

Glassy dynamics in geometrical confinement as studied by Broadband Dielectric Spectroscopy

F. Kremer

Universität Leipzig

**Co-authors: M. Treß, E.U. Mapesa, W. Kipnusu,
C. Iacob (Leipzig), Reiche (Halle), M. Erber,
K.-J. Eichhorn, B. Voit (Dresden),
A. Serghei (Lyon), C. Schick (Rostock)**

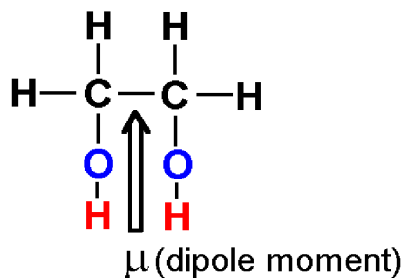
Outline

1. Experimental realization of **sub-nanometric** and **nanometric** (**one-dimensional** (1D) and **two-dimensional** (2D)) confinement
2. The **calorimetric glass transition temperature**, the **dynamic glass transition** and methods to measure it
3. The principle of Broadband Dielectric Spectroscopy (BDS)
4. Glassy dynamics in **sub-nanometric** geometrical confinement of zeolites
5. Polymethylphenylsiloxane (PMPS) in **1-D** and **2-D** geometrical constraints
6. Glassy dynamics of **condensed isolated polymer chains**.

1. Experimental realization of sub-nanometric and nanometric (one-dimensional (1D) and two-dimensional (2D)) confinement

sub-nanometric confinement – as realized with zeolites

ethylene glycol
(EG, ethanediol)

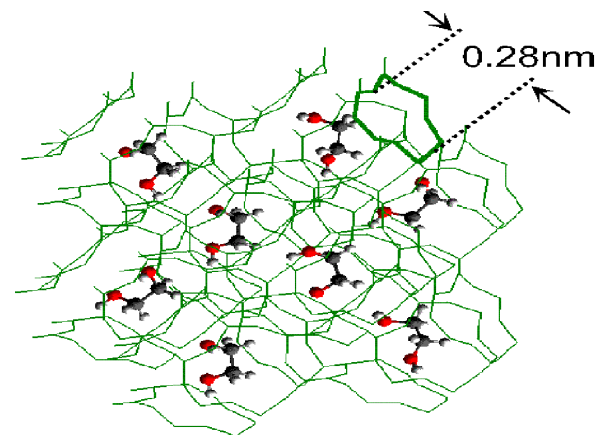


silica-sodalite (SiO_2)

cubic cages

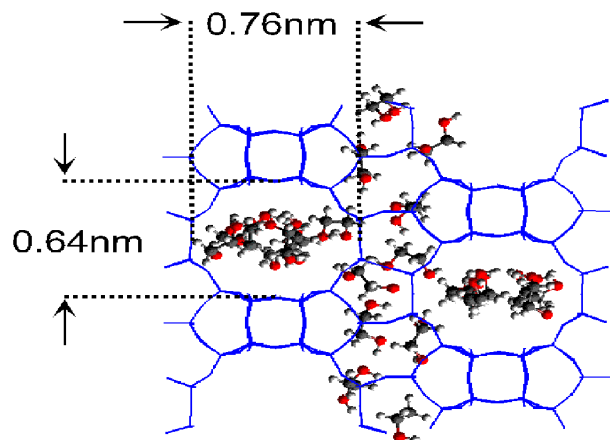
lattice constant 0.89nm

"one molecule per cage"



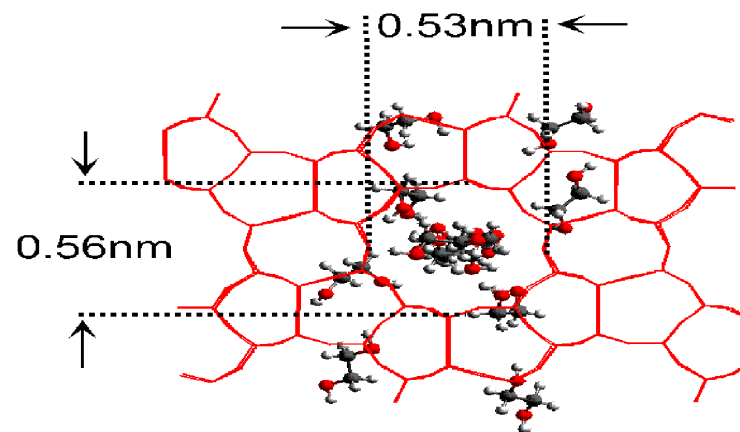
silicalite (SiO_2) channels

0.56nm x 0.53nm 0.55nm x 0.51nm



zeolite beta ($\text{SiO}_2/\text{Al}_2\text{O}_3$) Si : Al ratio 40

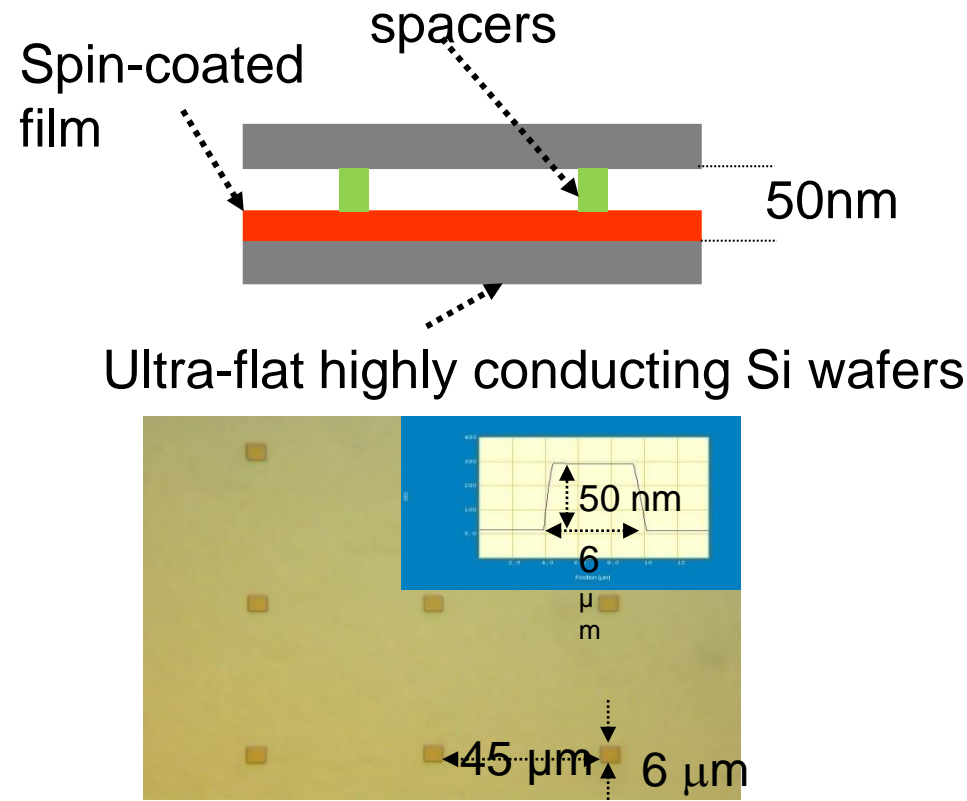
channels 0.76nm x 0.64nm 0.55nm x 0.55nm



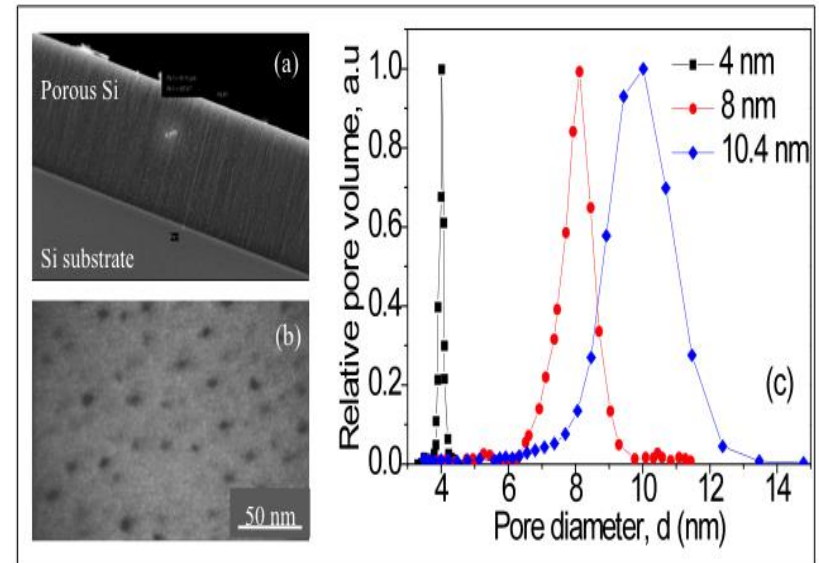
The chemical composition of all zeolites is nearly identical.

1D and 2D nanometric confinement

1D confinement



2D confinement



The **air-gap geometry** enables one to carry out BDS experiments on layers less than 5 nm without the possibility of electrical shorts. **No evaporated metal electrodes!**

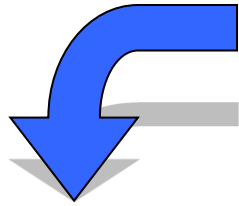
Uni-directional silica nanopores; (Electro-chemical etching of highly conductive silicon and subsequent oxidation)

Summary

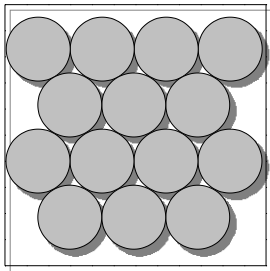
1. **Sub-nanometric**, two-dimensional confinement can be easily realized with zeolitic host systems.
2. **Nanometric layers** of thin polymer films can be easily prepared by spin-coating.
3. **Unidirectional** nanometric pores can be prepared down to diameters ≥ 4 nm.
4. With **silanization** the inner surfaces of the pores can be changed from hydrophilic to hydrophobic.

2. The calorimetric glass transition temperature, the dynamic glass transition and methods to measure it.

The (calorimetric) glass transition



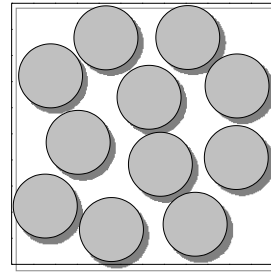
crystal



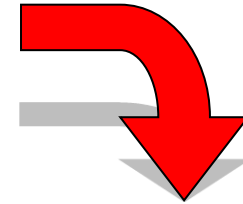
- long-range order
- scale invariant transition temperature



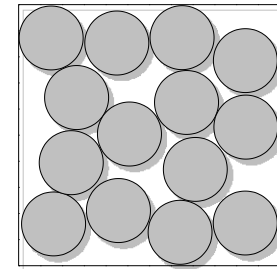
liquid



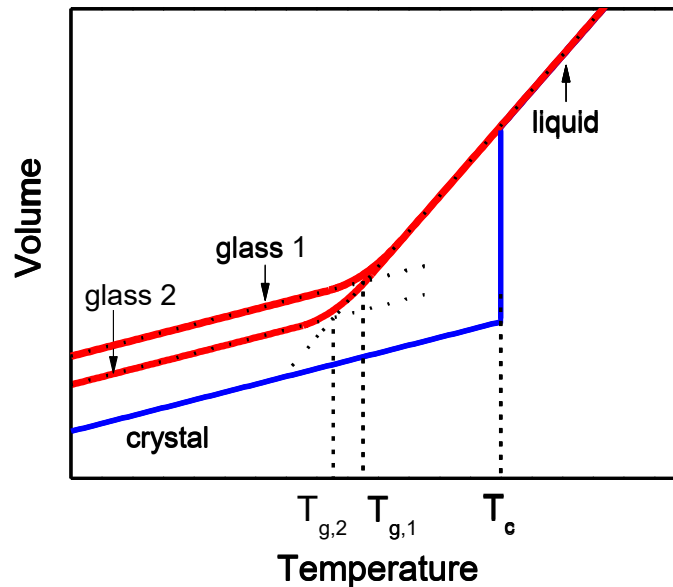
- no long-range order



glass

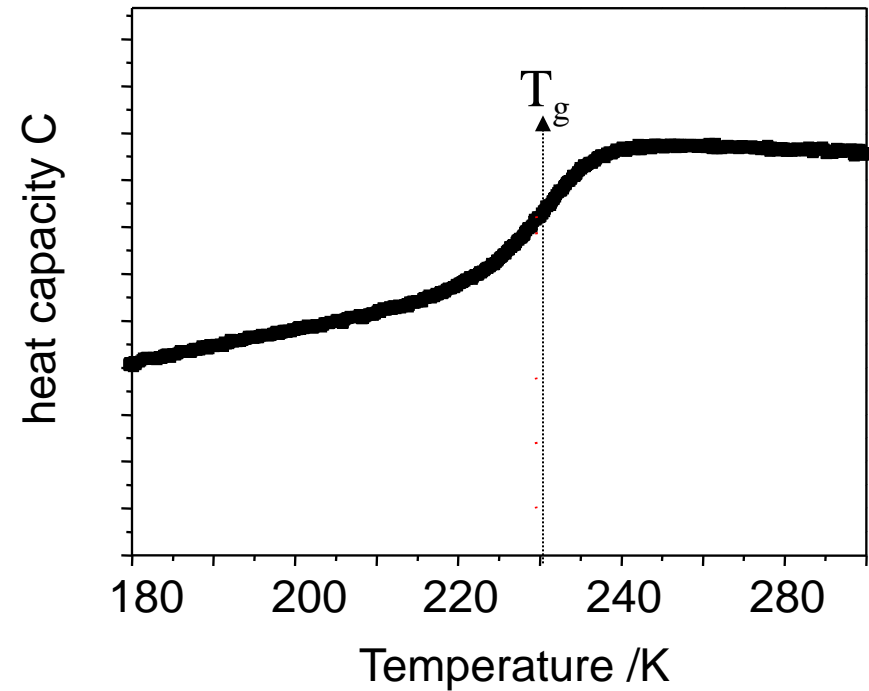
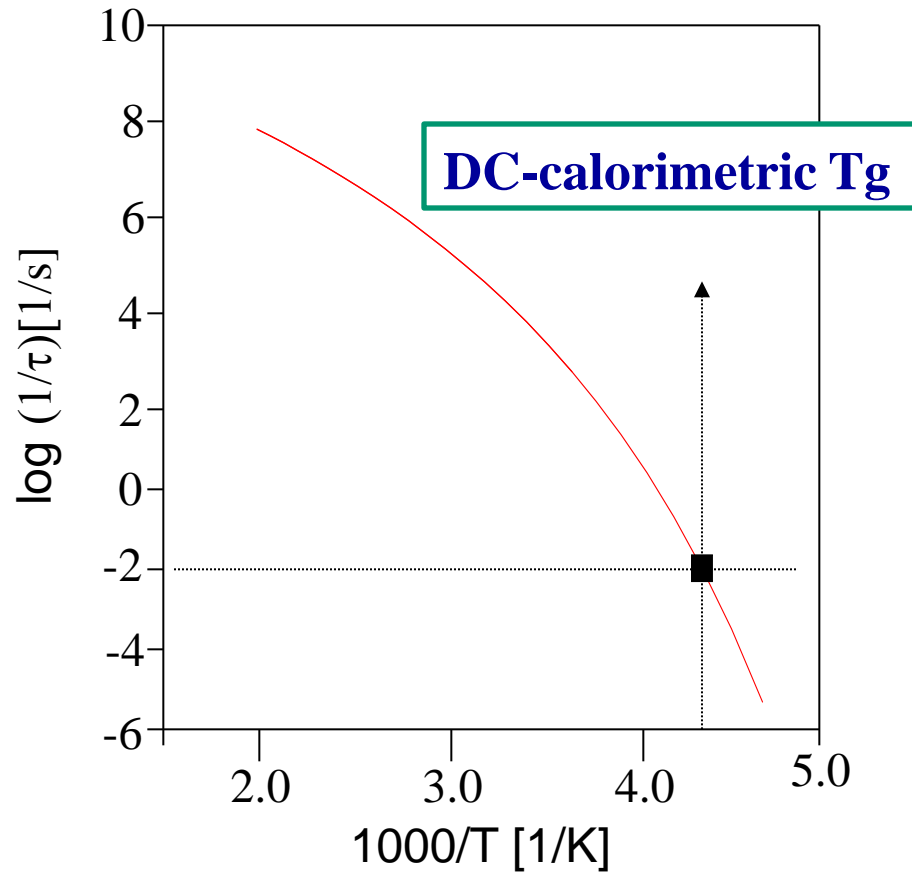


