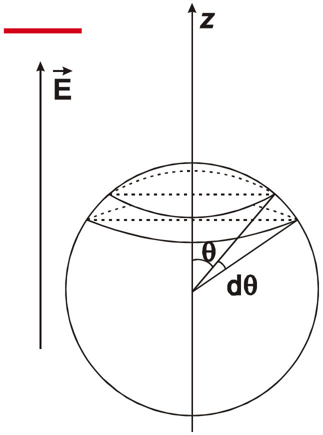
Electrical Energy

$$\langle\vec{\mu}\rangle = \frac{\int_{4\pi} \vec{\mu}\exp\left(\frac{\vec{\mu}\cdot\vec{E}}{kT}\right)d\Omega}{\int_{4\pi} \exp\left(\frac{\vec{\mu}\cdot\vec{E}}{kT}\right)d\Omega}$$

The factor gives the probability that the dipole moment vector has an orientation between Ω and Ω + dΩ.

Dielectric Spectroscopy

Dielectric relaxation strength



Spherical Coordinates:

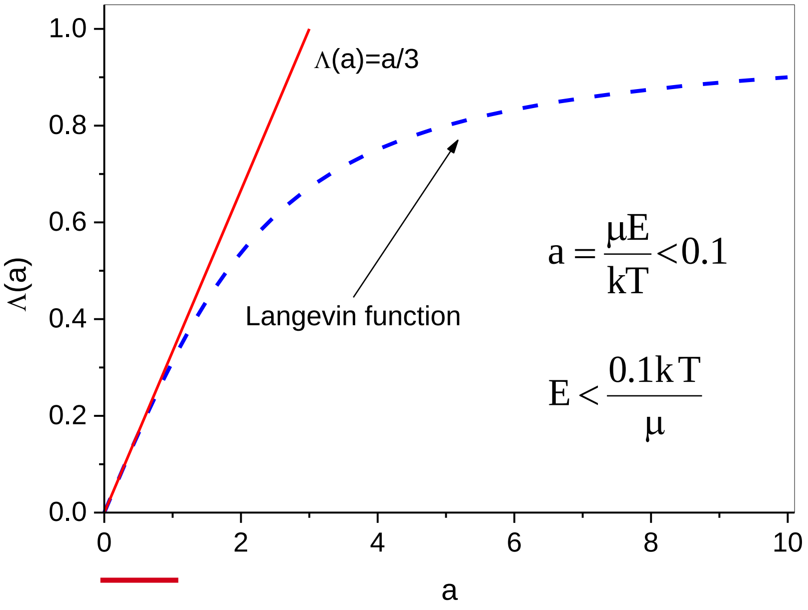
Only the dipole moment component which is parallel to the direction of the electric field contributes to the polarization

$$\langle\mu\rangle = \frac{\int_0^{\pi} \mu \cos\theta \exp\left(\frac{\mu E \cos\theta}{kT}\right) \frac{1}{2}\sin\theta \, d\theta}{\int_0^{\pi} \exp\left(\frac{\mu E \cos\theta}{kT}\right) \frac{1}{2}\sin\theta \, d\theta}$$

x = (μ E cos θ) / (kT)
a = (μ E) / (kT)

$$\langle\cos\theta\rangle = \frac{1}{a}\frac{\int_{-a}^{a} x \exp(x)\, dx}{\int_{-a}^{a} \exp(x)\, dx} = \frac{\exp(a)+\exp(-a)}{\exp(a)-\exp(-a)} - \frac{1}{a} = \Lambda(a)$$

Langevin function



Λ(a)≈a/3 →

$$\langle\mu\rangle = \frac{\mu^2}{3kT}E$$

↓

Debye-Formula →

$$\varepsilon_S - \varepsilon_\infty = \frac{1}{3\varepsilon_0}\frac{\mu^2}{kT}\frac{N}{V}$$

Dielectric Spectroscopy

Dielectric relaxation strength

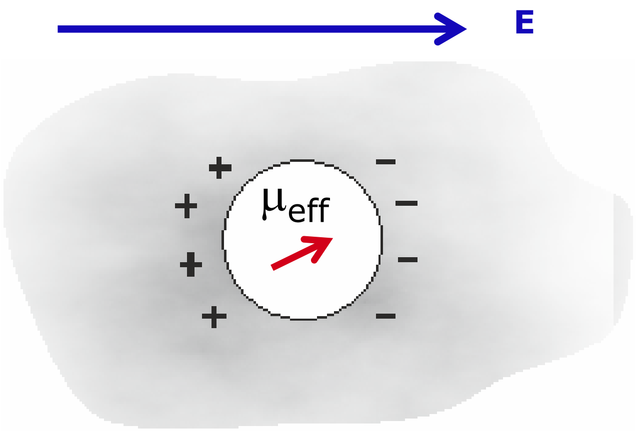
<u>Shielding effects:</u>

Polar Molecules; Onsager – Theory, Reactions Field

$\mu_{eff} = \mu + E_{loc}$

$$\varepsilon_S - \varepsilon_\infty = \frac{1}{3\varepsilon_0} F \frac{\mu^2}{kT} \frac{N}{V} \qquad F = \frac{\varepsilon_S(\varepsilon_\infty + 2)^2}{3(2\varepsilon_S + \varepsilon_\infty)}$$

Onsager Factor F= 2 … 3

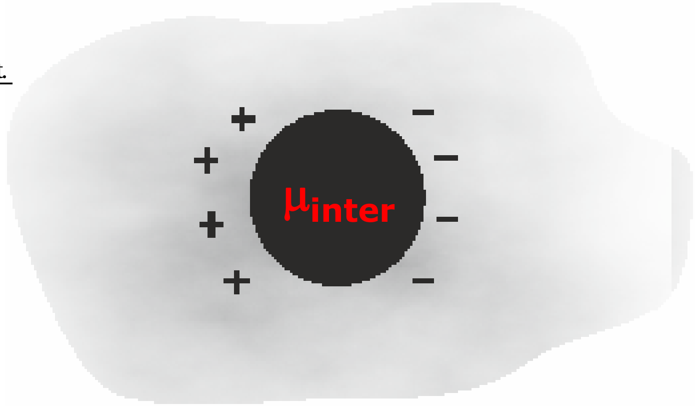


<u>Interaction effects:</u>

$$\varepsilon_S - \varepsilon_\infty = \frac{1}{3\varepsilon_0} gF \frac{\mu^2}{kT} \frac{N}{V} \qquad g = 1 + \frac{<\sum_i \sum_{i<j} \mu_i \mu_j>}{N\mu^2} = \frac{\mu^2_{Interact.}}{\mu^2}$$

Kirkwood / Fröhlich Correlation Factor g= 0.5 … 5

z nearest neighbors: $g = 1 + z < \cos\Psi >$



Dielectric Spectroscopy

Dynamics - Debye model

Dynamics is due to the dipole – dipole correlation function

$$\Phi(t)=\frac{\sum_i<\mu_i(0)\mu_i(t)>+2\sum_i\sum_{i<j}<\mu_i(0)\mu_j(t)>}{<(\sum_i\mu_i)^2>}$$

Debye model: Change of the polarization is proportional to the actual value

$$\frac{d\vec{P}(t)}{dt}=-\frac{1}{\tau_D}\vec{P}(t)$$

Time domain

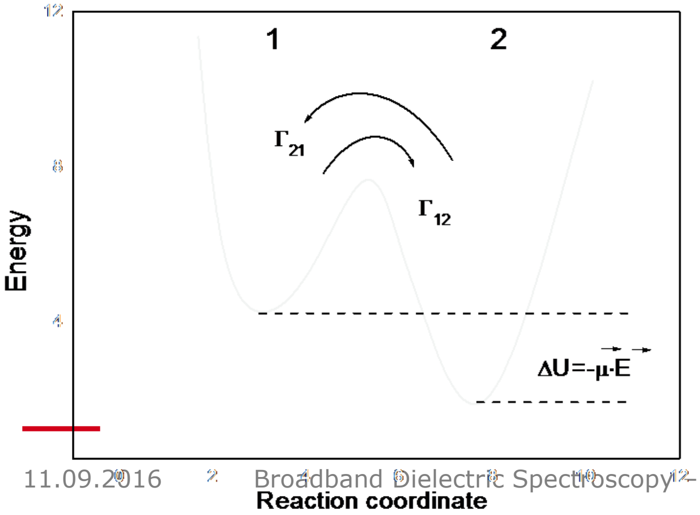
$$\Phi(t)=\exp\left[-\frac{t}{\tau_D}\right]$$

Frequency domain

$$\varepsilon^*(\omega)=\varepsilon_\infty+\frac{\Delta\varepsilon}{1+i\omega\tau_D}\qquad \varepsilon'=\varepsilon_\infty+\frac{\Delta\varepsilon}{1+(\omega\tau_D)^2}\qquad \varepsilon''=\Delta\varepsilon\frac{\omega\tau_D}{1+(\omega\tau_D)^2}$$

Double Potential Model

$$\frac{d\vec{P}}{dt}=\vec{\mu}\left[\frac{dn_1}{dt}-\frac{dn_2}{dt}\right]=-2\vec{\mu}\Gamma[n_1-n_2]=-2\Gamma\vec{P}(t)$$



Rotational Diffusion Model

A rigid isolated fluctuating dipole is regarded in viscous media under the influence of a stochastic force

$$\frac{\partial f(\vec{r},t)}{\partial t}=D_{Rot}\,\Delta\left[f(\vec{r},t)-\frac{\vec{\mu}\vec{E}(t)}{kT}f(\vec{r},t)\right]$$

$$\langle P_m(\cos\theta(0))P_m(\cos\theta(t))\rangle=\exp(-m(m+1)D_{Rot}t)$$

Dielectric Spectroscopy

Model functions

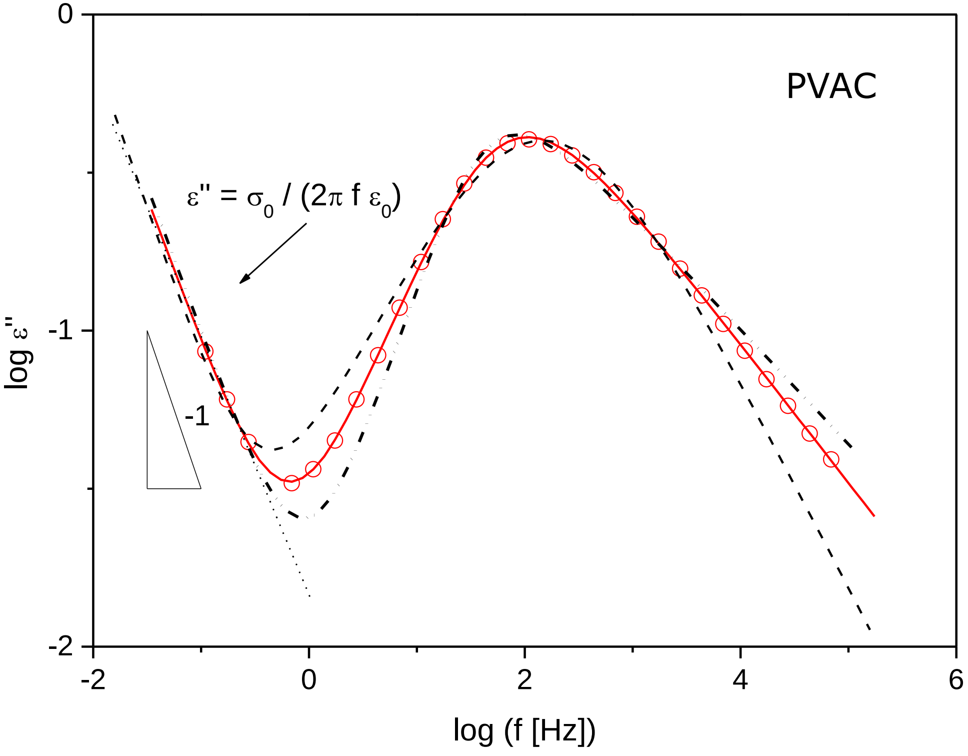
In most cases the half width of measured loss peaks is much broader than predicted by Debye equation and in addition their shapes are asymmetric.

