Molecular Dynamics in geometrical confinement

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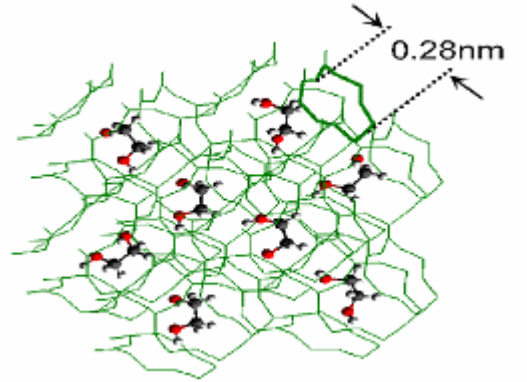
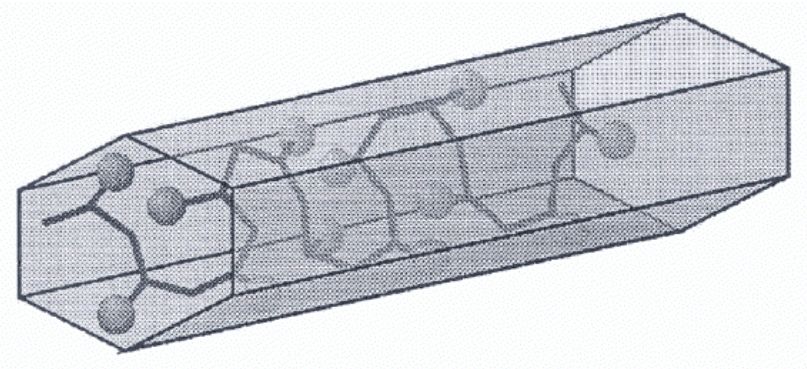
	L. Léger	Collège de France

Examples of geometrical confinement

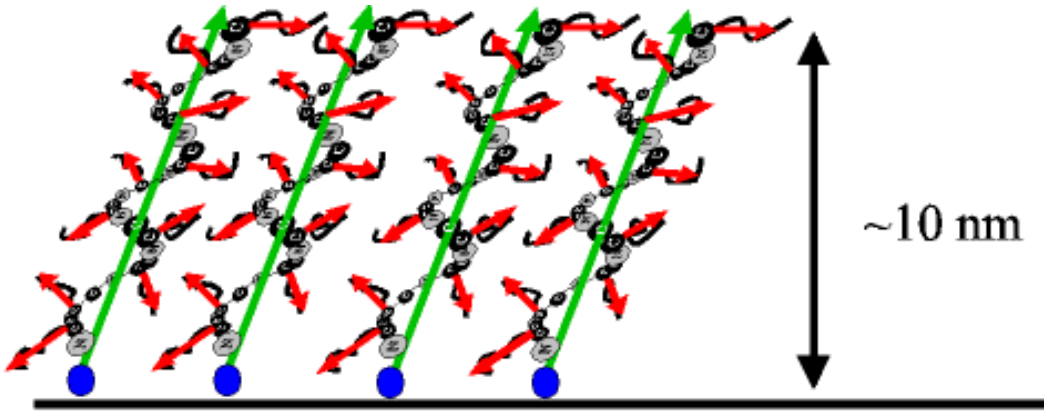
guest-molecules in (zeolitic) host-systems



single polymer chains in microporous channels of MCM



grafted polymers



Questions:

1. **What is the dynamics of a single molecule being isolated in a zeolitic cage?**

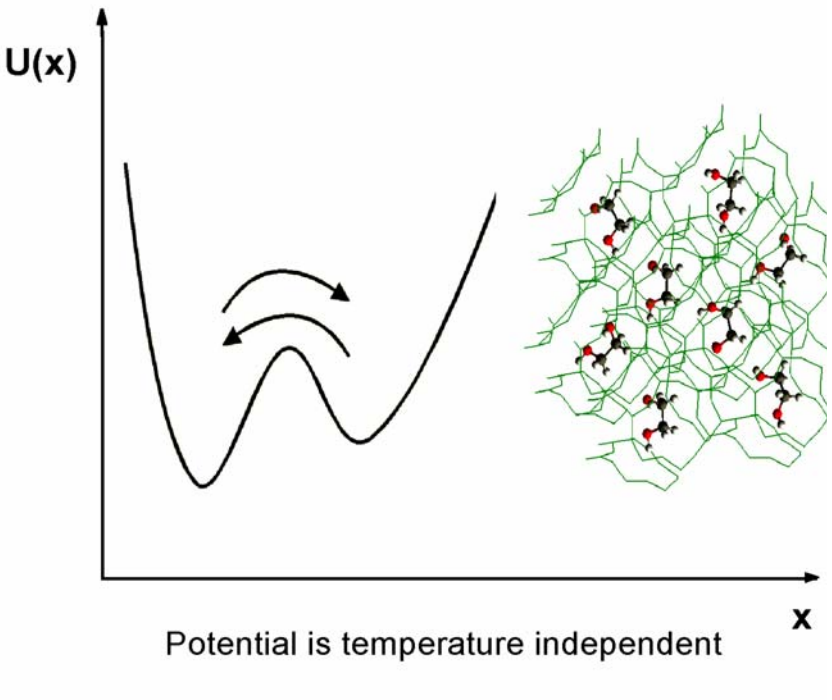
2. **How many molecules form a liquid?**

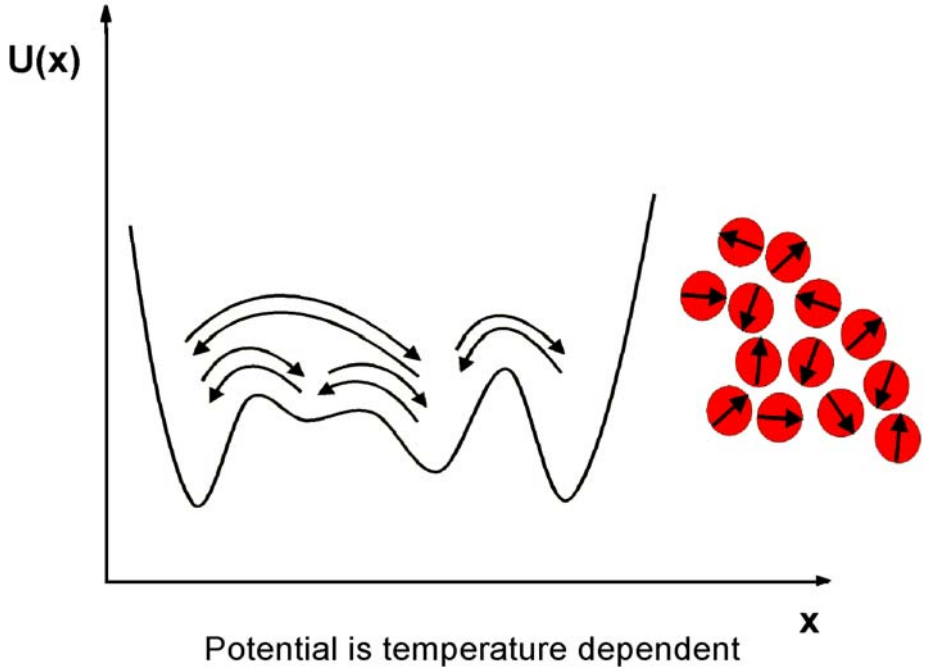
3. **What is the dynamics of an isolated polymer chain compared to the bulk?**

4. **What is the dynamics of polymers grafted onto a solid substrate?**

Single molecule relaxation

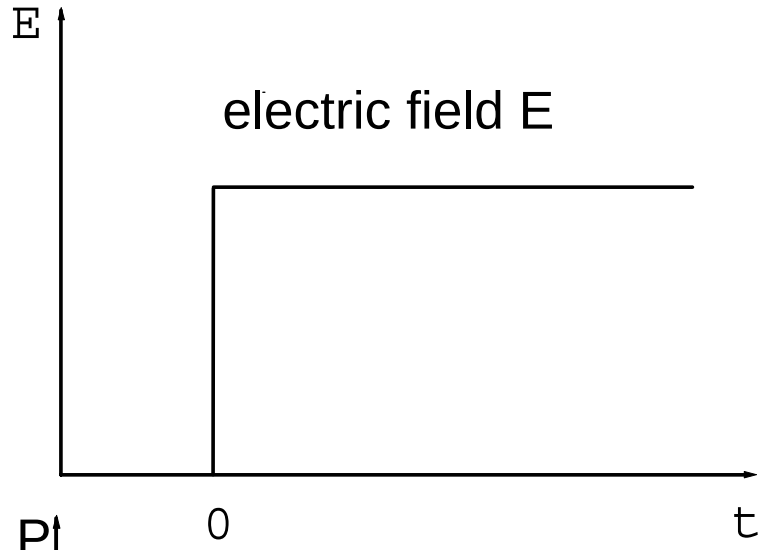
Liquid-like relaxation
(dynamic glass transition)

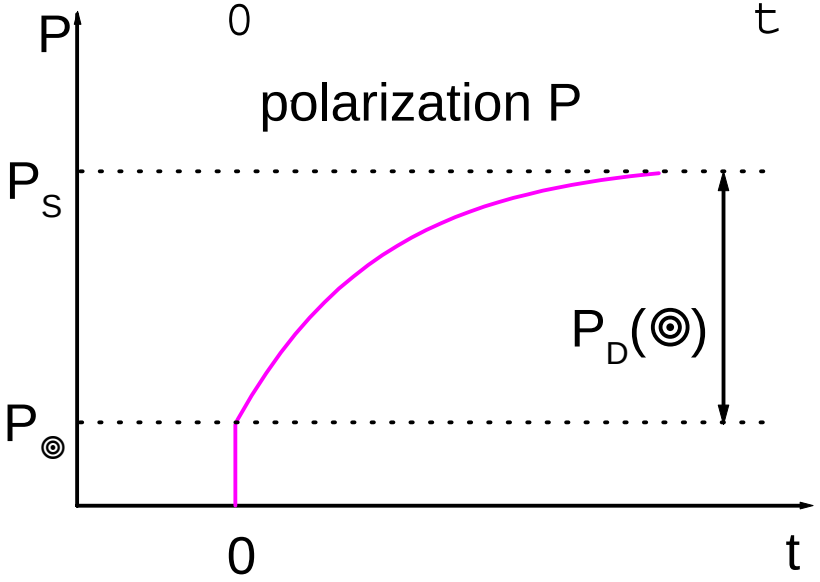




The temperature dependence of the relaxation rate enables one to distinguish between a single molecule and a liquid-like relaxation.