- no long-range order
- transition temperature depends on **cooling rate**



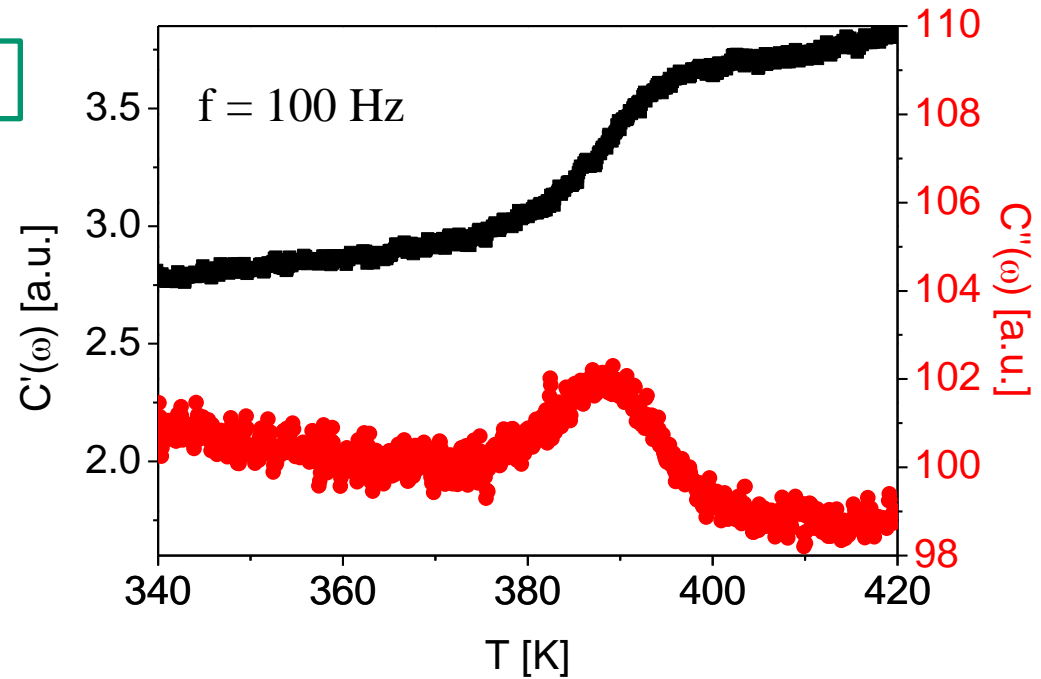
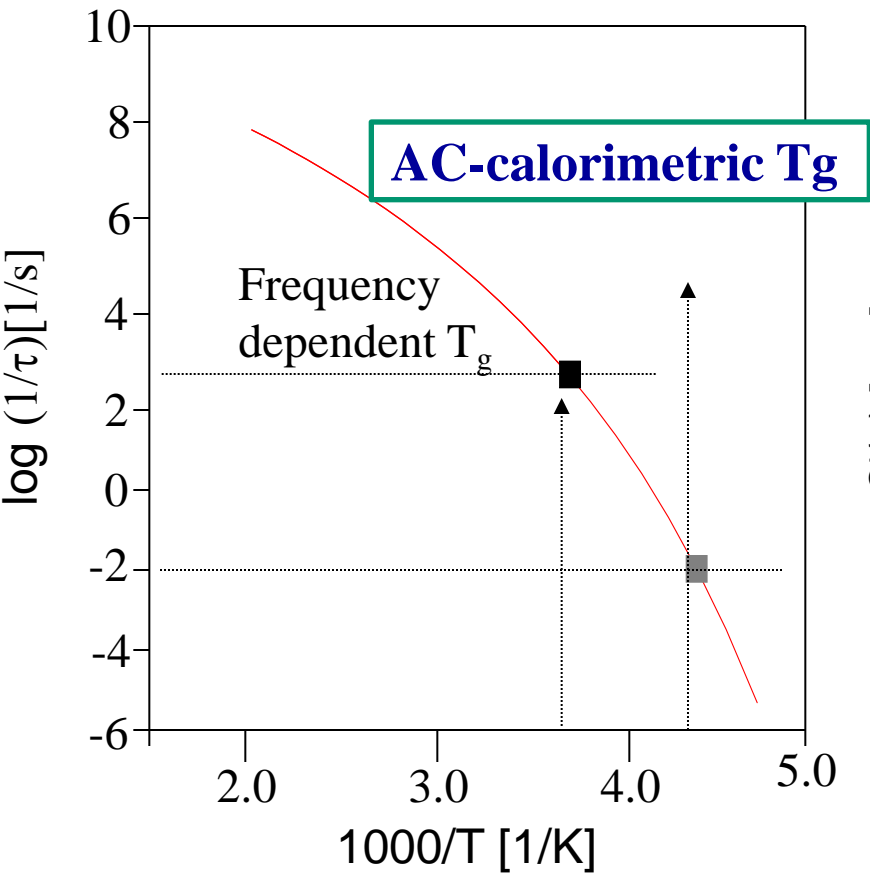
The glass transition is **no** phase transition!

The calorimetric glass transition temperature as measured by (DC-) Differential Scanning Calorimetry (DSC)



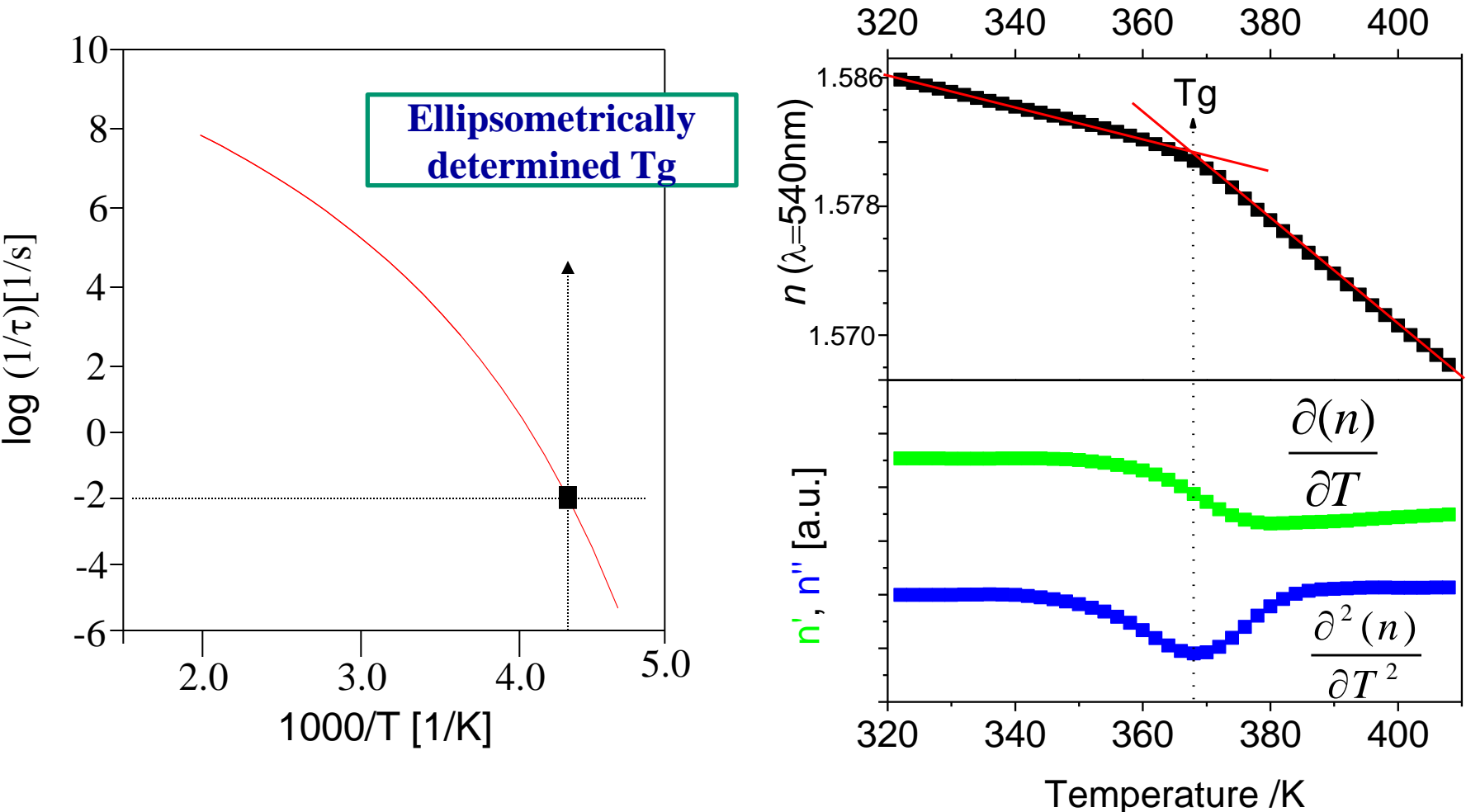
At the calorimetric glass transition temperature the dynamic glass transition has a typical relaxation rate of ~ 0.01 Hz

The **dynamic** glass transition as measured by **frequency-dependent (AC) calorimetry**



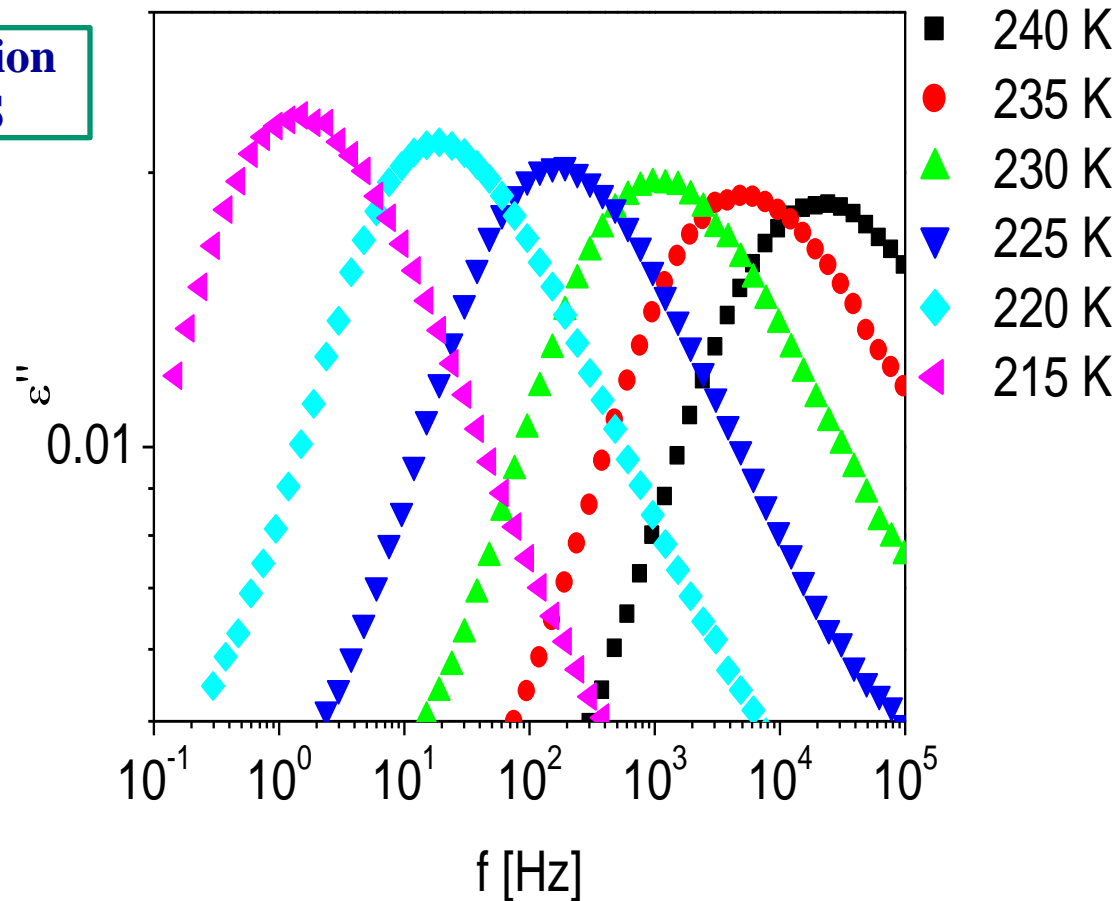
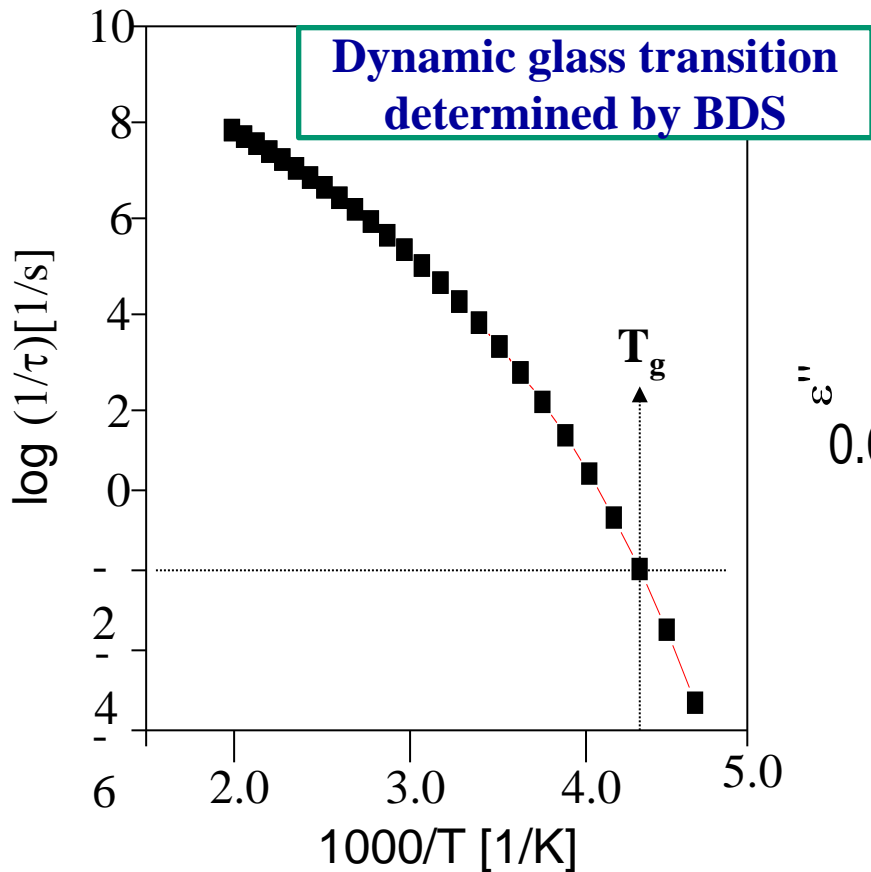
AC-calorimetry traces the **dynamic glass transition** over many orders of magnitude

Ellipsometric determination of the glass transition temperature



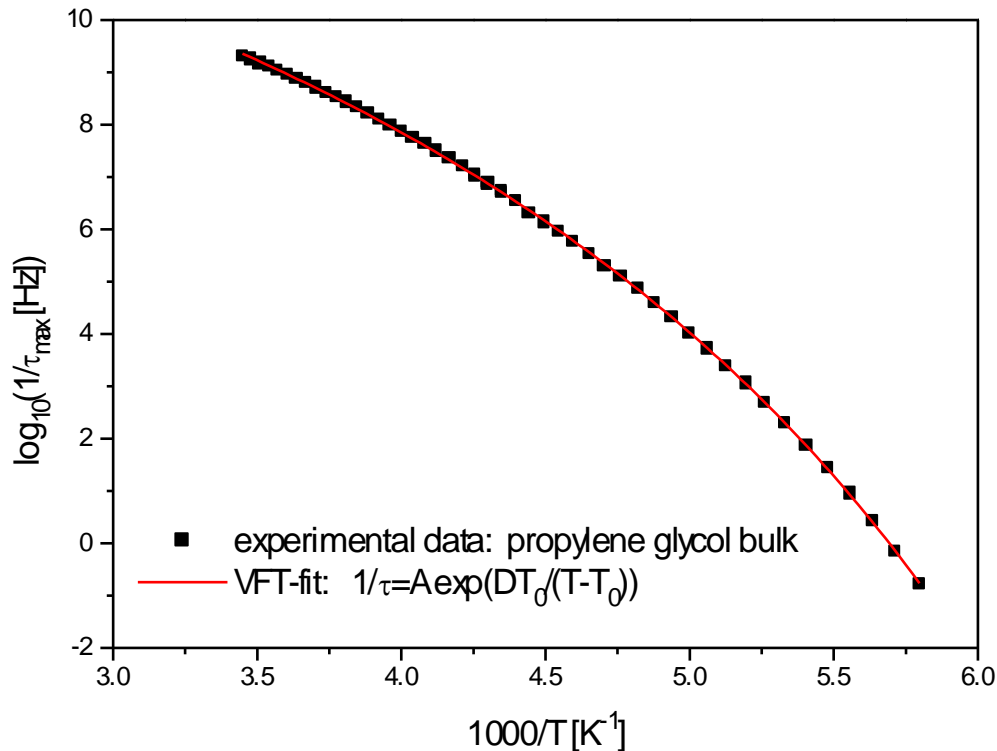
With ellipsometry a kink in the temperature dependence of n and d is found indicating T_g

The **dynamic** glass transition as measured by **Broadband Dielectric Spectroscopy (BDS)**



BDS measures the dynamic glass transition in a wide frequency and temperature range, including the **relaxation time distribution**

Glassy dynamics is characterized by a temperature dependence of the relaxation rate following the empirical Vogel-Fulcher-Tammann (VFT)-equation



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

(D is a constant and T_0 the Vogel temperature)

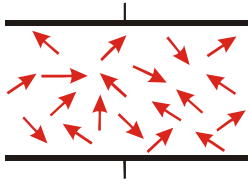
At the calorimetric glass transition temperature T_g the relaxation rate has a typical value of .01 Hz.