Debye function:	$\varepsilon^*(\omega) = \varepsilon_\infty + \dfrac{\Delta\varepsilon}{1+i\omega\tau_D}$		symmetric
Cole/Cole function:	$\varepsilon^*_{CC}(\omega) = \varepsilon_\infty + \dfrac{\Delta\varepsilon}{1+(i\omega\tau_{CC})^\beta}$	$0<\beta\leq 1$	symmetric broadening
Cole/Davidson function:	$\varepsilon^*_{CD}(\omega) = \varepsilon_\infty + \dfrac{\Delta\varepsilon}{(1+i\omega\tau_{CD})^\gamma}$	$0<\gamma\leq 1$	asymmetric broadening
Havriliak/Negami function:	$\varepsilon^*_{HN}(\omega) = \varepsilon_\infty + \dfrac{\Delta\varepsilon}{(1+(i\omega\tau_{HN})^\beta)^\gamma}$	$0<\beta;\ \beta\gamma\leq 1$	asymmetric and symmetric broadening

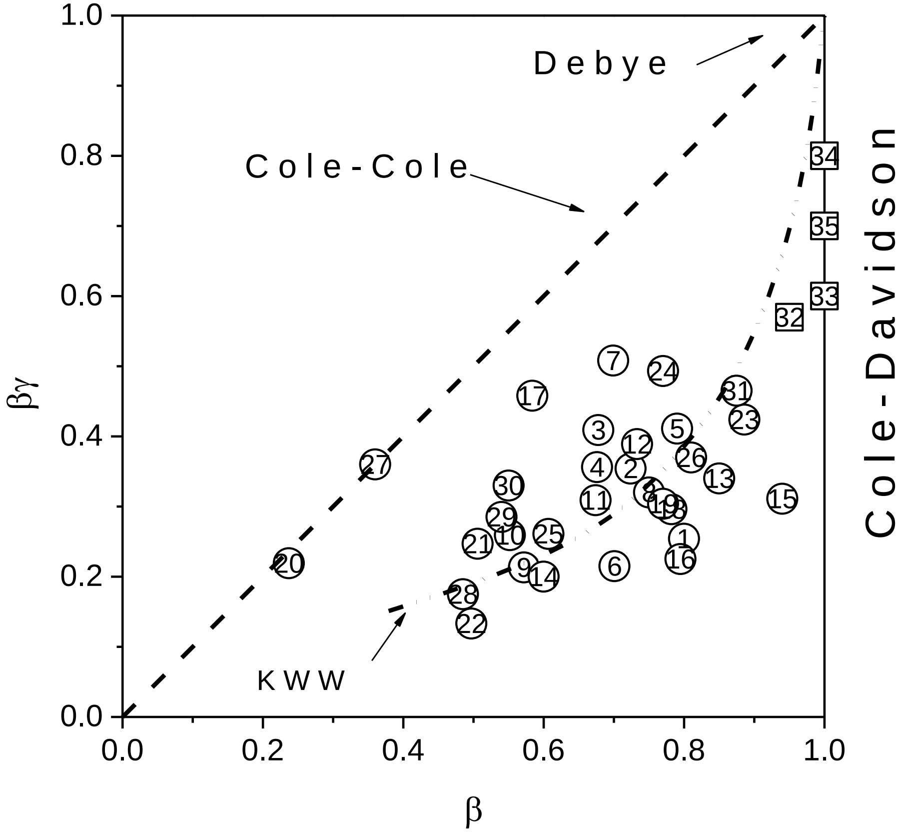
Dielectric Spectroscopy

Data Analysis

$$\sum_i w_i \left[\varepsilon^*_i - \varepsilon^*_{Model}(f_i)\right]^2 \longrightarrow \min$$



Most general function is the formula of Havriliak / Negmai

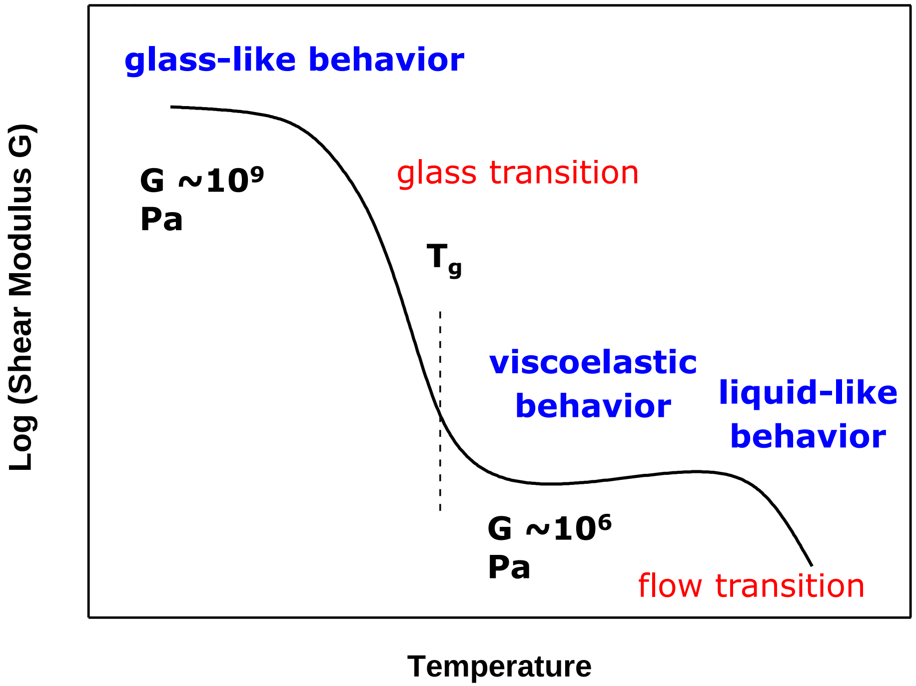


Overview about the dynamics of polymers

Polymers are complex systems

For an isolated macromolecule a large number of atoms (100 to 1000 000) are covalently bonded.

Shear modulus vs. Temperature



Almost unlimited number of conformations in space and time.

Most properties depend on this large conformation.

Chain flexibility

Mean End-to-End vector (shape)

Mean Square dipole moment

… and many more

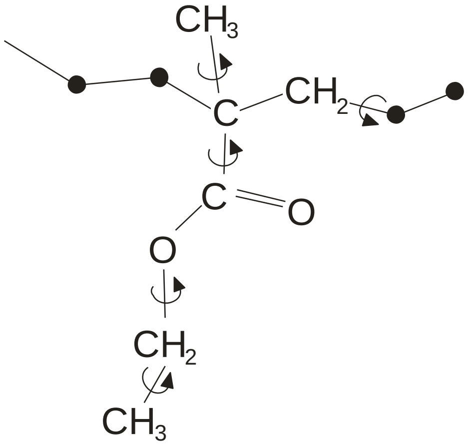
Behavior is complex ….

… and related to the molecular mobility

Molecular dynamic in polymers

“Glassy State”

ξ_{Local}



Local Motion

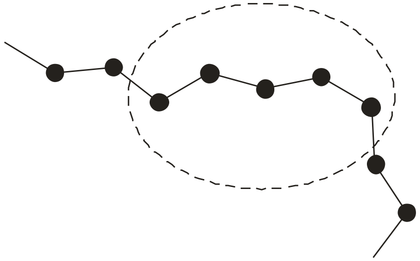
Localized bond rotations

Fluctuations in a side group

$\xi_{\text{LOCAL}} < 1$ nm

Glass Transition,
α-Relaxation

ξ_{Seg}

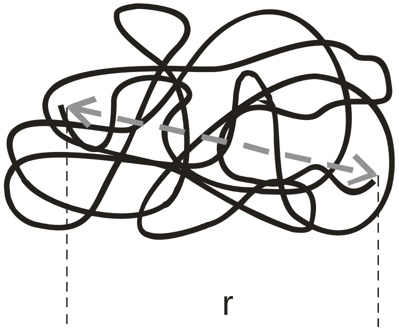


Segmental Motion

$\xi_{\text{SEG}} \sim 1 .. 2$ nm

Flow Transition

ξ_{Chain}



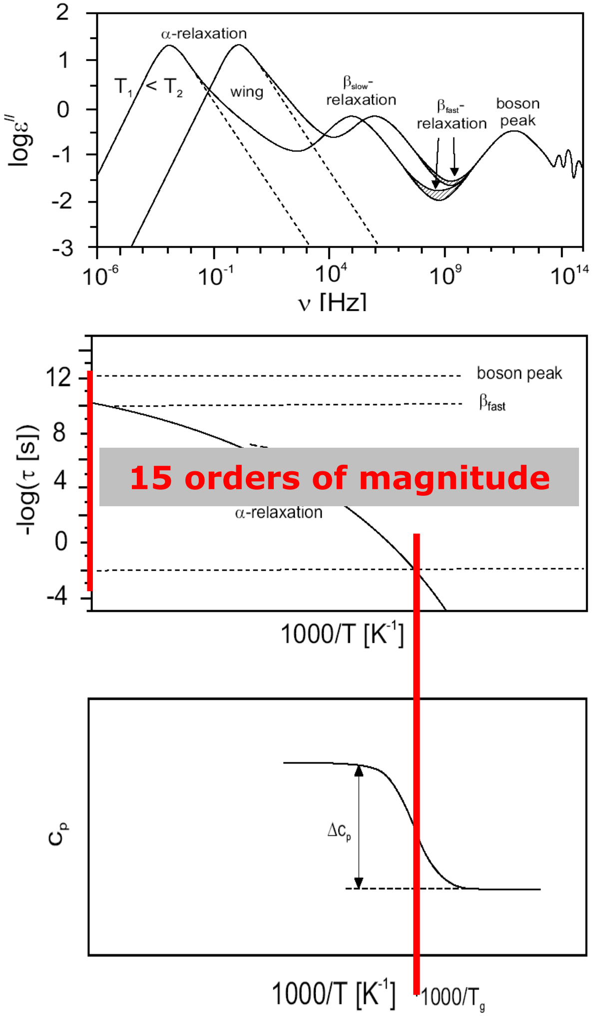
Chain Motion

$\xi_{\text{Chain}} <= r$

Scaling of segmental dynamics

Dynamic glass transition

Dynamics in glass-forming materials



Dynamic Response

α-relaxation, dynamic glass transition

β_{Slow}-relaxation

β_{Fast}-relaxation

Boson-peak

Activation Diagram

β_{Slow}-relaxation

$$\nu(T) = \nu_\infty \exp\left(\frac{-E_A}{kT}\right)$$

α-relaxation

$$\nu(T) = \frac{1}{2\pi\tau(T)} = \nu_\infty \exp\left[\frac{-DT_0}{T-T_0}\right]$$

Thermal Response

The temperature dependence of the dynamical relaxation times correlates with the glass transition temperature at ca. 10^2 s.