Dielectric spectroscopy

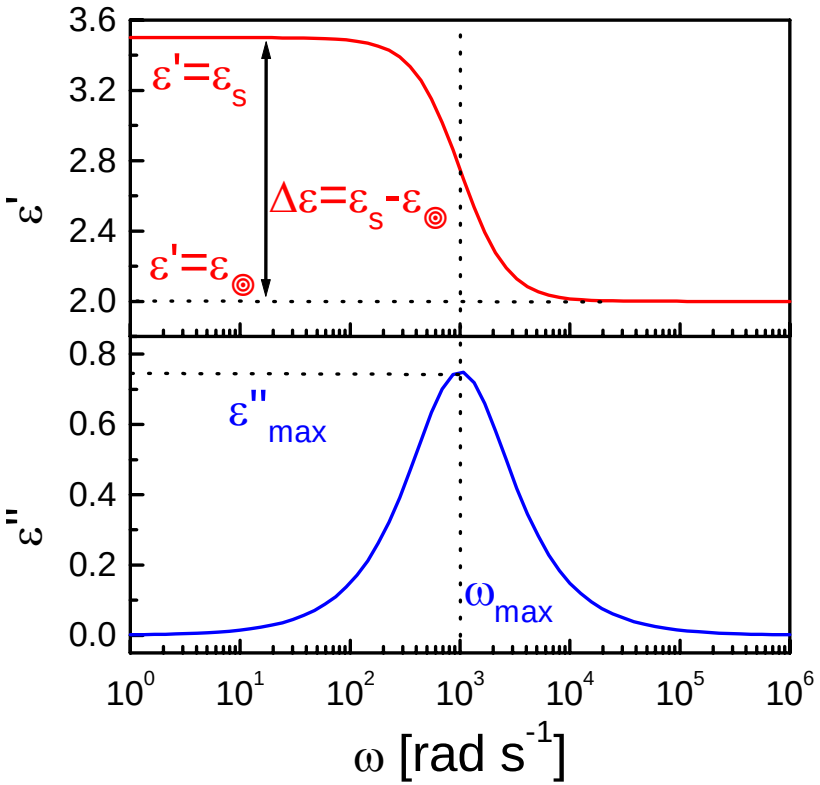




complex dielectric function $\epsilon^*(\omega, T)$

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

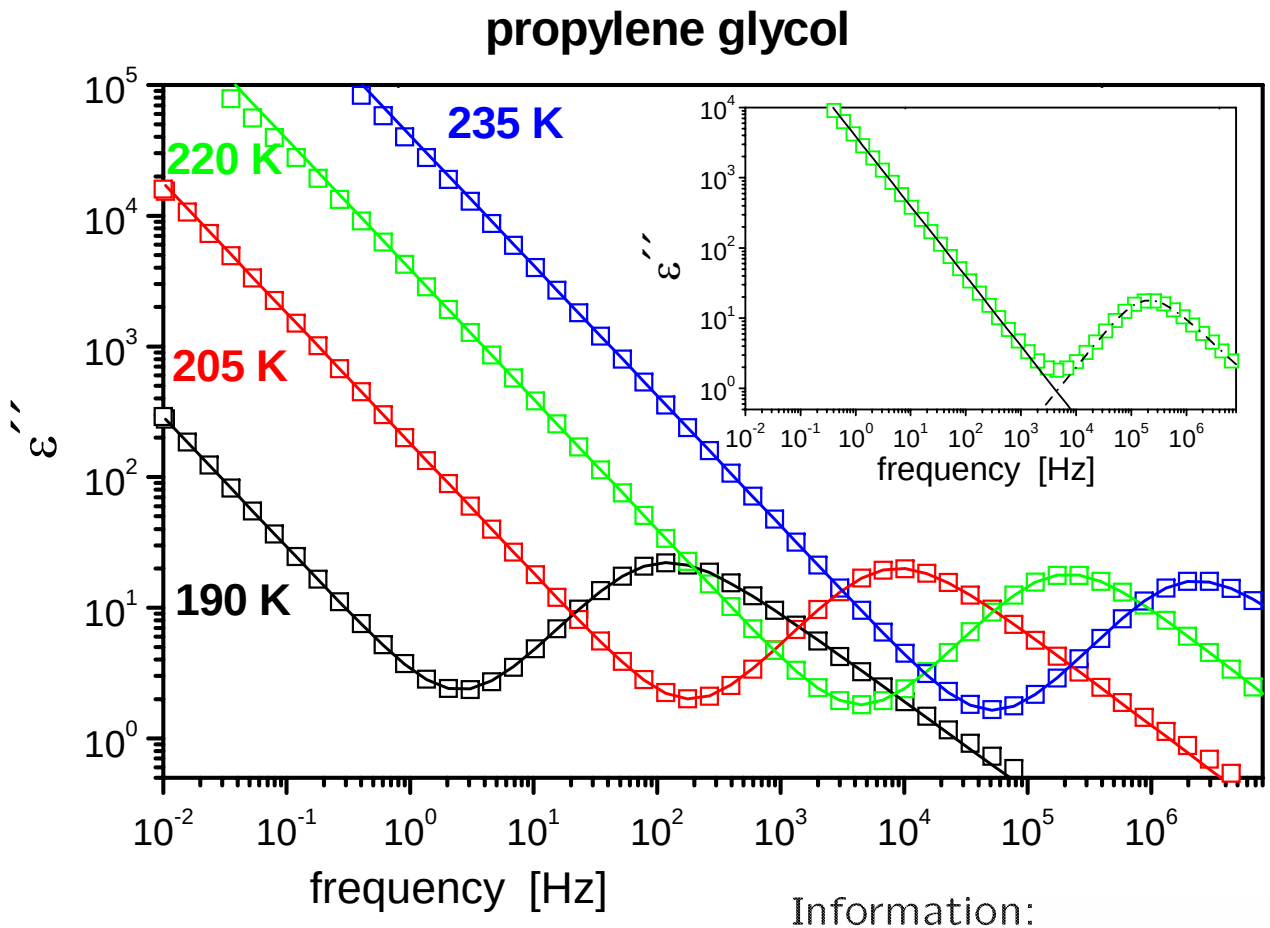
Debye relaxation $\varepsilon^* = \varepsilon_\infty + \dfrac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)}$



$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\ \tau)^2}$$

$$\varepsilon''(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega\ \tau)^2}\omega\ \tau$$

Analysis of the dielectric data



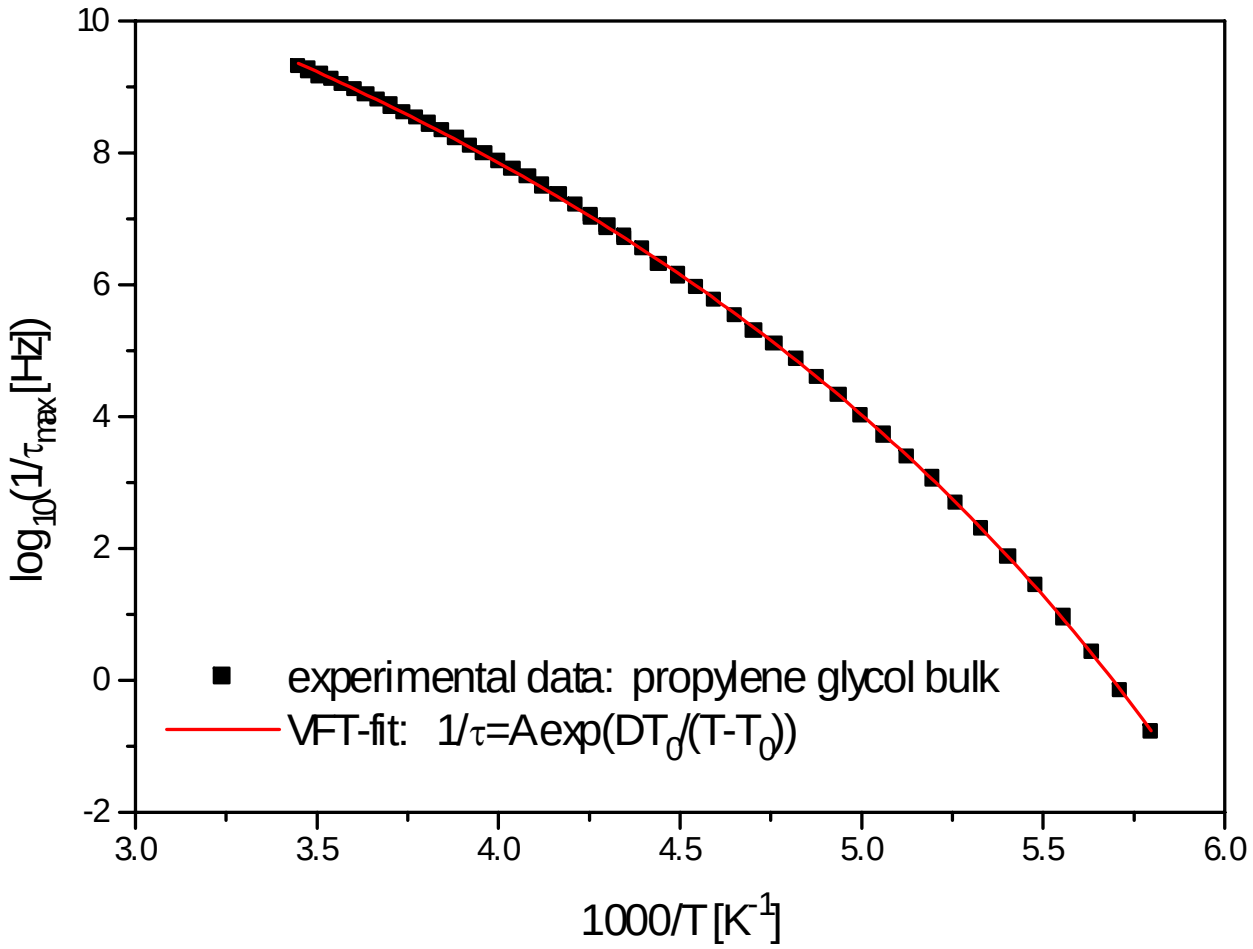
Havriliak-Negami fit function:

$$\epsilon'' = \frac{\sigma_0}{\epsilon_0} \cdot \frac{a}{\omega^s} - \Im\left[\frac{\Delta\epsilon}{(1+(\imath\omega\tau)^\alpha)^\gamma}\right]$$

Information:

- relaxation time τ
- relaxation time distribution $g(\tau)$, parameters α and γ
- dielectric strength $\Delta\epsilon \propto n \cdot \frac{\mu^2}{3kT}$

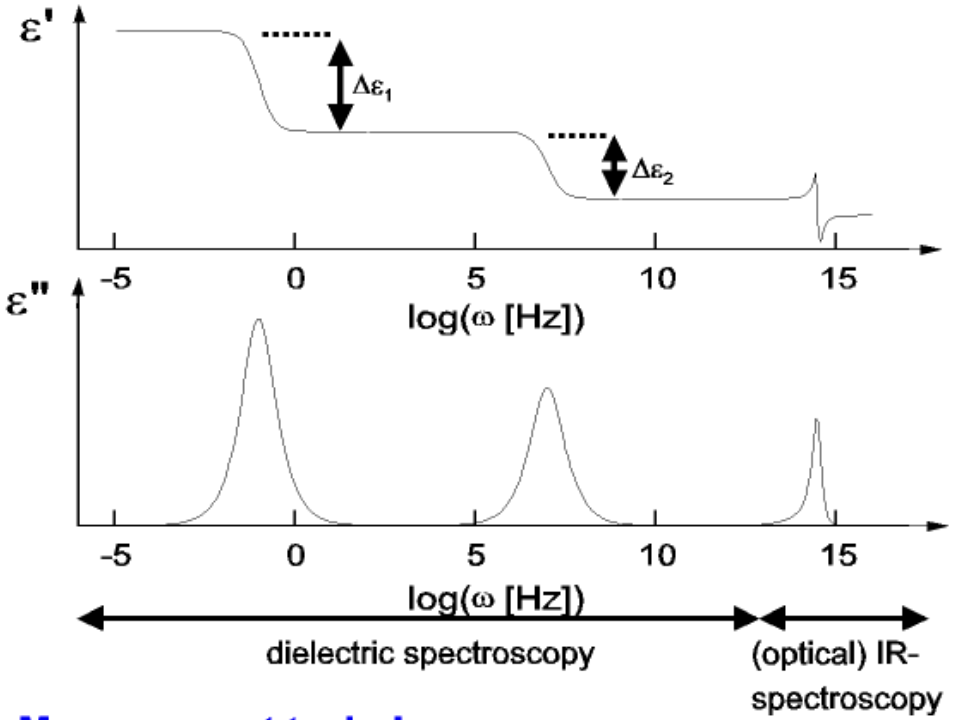
Analysis of the dielectric data



Information:

- type of thermal activation (VFT -or Arrhenius-like)

Broadband dielectric measurement techniques



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

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

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

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

(Sample amount required <5mg)

Measurement techniques:

Time-domain spectrometer

Frequency response analyser

AC-bridges

Coaxial line reflectometer

Network analyser

Wave-guides-techniquies

KREMER · SCHÖNHALS (Eds.)
Broadband Dielectric Spectroscopy

The interaction of electromagnetic waves with matter in the frequency range between 10^{-6} and 10^{15} 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