Summary

1. The calorimetric and the dynamic glass transition are interlinked by the (empirical) Vogel-Fulcher-Tammann (VFT) relationship.
2. There are manifold ways to measure the dynamic glass transition (AC- and DC-calorimetry, dilatometry, viscosimetry, scattering techniques, ellipsometry, **Broadband Dielectric Spectroscopy** etc). The latter has the advantage to cover an extraordinarily broad spectral range.
2. The dynamic glass transition is assigned to **relaxations between structural substates**. It corresponds to a **continuous slowing down** of the molecular dynamics upon cooling which is described by the **empirical** Vogel-Fulcher-Tammann (VFT) dependence.

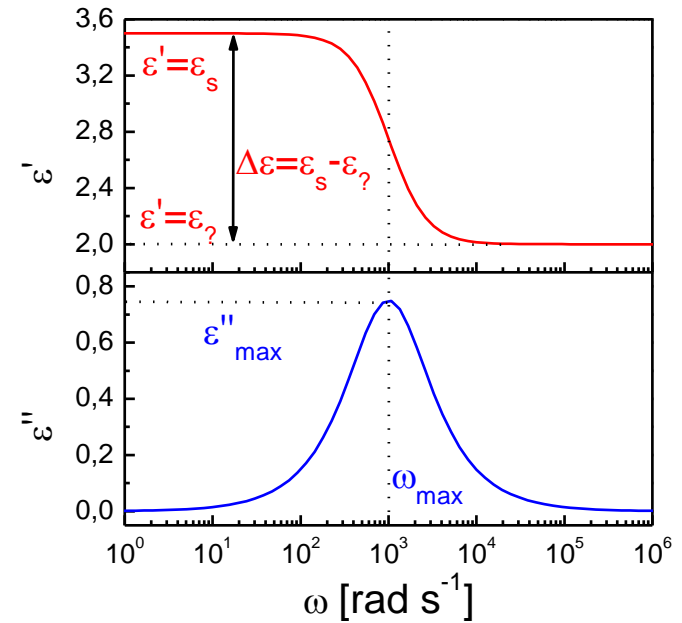
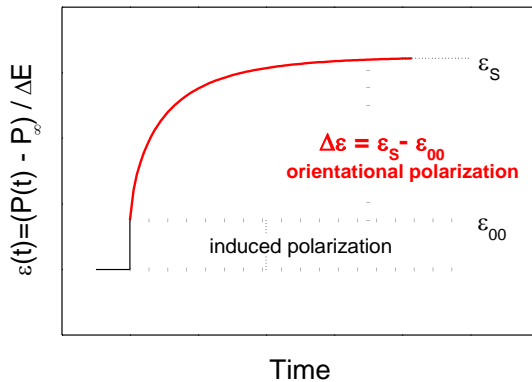
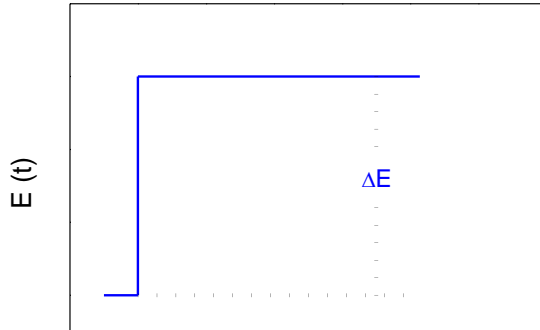
3. The principle of Broadband Dielectric Spectroscopy (BDS)?

Purely insulating samples: orientational polarisation:



Capacitor with N permanent dipoles, dipole Moment μ

Debye relaxation $\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau}$



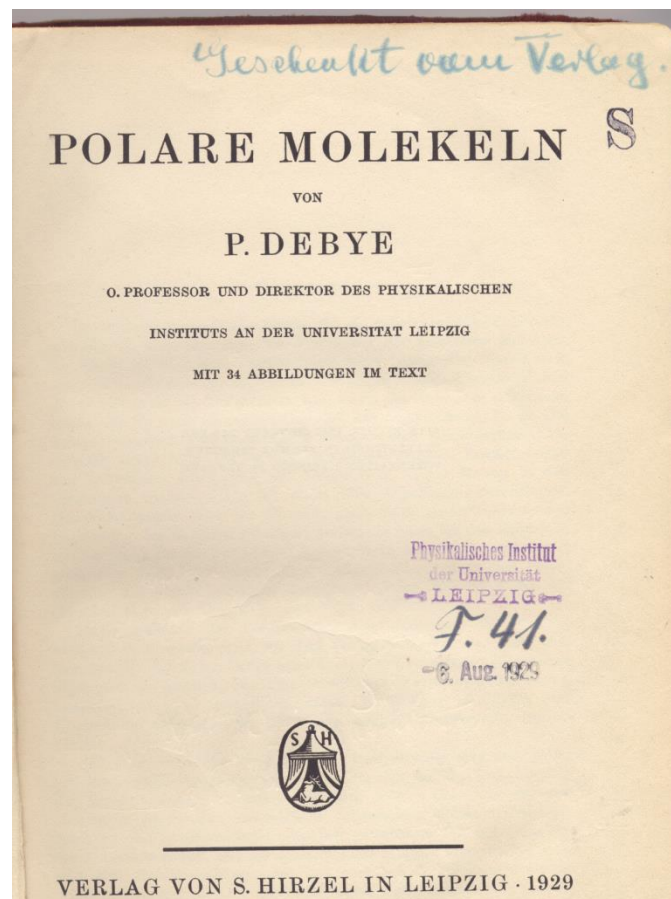
complex dielectric function $\epsilon^* (\omega, T)$

$$P (\omega, T) = (\epsilon^* (\omega, T) - 1) E (\omega)$$

$$\epsilon'(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (\omega \tau)^2}$$

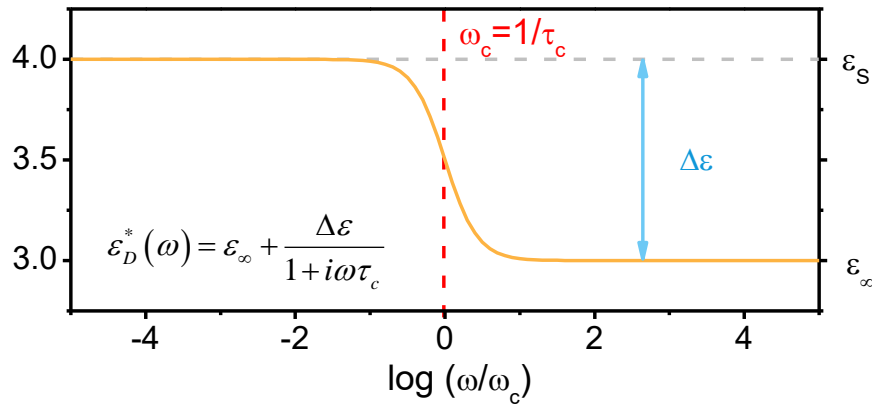
$$\epsilon''(\omega) = \frac{\epsilon_s - \epsilon_\infty}{1 + (\omega \tau)^2} \omega \tau$$

P. Debye, Director (1927-1935) of the Physical Institute at the university of Leipzig (Nobelprize in Chemistry 1936)

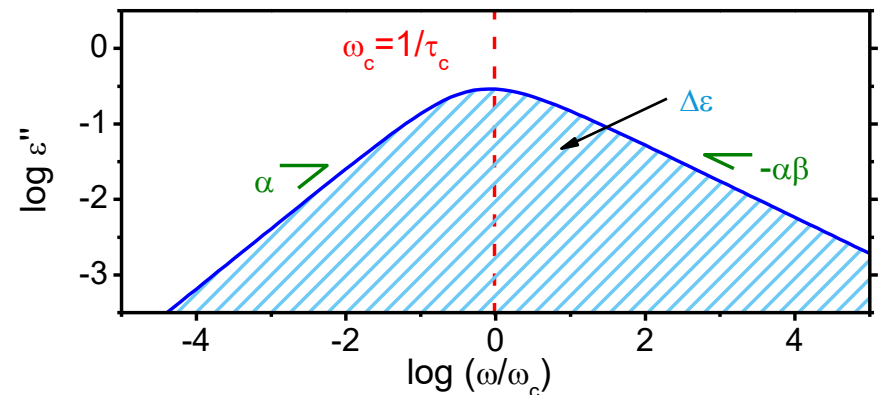
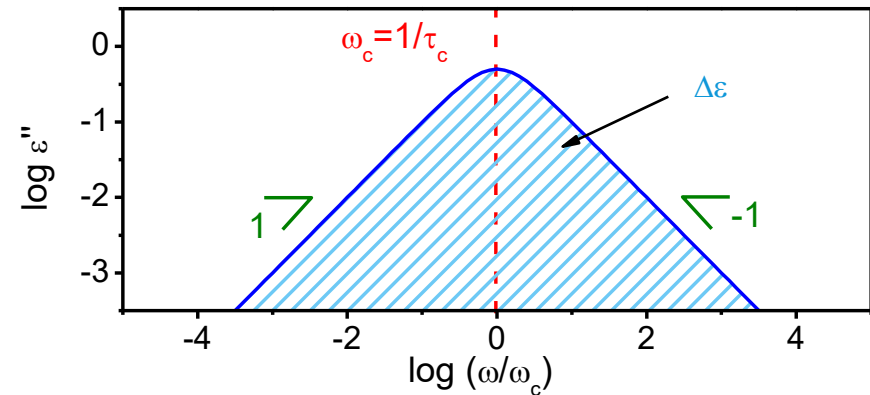
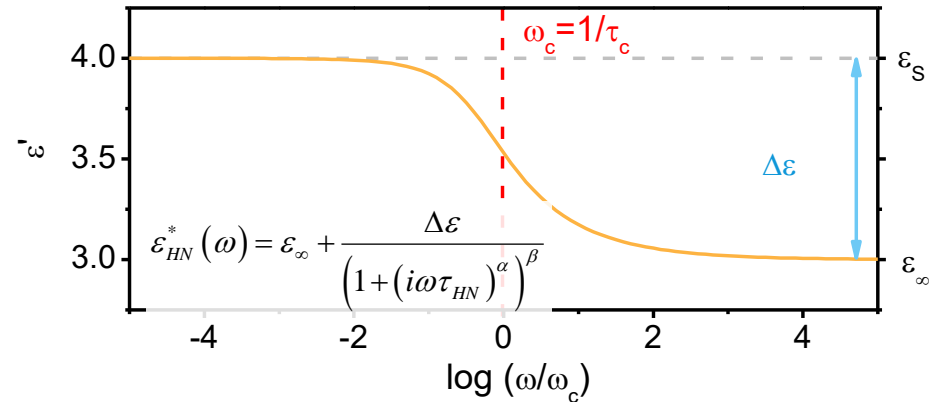


information content of dielectric spectra

Debye-Relaxation



Generalized Relaxation: Havriliak-Negami function



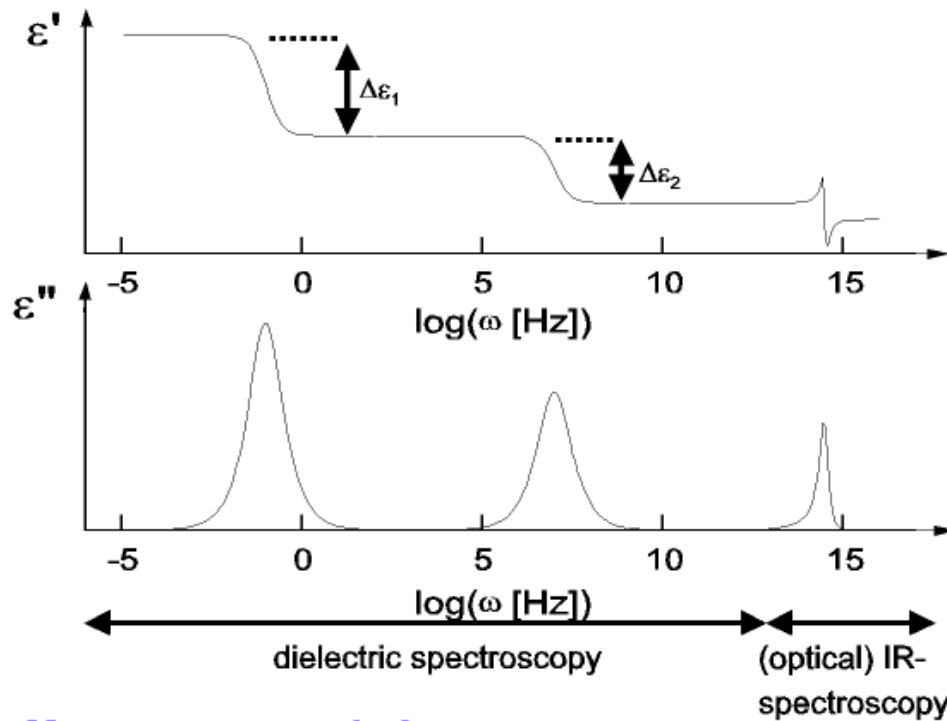
Mean relaxation time τ_c :
$$\tau_c = \tau_{HN} \left[\sin\left(\frac{\alpha\pi}{2+2\beta}\right) \right]^{1/\beta} \left[\sin\left(\frac{\alpha\beta\pi}{2+2\beta}\right) \right]^{-1/\beta}$$

Relaxation strength $\Delta\varepsilon$:
$$\Delta\varepsilon = \frac{\mu^2 N/V}{3\varepsilon_0 k_B T}$$

Relaxation time distribution $L(\tau)$: $L_D(\tau) = \delta(\tau - \tau_c)$ $L_{HN}(\tau) = f(\tau_{HN}, \alpha, \beta)$

Temperature dependence of τ_c : Arrhenius or Vogel-Fulcher Tammann (VFT)

Broadband dielectric measurement techniques



Dual-phase lock-in amplifier (SR 830) ($10^{-3}\text{Hz} - 10^5\text{Hz}$)