Dynamics in glass-forming materials

- Non-Debye behavior of the Relaxation function

  $$\sim \exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right)$$ KWW-function

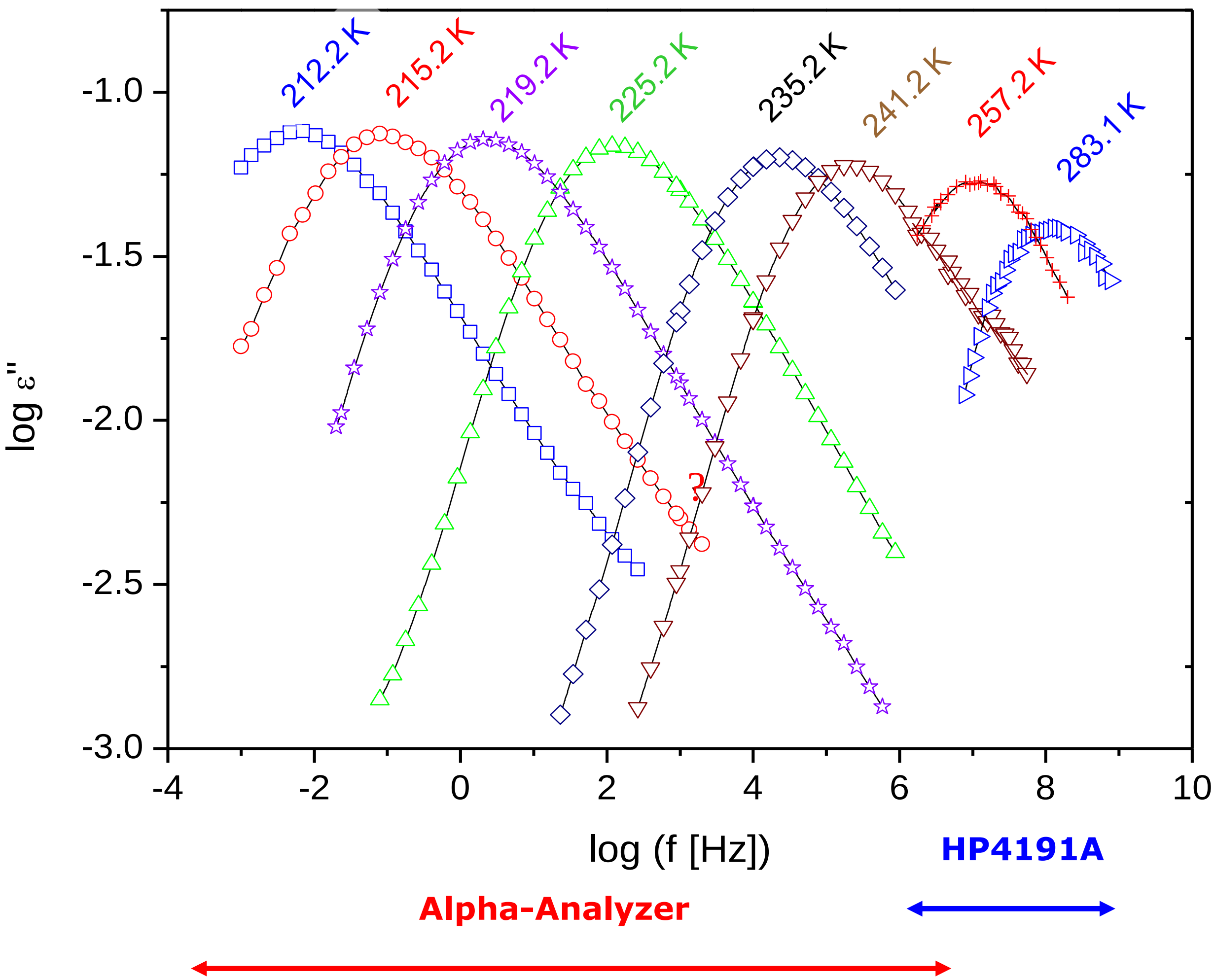
- Crossover Phenomena form a high to a low temperature regime at $T_B \sim 1.2 .. 1.3\, T_g$

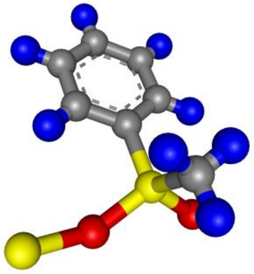
- Formation of dynamic heterogeneities below T_B

  Size : few nanometers

Dielectric Spectroscopy

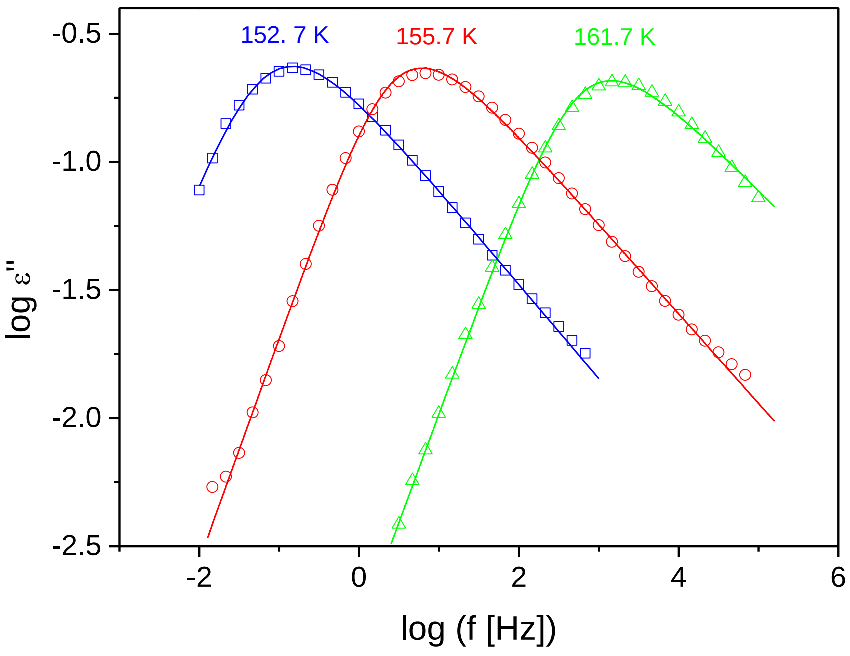
Poly(methyl phenyl siloxane) (PMPS) ; M_w=1000 g/mol



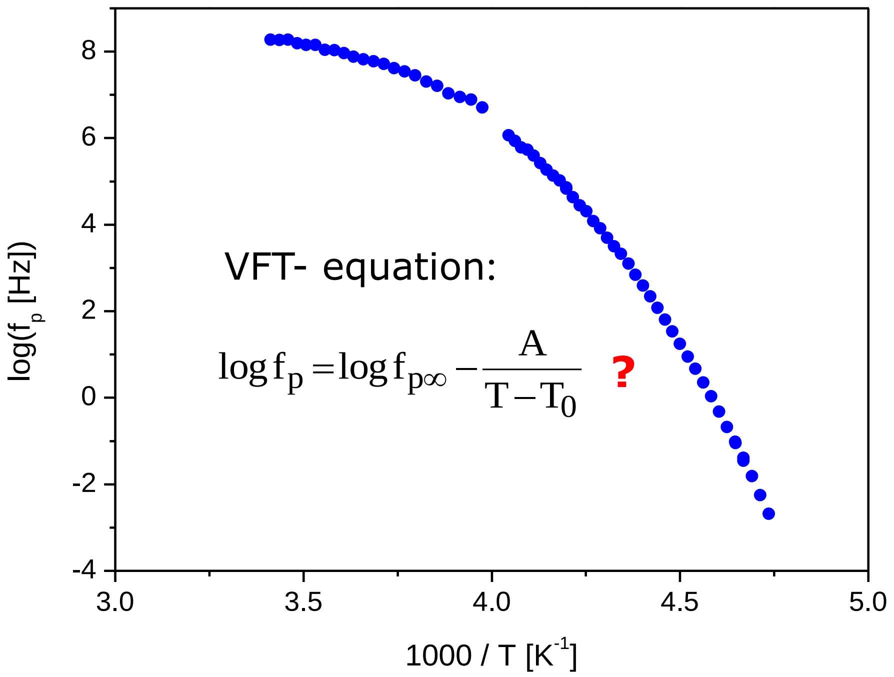


Dielectric Spectroscopy

Poly(methyl phenyl siloxane) (PMPS) ; M_w=1000 g/mol



$$\varepsilon^*_{HN}(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1+(i\omega\tau_{HN})^{\beta})^{\gamma}}$$



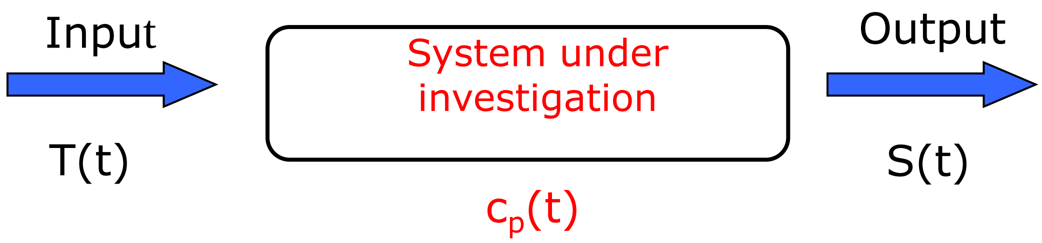
VFT- equation:

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

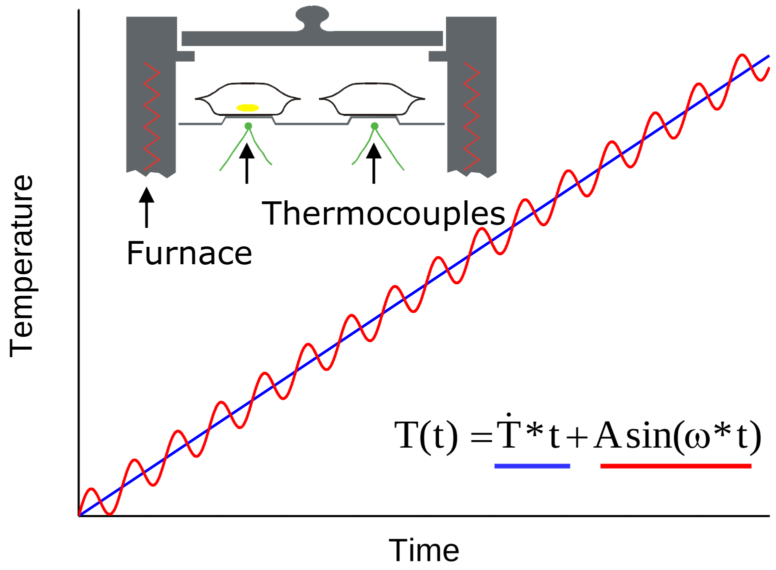
Mean Relaxation Rate f_p

Dielectric Strength $\Delta\varepsilon$

Specific Heat Spectroscopy



Temperature Modulated DSC



$$T(t) = \underline{\dot{T} * t} + \underline{A \sin(\omega * t)}$$

The modulated temperature results in a modulated heat flow

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

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

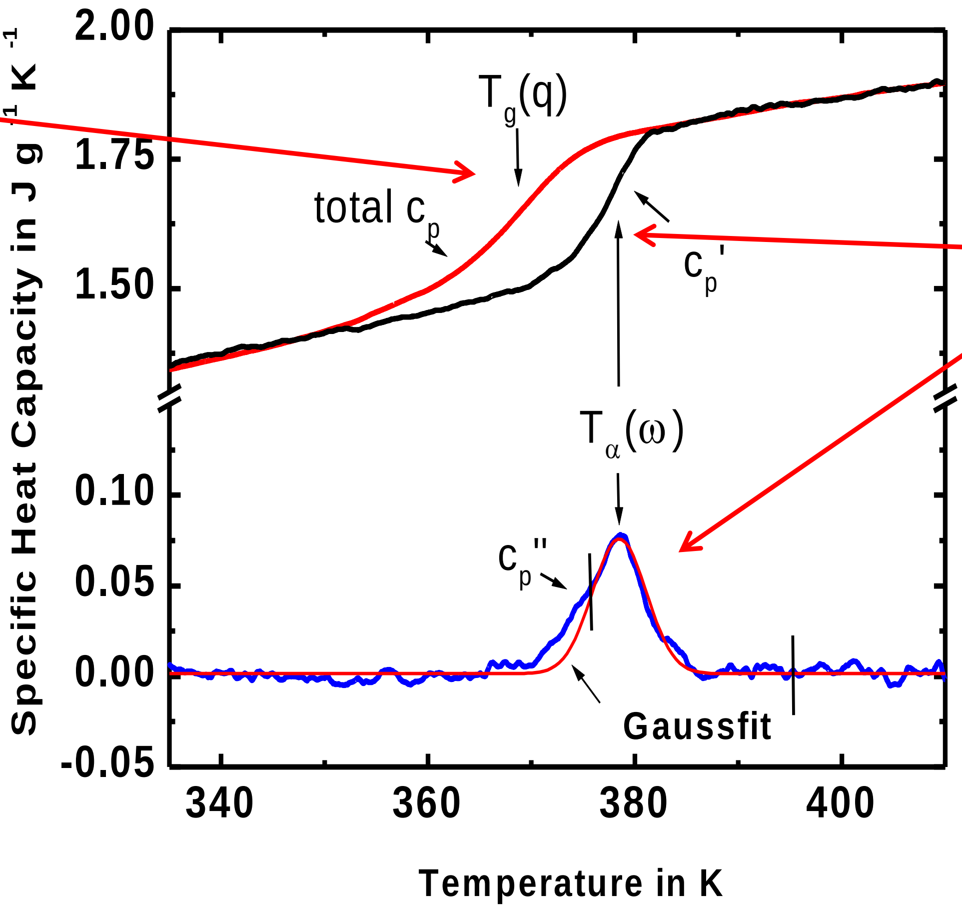
Ch. Schick, Temperature Modulated Differential Scanning Calorimetry - Basics and Applications to Polymers in Handbook of Thermal Analysis and Calorimetry edited by S. Cheng (Elsevier, p 713. Vol. 3, 2002).