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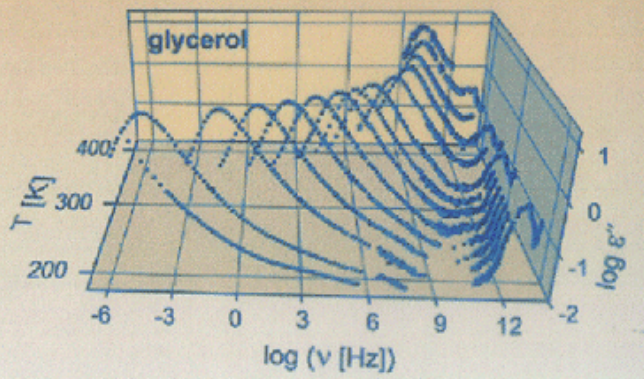
Broadband Dielectric Spectroscopy

Friedrich Kremer
Andreas Schönhals
Editors

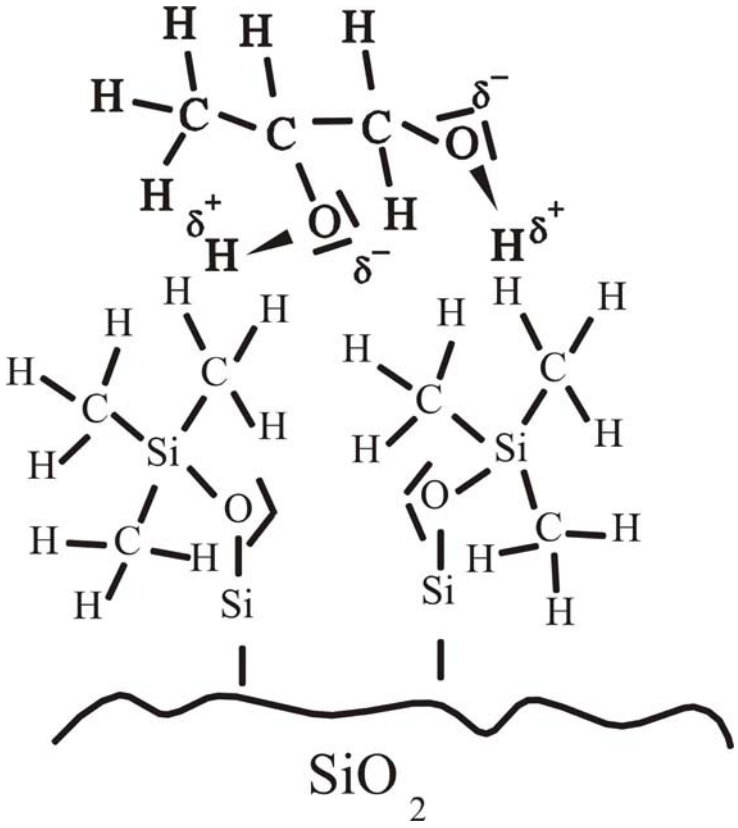
Broadband Dielectric Spectroscopy

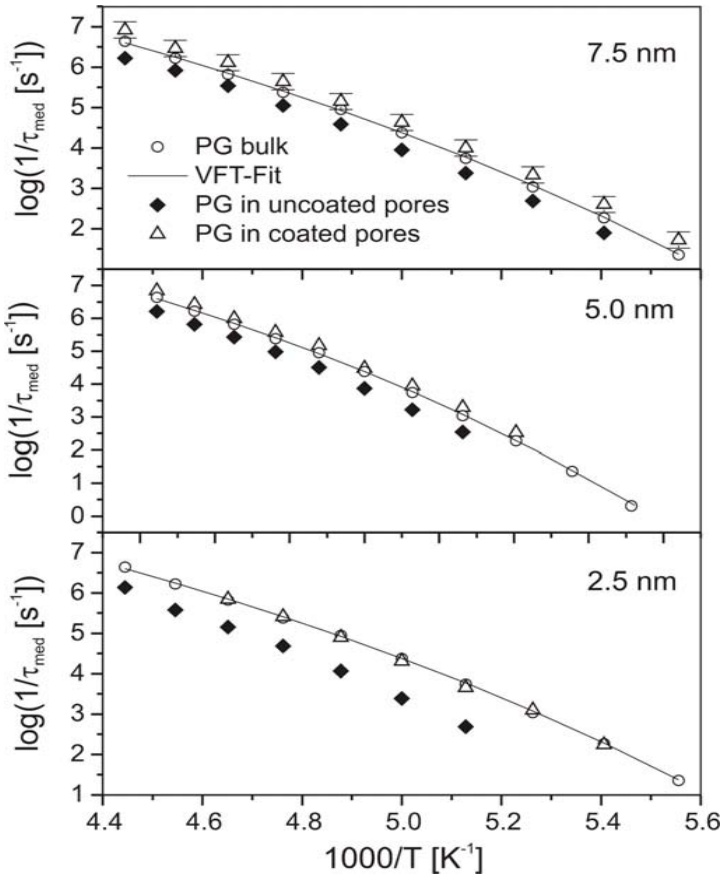


Springer

What controls the dynamics of (low molecular weight) molecules in confinement?

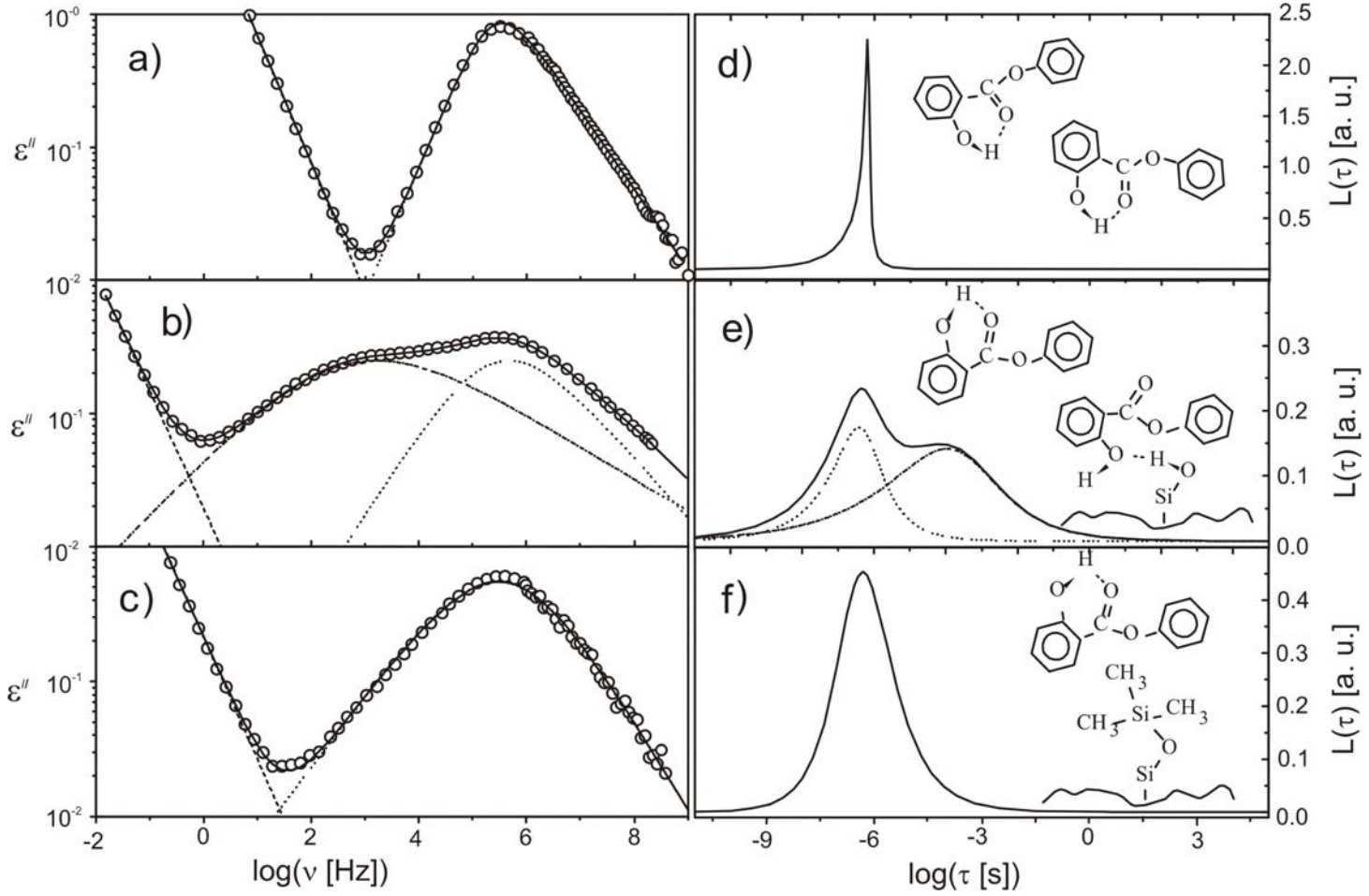
Attractive vs. repulsive interactions between guest and host (e.g. Propylenglycol in uncoated and silanised SiO2 surfaces of Sol-gel glasses)





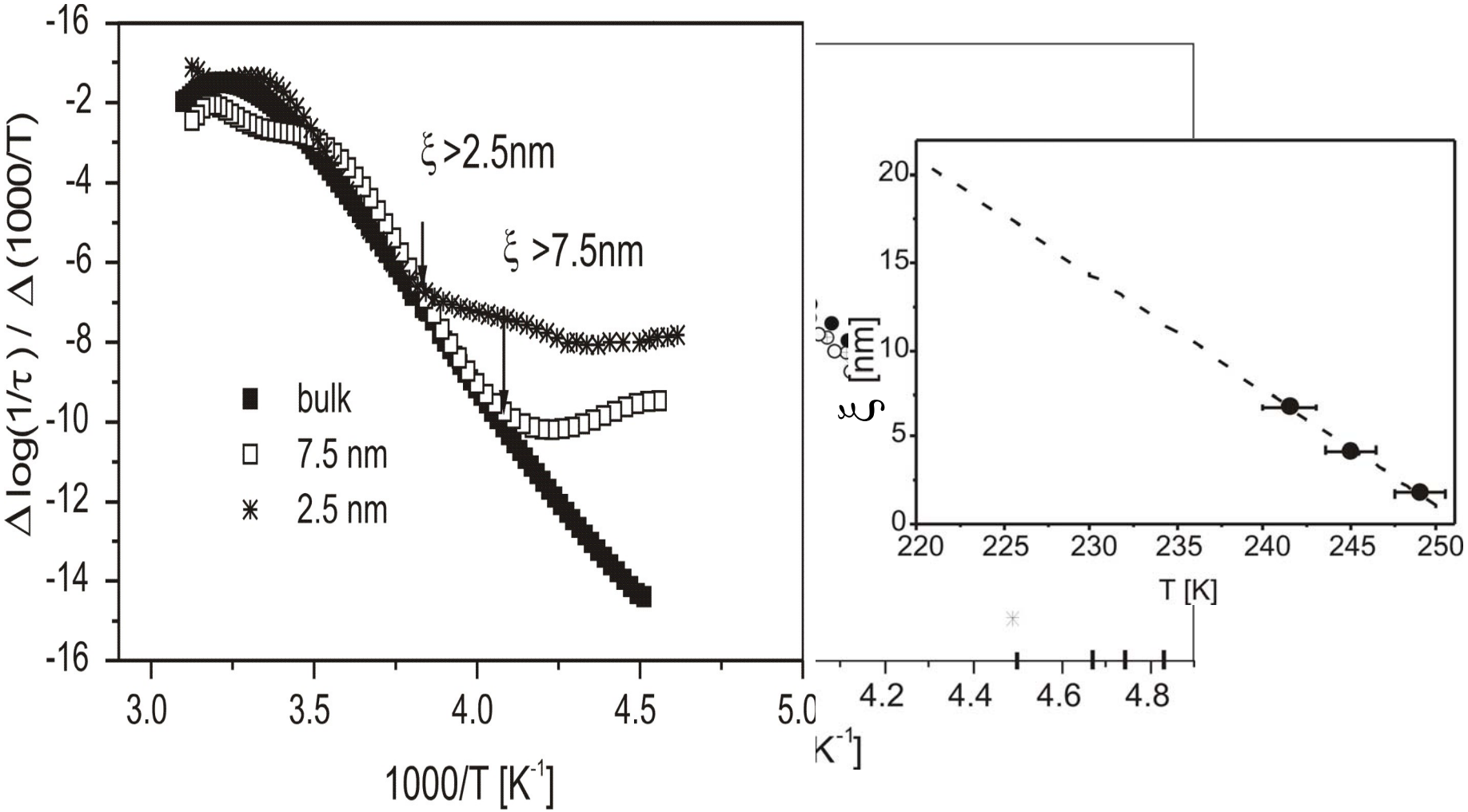
The attractive interaction between guest and host causes a slowing down of the molecular dynamics (Surface effect).Due to the silanization this effect is fully removed and a dynamics becomes comparable to that of a bulk liquid .