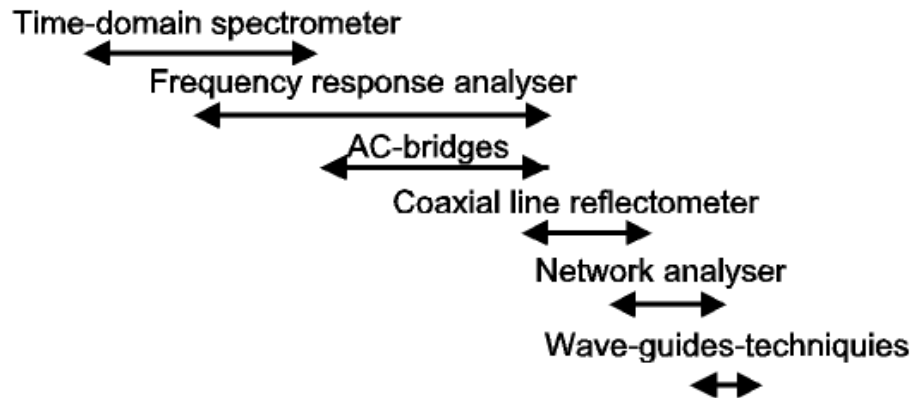
Impedance analyser (HP 4284 A) ($20 \text{ Hz} - 10^6\text{Hz}$)

Frequency-response-analyser (SI 1260) ($10^{-4}\text{Hz} - 10^7\text{Hz}$)

Coaxial line reflectometer (HP 4291 A) ($10^6\text{Hz} - 10^9\text{Hz}$)

(Sample amount required $<5\text{mg}$)

Measurement techniques:



In real samples **charge transport and orientational polarisation** take place in parallel

The *linear* interaction of electromagnetic fields with matter is described by one of **Maxwell's equations**

$$\text{curl } H = j + \frac{\partial D}{\partial t}$$

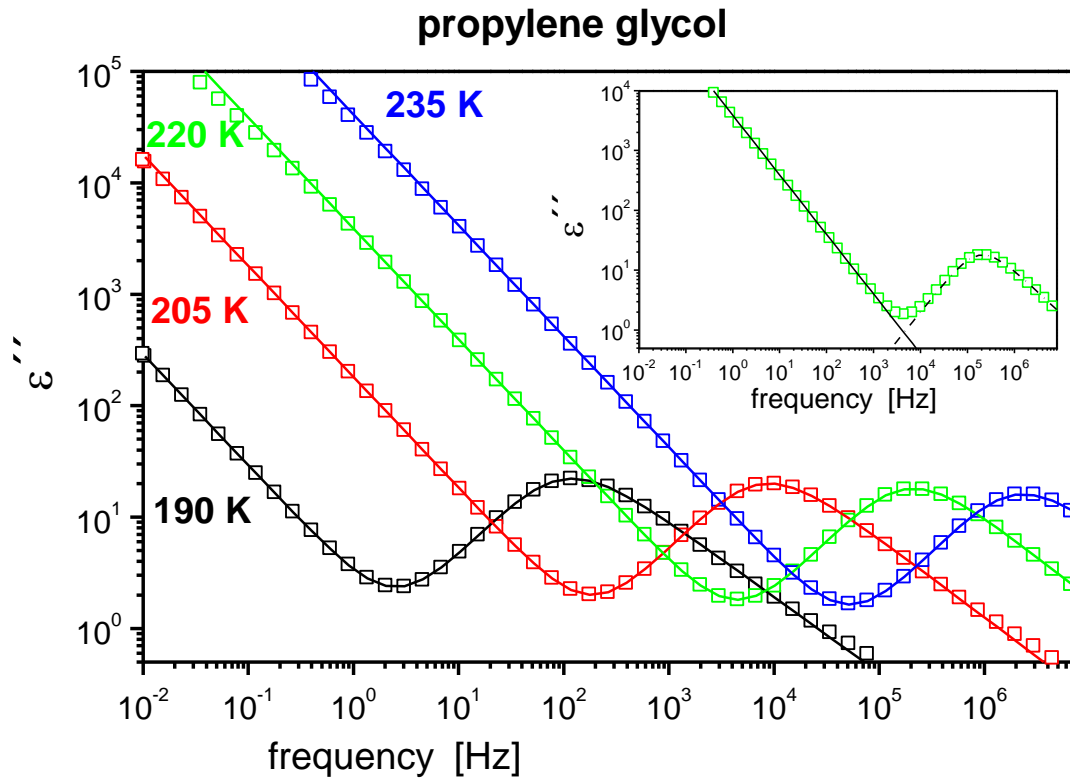
$$D = \varepsilon^* \varepsilon_0 E \quad j = \sigma^* E \quad (\text{Ohm's law})$$

(Current-density and the time derivative of D are equivalent)

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

$$\sigma^* = i\omega\varepsilon_0\varepsilon^*$$

Dielectric spectra as characterized by **charge transport and electrode polarisation in parallel**



Charge transport and orientational polarisation have quite different frequency dependencies

Summary concerning the principle of Broadband Dielectric Spectroscopy (BDS) and the information-content of dielectric spectra.

1. BDS covers a **huge spectral range** of about 15 decades from THz to below mHz.
2. Due to Maxwell's equations the **complex dielectric function $\epsilon^*(\omega)$** and the **complex conductivity $\sigma^*(\omega)$** are directly interrelated.
3. From dielectric spectra the **relaxation rate** of fluctuations of a **permanent molecular dipole** and its relaxation time distribution function can be deduced.
4. The capacitance of a sample capacitor and hence **the sensitivity** of the measurement **increases** with decreasing separation between the electrodes. The **sample amount** required for a measurement can be reduced to that of **isolated molecules**.

KREMER · SCHÖNHALS (Eds.)
Broadband Dielectric Spectroscopy

The interaction of electromagnetic waves with matter in the frequency range between 10^{-6} and 10^{14} Hz is the domain of broadband dielectric spectroscopy. In this extraordinarily extended dynamic range molecular and collective dipolar fluctuations, charge transport and polarisation effects at inner and outer boundaries take place and determine the dielectric properties of the material being studied. Hence, broadband dielectric spectroscopy enables one to gain a wealth of information on the dynamics of bound (dipoles) and mobile charge carriers depending on the details of a molecular system.

It is the intention of this book to be both an introductory course to broadband dielectric spectroscopy as well as a monograph describing recent dielectric contributions to current topics like the scaling of relaxation processes, molecular dynamics in confinement or non-resonant dielectric hole burning, just to name a few. In this respect the book will correspond to the needs of graduate students but also to specialized researchers, molecular physicists, polymer scientists and materials scientists in academia and industry.

ISBN 3-540-43407-0



9 783540 434078

<http://www.springer.de>

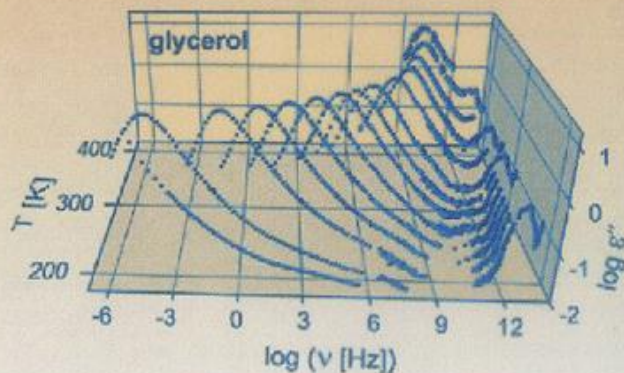
Kremer · Schönhals (Eds.)



Broadband Dielectric Spectroscopy

Friedrich Kremer
Andreas Schönhals
Editors

Broadband Dielectric Spectroscopy

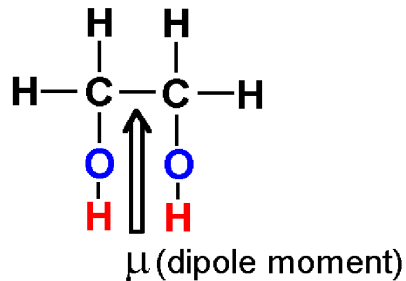


Springer

4. Glassy dynamics in **sub-nanometric geometrical confinement of zeolites.**

Ethylene glycole as guest molecule in zeolites

ethylene glycol
(EG, ethanediol)

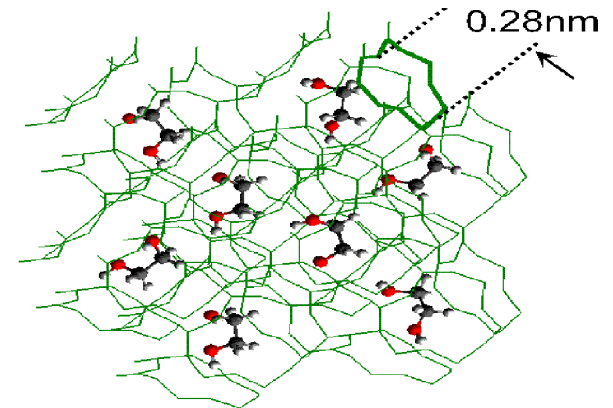


silica-sodalite (SiO_2)

cubic cages

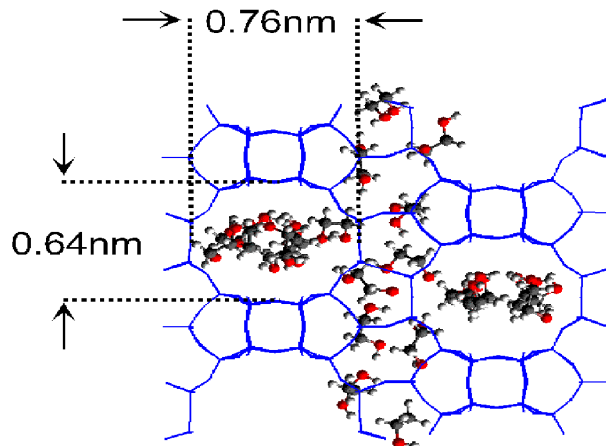
lattice constant 0.89nm

"one molecule per cage"



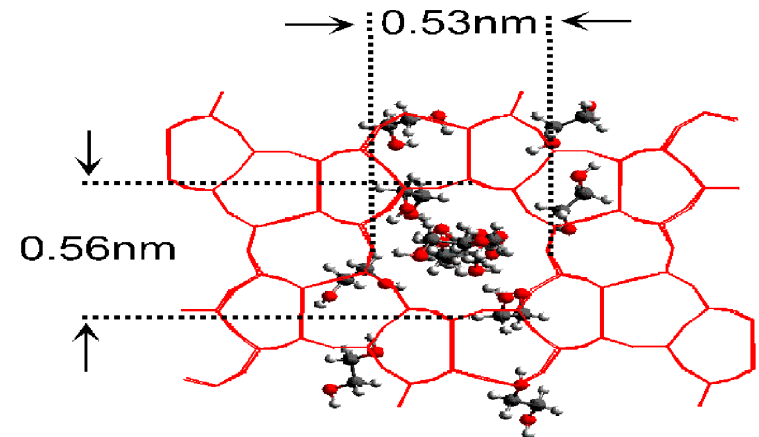
silicalite (SiO_2) channels

0.56nm x 0.53nm 0.55nm x 0.51nm



zeolite beta ($\text{SiO}_2/\text{Al}_2\text{O}_3$) Si : Al ratio 40

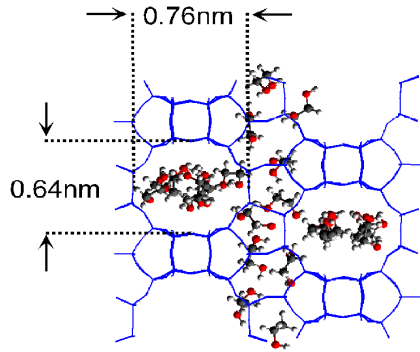
channels 0.76nm x 0.64nm 0.55nm x 0.55nm



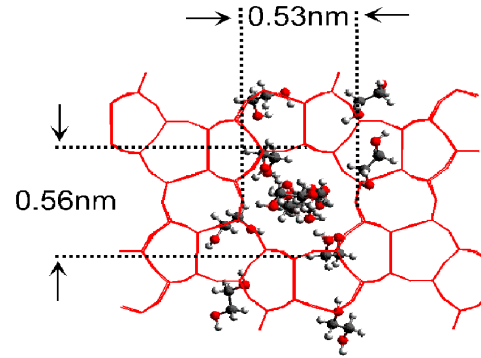
The chemical composition of all zeolites is nearly identical.

Dielectric spectra of ethylene glycole in different zeolitic host systems

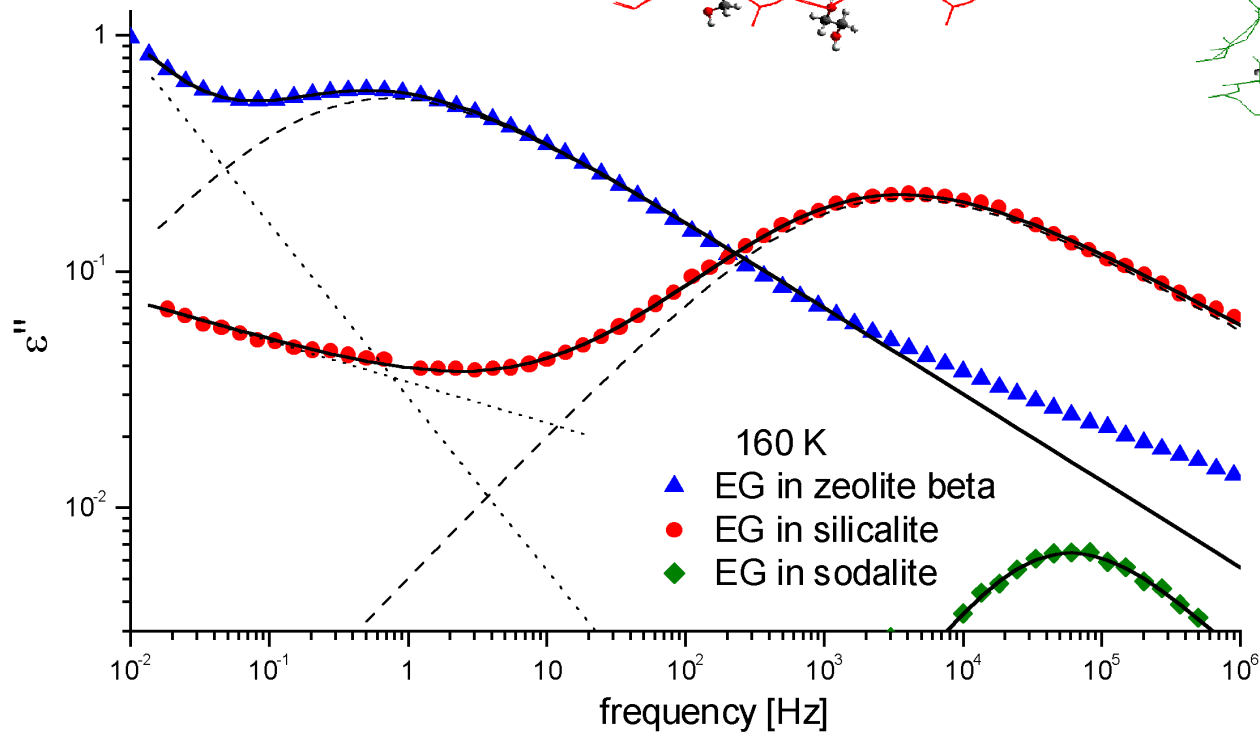
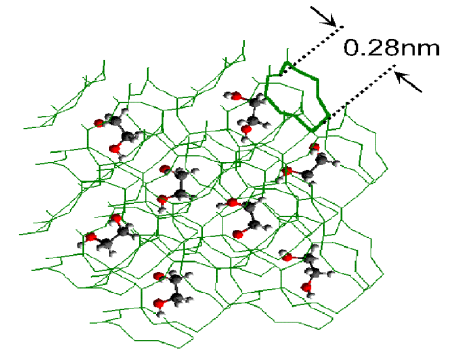
zeolite beta



