Glass transition effects in ultra-thin polymer films

Wierzba, 12 May 2004

Michael Wübbenhorst

TU Delft
Delft University of Technology

Outline

1. Introduction
2. Phenomenology of the glass transition
3. Polymer chains in nano-scale geometry – general issues
4. Glass transitions effects in ultra-thin polymer films – main findings and models
5. Dielectric relaxations in ultra-thin polymer films – basic issues
6. DRS results on ultra-thin PMMA films
7. Liquid-like surface mobility in supported PS-films
8. Summary and Future work

1. Introduction

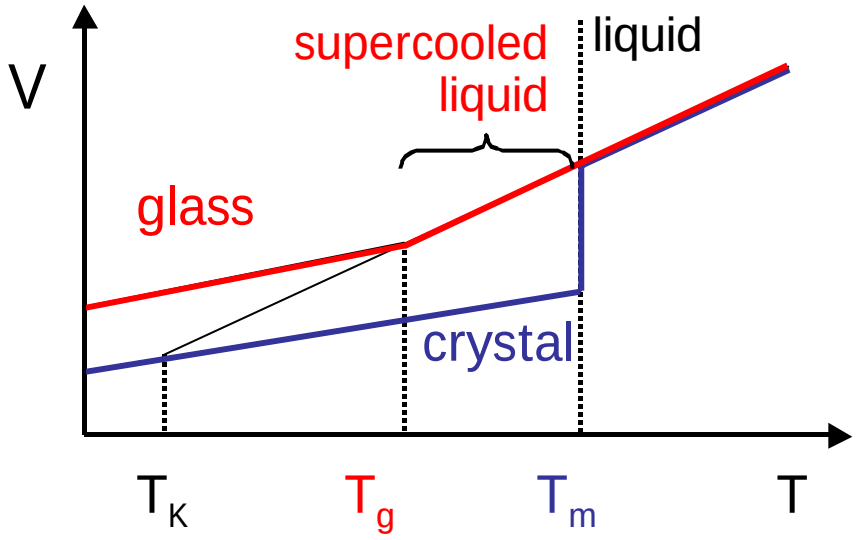
Motivation of this lecture:

1. **new materials**:
   - clay-based "nano"composites, other materials containing "nanofillers",
   - nano-structured materials, e.g. alignment layers, nano-porous materials
2. ongoing **miniaturization** of devices and structures, lithographic structurizing below 100 nm !
3. new insights in **physics of macromolecules** and the **glass transition**

2. Phenomenology of the glass transition

The glass transition:

2nd route from liquid to solid state by avoiding crystallization



$T_g < T < T_m$:

Viscosity and structural relaxation time τ obey Vogel-Fulcher-Tammann (VFT) law:

$$t(T) = t_\infty \exp\left(-\frac{E_V}{k(T - T_V)}\right)$$

Example:

Crystallization of a supercooled liquid (sodiumacetate/water)

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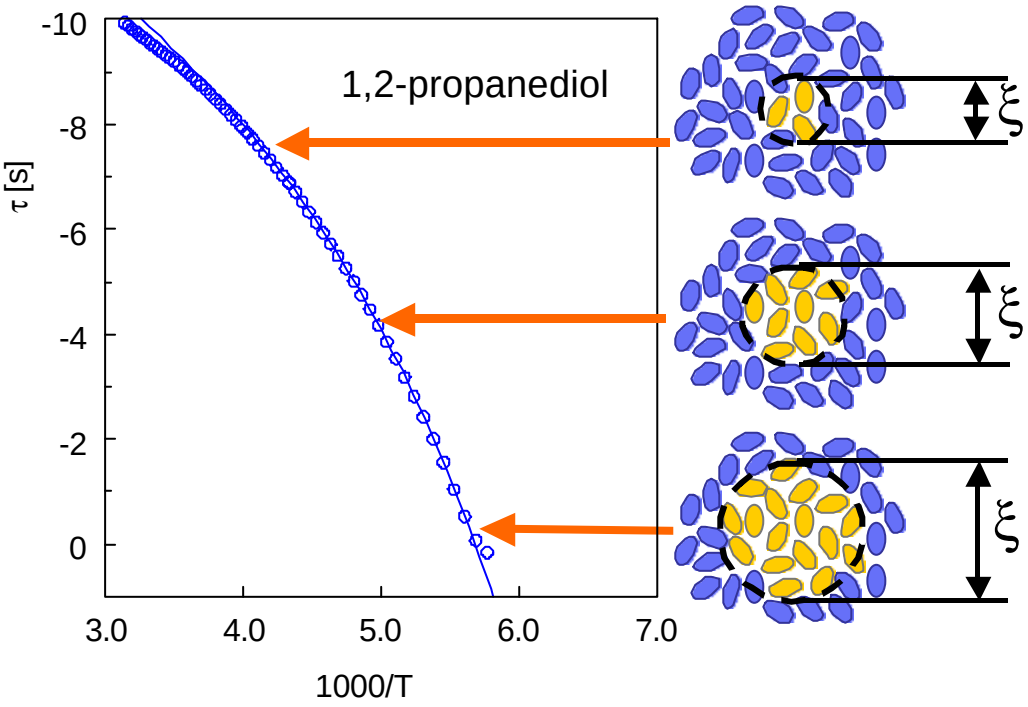
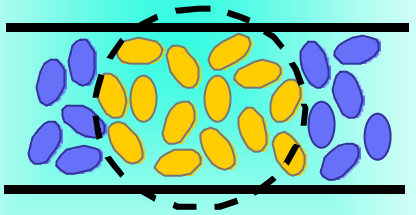
Rationalization of VFT law:

Temperature dependent length scale $\xi=\xi(T)$ of cooperatively rearranging regions (CRR) (Adam and Gibbs, 1965)



CRR's in confined geometry:

deviations of $\xi(T)$ from bulk behaviour likely



→ finite size effects

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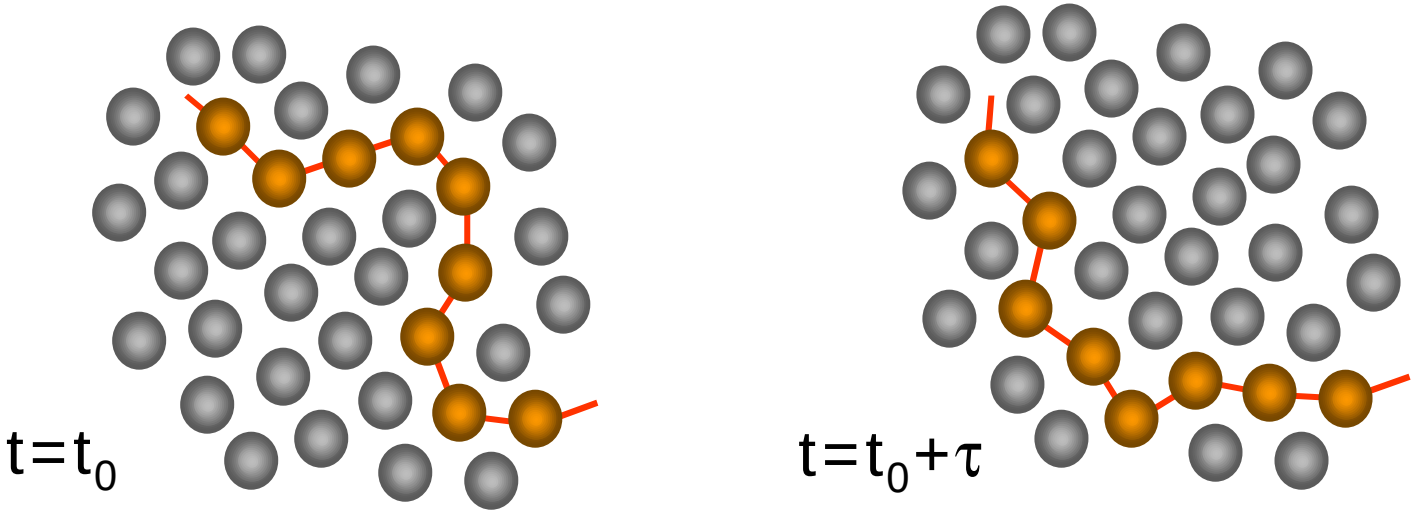
Dynamic glass transition

In polymers:

Additional contribution of chain connectivity expected



cooperative motions of a few monomer units (polymer segments) at $T>T_g$

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Dynamic glass transition

more or less pronounced curvature of η(1/T) dependence

classification into **fragile** and **strong** glass formers

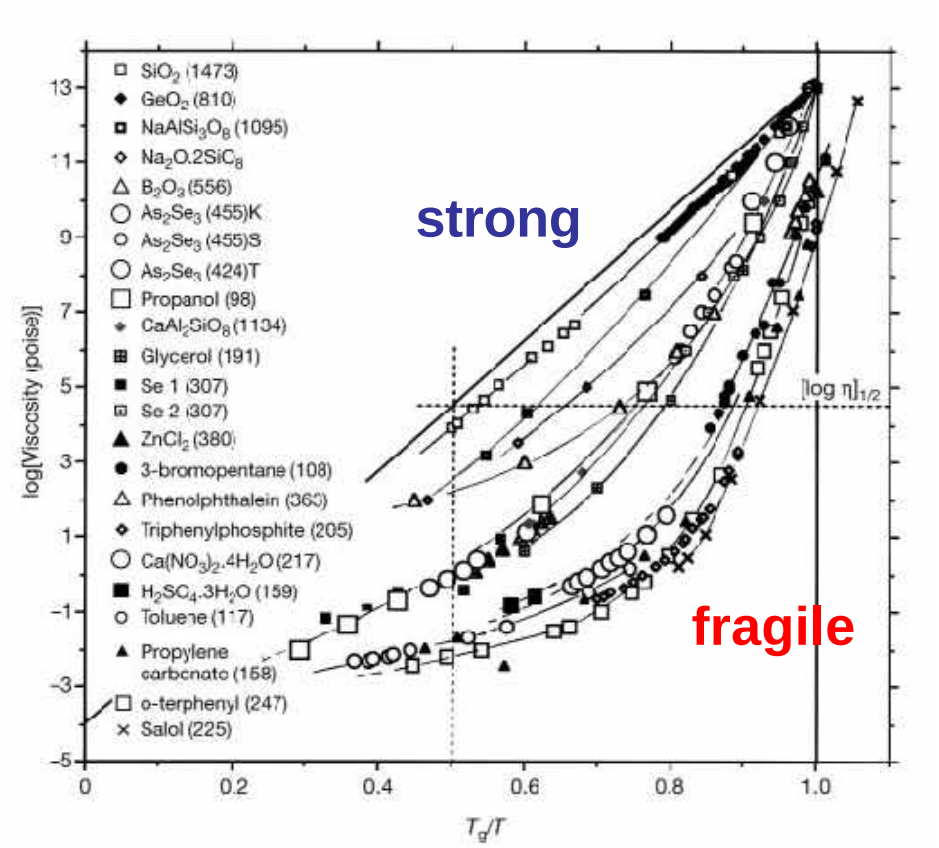
fragility: nothing to do with mechanical "fragile" behaviour

fragility or steepness index:

$$m = \left. \frac{\mathrm{d} \log \langle \tau \rangle}{\mathrm{d}(T_\mathrm{g}/T)} \right|_{T=T_\mathrm{g}}$$

linked to VFT parameters

$$m = \frac{E_\mathrm{V}}{2.303R} \frac{T_\mathrm{g}}{(T_\mathrm{g} - T_\mathrm{V})^2}$$



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Dynamic glass transition – theoretical concepts

1. Free volume approach

$$1/t \propto \exp\left(v_f / v\right)$$

- assumption of an activation volume ($\propto$ free volume) which links dynamics to specific volume/density
- Lowering the temperature results in progressive slow-down in relaxation rate due to faster decrease in the free volume v_f → effective barrier changes with T

Free volume concept:

- rationalises the VFT behaviour, works reasonably well for many polymers
- fails to predict the pressure dependence $\tau(p)$ and $T_g(p)$

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Dynamic glass transition – theoretical concepts

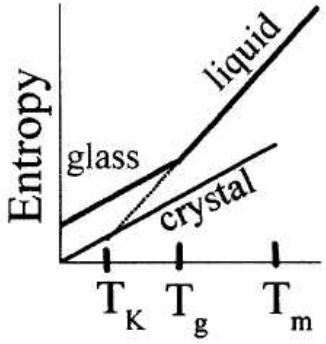
2. Adams-Gibbs theory

$$\log(t / s) = A_{AG} + \frac{C}{S_C(T) \cdot T}$$

- assumption of cooperatively rearranging regions (CRR)
- links transition probability $W \propto \tau^{-1}$ to temperature dependent configurational entropy $S_c(T)$:

$$S_c(T) = S_{melt} - S_{crystal}$$

- AG theory introduces cooperativity
- Unfortunately no predictions about length scale of CRRs



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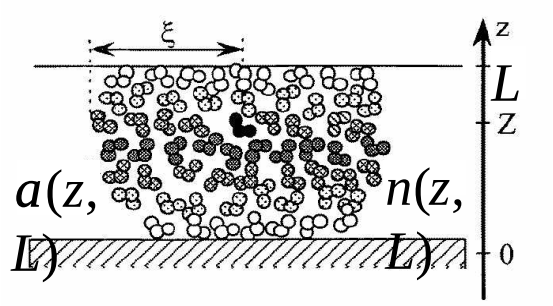
Dynamic glass transition – theoretical concepts

3. Fluctuation approach (Donth)

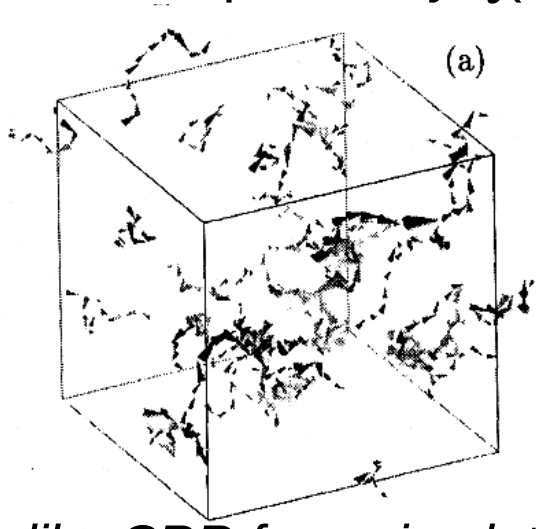
$$x(T) \propto \frac{1}{(T - T_0)^{2/3}}, \quad x(T_g) \approx 2 - 3nm$$

- allows determination of length scale of cooperativity $\xi(T)$ from $C_p(T)$ steps at T_g

How does CRR look like ?



classical picture



string-like CRR from simulations

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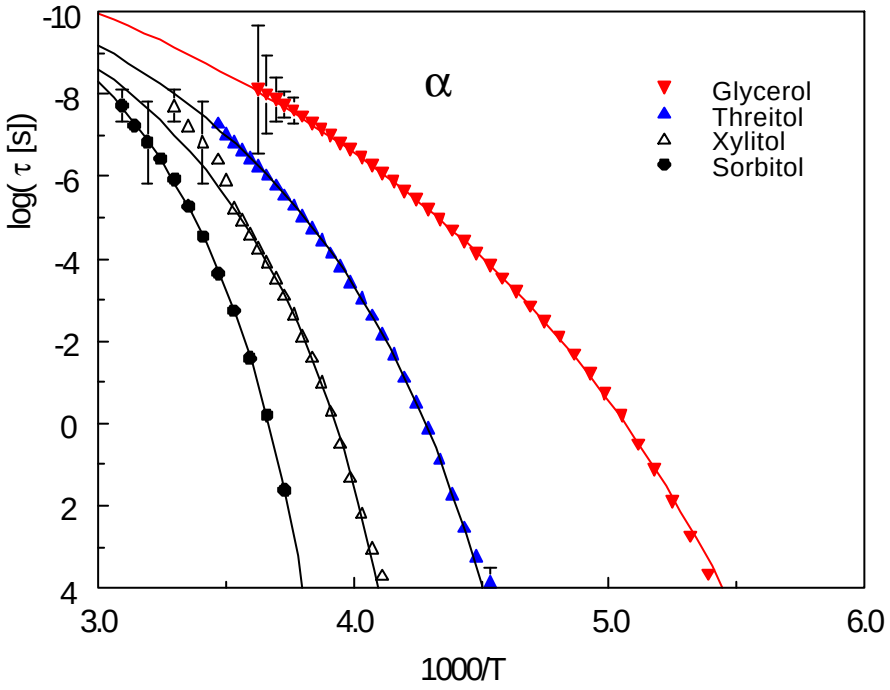
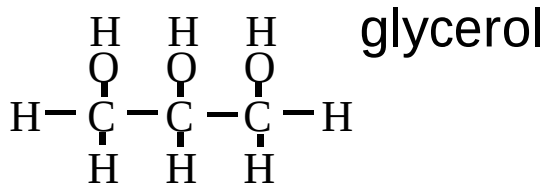
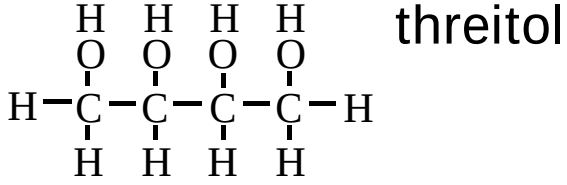
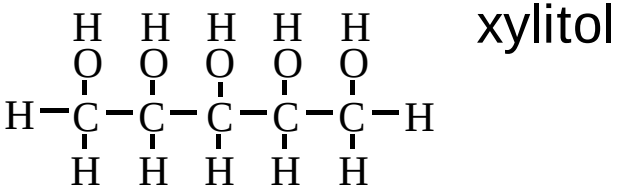
Dynamic glass transition – simple liquids