Another example:Salol in coated and non-coated Sol-Gel glasses



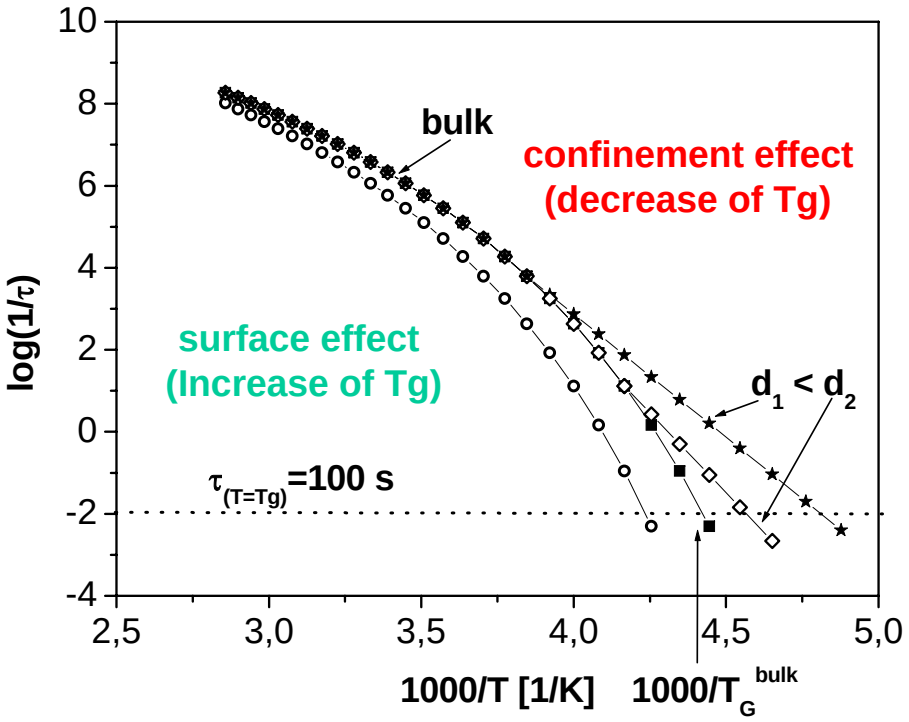
In uncoated nanopores two relaxation processes are observed due to the adsorbed and "free" salol molecules.In silanized nanopores the suface effect is fully removed.

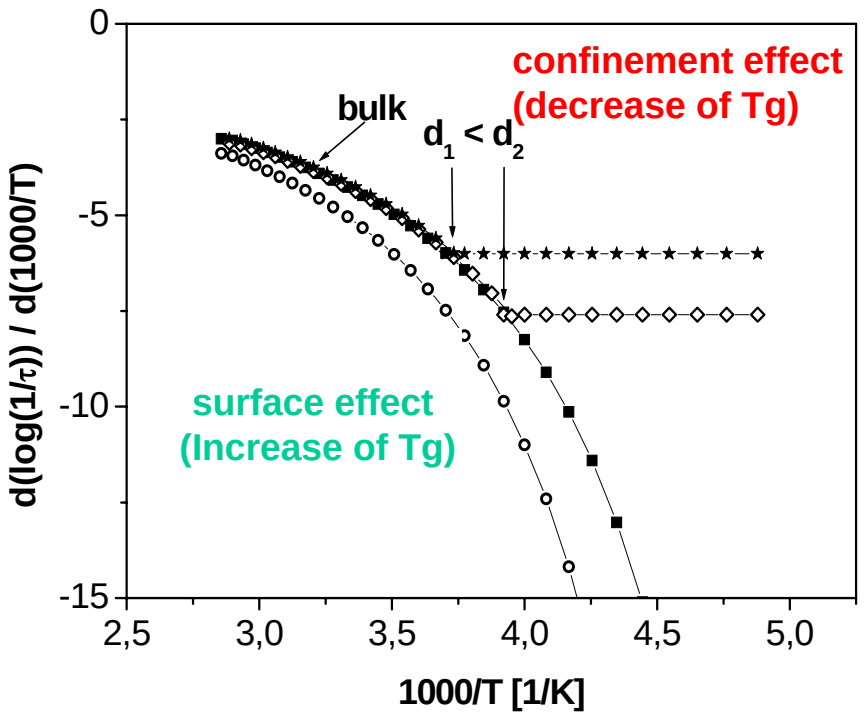
Salol in silanized nanopores



Confinement effect:The molecular dynamics becomes faster with increasing confinement.An inherent length-scale exists for the dynamic glass transtion.

A first conclusion: The molecular dynamics in confinement is the result of a counterbalance between surface and confinement effects.





Surface effect: Due to the attractive interaction between host and guestsystem the molecular dynamics is slowed down

Confinement effect: The growth of the inherent lengthscale of the dynamic glass transition is limited by the external confinement.This causes a change from a VFT- to an Arrehnius temperature dependence

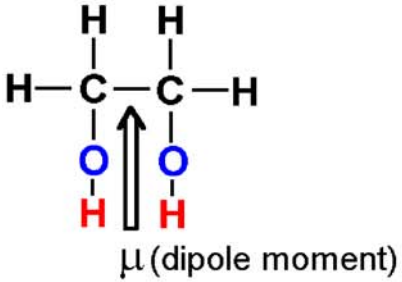
Ethylene glycol in zeolites: From the single molecule to the bulk liquid

or

“How many molecules form a liquid?“

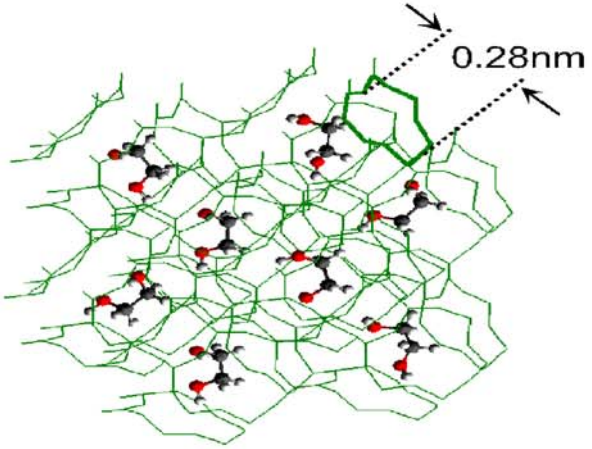
Ethylene glycol in zeolitic host systems

ethylene glycol
(EG, ethanediol)



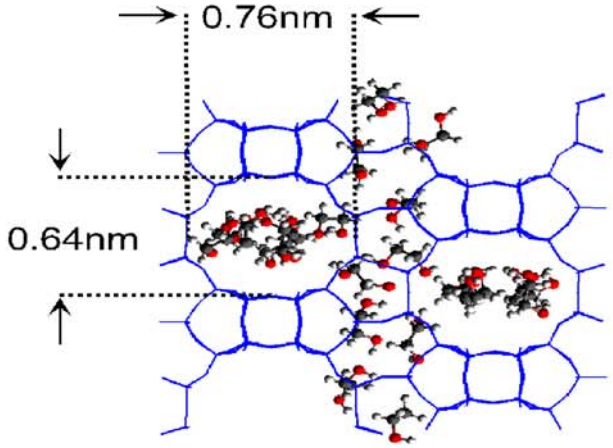
silica-sodalite (SiO_2)

cubic cages
lattice constant 0.89nm
"*one* molecule per cage"



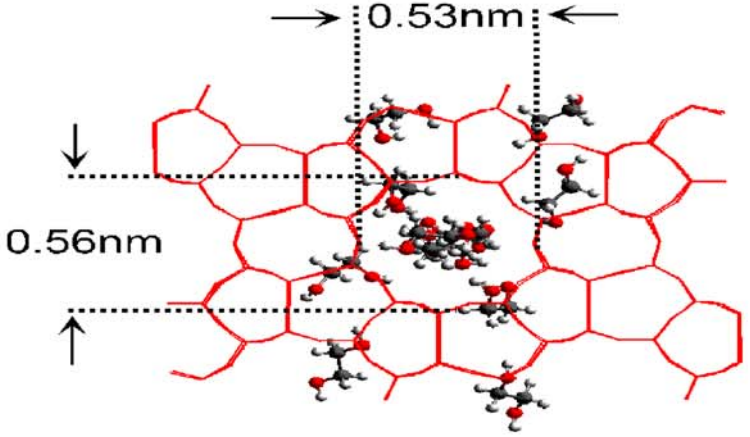
silicalite (SiO_2) channels

0.56nm x 0.53nm 0.55nm x 0.51nm



zeolite beta (SiO_2/Al_2O_3) Si : Al ratio 40

channels 0.76nm x 0.64nm 0.55nm x 0.55nm



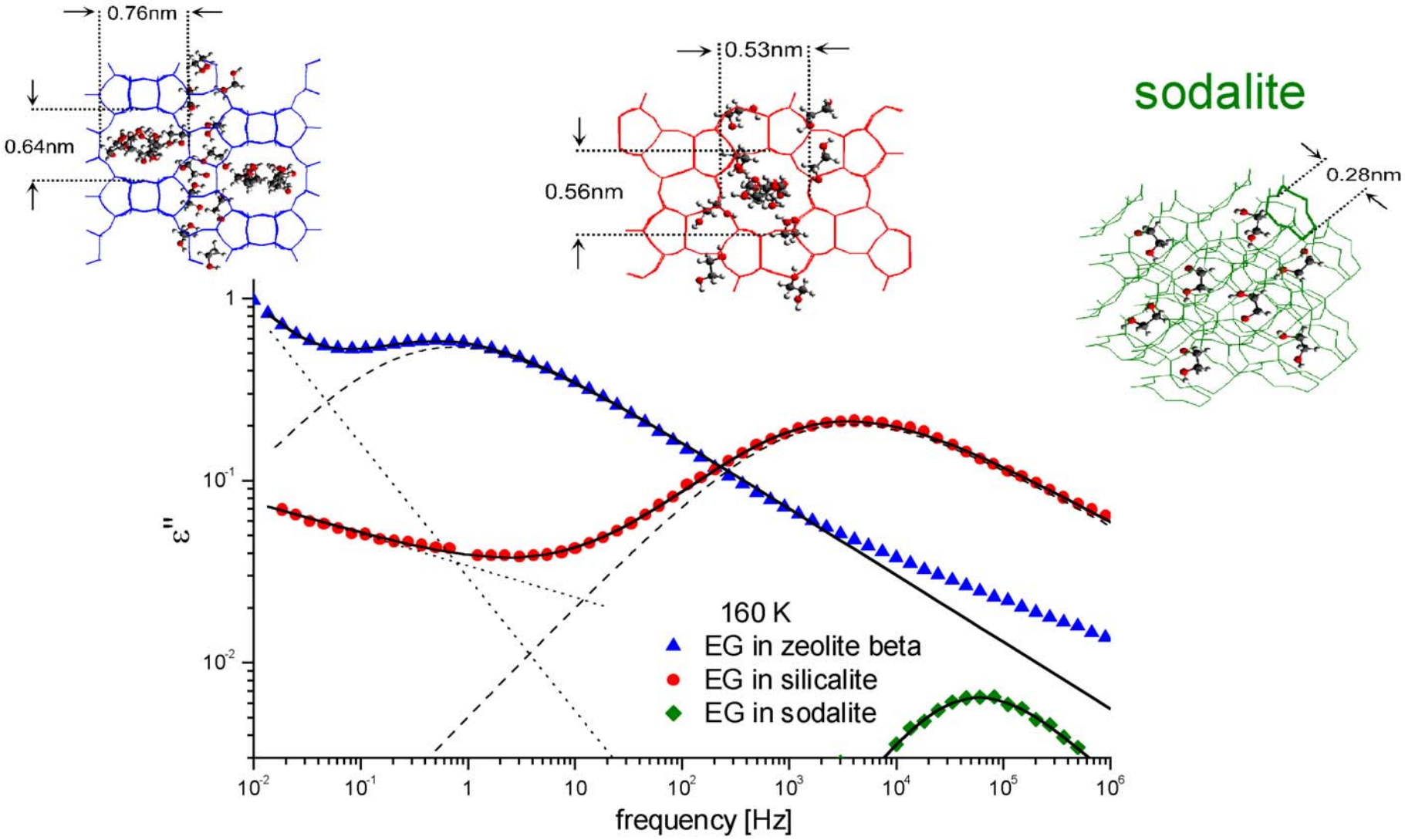
The chemical composition of all zeolites is nearly identical.