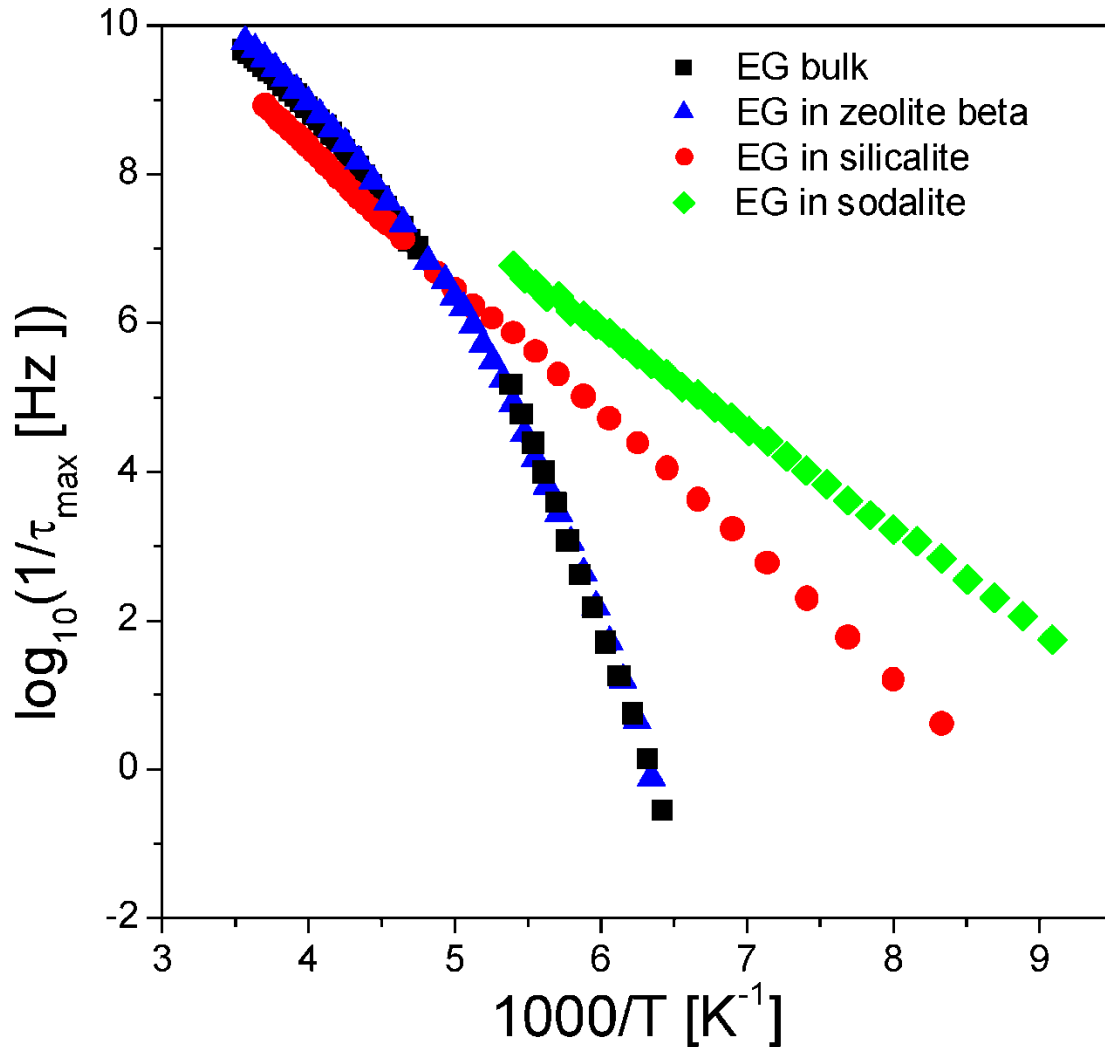
silicalite



sodalite



ethylene glycole in the bulk and in different zeolitic host systems



The temperature dependence of EG in the bulk liquid and in zeolite beta is identical. EG in silicalite and in sodalite shows an Arrhenius like temperature dependence with different activation energies.

Summary for low molecular weight systems (e.g. ethylene glycole) in zeolitic host systems

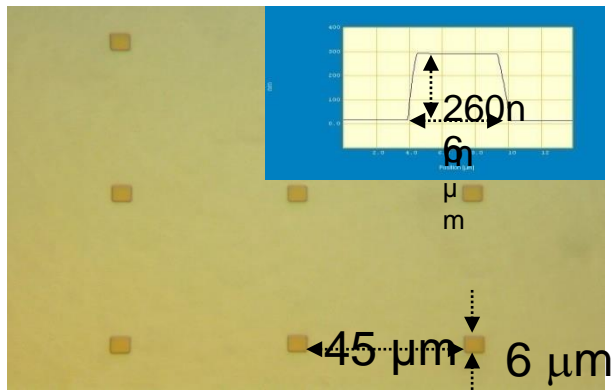
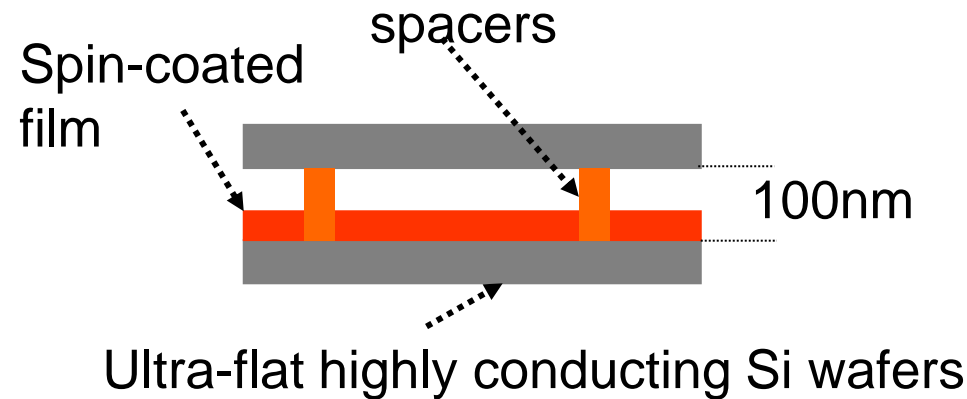
1. A **single molecule dynamics** is characterized by an Arrhenius temperature dependence - a **liquid-like dynamics** by a Vogel-Fulcher-Tammann (VFT) temperature dependence.
2. For ethylenglycol in zeolites a **sharp transition** from a **single molecule** to a **liquid-like dynamics** is observed.
3. An ensemble as small as **6 ethylenglycol molecules** is sufficient to **perform a liquid-like dynamics**.

R.Stannarius et al. PRL 75,4698(1995); M.Arndt et al.PRL 79,2077(1997); A.Huwe et al. PRL 82,2338 (1999); F.Kremer et al. J.Phys.Cond.Matter 11:A175 (1999);F.Kremer et al. Chap.6 in: „Broadband Dielectric Spectroscopy“ (Eds.:F.Kremer and A.Schönhals),Springer (2002)

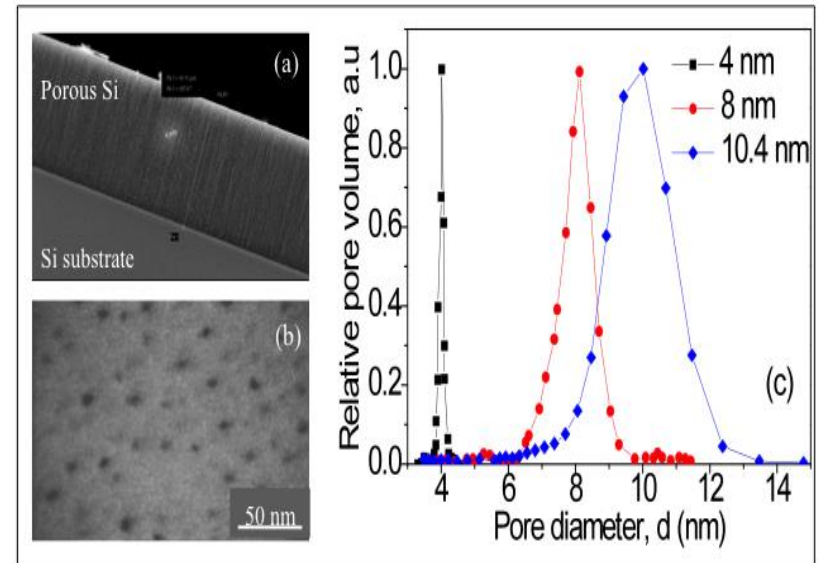
5. Polymethylphenylsiloxane (PMPS) in 1-D and 2-D geometrical confinement

1D and 2D confinement – a comparison

1D confinement



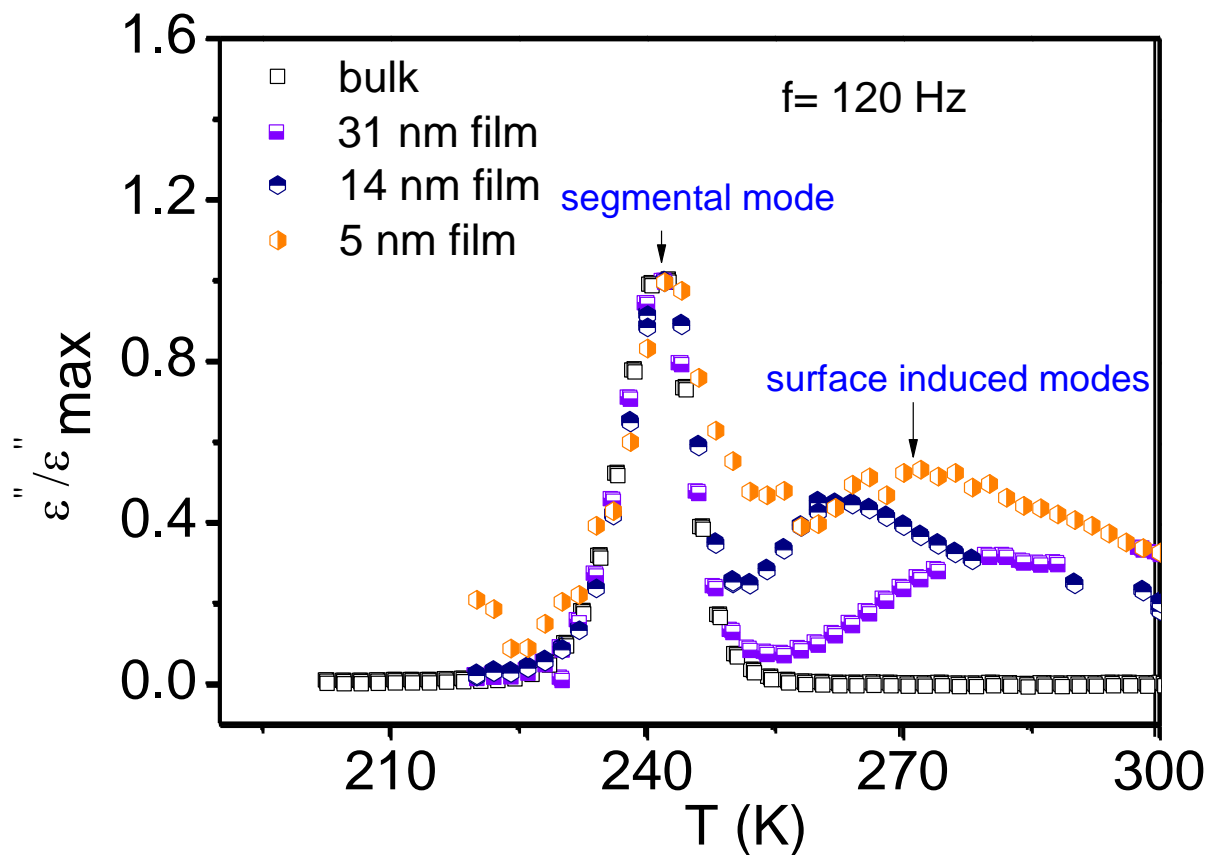
2D confinement



The **air-gap geometry** enables one to carry out BDS experiments on layers less than 5 nm without the possibility of electrical shorts. **No evaporated metal electrodes!**

Uni-directional silica nanopores; (Electro-chemical etching of highly conducting silicon and subsequent oxidation)

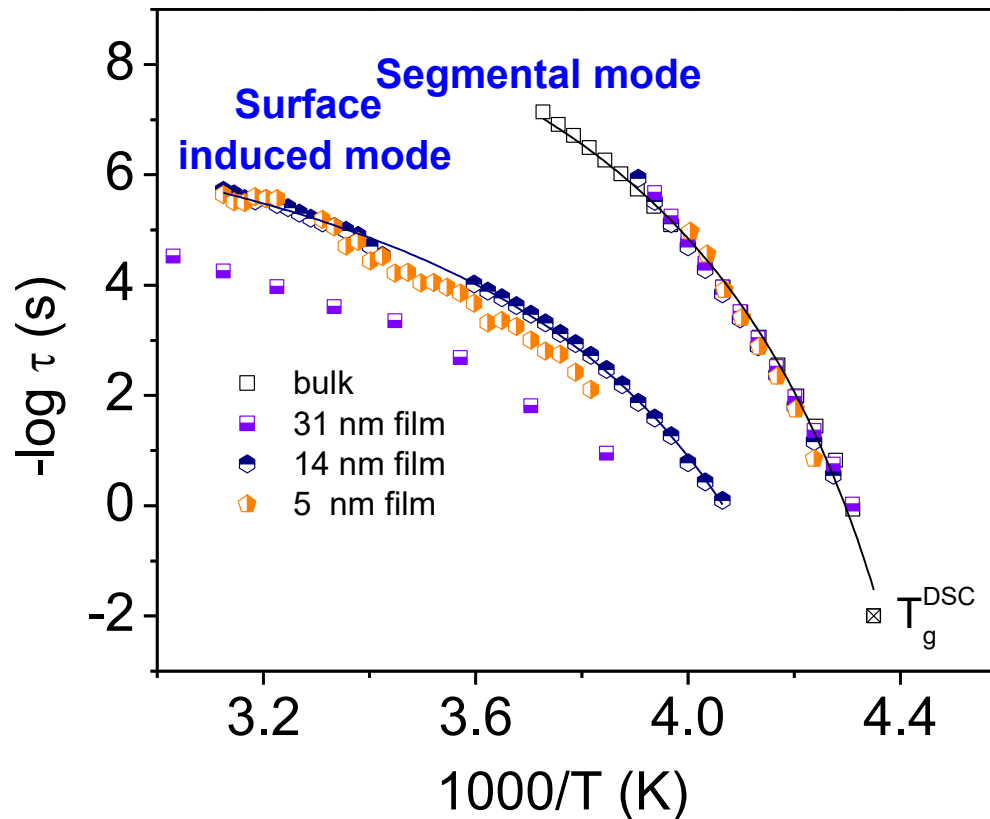
PMPS in 1D confinement and in bulk



Segmental mode: not broadened, peak position not shifted compared to bulk.

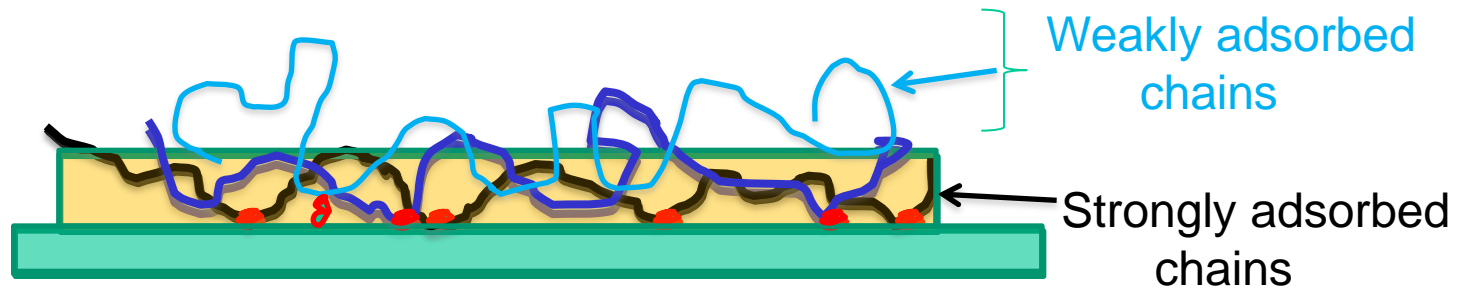
Surface induced mode: intensity increases with decreasing thickness

Activation plot: bulk and 1D confinement of PMPS



Segmental mode: not shifted compared to bulk
Surface induced mode: spectral position seems to be not only dependent on the thickness.