Specific Heat Spectroscopy

Example - Polystyrene

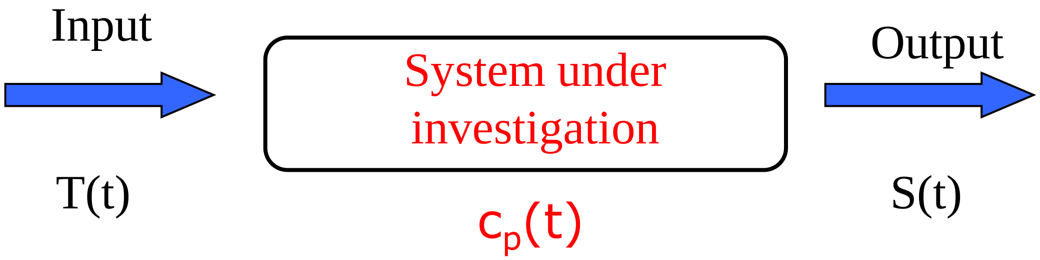
Due to heating rate

Due to modulation



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

Specific Heat Spectroscopy



Input

T(t)

System under investigation

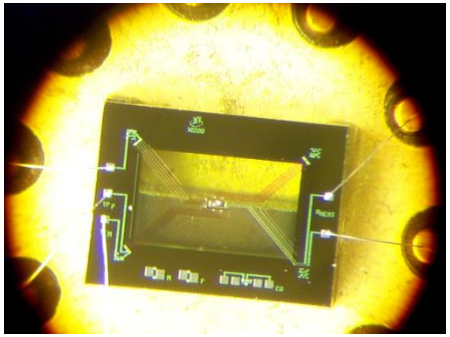
$c_p(t)$

Output

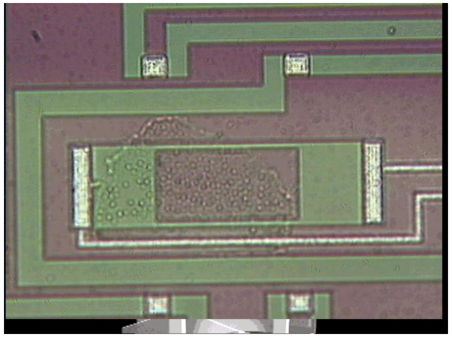
S(t)

AC Chip calorimetry → Pressure gauge, Xsensor Integration

10 mm



2 mm

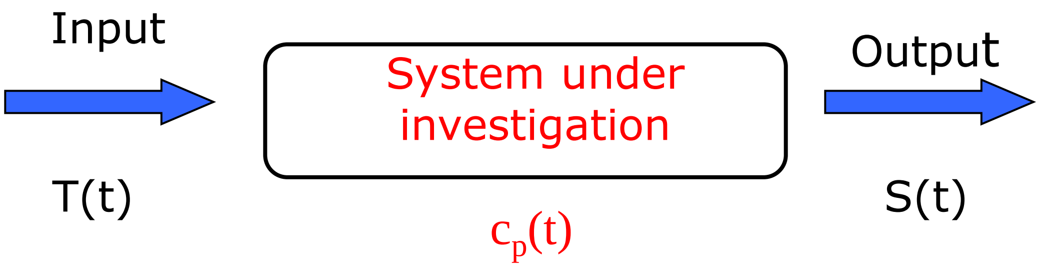


0.1 mm

Fast heating and cooling

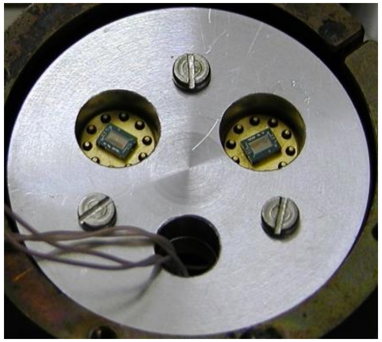
H. Huth, A. Minakov, Ch. Schick, Polym. Sci. B Polym. Phys. **44**, 2996 (2006).

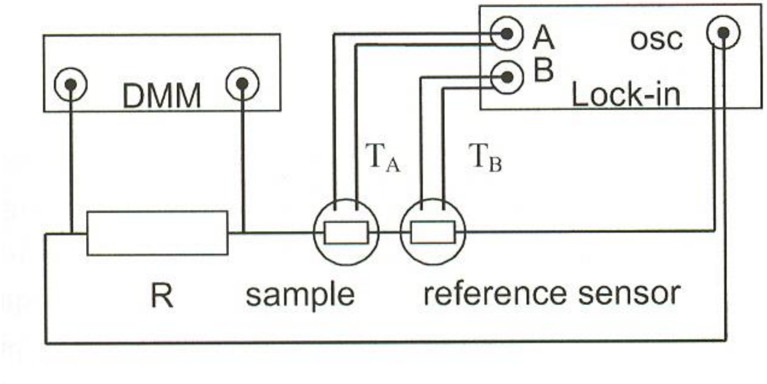
Specific Heat Spectroscopy



Input → System under investigation → Output

T(t) — $c_p(t)$ — S(t)





→ ΔU^*

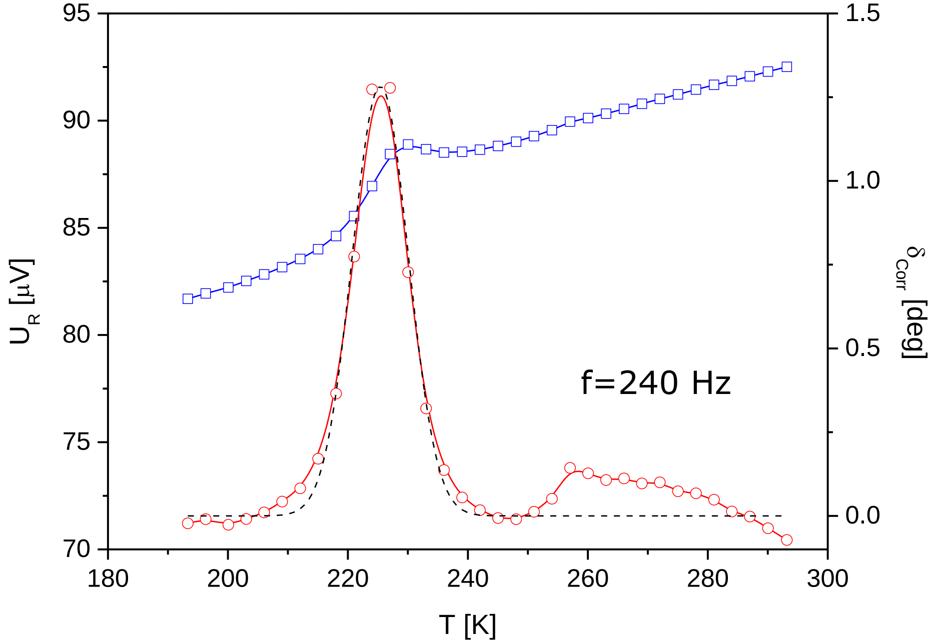
Complex differential Voltage

Differential setup → Increase of sensitivity

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

Specific Heat Spectroscopy

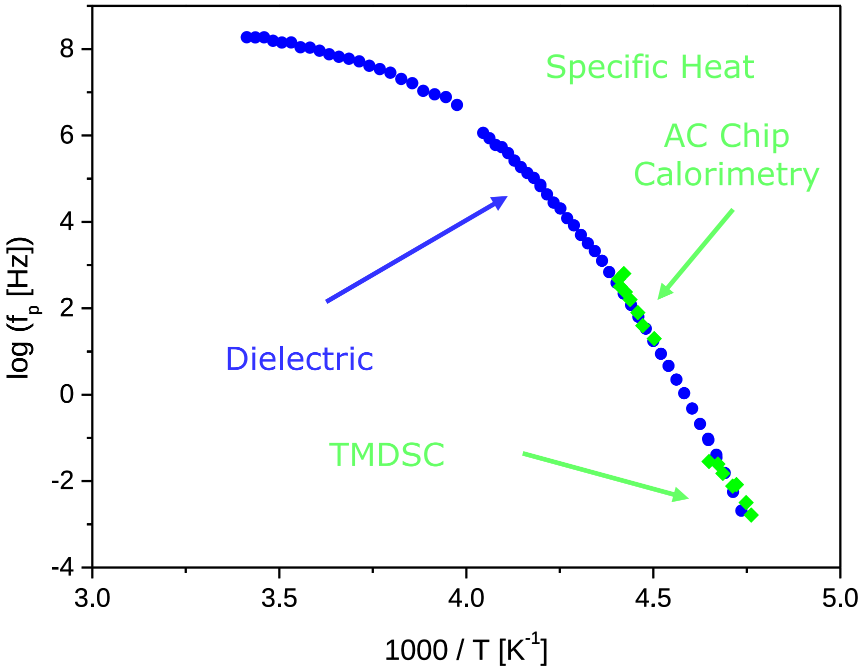
Example - PMPS



Frequency range : 10 Hz …. 5000 Hz

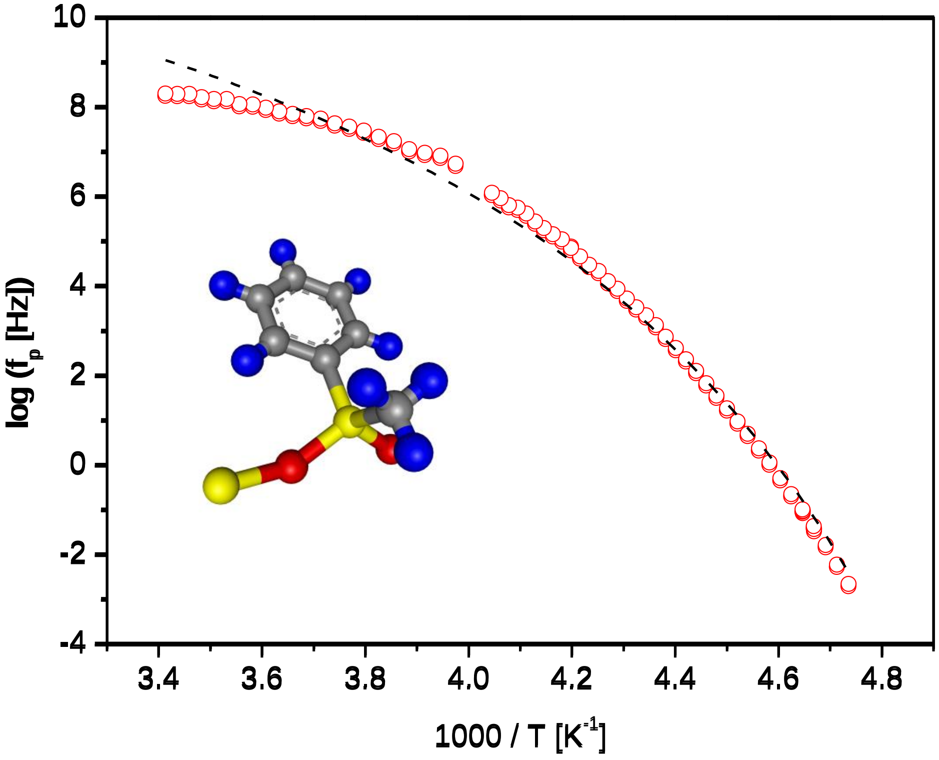
Both methods measure the same process….