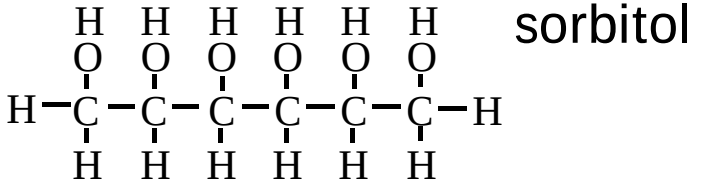
Homologue series of alcoholes











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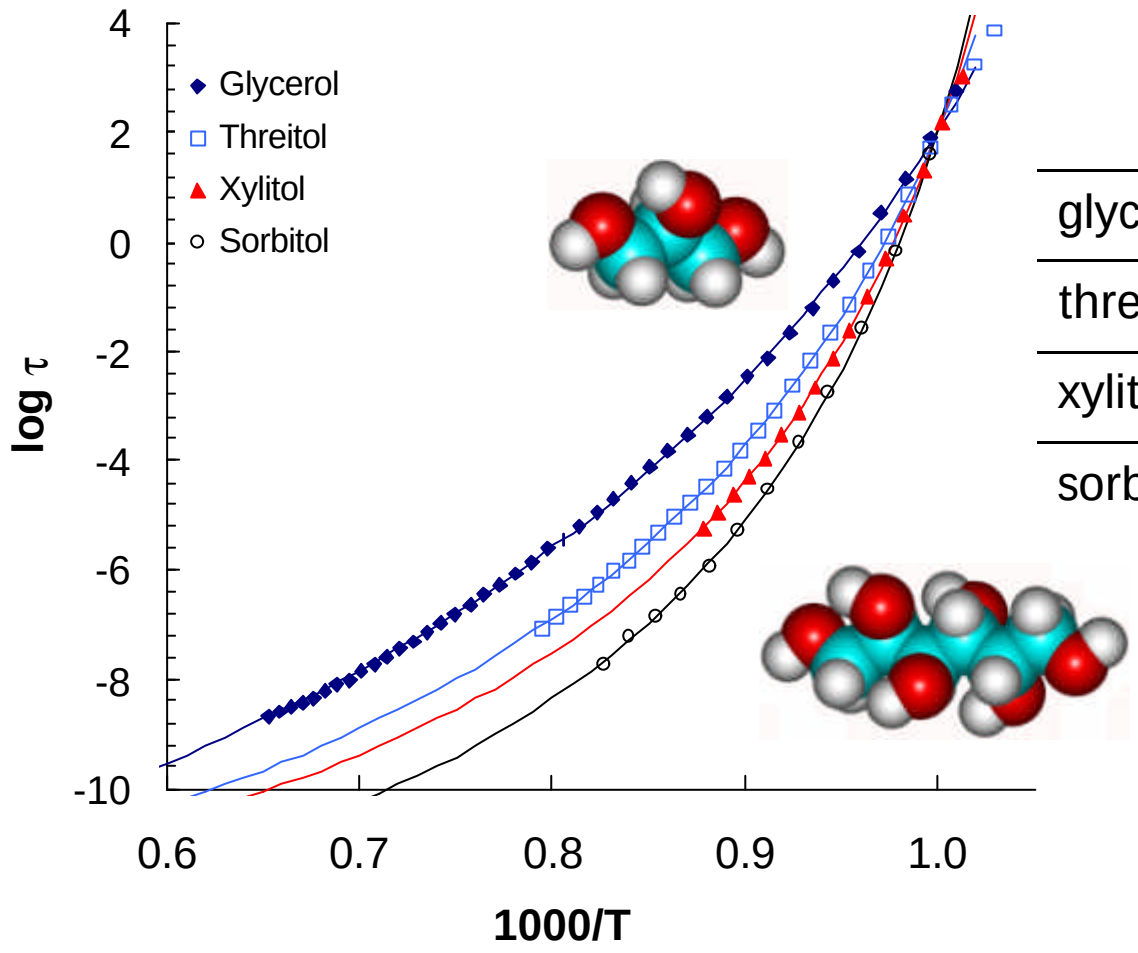
Fragility classification



	T_g [C]	m
glycerol	-83.3	55.5
threitol	-46.0	79.9
xylitol	-24.5	97.2
sorbitol	-6.0	112.1

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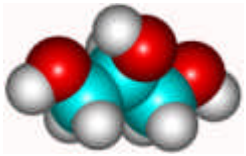
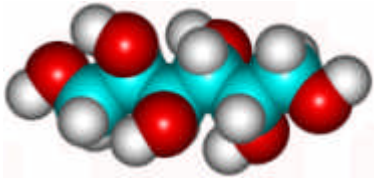
Fragility classification

Interpretation of fragility / steepness index:



	m
glycerol	55.5
threitol	79.9
xylitol	97.2
sorbitol	112.1

$$m \propto \frac{\text{intermolecular } \textit{cooperativity}}{\text{intramolecular } \textit{cooperativity}}$$



alcoholes: H-bonding glass formers
number of OH-groups/molecule varies from 3 → 6

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Dynamic glass transition – effect of confinement

First: simple glass formers (low molecular mass)

1st example:

Confining ethylene glycol (EG) in zeolites

[Huwe et al., PRL 1999]

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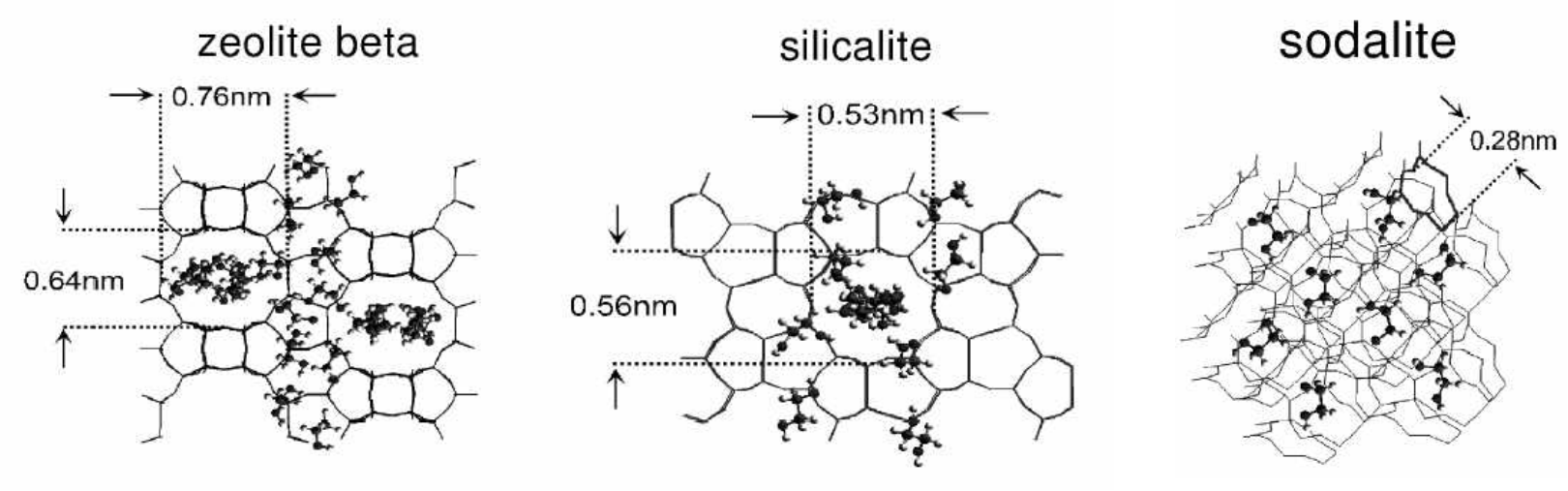
Study of glass transition of ethylene glycol (EG) in different confinement

Confined geometry provided by various zeolites having channels or cages of different shape and size



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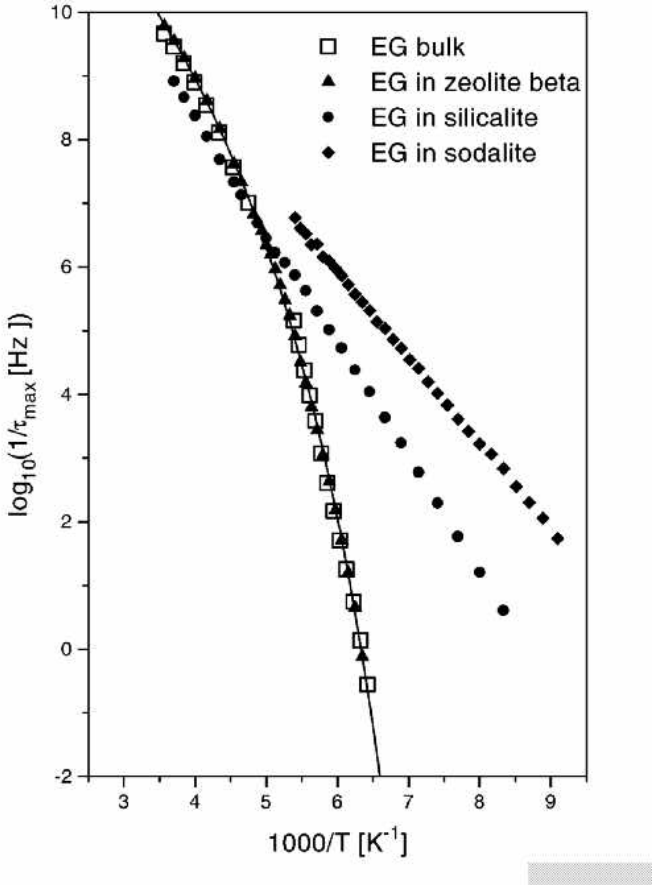