Origin of surface induce relaxation mode



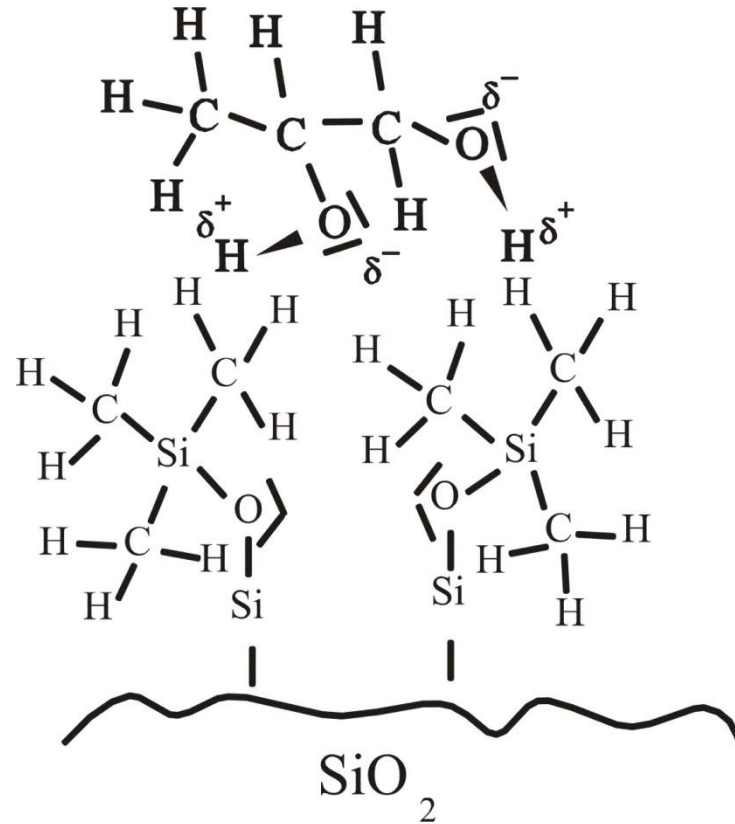
Adsorption and desorption process

Summary: PMPS in 1D confinement

1. Segmental dynamics: **not shifted** compared to bulk **down 5 nm**; **not broadened** with respect to bulk.
2. Surface induced mode: **increases in intensity** with decreasing thickness; **VFT-like temperature dependence**; **spectral position** seems to depend **not only on the thickness**; it is presumably assigned to **adsorption and desorption processes**.

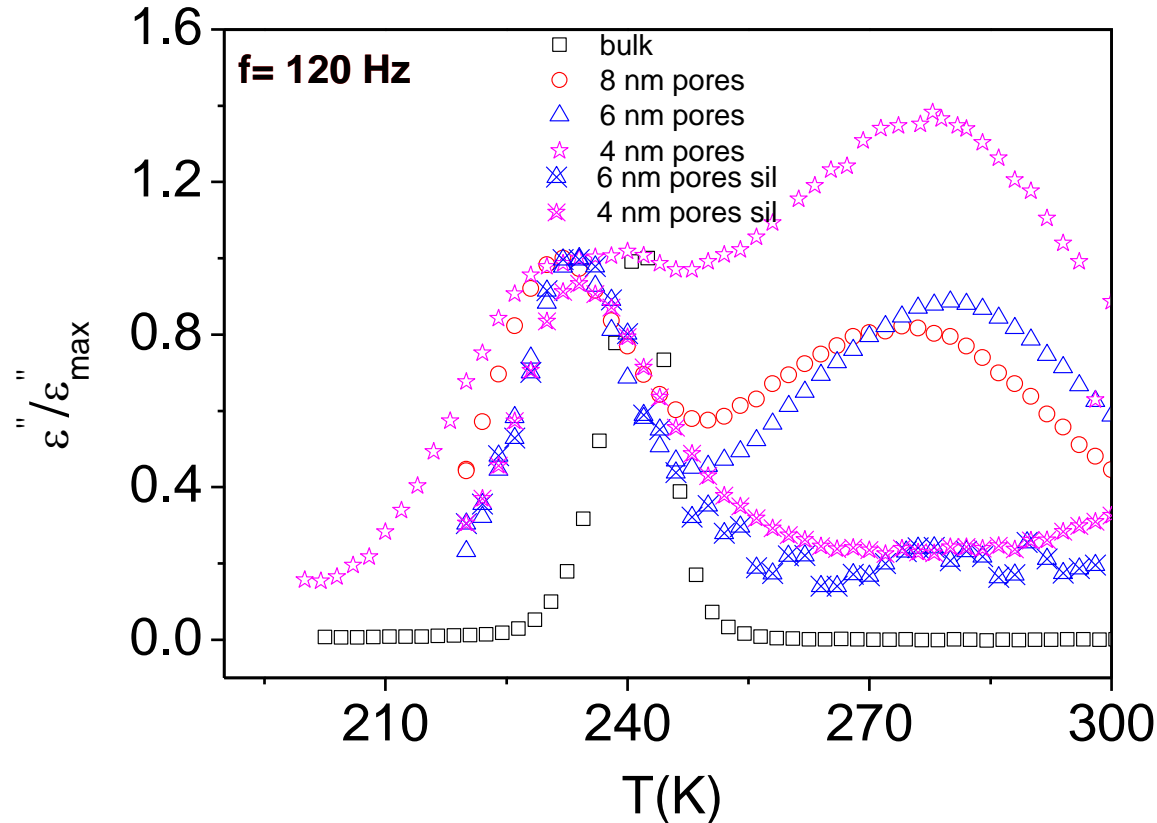
Dynamics of PMPS in 2D confinement

Due to **silanization** the **SiO₂** surfaces become hydrophobic



The attractive interaction between guest and host causes a slowing down of the molecular dynamics (Surface effect). Due to the silanization this effect is fully removed and a dynamics becomes comparable to that of a bulk liquid.

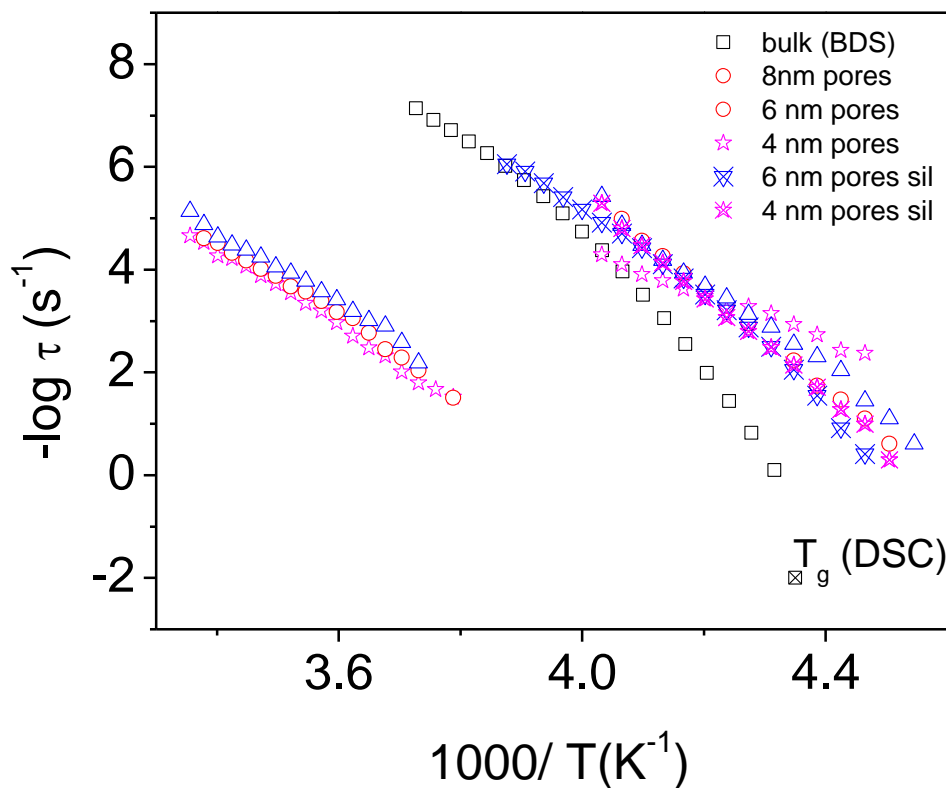
PMPS in 2D confinement and in bulk



Segmental mode: broadening in pores, which is removed by silanization, peak position shifted compared to bulk.

Surface induced mode: intensity increases with decreasing pore diameter; removed by silanization

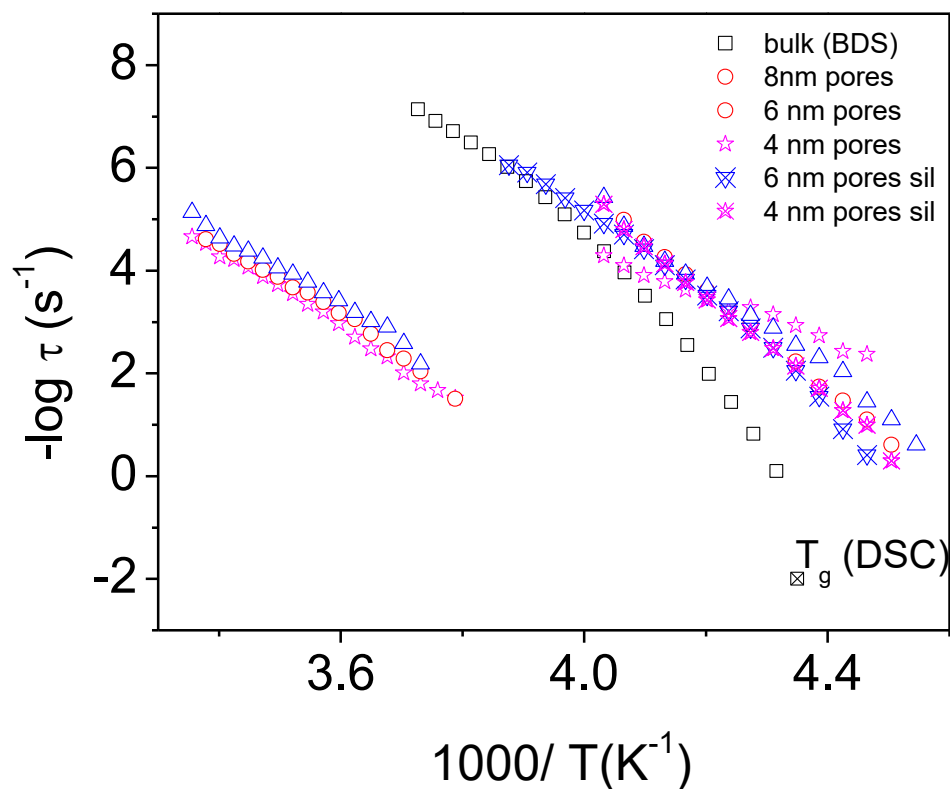
Activation plot: PMPS in 2D confinement and in bulk



Segmental mode: faster for smaller pore sizes; slower in silanized pores

Surface induced mode: no thickness dependence; much slower than segmental mode

Activation plot: PMPS in 2D confinement and in bulk



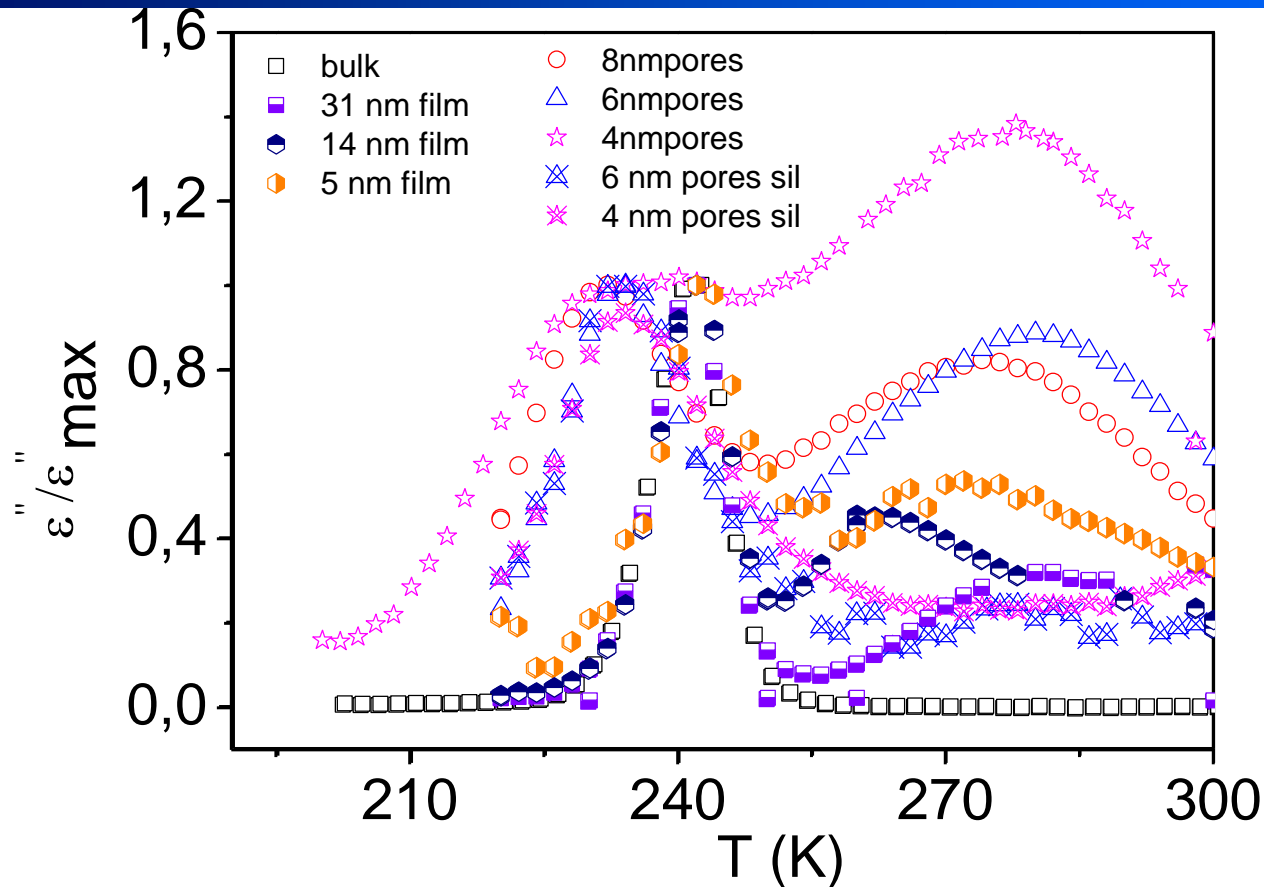
Segmental mode: faster for smaller pore sizes; slower in silanized pores

Surface induced mode: no thickness dependence; much slower than segmental mode

Summary: PMPS in 2D confinement

1. Segmental dynamics: **increases** with decreasing pore sizes; slower in silanized pores.
2. Surface induced mode: removed by silanization, no simple thickness dependence.

