Glassy dynamics in geometrical confinement as studied by Broadband Dielectric Spectroscopy

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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

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)

H\ H
H–C–C–H
O|O
H \ H
\ \ \ \ \ \ \ \ \ \ μ (dipole moment)

silica-sodalite (SiO₂)
cubic cages
lattice constant 0.89nm
"one molecule per cage"

silicalite (SiO₂) channels
0.56nm x 0.53nm  0.55nm x 0.51nm

zeolite beta (SiO₂/Al₂O₃) Si : Al ratio 40
channels 0.76nm x 0.64nm 0.55nm x 0.55nm

The chemical composition of all zeolites is nearly identical.
The *air-gap geometry* enables one to carry out BDS experiments on layers less than 5nm 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 $\geq 4$ 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

- long-range order
- scale invariant transition temperature

The glass transition is no phase transition!
At the calorimetric glass transition temperature as measured by (DC-) Differential Scanning Calorimetry (DSC), 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.

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

(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 $\mu$

Debye relaxation

$$\varepsilon^*(\omega, T) = \varepsilon' + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}$$

Complex dielectric function

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

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

$$\varepsilon''(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega \tau)^2} \omega \tau$$
P. Debye, Director (1927-1935) of the Physical Institute at the university of Leipzig (Nobelprixe in Chemistry 1936)
information content of dielectric spectra

Debye-Relaxation

\[ \varepsilon_D^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + i\omega\tau_c} \]

Generalized Relaxation: Havriliak-Negami function

\[ \varepsilon_{HN}^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{(1 + (i\omega\tau_{HN})^\alpha)^\beta} \]

Mean relaxation time \( \tau_c \):

\[ \tau_c = \tau_{HN} \left[ \sin \left( \frac{a\pi}{2 + 2\beta} \right) \right]^{1/\beta} \left[ \sin \left( \frac{a\beta\pi}{2 + 2\beta} \right) \right]^{-1/\beta} \]

Relaxation strength \( \Delta \varepsilon \):

\[ \Delta \varepsilon = \frac{\mu^N}{3e_0k_BT} \]

Relaxation time distribution \( L(\tau) \):

\[ L_D(\tau) = \delta(\tau_c) \quad L_{HN}(\tau) = f(\tau_{HN}, \alpha, \beta) \]

Temperature dependence of \( \tau_c \): Arrhenius or Vogel-Fulcher-Tammann (VFT)
Broadband dielectric measurement techniques

Measurement techniques:
- Time-domain spectrometer
- Frequency response analyser
- AC-bridges
- Coaxial line reflectometer
- Network analyser
- Wave-guides-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 <5mg)
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 \( \varepsilon^*(\omega) \) 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.
The interaction of electromagnetic waves with matter in the frequency range between $10^4$ 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 polarization 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 holeburning, 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.
4. Glassy dynamics in sub-nanometric geometrical confinement of zeolites.
Ethylene glycol as guest molecule in zeolites

ethylene glycol (EG, ethanediol)
\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{O} & \quad \uparrow \quad \text{O} \\
\text{H} & \quad \quad \text{H}
\end{align*}
\]
$\mu$ (dipole moment)

silica-sodalite ($\text{SiO}_2$)
cubic cages
lattice constant 0.89nm
"one molecule per cage"

silicalite ($\text{SiO}_2$) 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
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The chemical composition of all zeolites is nearly identical.
Dielectric spectra of ethylene glycol in different zeolitic host systems

zeolite beta

silicalite

sodalite

160 K

- EG in zeolite beta
- EG in silicalite
- EG in sodalite

frequency [Hz]
ethyleneglycol 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.

5. Polymethylphenylsiloxane (PMPS) in 1-D and 2-D geometrical 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)
Segmental mode: not broadened, peak position not shifted compared to bulk.

Surface induced mode: intensity increases with decreasing thickness
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
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 SiO$_2$ 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.
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
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.
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.**

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 $M_n = 1510$ kg/mol:

$$V_{\text{chain}} = 2251 \text{ nm}^3$$

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

$$V_{\text{coil}} = 2030 (\pm 500) \text{ nm}^3$$

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$V_{\text{coil}} = 2030 \pm 500 \text{ nm}^3$

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

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 ~ 2 - 3 polymer segments i.e. a length scale of about 5Å 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.

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