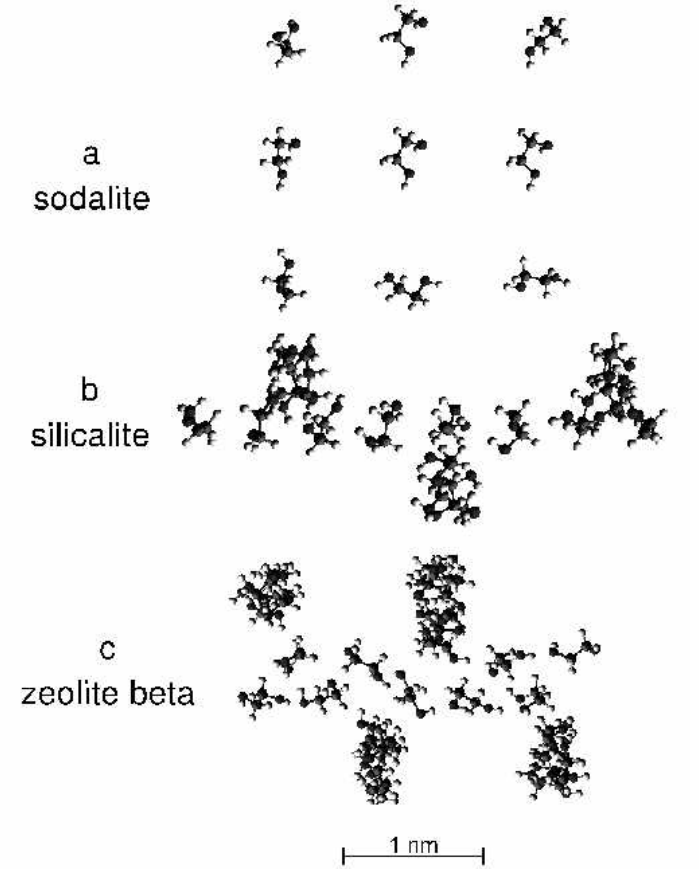

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Interpretation of results from ethylene glycol/zeolite systems:

→ **Minimum number of nearest neighbors of 6 required to establish VFT-type dynamics**

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Dynamic glass transition – effect of confinement

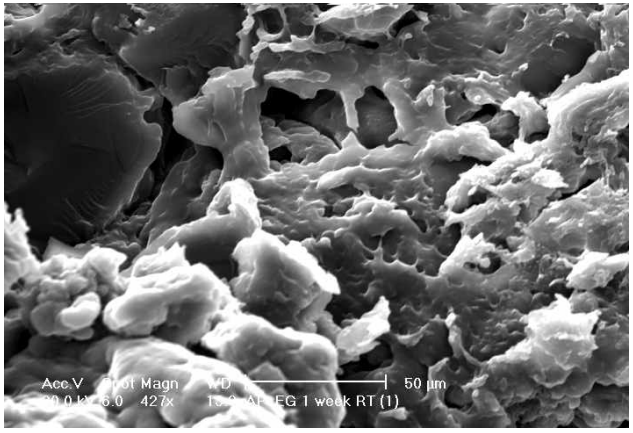
2nd example:

α-relaxation of ethylene glycol (EG) in Amylopectine/ethyleneglycol (AP/EG) mixtures:

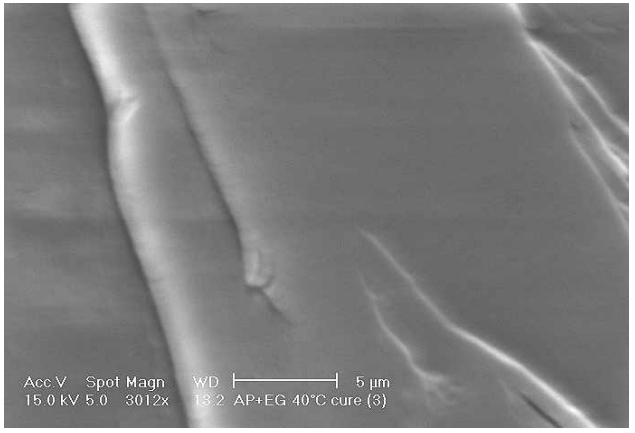
formation of *nm*-sized droplets of EG due to physical network formation between EG/starch

→ **3-dim. Confinement**

J. Phys. Chem B, Smits et al., 2001



freshly mixed



annealed sample

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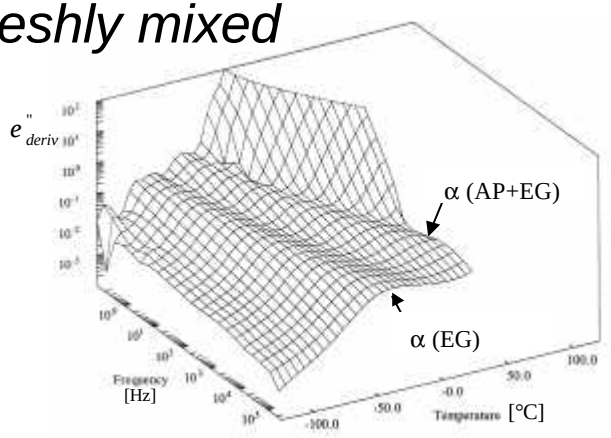
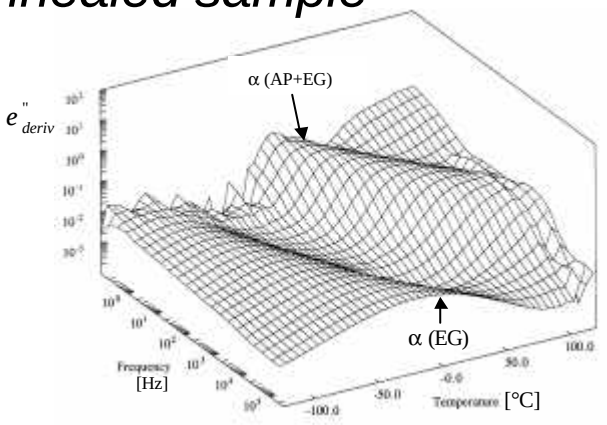
Dynamic glass transition – effect of confinement

a-relaxation of amylopectine / ethyleneglycol mixtures:

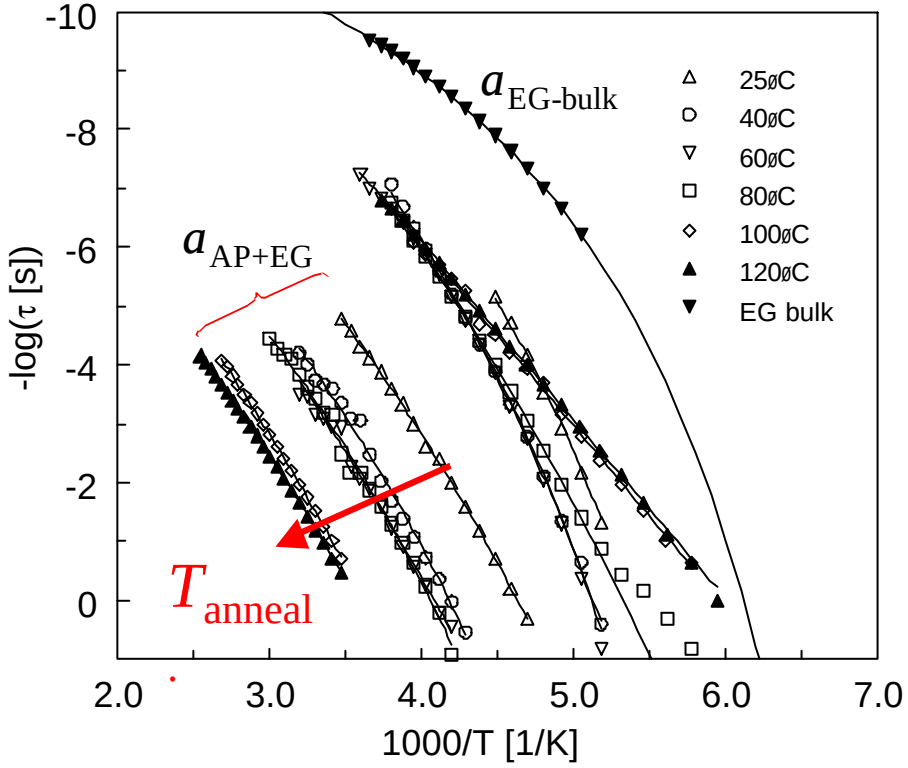
freshly mixed



annealed sample



2 separate glass transitions of EG and AP/EG phase



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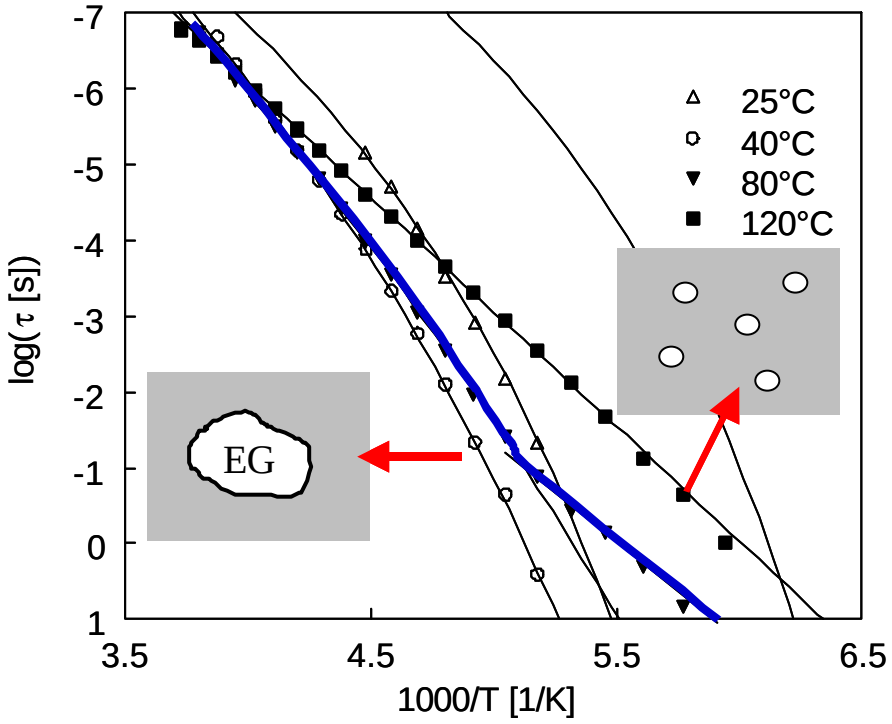
a-relaxation of amylopectine / ethyleneglycol mixtures:



α-process of EG senses size reduction from "bulk" droplets to nm-sized EG clusters

evolution of structure

→ **time-dependent confinement**

Clear transition from VFT behaviour → Arrhenius law

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Dynamic glass transition – effect of confinement

3rd example:

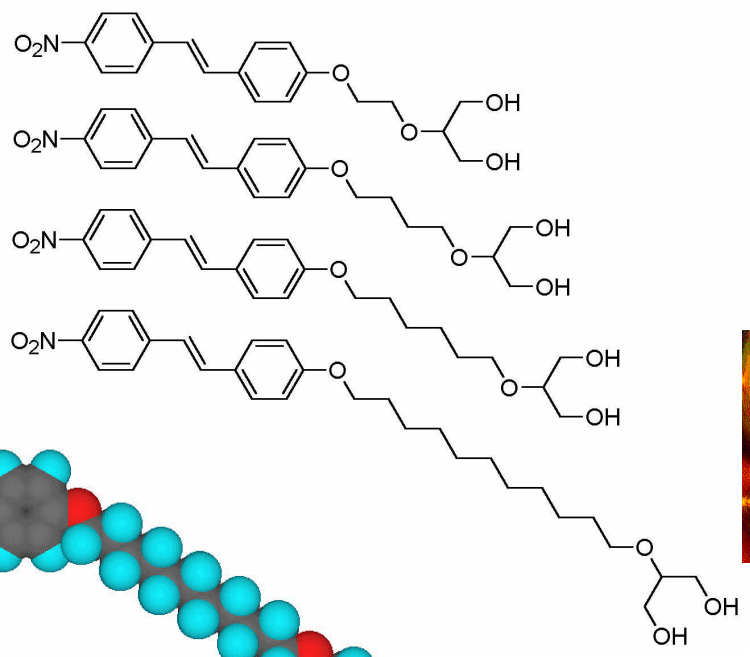
Mesogenic nitrostilbene diols of various methylene spacer lengths (LC monomers):

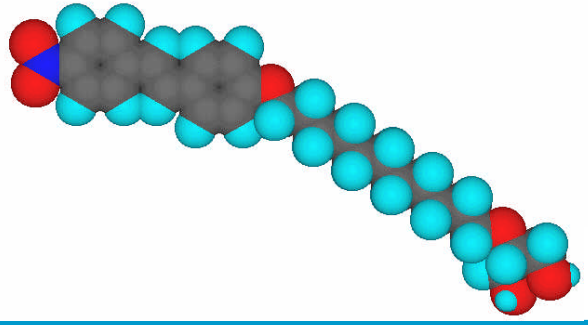
8a *(n=2)*

8b *(n=4)*

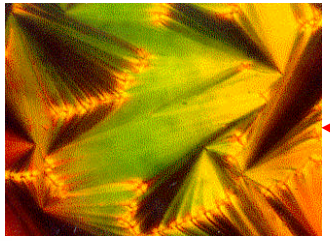
8c *(n=6)*

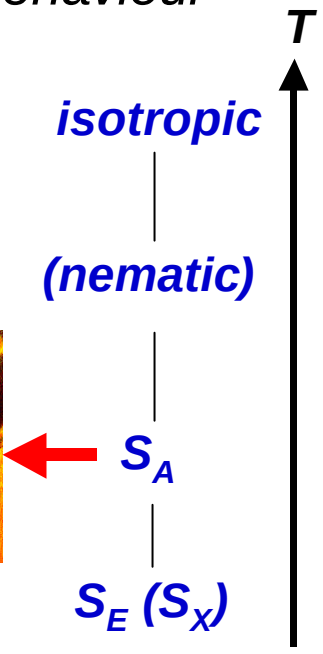
8d *(n=11)*





Phase behaviour





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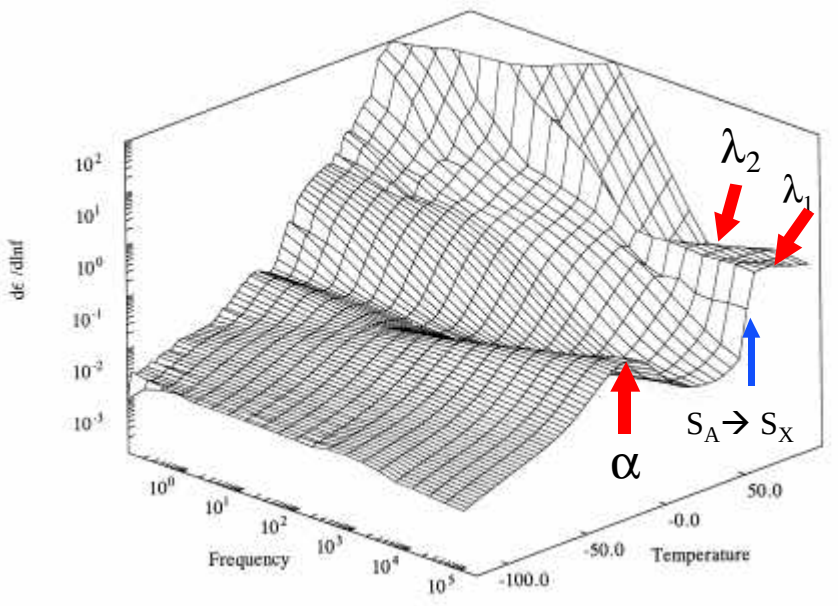
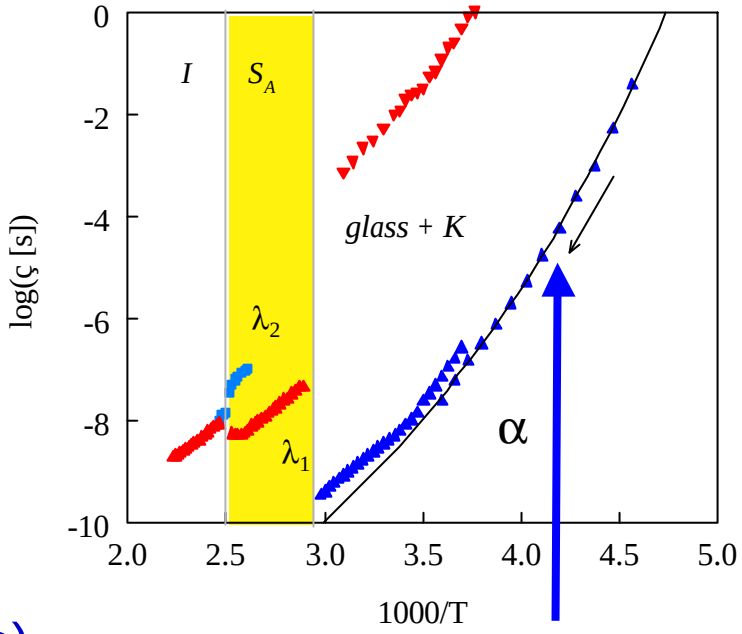
Dielectric spectrum of C_6-compound:



Relaxation map



- 2 mesogenic relaxations (in S_A state)
- 2 phase transitions

unexpected "VFT-process"