Dielectric spectra of ethylene glycol (EG) in different zeolitic host systems

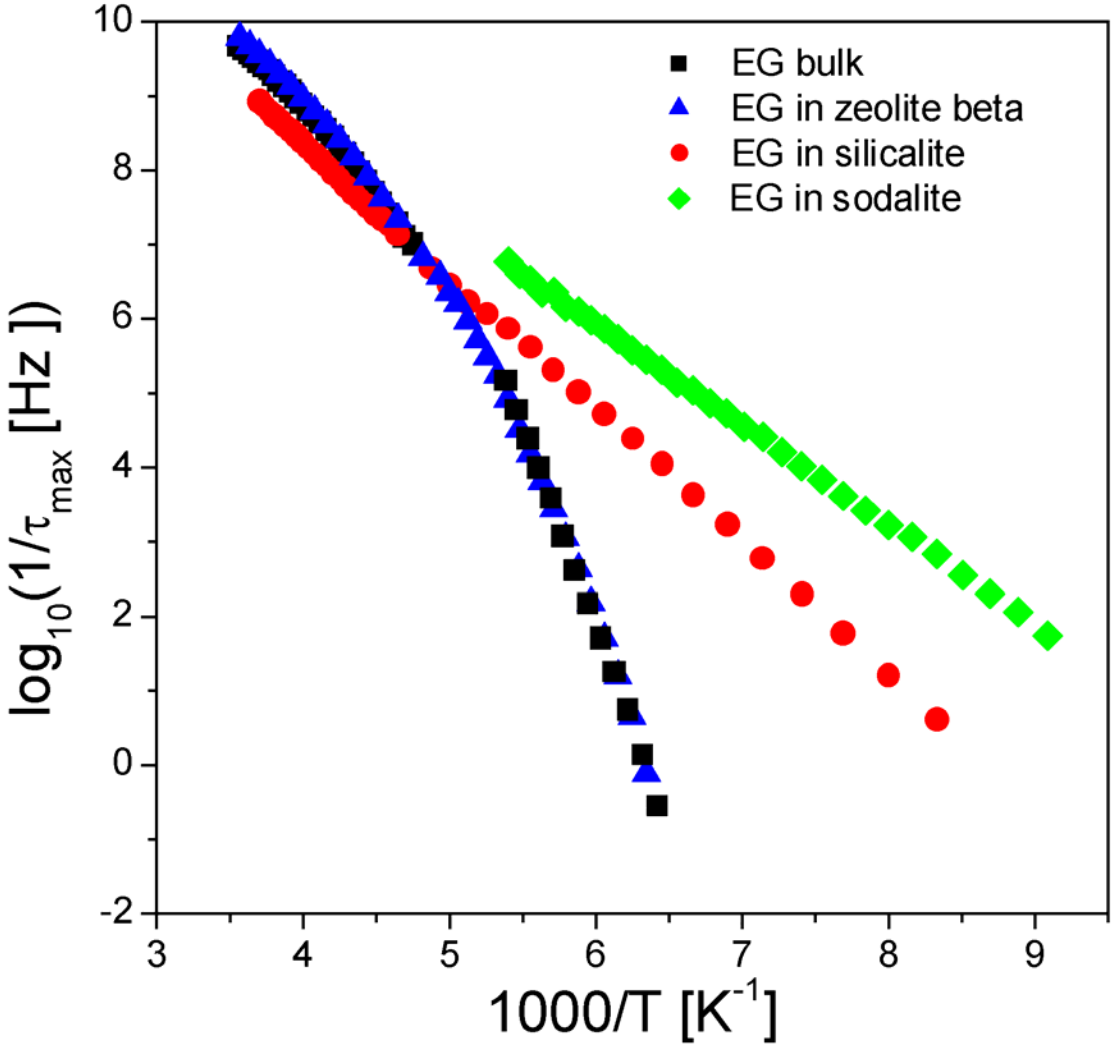
zeolite beta

silicalite

sodalite



EG in the bulk and in zeolitic host systems



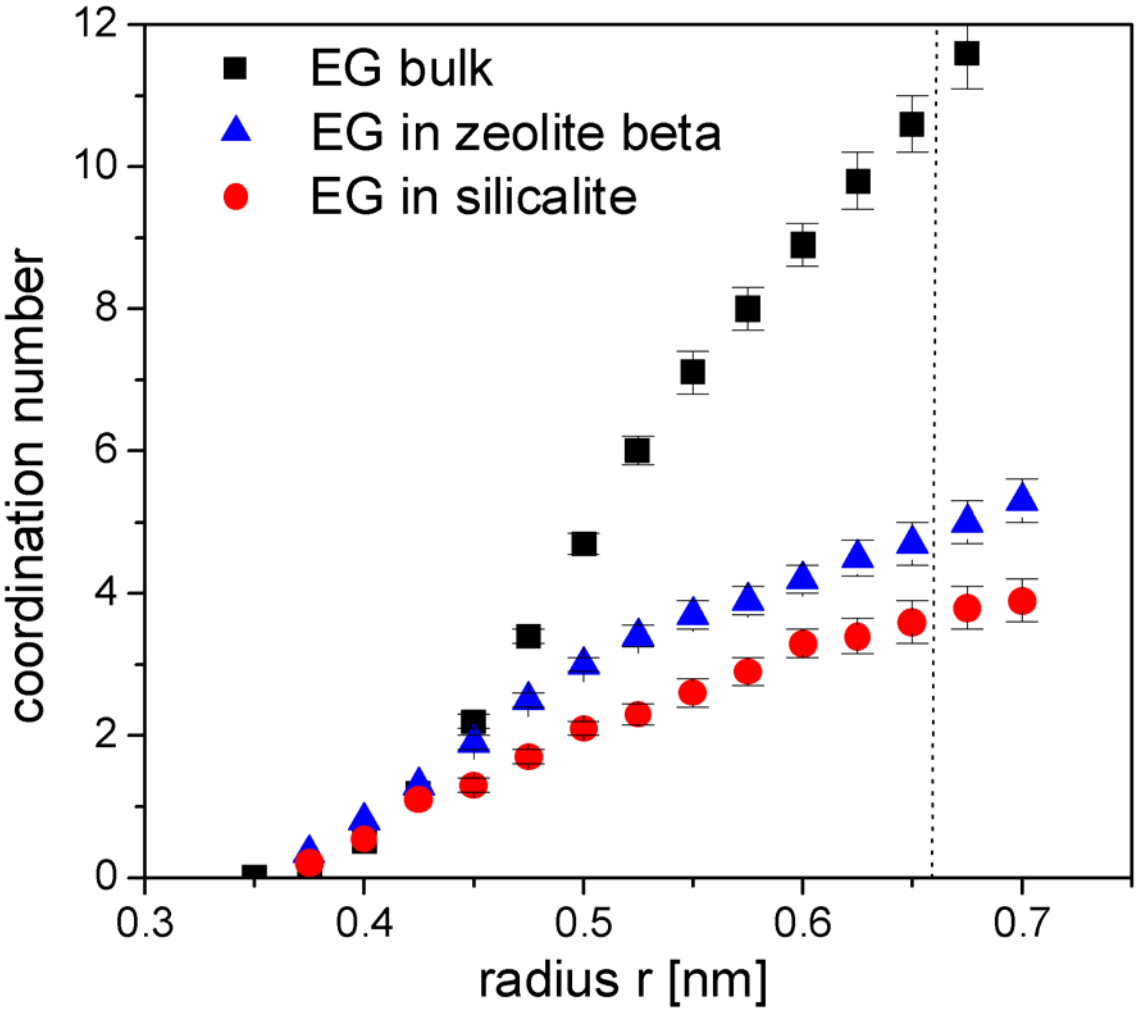
The temperature dependence of EG in the bulk liquid and in zeolite beta is identical. EG in silicalite and in sodalite shows an Arrhenius like temperature dependence with different activation energies.

Quantitative analysis of the molecular arrangement of the guest molecules in host systems, as deduced by computer simulations (Cerius^2).

	bulk liquid	zeolite beta	silicalite
distance between molecules [nm]	0.42±0.01	0.41±0.01	0.42±0.01
average length of H-bonds [nm]	0.23±0.02	0.25±0.02	0.24±0.02
density [g/cm^3]	1.113	1.0±0.1	1.0±0.1

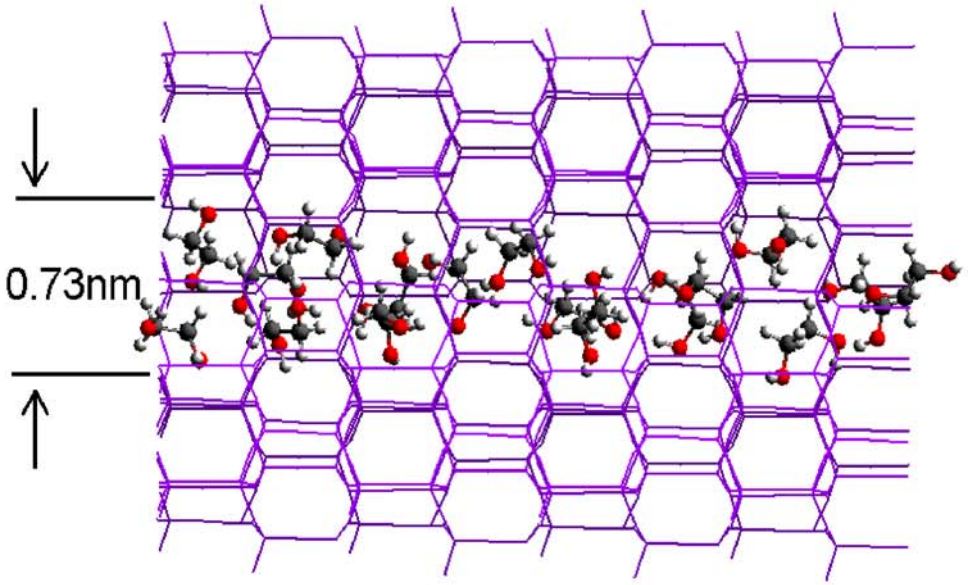
Neither for the distance between molecules nor the length of hydrogen-bonds or the density a significant change is found.

Number of neighboring molecules (coordination number) in a sphere of radius r



EG in zeolite beta (VFT-type temperature dependence) has 5 neighboring molecules.
EG in silicalite (Arrhenius-type dependence) has 4 neighboring molecules.