… Glassy dynamics of PMPS



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

Analysis of the temperature dependence of the relaxation rate



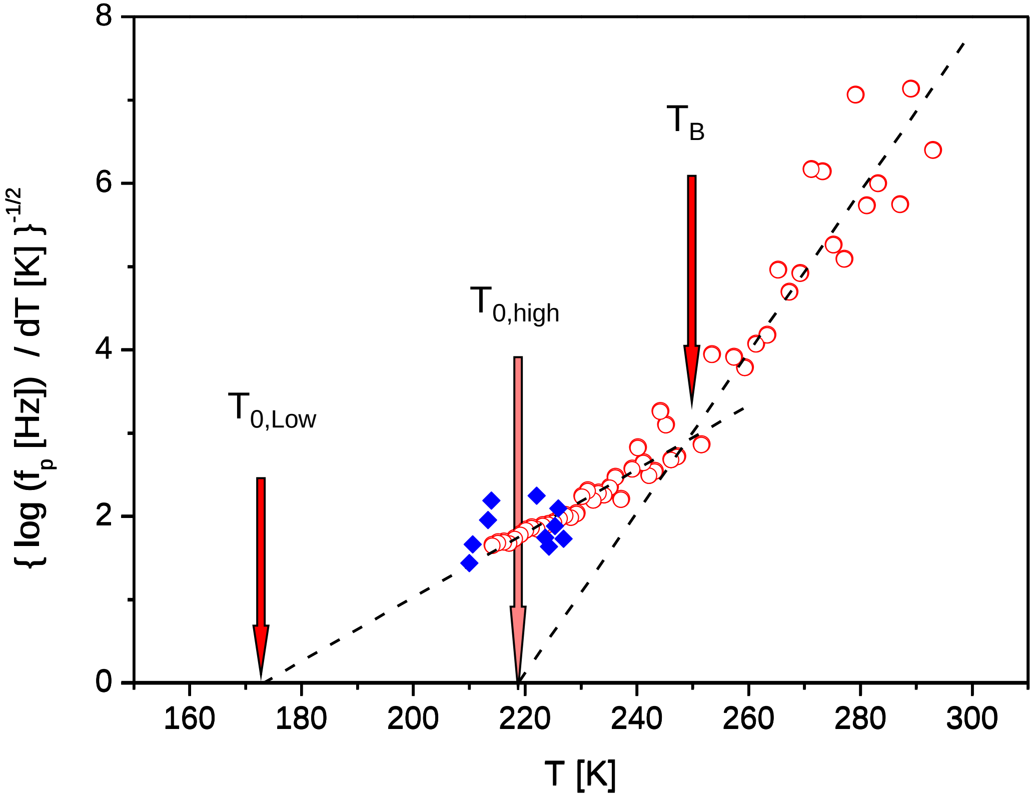
… cannot be described by the VFT-equation in the whole temperature range

VFT- equation: $\log f_p = \log f_{p\infty} - \dfrac{A}{T - T_0}$

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

Straight Line, $T_0 > 0$

Analysis of the temperature dependence of the relaxation rate



red : dielectric data

blue: thermal data

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

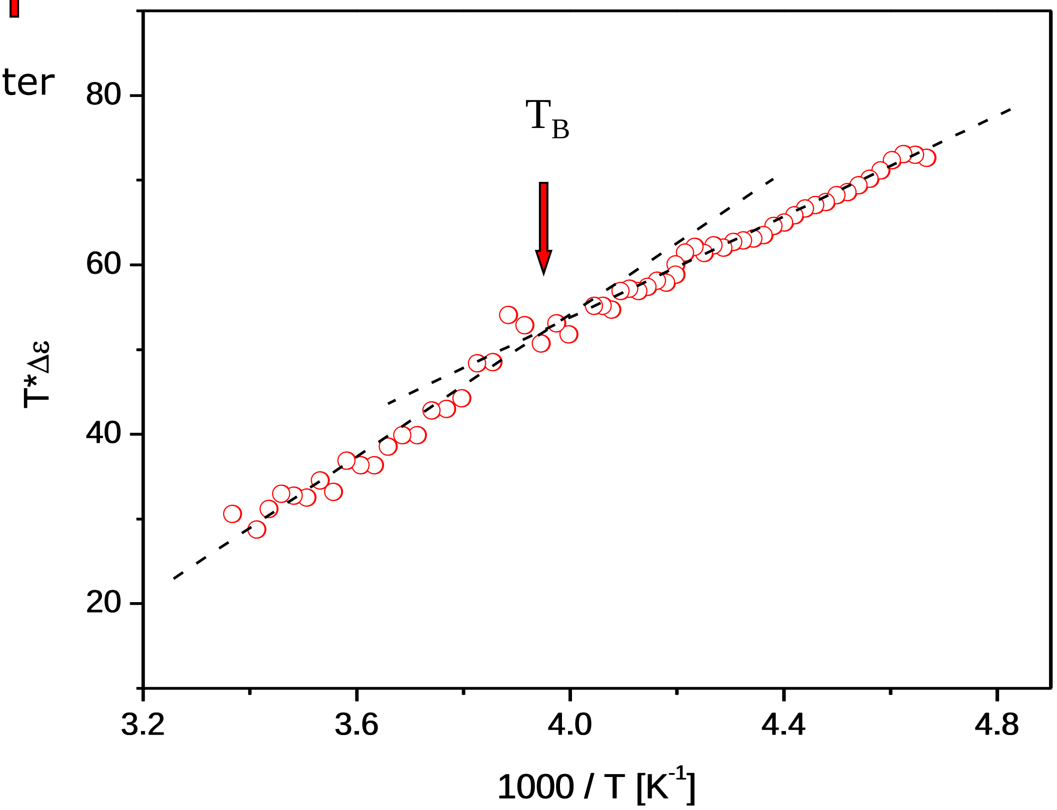
  $T_B = 250$ K
- Thermal and dielectric data have the same temperature dependence

Analysis of the temperature dependence of the dielectric 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

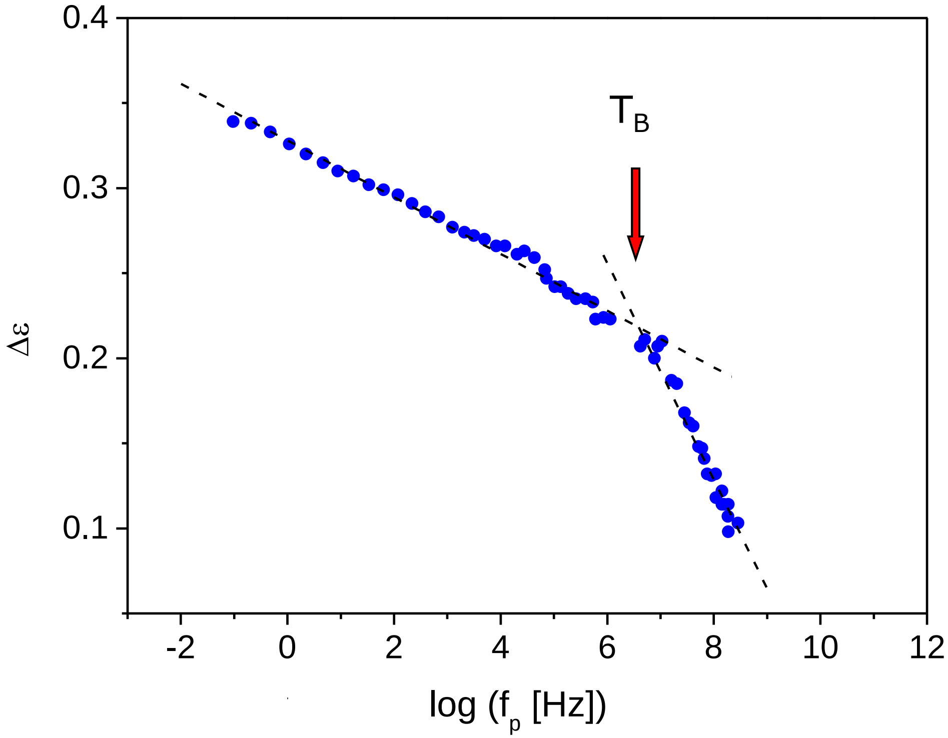
Analysis of the temperature dependence of the dielectric strength

The change in the temperature dependence of Δε is not much pronounced

Plot of Δε vs. log f_p

Sharp transition from a low temperature to a high temperature branch

The crossover frequency corresponds to T_B



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

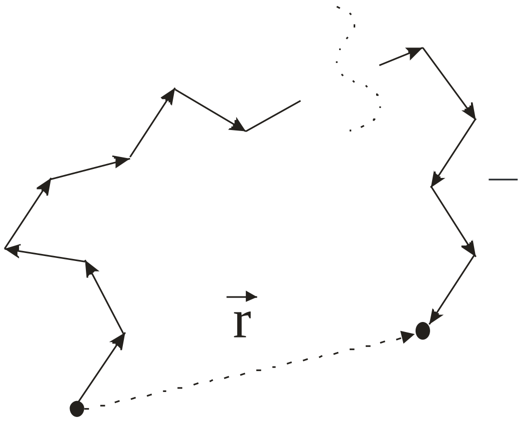
Chain dynamics

Normal mode

Dipole moments of polymers

Type A

Chain Dynamics



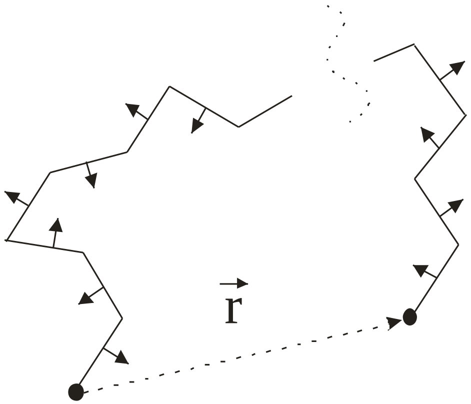
Dipole Moment
"Parallel" to the Chain

Poly(cis-1,4-isoprene)

Poly(propylene glycol)

Type B

Segmental Dynamics



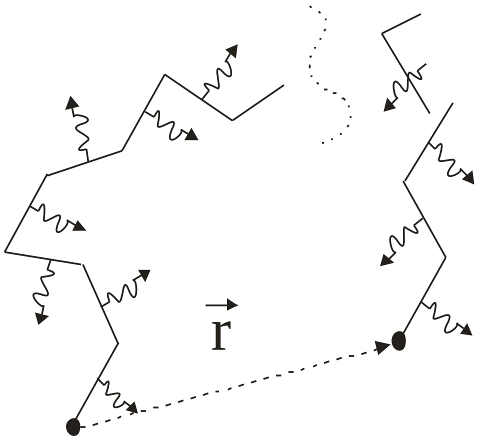
Dipole Moment
"Perpendicular" to the Chain

Polystyrene

Poly(vinyl chloride)

Poly(methyl phenyl siloxane)

Type C



Dipole Moment in a Side Group

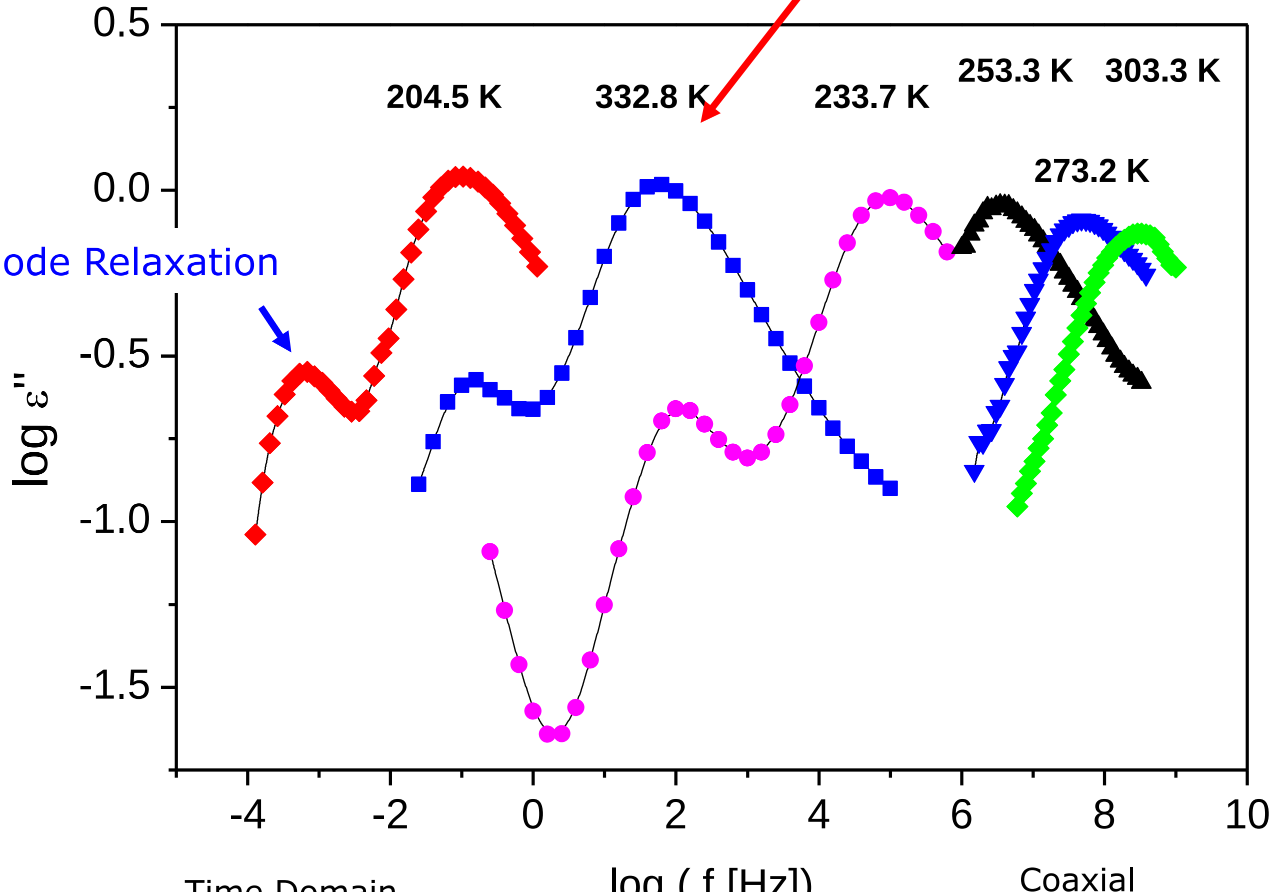
Poly(methyl methacarylate)