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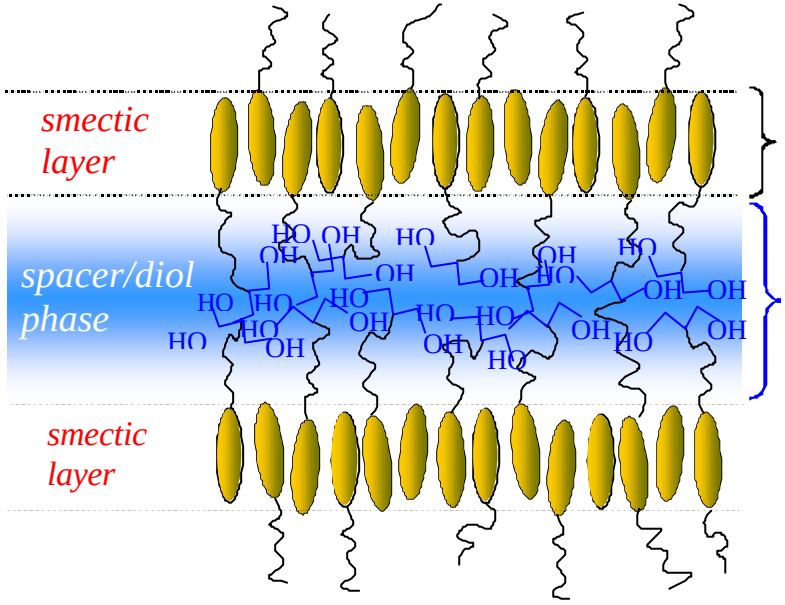
Dynamic glass transition – effect of confinement

Coexistence of glass forming (liquid) phase and crystalline mesogenic order

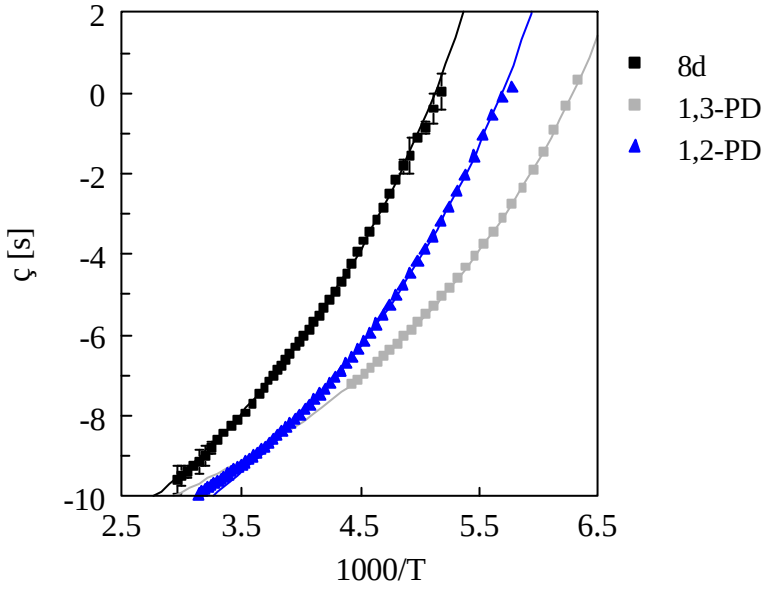


Rigid Fraction

Mobile fraction

- Analogy to H-bonded liquids ?

Comparison with diols 1,3-PD and 1,2-PD



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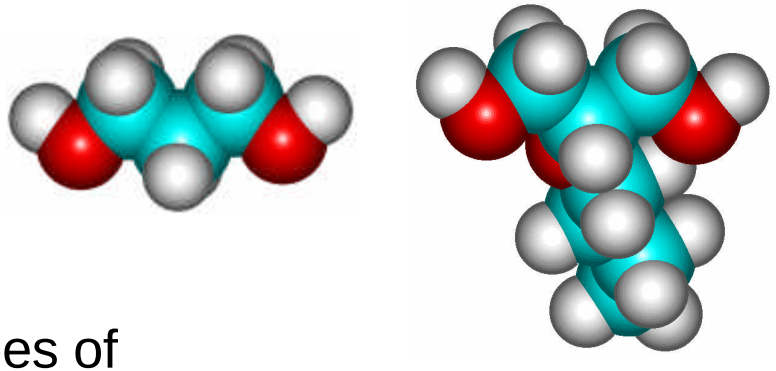
Dynamic glass transition – effect of confinement

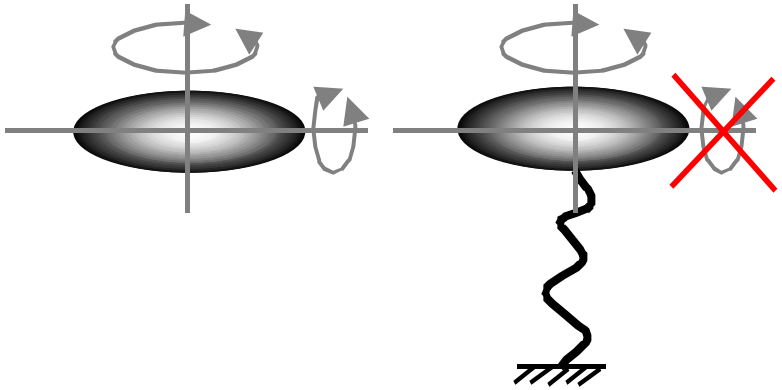
High frequency relaxation rate: single molecule behaviour

1,3-propanediol



***1,3-PD** with attached alkoxy-spacer*

rotational degrees of freedom:



difference in high frequency relaxation rate by < 1 decade plausible

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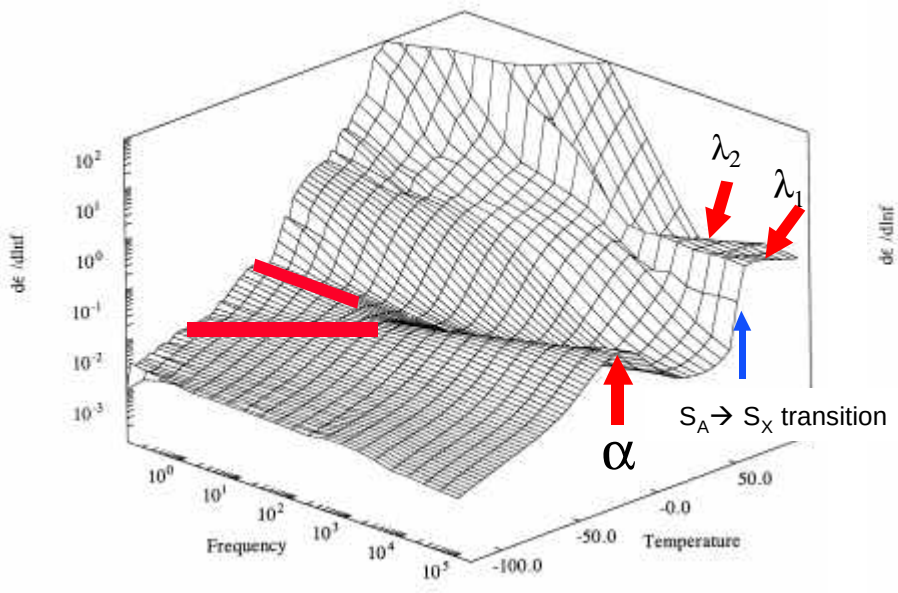
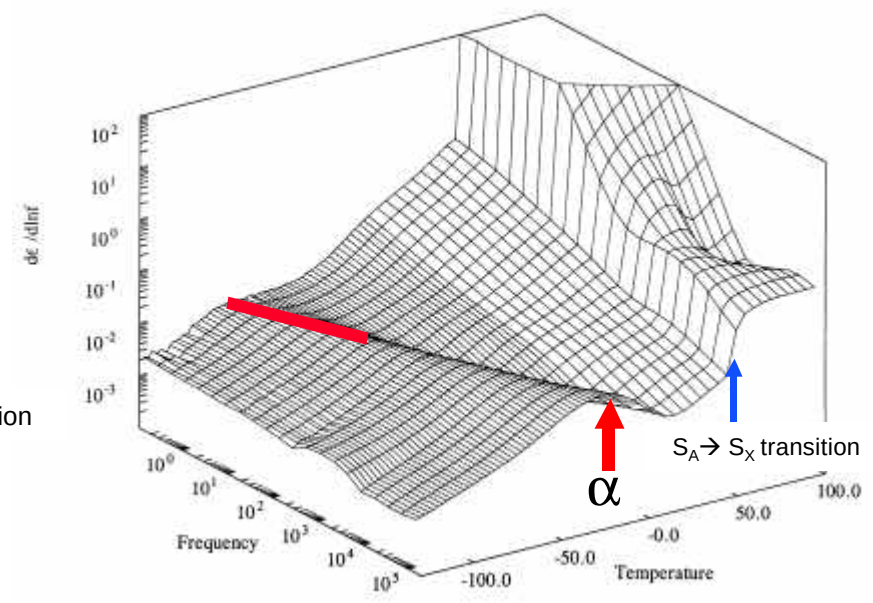
Low frequency relaxation behaviour

8c *(C_6-spacer)*



8d *(C_{11}-spacer)*



Splitting of α-process for short spacers lengths (n £ 6)