$AlPO_4$-5



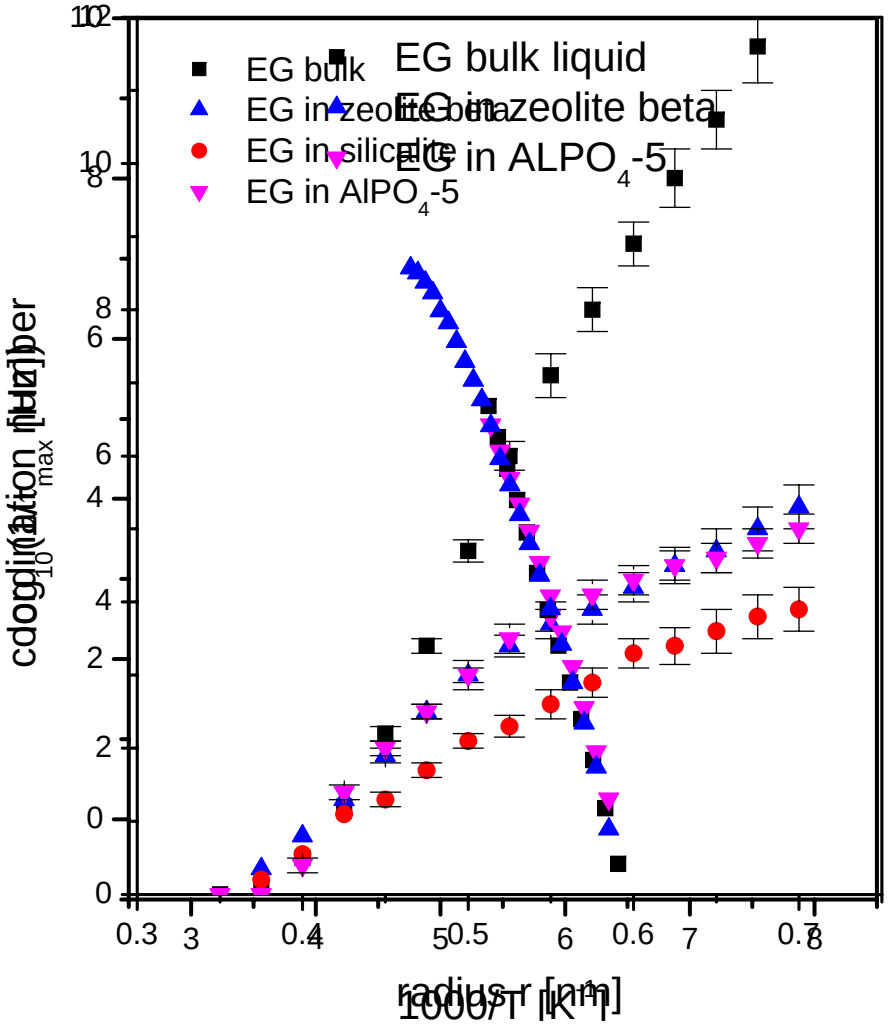
one-dimensional channels, diameter 0.73nm

One molecule has about 5 neighbors
in sphere of r = 0.7 nm

Ethylene glycol in $ALPO_4$-5

Simulation

Experiment

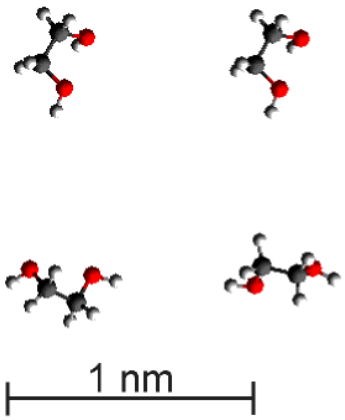


EG in $AlPO_4$-5 shows a VFT-dependence as in the bulk and for EG in zeolite beta.

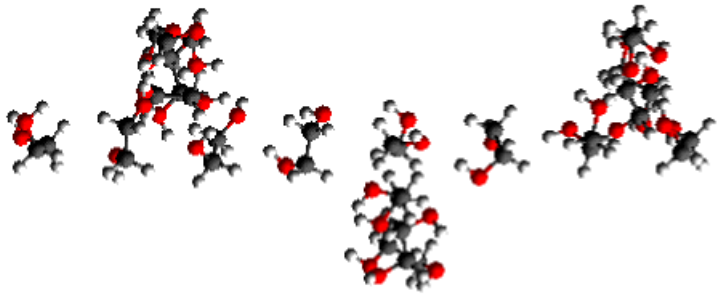
The coordination number at r = 0.7 nm is 5.

Summary

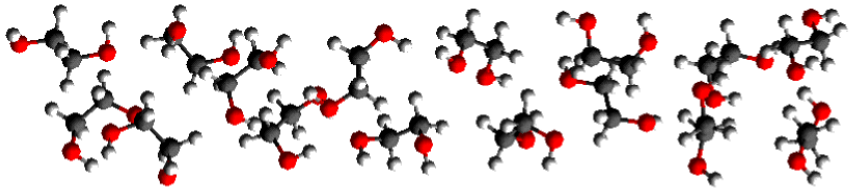
(a) Sodalit



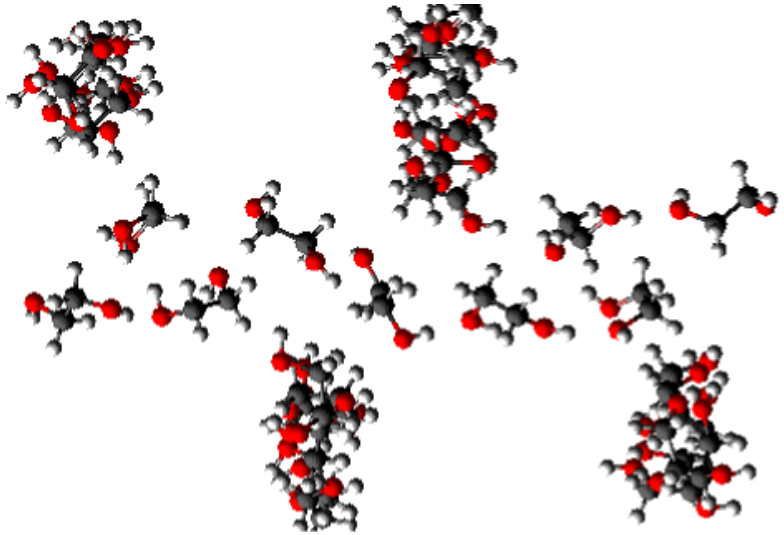
(b) Silikalit



(c) $AlPO_4$-5



(d) Zeolite beta



Summary for low molecular weight systems

The molecular dynamics in confinement is determined by the counterbalance between surface- and confinement effects

A single molecule dynamics is characterized by an Arrhenius temperature dependence - a liquid-like dynamics by a Williams-Landel-Ferry (WLF) temperature dependence

For ethylenglycol in zeolites a sharp transition from a single molecule to a liquide-like dynamics is observed

An ensemble as small as 6 ethylenglycol molecules is sufficient to perform a liquid-like dynamics

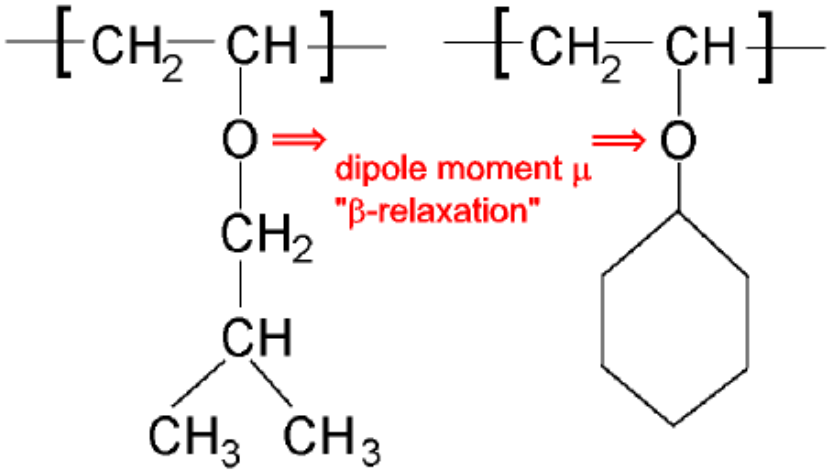
R.Stannarius et al. PRL 75,4698(1995); M.Arndt et al.PRL 79,2077(1997); A.Huwe et al. PRL 82,2338 (1999); F.Kremer et al. J.Phys.Cond.Matter 11:A175 (1999);F.Kremer et al. Chap.6 in: „Broadband Dielectric Spectroscopy“ (Eds.:F.Kremer and A.Schönhals),Springer (2002)

Single polymer chains confined to separated nanoporous channels of MCM („Mobil Composition of Matter“)

(collaboration with S.Spange and A.Grässer, university of Chemnitz)

Polymers confined to mesoporous channels of MCM's

Synthesized Polymers



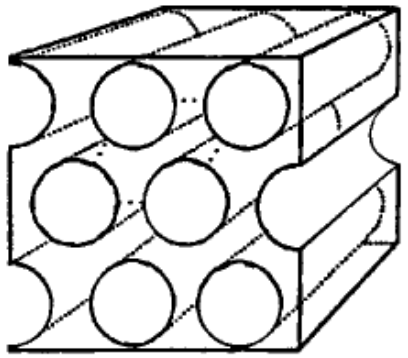
Polyisobutylvinylether (PIBVE) T_g=244 K

Polycyclohexylvinylether (PCHVE) T_g=310 K

relaxation between structural substates:
"dynamic glass transition"

MCM-41

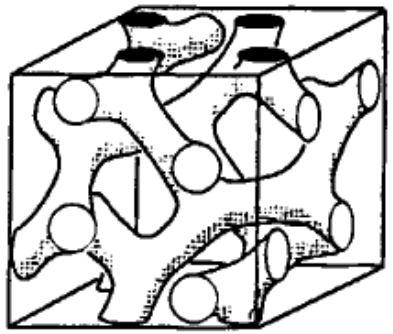
one-dimensional channels



pore-diameter: 3.7nm

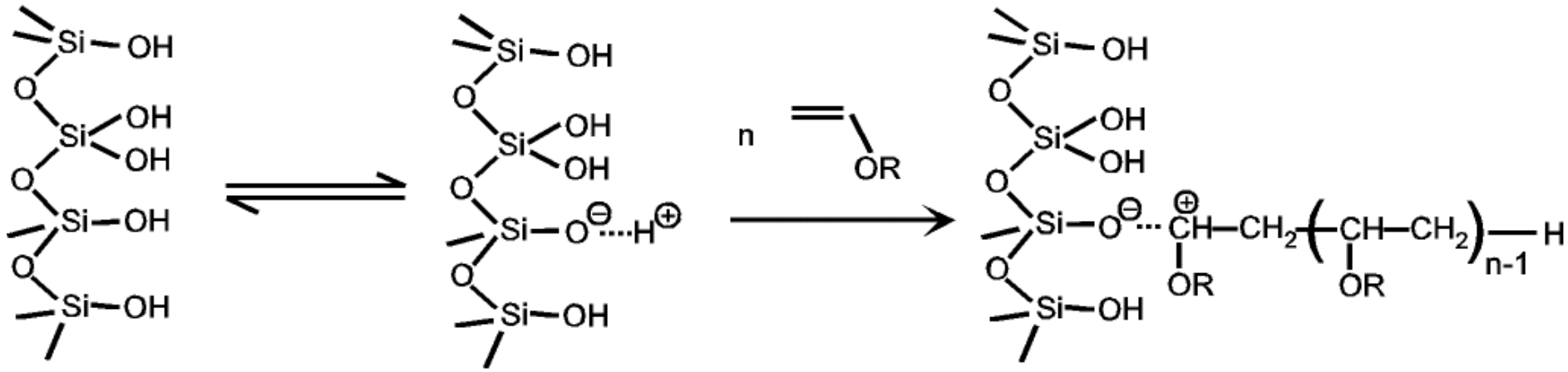
MCM-48

three-dimensional poresystem



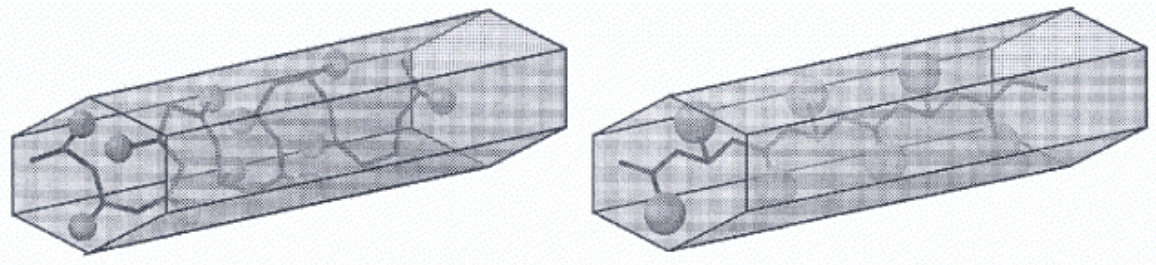
pore-diameter: 2.5nm

Cationic host-guest-polymerization by initiation using a silanolgroup of MCM



R = $CH_2CH(CH_3)_2$ Polyisobuthylvinylether (PIBVE)