Dielectric Spectroscopy

Polypropylene glycol; M_w=4000 g/mol

Dynamic Glass Transition,
α- relaxation

Normal Mode Relaxation

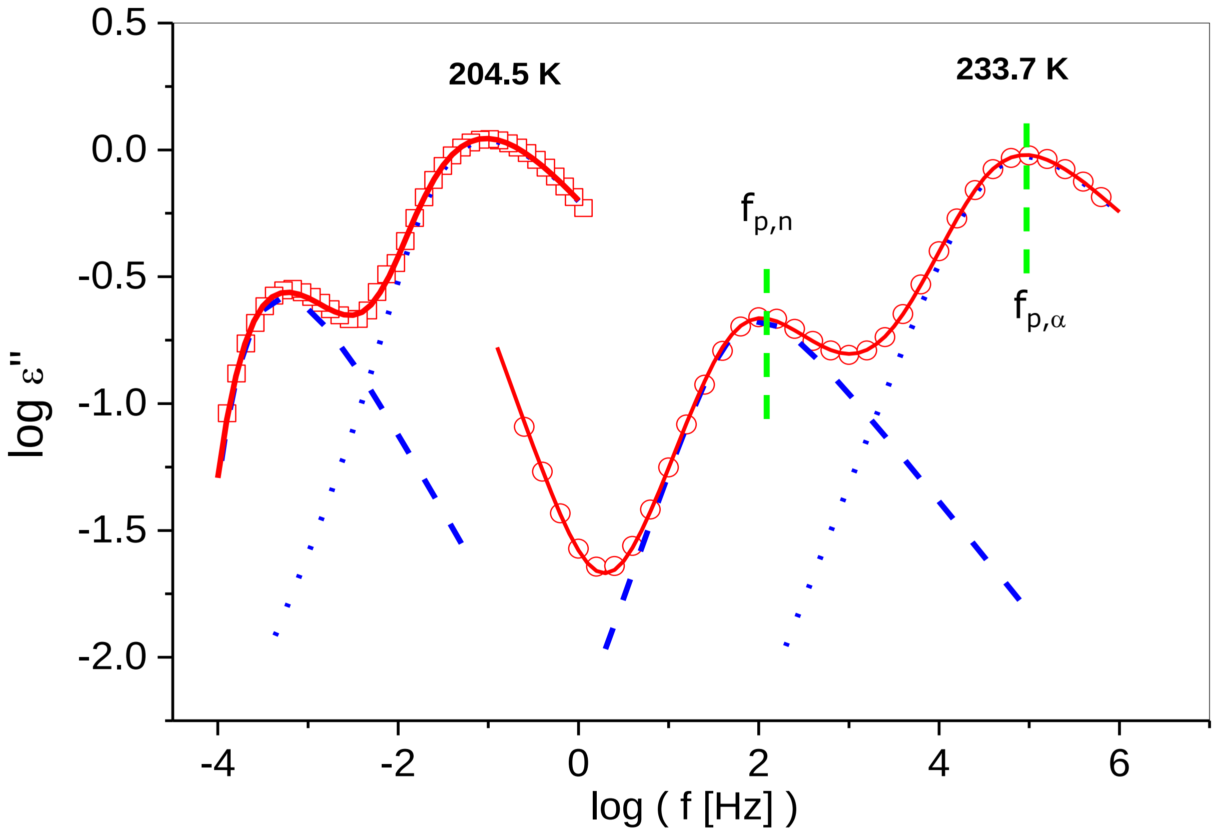


Time Domain Spectrometer

Frequency Response Analysis

Coaxial Reflectometer

Data analysis



The two model function of Havriliak and Negami are fitted to the data.

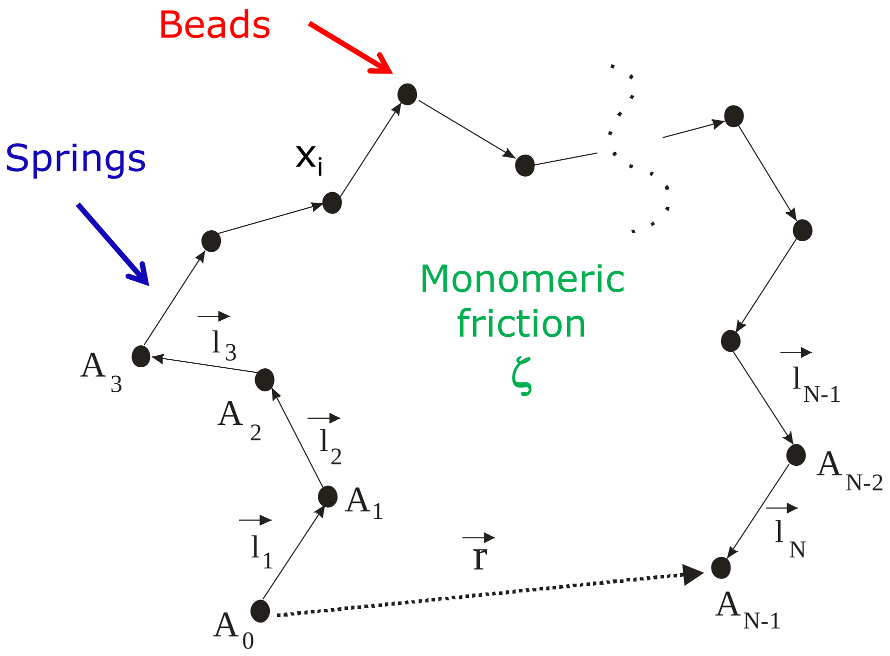
Relaxation rate f_p

Dielectric strength $\Delta\varepsilon$

… for each process

Theory of chain dynamics

Rouse motion, Reptation



Rouse Model:

$$\zeta \frac{dx_i}{dt} + 3\,kT\,(2x_i - x_{i-1} - x_{i+1}) = 0$$

Friction

Chain connectivity (Entropy springs)

Solution:

$$\Phi(t) = \frac{<\vec{r}(0)\,\vec{r}(t)>}{<r^2>} = \frac{8}{\pi^2} \sum_{p=1}^{N} \frac{1}{p^2} \exp\left(-t/\tau_p\right)$$

Short chains:

$$\tau_p = \frac{\zeta\, N^2 b^2}{3\pi^2 kT\, p^2} \sim M^2 \;,\; p = 1, 3 \ldots$$

Long chains (Entanglements):

$$\tau_p = \frac{\zeta\, N^3 b^4}{\pi^2 kT\, a^2 p^2} \sim M^3$$

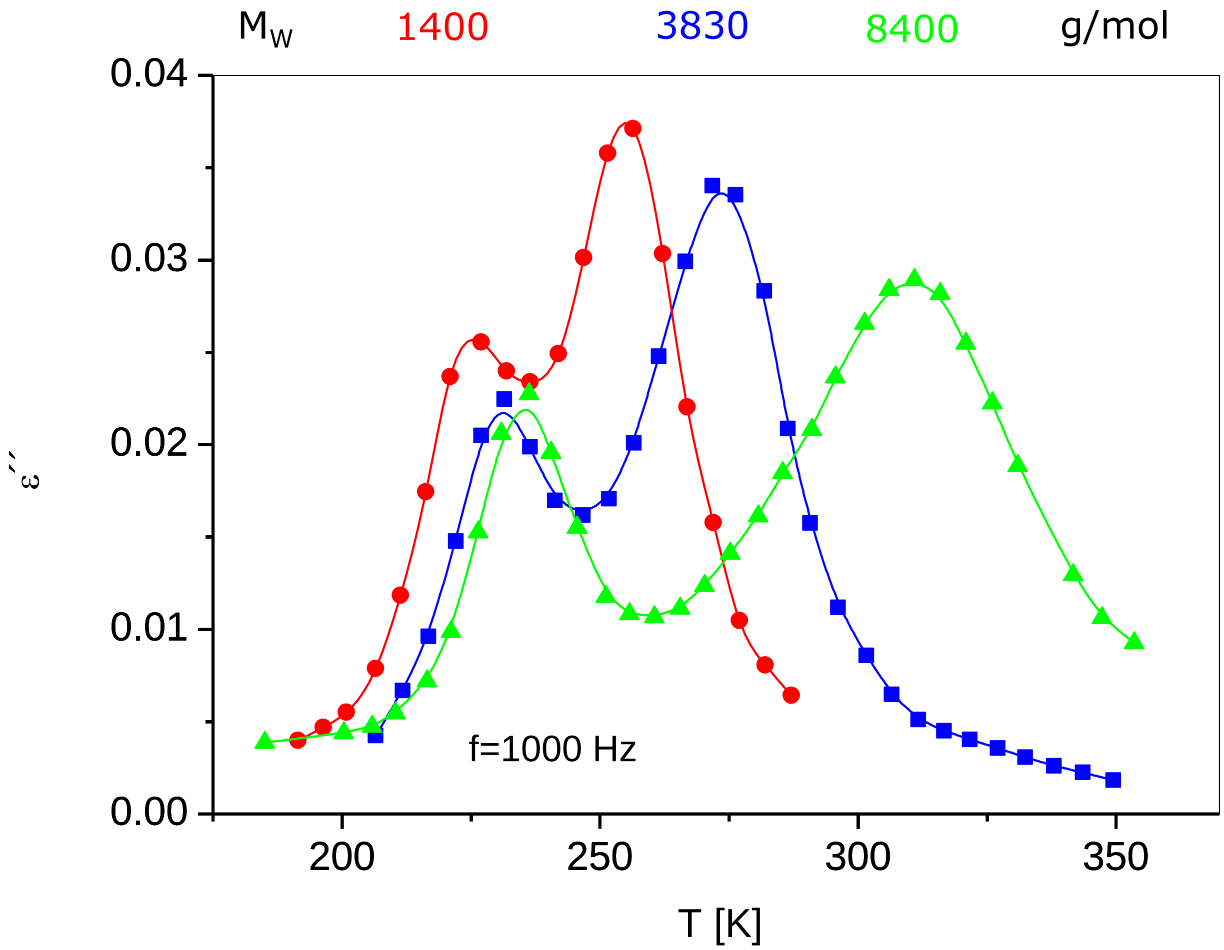
Predictions:

Molecular weight dependence

Temperature dependence of the relaxation rates of segmental and chain dynamics should be similar

Chain dynamics – Normal mode

Poly(cis-1,4 isoprene)