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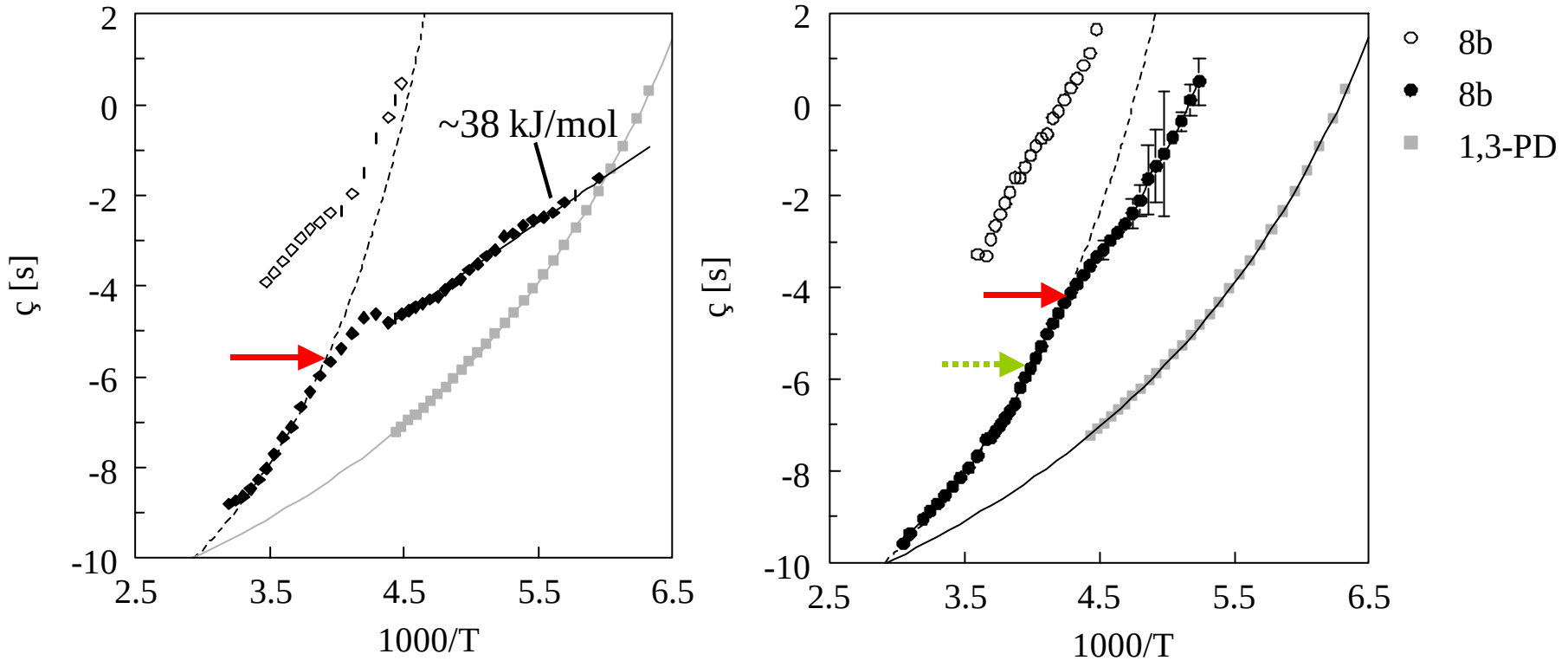
Dynamic glass transition – effect of confinement

Fit-results: peak relaxation time t_a – details

a) C_2-spacer

b) C_4-spacer



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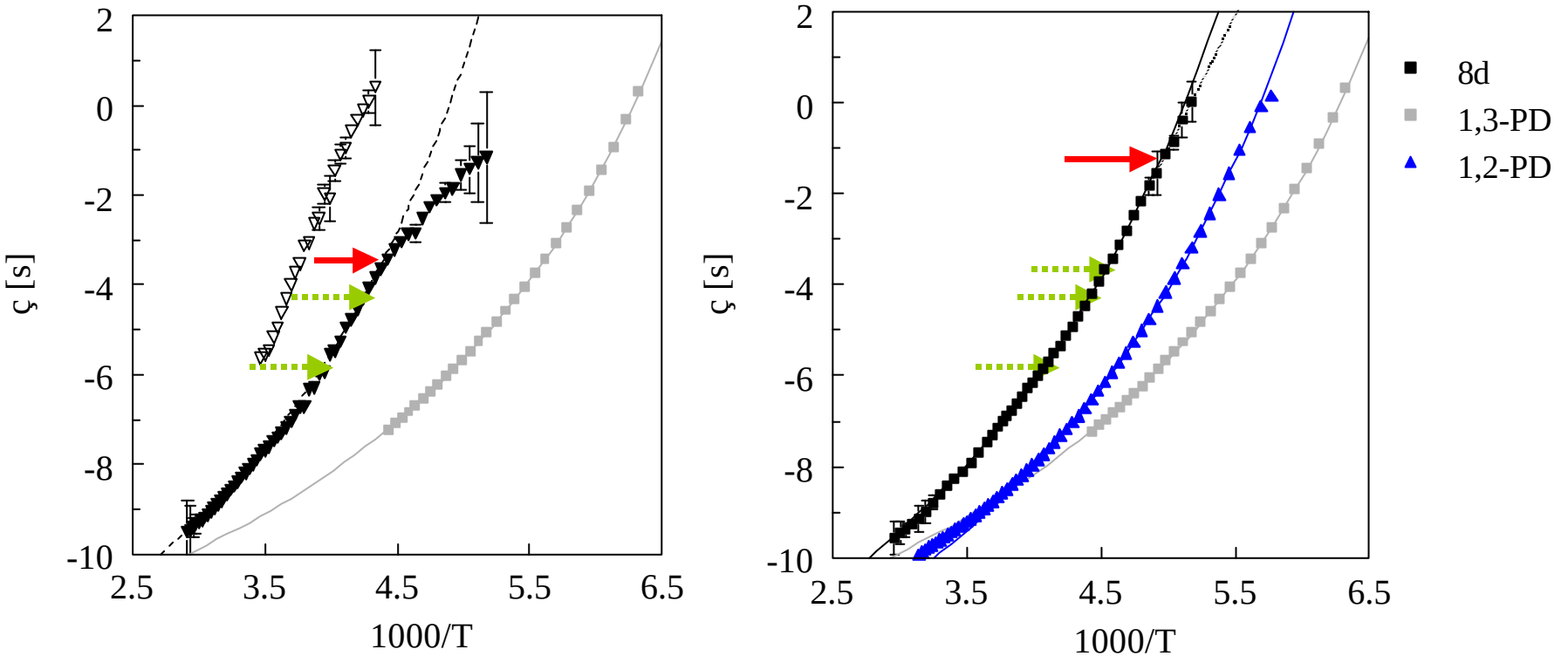
Fit-results: peak relaxation time t_a – details

c) C_6-spacer

d) C_{11}-spacer



Crossover-frequency f_c* : function of spacer length *n

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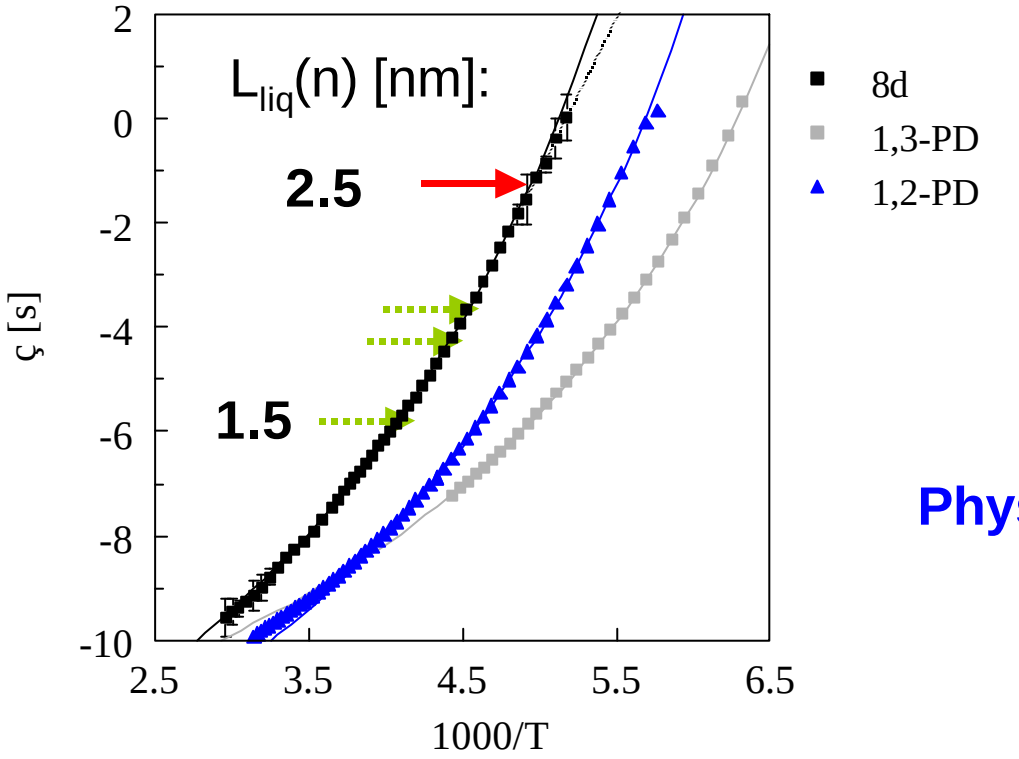
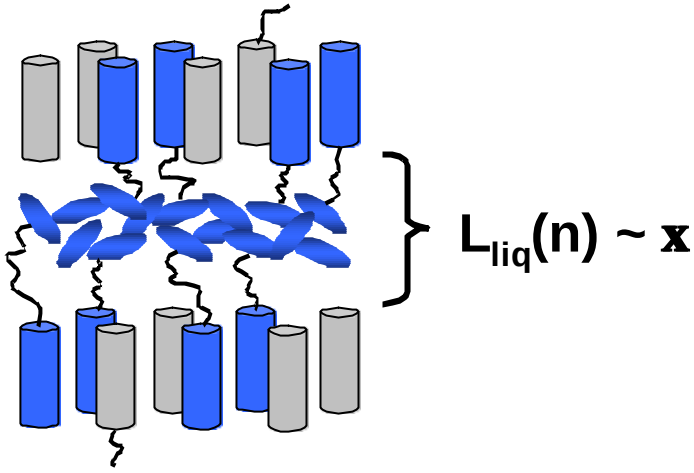
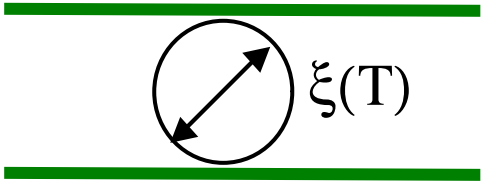
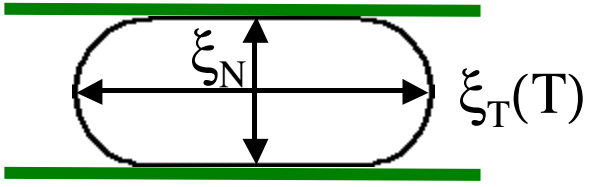