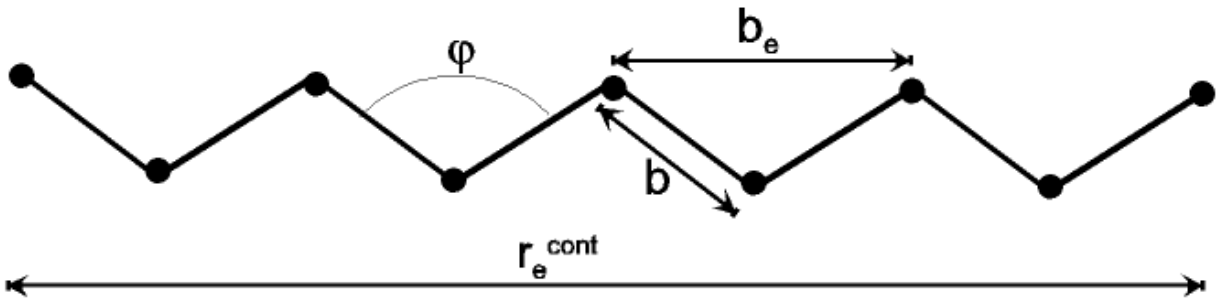
R = C_6H_{11} Polycyclohexylvinylether (PCHVE)



A. Gräser, S. Spange, Polymerchemie
Technische Universität Chemnitz

Contour length of polymers

Effective contour length r_e^{cont} of a single chain



b: bond length = 0.15nm

φ: angle between C-C bonds = 112°

b_e: effective bond length = segment length = 0.26nm

N: number of C-C bonds

N_e: number of monomer units

From BET-analysis:

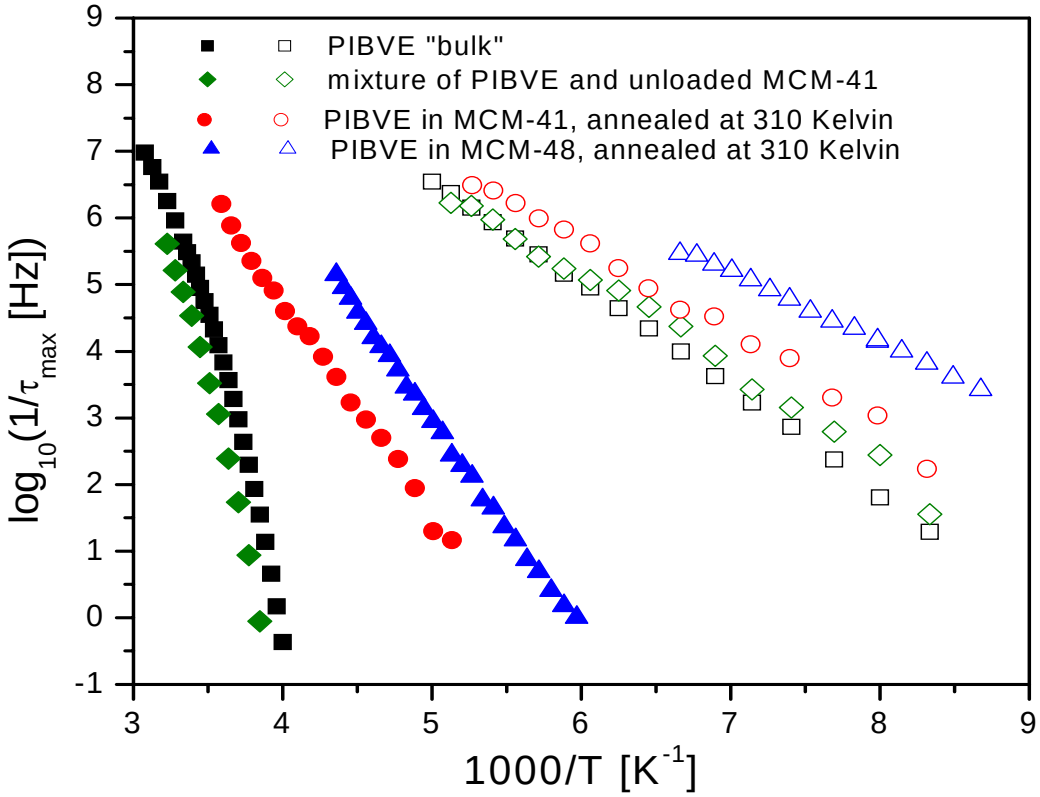
channel length / g(MCM-41) = $6.7 \cdot 10^{10}$m / g(MCM-41)

From GPC (for PIBVE):

M_n=4 370 g / mol, M_w=14 800 g / mol, N_e=44

Averaged load ratio: 30-60 vol. %

Dynamics of PIBVE in MCM-41 (∅ 3.7nm), in MCM-48 (∅ 2.5nm) and adsorbed to the surfaces of the unloaded microcrystals



- The dynamic glass transition shows a pronounced confinement effect if the polymers are embedded in the nanoporous channels of MCM's.
- If the polymers are adsorbed to the (unloaded) microcrystals of MCM's a (weak) surface effect is observed.
- The (local) β-relaxation is also influenced by the confinement of MCM's proving the strong interaction between the polymers and the inner surfaces.

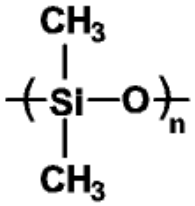
Summary

- Using a surface induced initiation it is possible to polymerize polyvinylethers in mesoporous media ($\varnothing \sim 2$ - 4 nm).
- Two relaxation processes are observed: the dynamic glass transition (α-relaxation) and a secondary relaxation (β-relaxation).
- In MCM-48 (diameter 2.5nm) the dynamic glass transition is faster than in MCM-41 (diameter 3.7nm) -confinement effect.
- Polymers adsorbed on the surface of the (unloaded) microcrystals of MCM show a (weak) surface effect.
- The observed surface- and confinement effects are in full agreement with our studies on low molar mass systems.

F.Kremer et al.in Chapter 6 of „Broadband Dielectric Spectroscopy“(Eds.:F.Kremer and A.Schönhals)

Sample preparation - PDMS

poly (dimethyl siloxane) (PDMS)



- **bulk**
- **grafting-on-films (Prof. L. Léger, Paris)**
- **spin coated films**

M_w [g mol^{-1}]	R_g^{ideal} [nm]	d_{diel} [nm]
170000	21	41, 11
96000	15	15, 8
139000	18	14...345

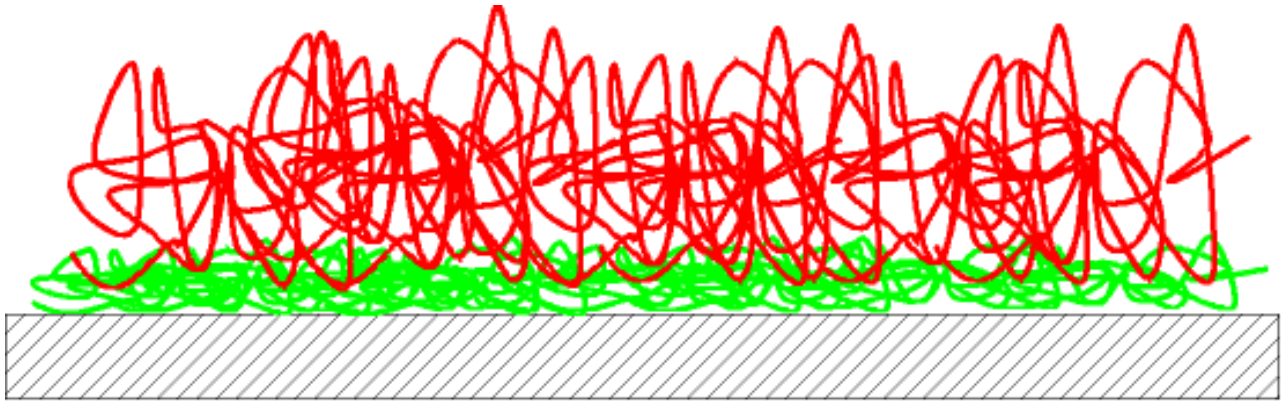
to avoid crystallisation the samples were quenched in liquid N_2 ($\Delta T/\Delta t \sim 50$ K min^{-1})

spin coated films

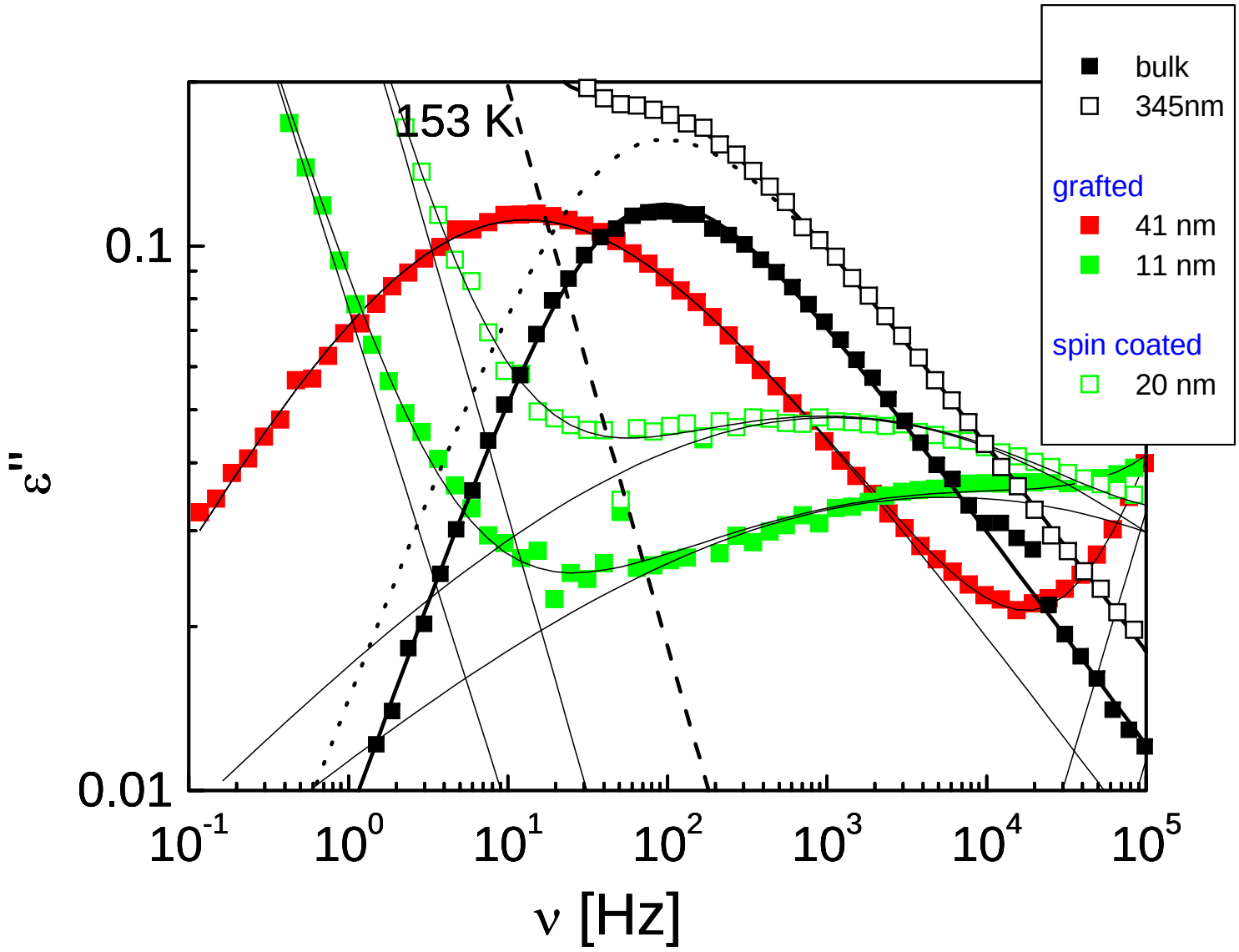
from a diluted solution of PDMS in Toluol spin-cast at 3000 rpm