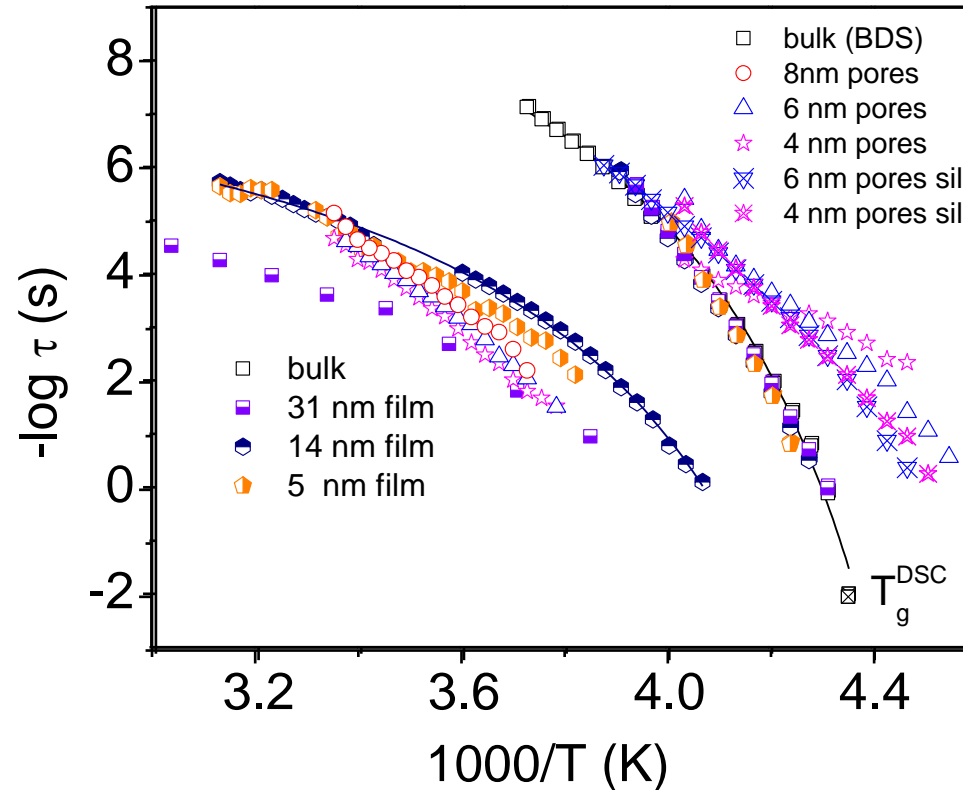
Normalized dielectric loss: 1D & 2D confinement



1D: Segmental mode: **not** broadened, peak position **not** shifted
surface induced mode: **weak** thickness dependence, if any

2D: Segmental mode: **shifted from bulk, strongly broadened**
Surface induced mode: stronger than in 1D, removed by silanisation

Activation plot: PMPS in 1D&2D confinement



1-D: Segmental: not shifted compared to bulk

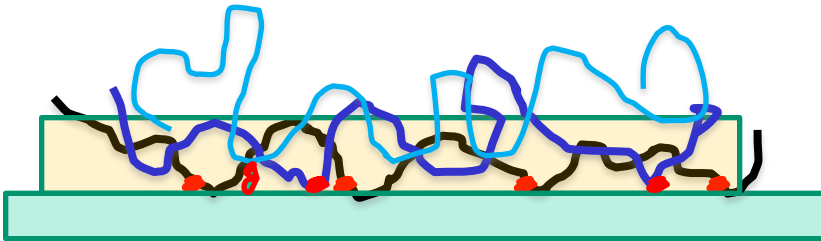
surface induced mode: Weak thickness dependence, if any weak

2-D: Segmental: the faster, the smaller the pores; silanization
causes removal of the surface effect

Surface induced mode: **no thickness** dependence

Consistent interpretation for PMPS in 1-&2-D confinement

1D

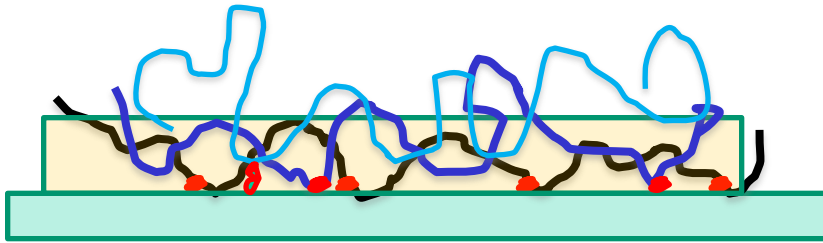


Segmental mode: not broadened, peak position not shifted, but confinement induced process.

Conclusion: The density is not changed, hence the dynamics is not altered. Due to surface effect surface induced modes.

Consistent interpretation for PMPS in 1D&2D conf.

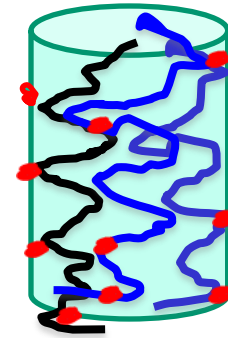
1D



Segmental mode: not broadened, peak position not shifted, but confinement induced process.

Conclusion: The density is not changed, hence the dynamics is not altered. Due to surface effect surface induced modes.

2D



In unsilanized pores, strong interaction with inner surfaces, thus a less efficient packing and hence a reduced density and more free volume resulting in a faster dynamics – confinement effect.

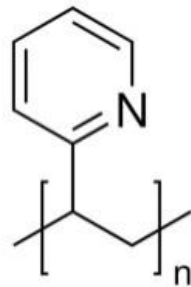
In silanized pores the surface interaction is suppressed, but the confinement effect is still visible for small pores.

Conclusions

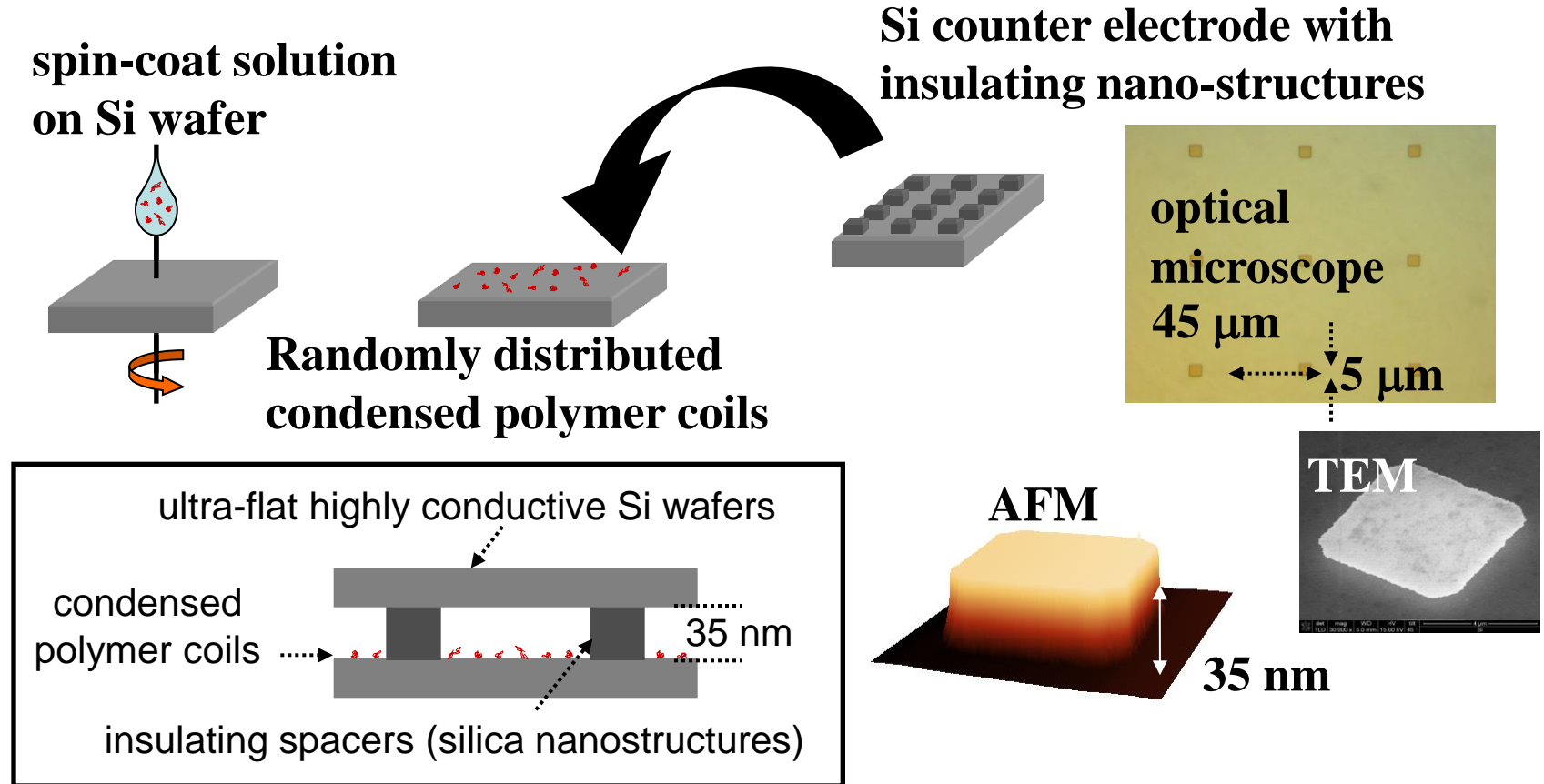
- 1. Dimensionality of confinement impacts the inter-molecular dynamics differently**
- 2. Segmental dynamics in 2D becomes faster in smaller pores due to a confinement effect but remains bulk-like in 1D confinement.**
- 3. Dynamics of the surface induced mode in both, 1D and 2D confinement show no systematic thickness dependence.**

Kipnusu, W.K. et al., *ACS Appl. Mater. Interfaces*, **7**, 12328–12338 (2015); Kipnusu, W.K. et al., *J. Phys. Chem. Lett.* **6**, 3708-3712 (2015); Kipnusu W.K. et al., *J. Chem. Phys.* **146**, 203302 (2017)

6. Glassy dynamics of **condensed isolated polymer chains** (polyvinylpyridin (P2VP))

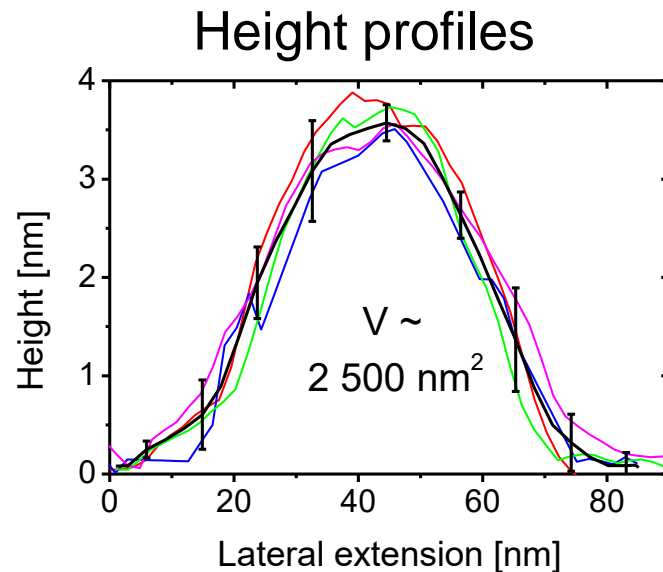
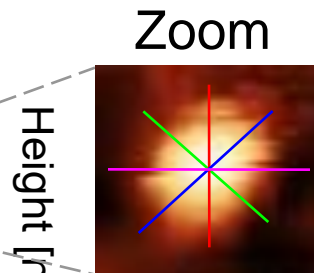
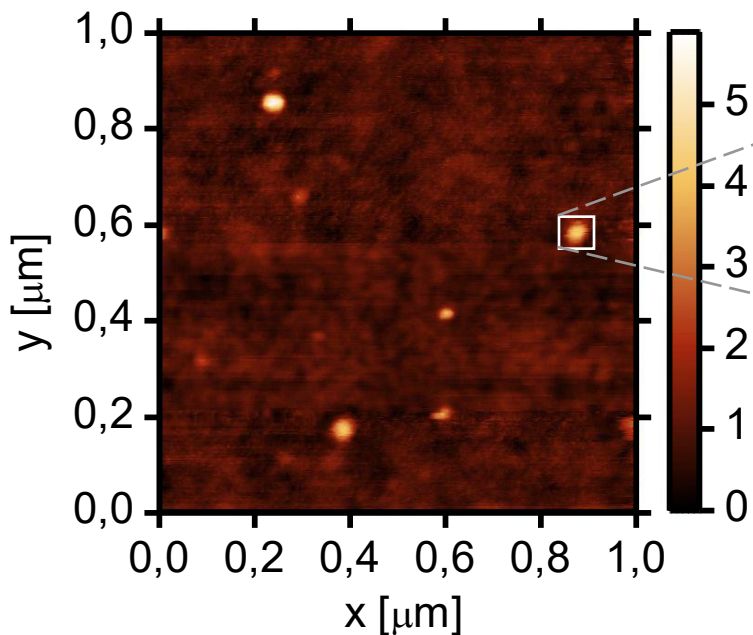


Nanostructured electrodes enable one to measure both in parallel, structure (by AFM) and dynamics (by BDS)



- **nano-structured electrodes** enable one to avoid evaporation of a counterelectrode.
- For the **identical sample dynamics** by BDS and structure by AFM can be measured.

Isolated polymer chains: AFM characterization



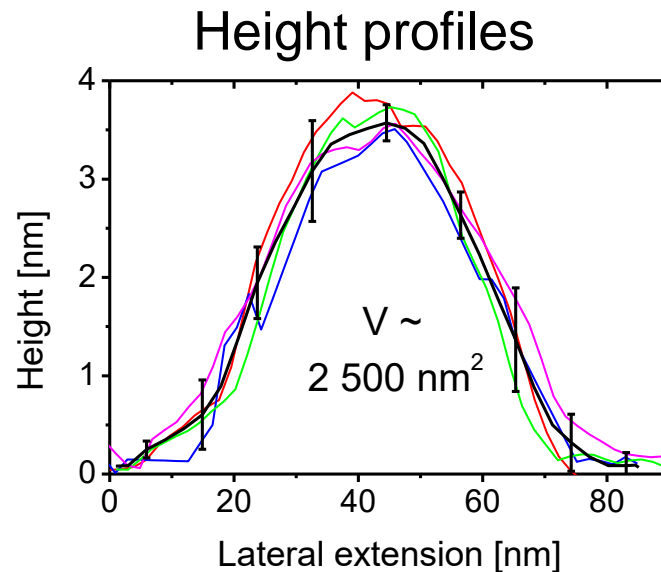
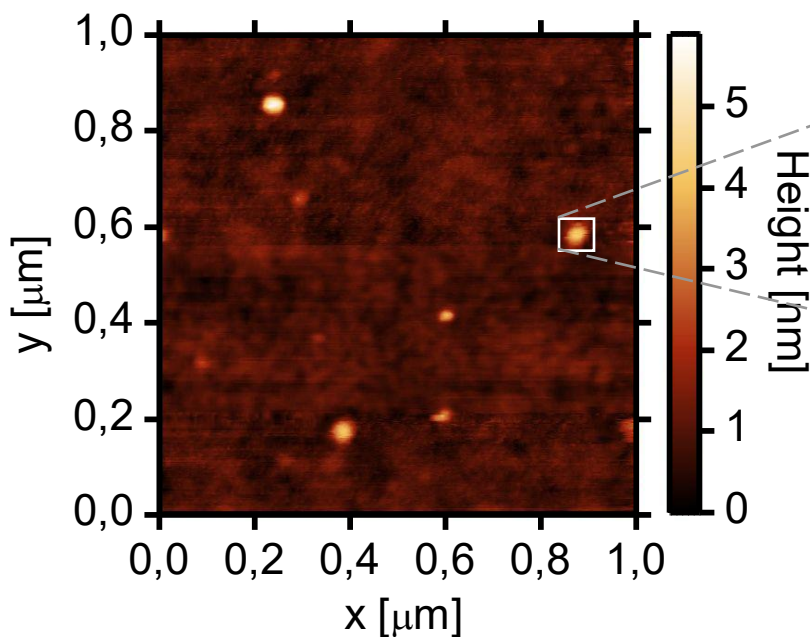
Calculated single chain volume
(assuming bulk density) for M_n
 $= 1\,510\text{ kg/mol}$:

$$V_{\text{chain}} = 2\,251\text{ nm}^3$$

Experimental (AFM) mean coil volume
(55 “droplets”):

$$V_{\text{coil}} = 2\,030 (\pm 500)\text{ nm}^3$$

Isolated polymer chains: AFM characterization



Calculated single chain volume
(assuming bulk density) for M_n
= 1 510 kg/mol:

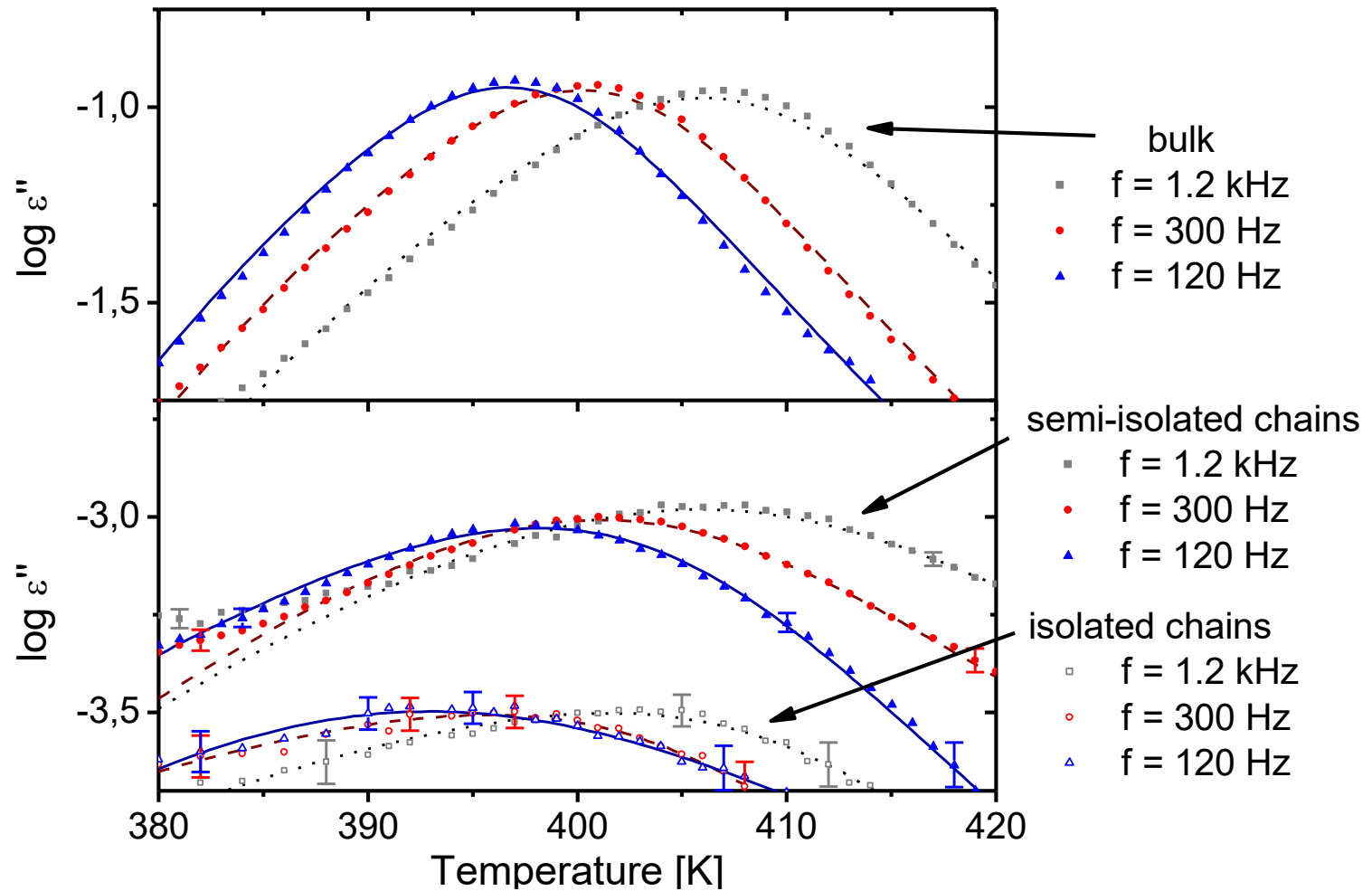
$$V_{\text{chain}} = 2\,251 \text{ nm}^3$$

Experimental (AFM) mean coil
volume (55 “droplets”):

$$V_{\text{coil}} = 2\,030 (\pm 500) \text{ nm}^3$$

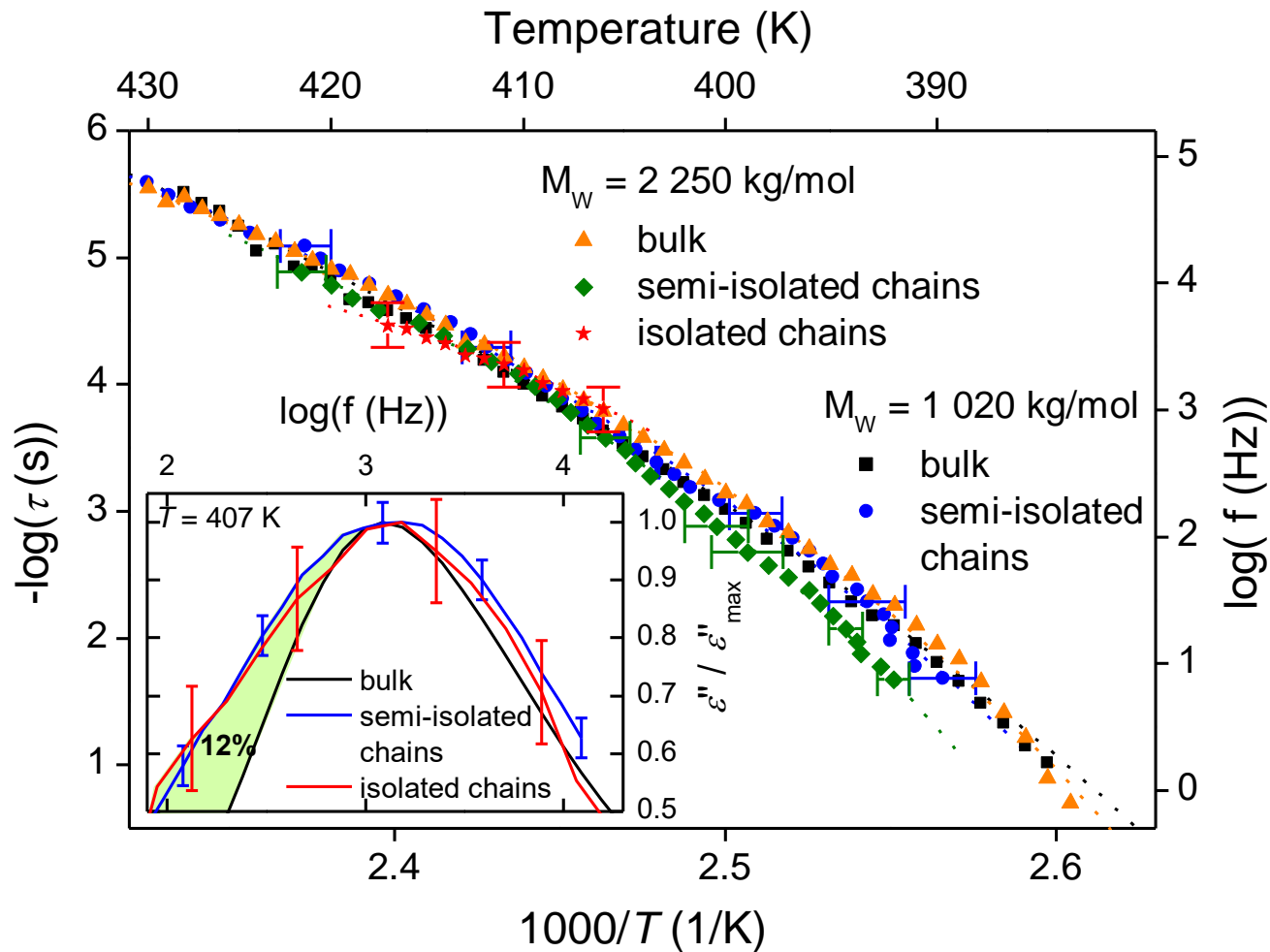
$$V_{\text{chain}} / V_{\text{coil}} = 1.1 \pm 0.2$$

The dynamics of condensed (semi)-isolated chains



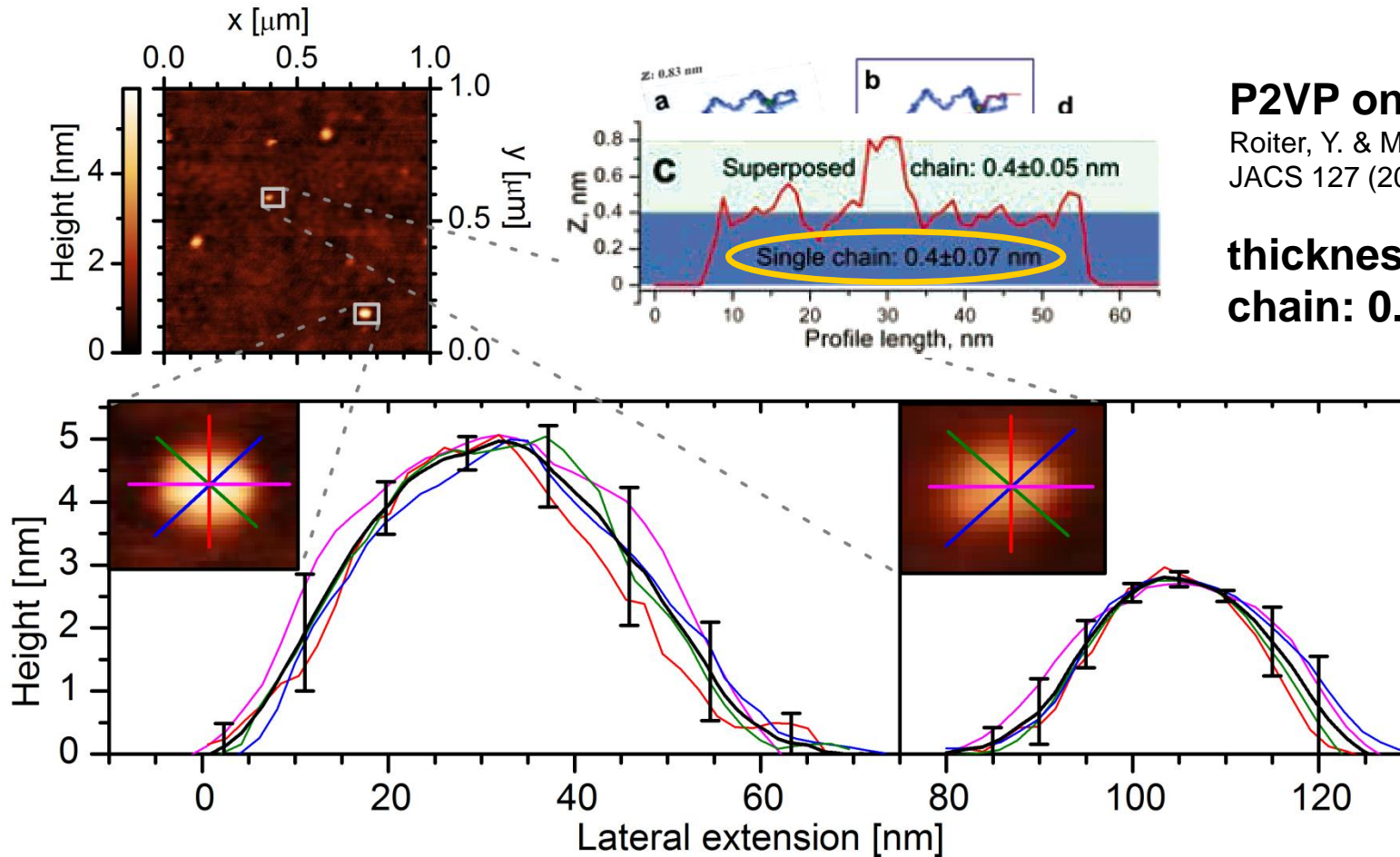
(semi)-isolated P2VP chains perform a dynamic glass transition

The dynamics of condensed (semi)-isolated chains



- The mean relaxation rate of (semi)-isolated P2VP chains time is **bulk-like with a VFT-temperature dependence;**
- The relaxation time distribution is **broadened on the low frequency side.**

AFM characterization



P2VP on mica

Roiter, Y. & Minko, S.,
JACS 127 (2005), 15688

**thickness of P2VP-
chain: 0.4 nm**

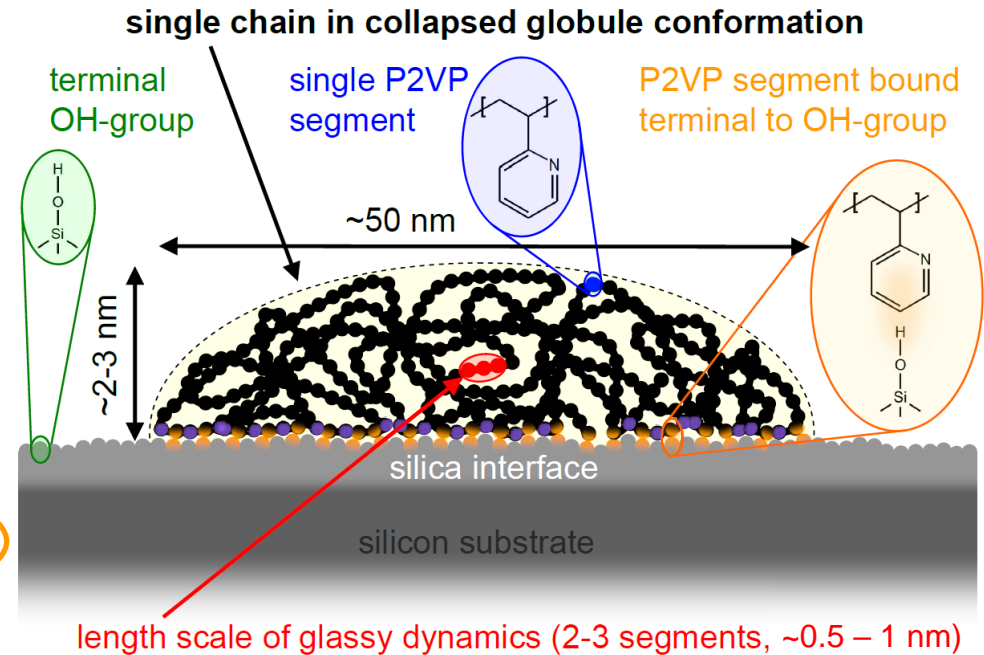
- ~30%** of segments contact the substrate **directly** (= 1st layer)
- factor of **~2 more** than broadening in BDS (~15% slowed fraction)
- only **~50%** of segments in 1st layer affected by the surface?

Glassy dynamics of isolated condensed P2VP chains

- mostly **bulk-like** glassy dynamics

• **~50%** of segments in 1st layer are **slowed**

• **~50%** of segments in 1st layer **establish bonds**

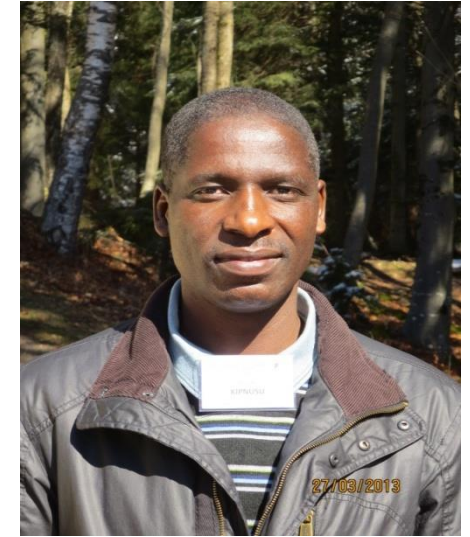


- studies on polymer adsorption* suggest: **bound segments** are largely **immobilized** and segments **in between** are **slowed**
- range of interfacial effects on glassy dynamics **~0.5 - 1 nm** (P2VP/ silica)

Final summary

1. Glassy dynamics is based on the fluctuation of $\sim 2 - 3$ polymer segments i.e. a length scale of about 5\AA still below the typical dimensions of nanometric (1-D or 2-D) confinement.
2. For segmental fluctuations (**dynamic glass transition**) **no thickness** and **no molecular weight** dependence is found. Even a broadening of the relaxation – time distribution function is not detected in nanometric layers.
3. **Dimensionality of confinement** impacts the inter-molecular dynamics differently
4. Segmental dynamics in 2D becomes faster in smaller pores due to a **confinement effect** but **remains bulk-like in 1D confinement**.

Thanks to



**K.-J. Eichhorn, B. Voit,
IPF (Dresden)**

**C. Schick,
(Rostock)**

**M. Reiche
(Halle)**

**W. Paul. M. Solar
(Halle)**