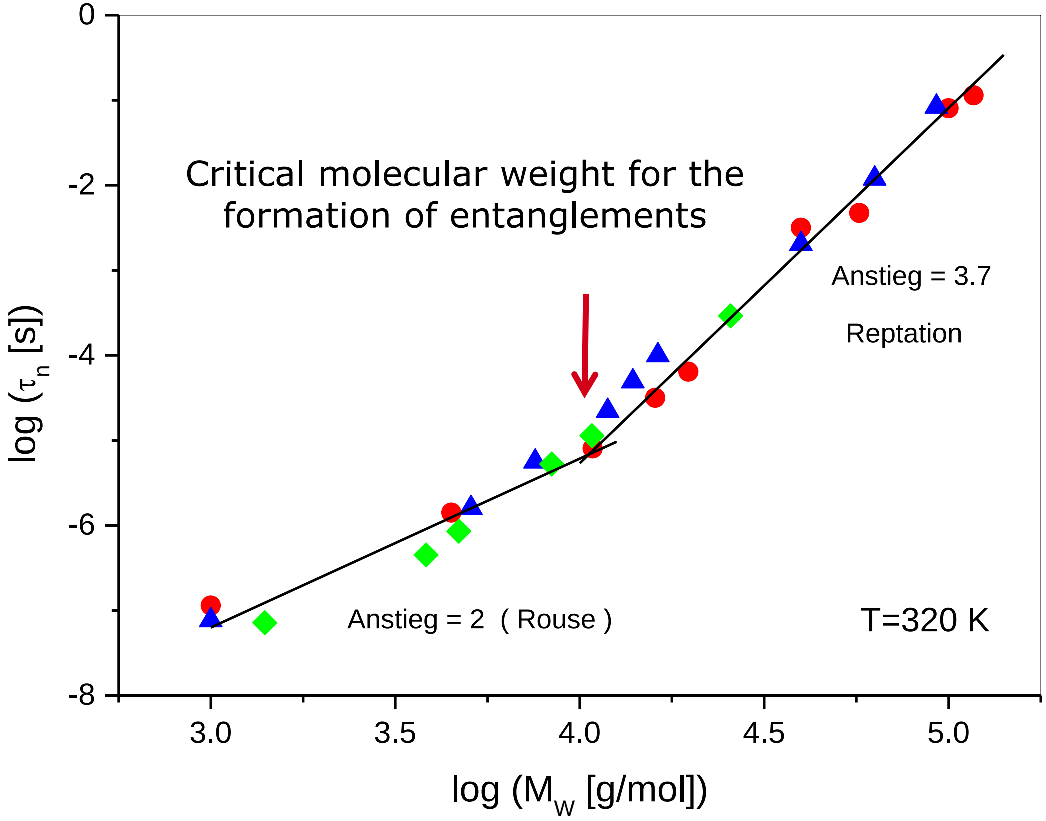
Schönhals, A. Macromolecules **26** (1993) 1309

Chain dynamics – Normal mode

Poly(cis-1,4 isoprene)

$$\tau_p = \frac{\zeta\ N^2 b^2}{3\pi^2 kT p^2} \sim M^2$$

$$\tau_p = \frac{\zeta\ N^3 b^4}{\pi^2 kT a^2 p^2} \sim M^3$$



Chain dynamics – Normal mode

Self diffusion

Relaxation times: $$\tau_p = \frac{\zeta\ N^2 b^2}{3\pi^2 kT\, p^2}$$

↪ $$D_{Self} = \frac{< r^2 >}{3\pi^2\, p^2 \tau_p}$$

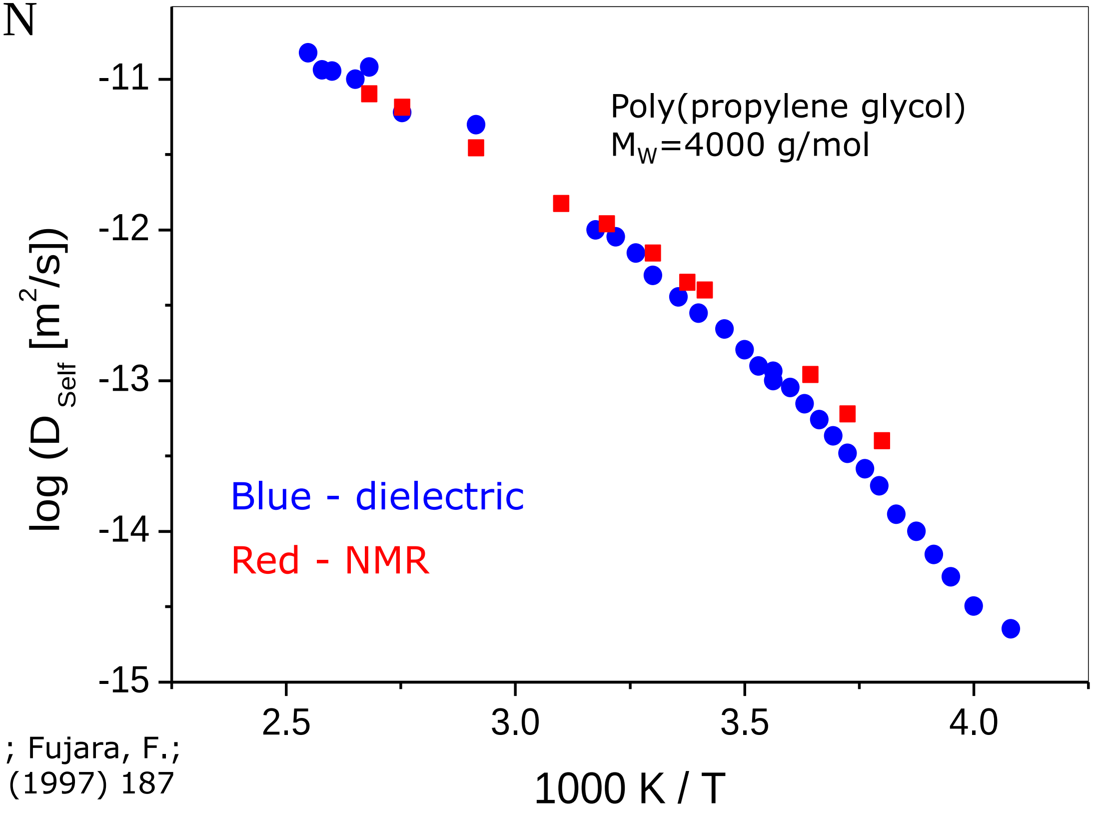
Diffusion coefficient: $$D_{Self} = \frac{kT}{\zeta N}$$

D_{Self} can be measured by Pulsed Field Gradient NMR

Both quantities agree in both there absolute values and in there temperature dependence

↪

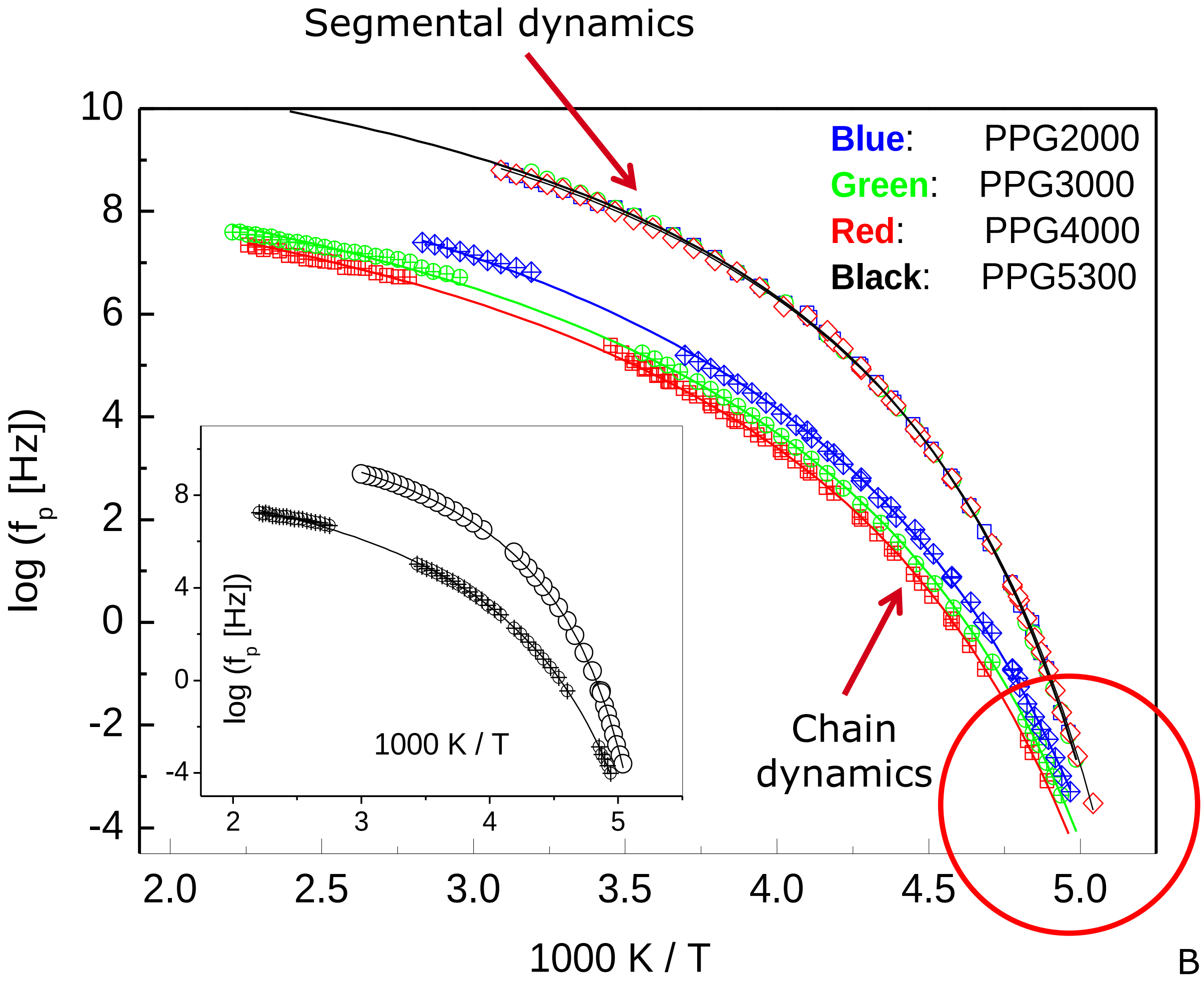
Normal mode corresponds to translatorial diffusion



Appel, M.; Fleischer, J. Kärger, G.; Chang, I.; Fujara, F.; Schönhals, A.; Colloid and Polymer Sci. **275** (1997) 187

Chain dynamics

Temperature dependence relaxation rates



The relaxation rates of the segmental dynamics are independent of the molecular weight.

The relaxation rates of the chain dynamics depends of the molecular weight.

The temperature dependence of both relaxation rates seems to follow the Vogel/Fulcher/Tammann formula.

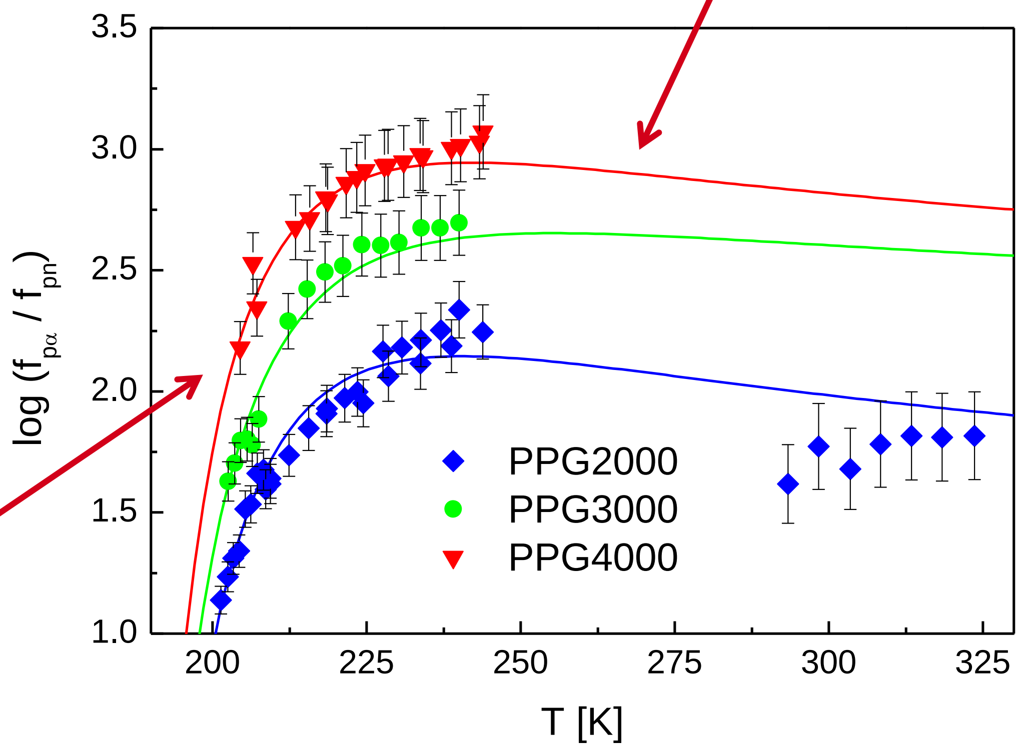
$$\log f_p = \log f_{p\infty} - \frac{A}{T - T_0}$$

Both processes seems to merge close to T_g.