grafted films

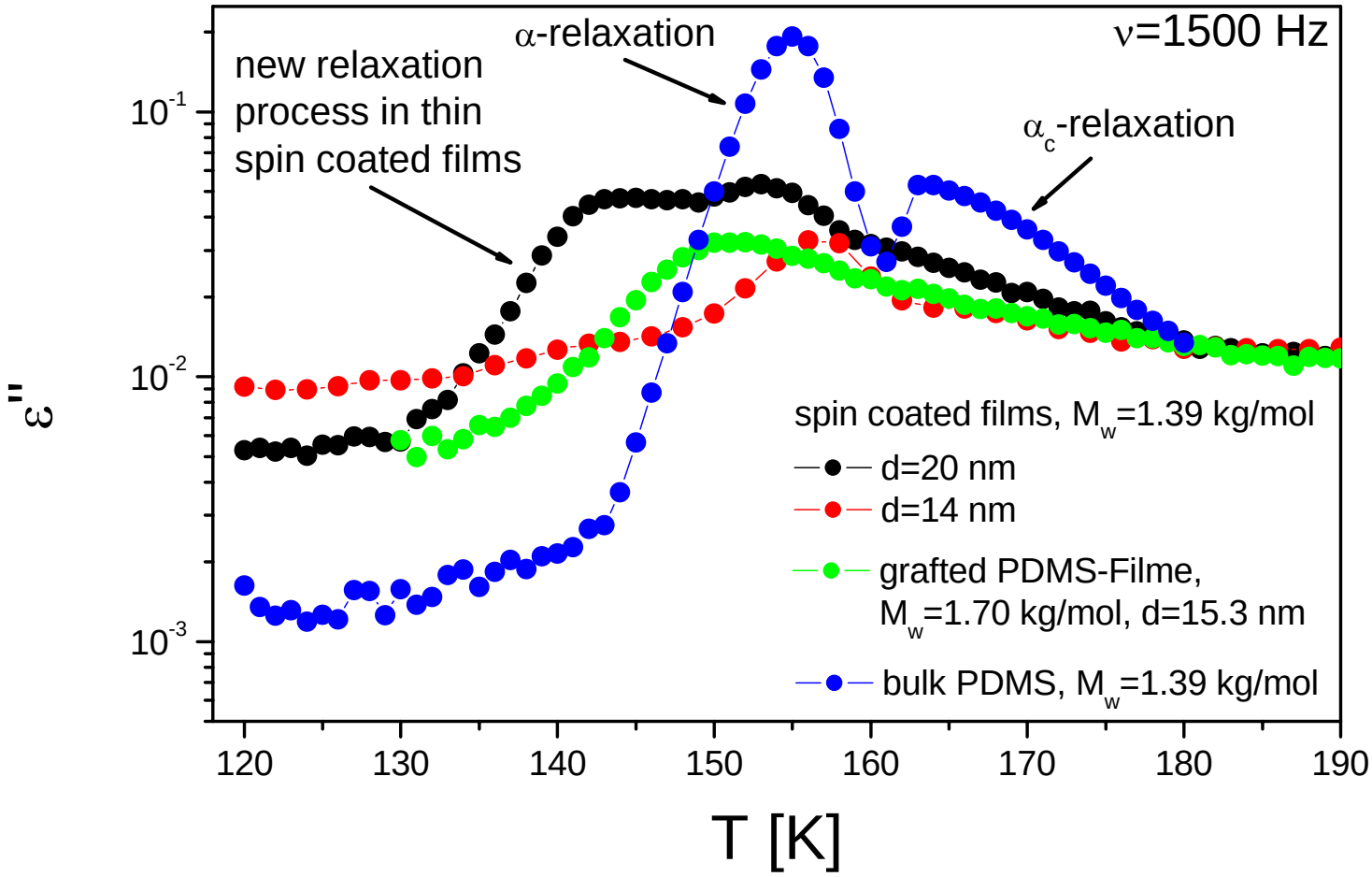
layer of short (M_w=5k) chains to prevent adsorption of long chains



Dielectric loss of PDMS in the bulk, as grafted layer and as spincoated film



A new relaxation process in thin spin coated films of PDMS

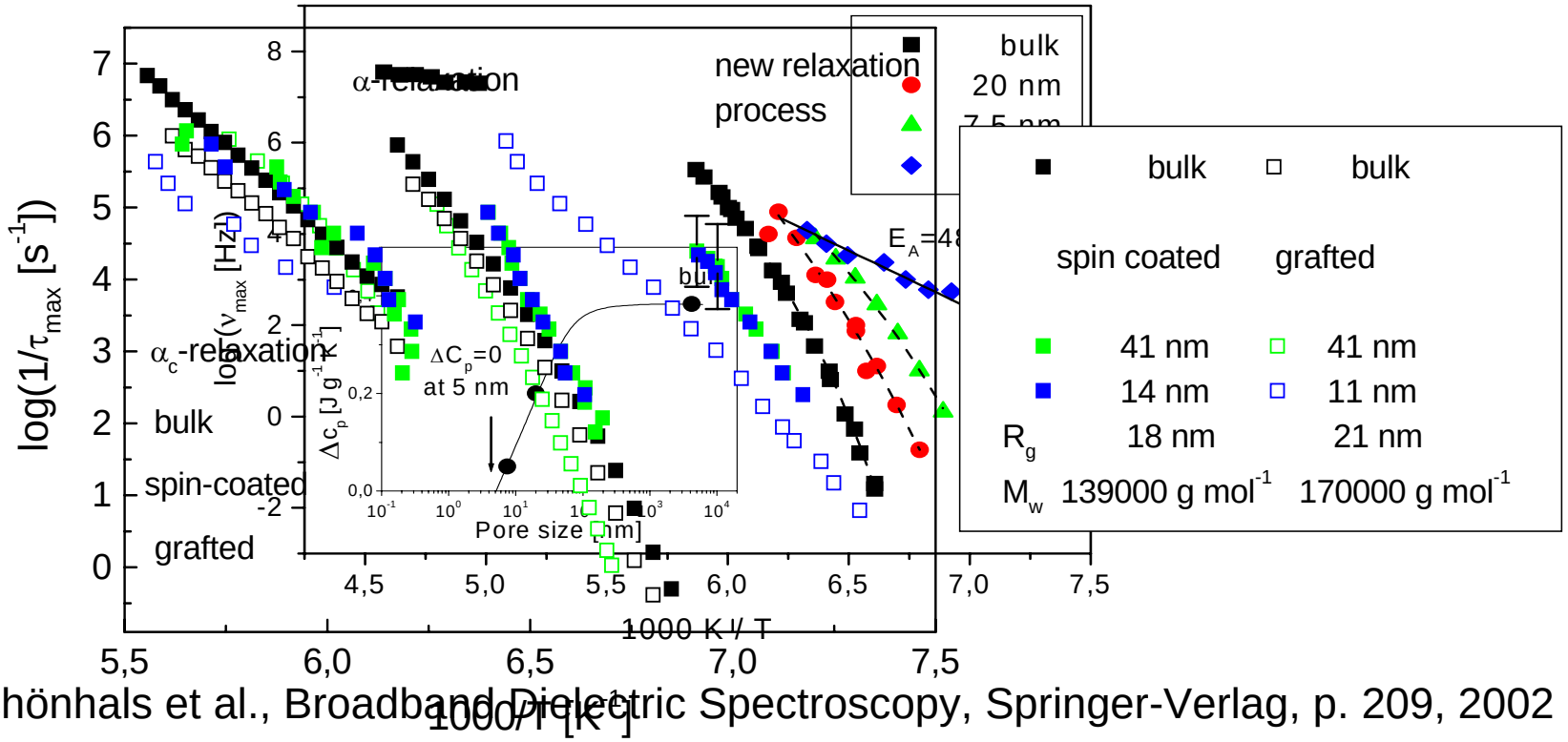


α-relaxation (dynamic glass transition)

α_c-relaxation (dynamic glass transition in the partially crystalline sample)

„new relaxation process“ in spin coated films

Activation plot – PDMS in thin grafted and spin-coated layers



A. Schönhals et al., Broadband Dielectric Spectroscopy, Springer-Verlag, p. 209, 2002

For the grafted and the spin-coated PDMS layers (11nm, 14nm) the molecular dynamics is by orders of magnitude faster compared to the bulk.

This resembles a confinement effect as observed also for PDMS in nanoporous media.

Summary – Comparison of PDMS as grafted and spin-coated films

In both grafted and spin-coated PDMS layers the molecular dynamics is by orders of magnitude faster compared to the bulk. This resembles well confinement effects as observed for PDMS in nanoporous media.

$d<R_g$ For the grafted layer the spectra are fully reversible in contrast to the spin-coated sample.

$d>R_g$ The dynamics of the grafted and the spin-coated layer resembles that of the bulk.

In all cases a cold crystalization is observed.

L. Hartmann, F. Kremer, P. Pouret, L. Leger, J. Chem. Phys. **118**, 13 (2003), F.Kremer et al. EJPE **12**,139-142, (2003)

Final Summary

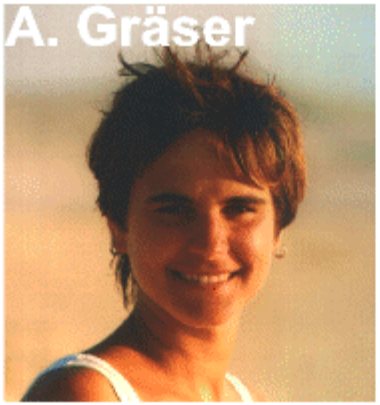
1. Broadband dielectric spectroscopy (BDS) has the essential advantage that it measures a well defined molecular quantity, i.e. the fluctuations of polar moieties in a molecular system.

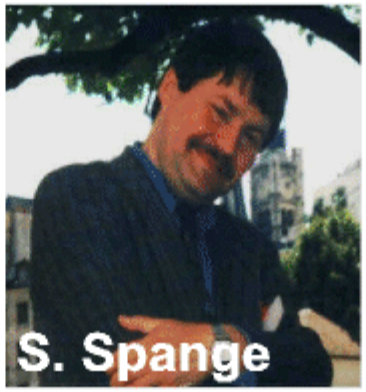
2. BDS is broadband in frequency.

3. Separately the relaxation-time, the type of it´s thermal activation, the relaxation-time distribution function and the dielectric strength are determind.

4. For measurements on thin (polymer)-films the sensitivity of the experiment increases with decreasing thickness, i.e. decreasing amount of sample-material.

Thanks to...





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