Chain dynamics

Temperature dependence relaxation rates

Ratio of both relaxation rates



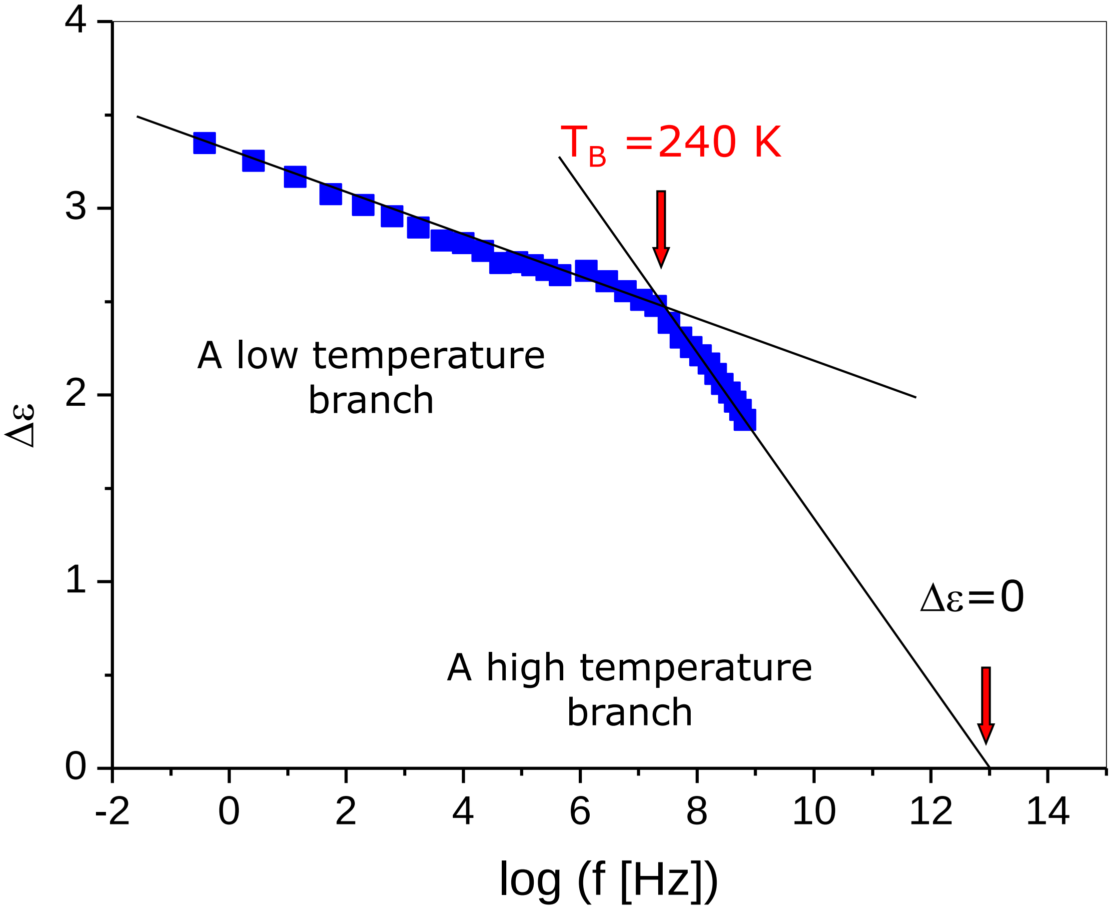
Plateau

Decrease

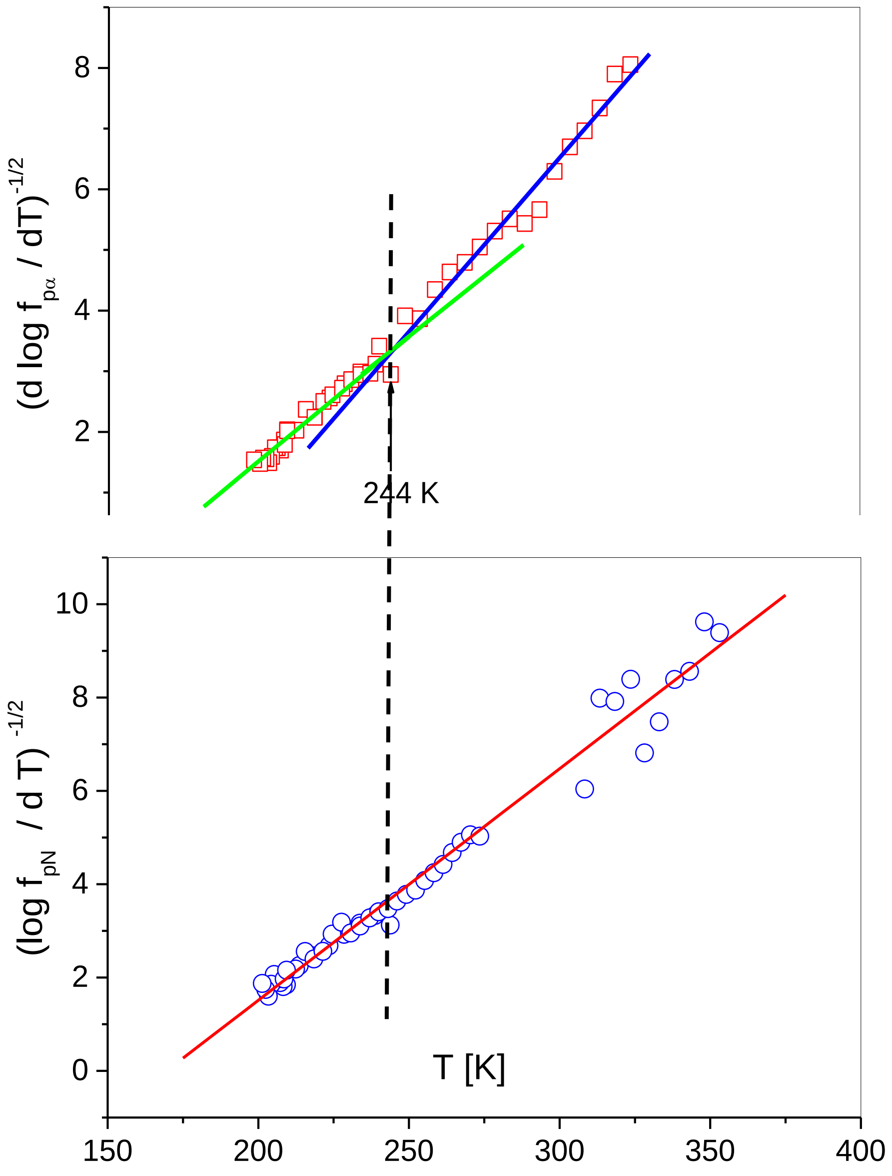
Detailed investigation of the temperature dependence of the relaxation rates!

Chain dynamics – Normal mode
Crossover of segmental dynamics

Polypropylene glycol; M_w=4000 g/mol



Chain dynamics – Normal mode



Derivative:

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

The temperature dependence of the α-relaxation rate shows a change at T=244 K as it was observed also for the dielectric strengths

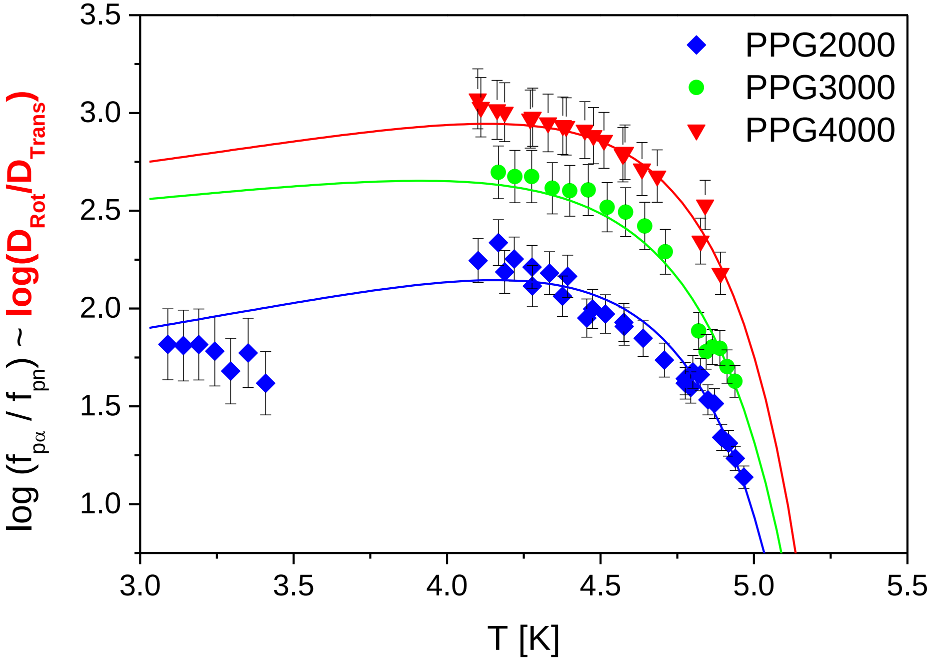
No change of the temperature dependence of the relaxation rate of the normal mode at $T_{B.}$

The reason for the different temperature dependencies of α- and normal mode relaxation is the crossover in the dynamic glass transition.

Decoupling of rotational and translatorial diffusion

Segmental dynamics – rotational diffusion

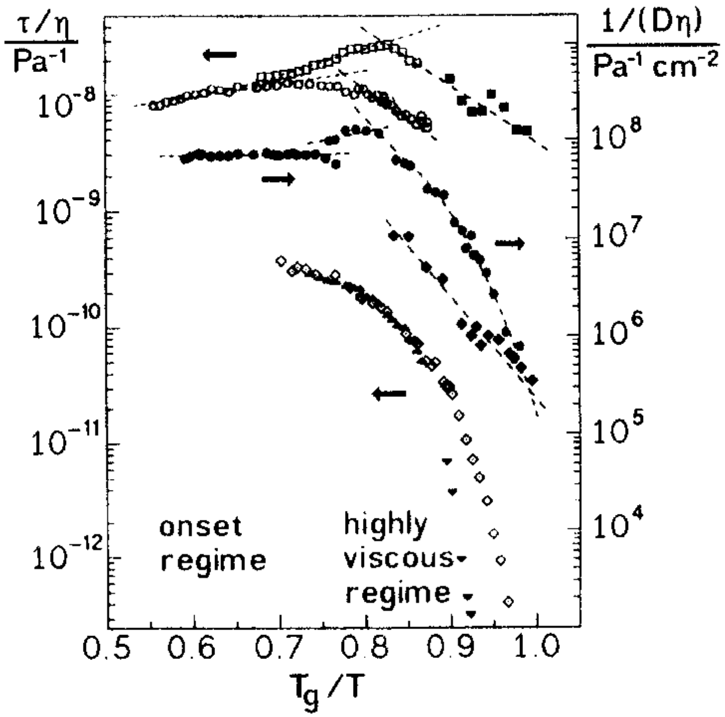
Chain dynamics – translatorial diffusion



Different temperature dependencies of α- and normal mode relaxation is due to the decoupling of rotational and translatorial diffusion at T_B.

Decoupling of Rotation and translation in low molecular weight glass-forming liquids

Rössler, E.; Phys. Rev. Lett. 69 (1992) 1620, 65 (1990) 1595



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

Conclusion

Dielectric spectroscopy is a powerful tool to study the structure and dynamics of matter.

- Extremely broad dynamical range.
- Extremely high sensitivity.

Careful data analysis is needed.

- This can be done by model functions.
- Employing theoretical approaches.

Combination with other spectroscopic methods.

- Mechanical spectroscopy
- Thermal spectroscopy
- Neutron spectroscopy
- NMR spectroscopy