Physical meaning of crossover frequency:

$$x(f_{ct}) \sim L_{liq}(n)$$





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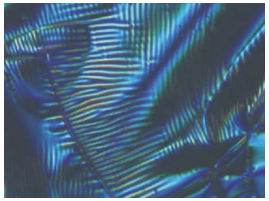
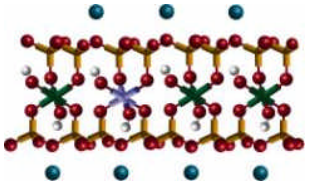
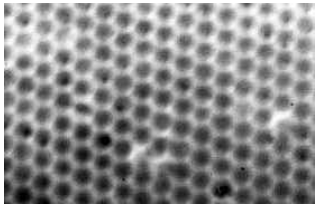
3. Polymer chains in nm-scale geometry

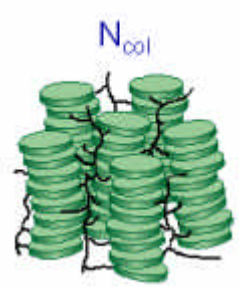
- ultra-thin polymer films
- clay-based nano-composites
- semicrystalline polymers
- liquid-crystalline polymers
- nano-structured materials

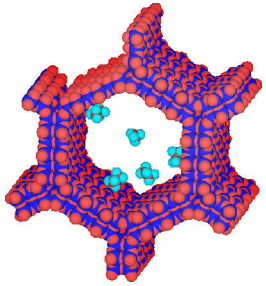




porous silica







MCM-41

Interference between intrinsic length scales of molecular dynamics and geometric dimensions expected

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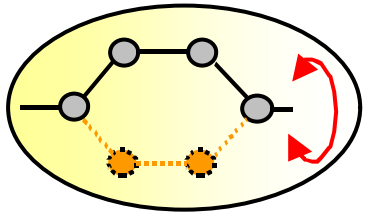
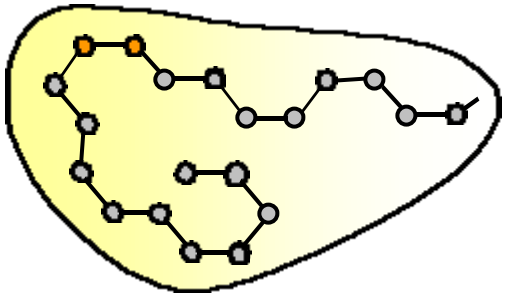
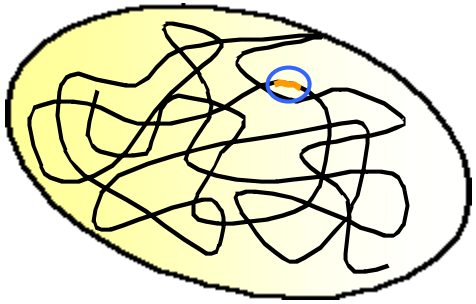
Length scales of motions in polymers

local motions, e.g. simple bond rotations	segmental motions (dynamic glass transition)	chain relaxation (Rouse, Reptation)
		
< 1 nm	$2 < \xi < 10$ nm	$10 < \xi < 200$ nm

increasing relaxation time, characteristic length scale

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Length scales of motions in polymers

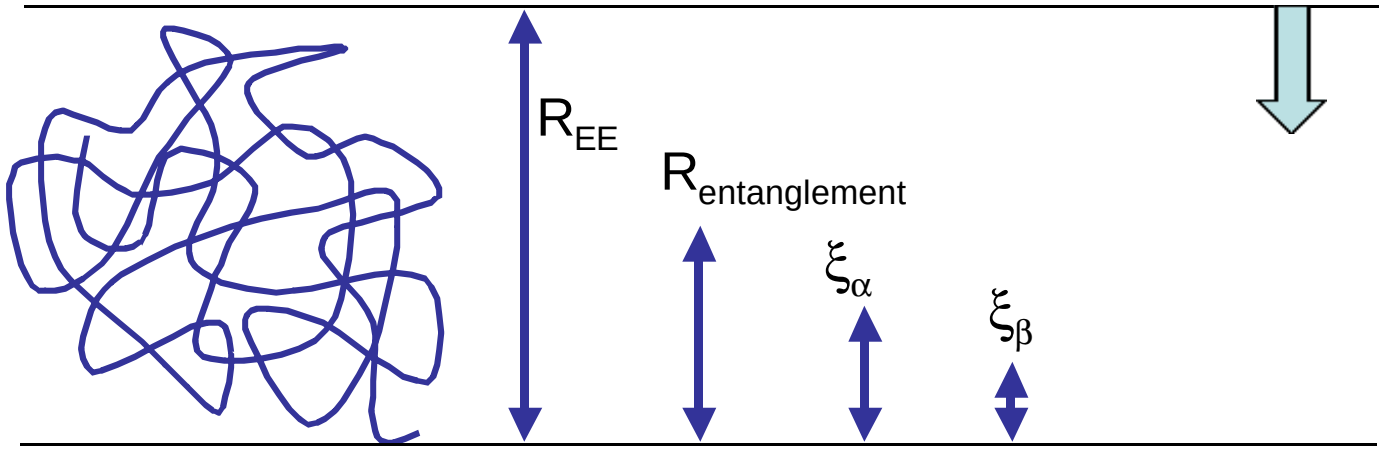
There are more length scales:

- reptation model: **tube dimensions** and there related relaxation times τ_d, τ_e, τ_r (lecture Prof. Kimmich)
- mean **distance between entanglements** (dependent on M_c and degree of chain coiling

Length scales of motions in polymers

Study of dynamics in confinement:

Successively break-down of molecular motions related to intrinsic length scales > L = imposed length of confined geometry



Ideally: Reduction of *L* only affects the larger processes

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Outline

1. Introduction
2. Phenomenology of the glass transition
3. Polymer chains in nano-scale geometry – general issues
4. Glass transitions effects in ultra-thin polymer films – main findings and models
5. Dielectric relaxations in ultra-thin polymer films – basic issues
6. DRS results on ultra-thin PMMA films
7. Liquid-like surface mobility in supported PS-films
8. Summary and Future work

4. Glass transitions effects in ultra-thin polymer films

In this section:

- Ultrathin polymer films: basic geometries and **preparation**
- 10 years study of T_g-effects on ultrathin polymer films: typical **results**
- What remains to be answered?
- How can Dielectric Relaxation Spectroscopy (DRS) contribute to solve the remaining questions?

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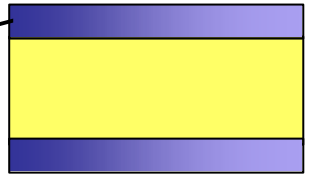
Ultrathin polymer films: thickness L < 100nm

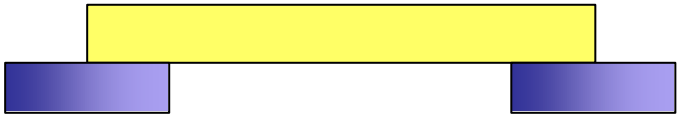
2 basic configurations

supported films (polymer on substrate):

capping layer



freely-standing films:



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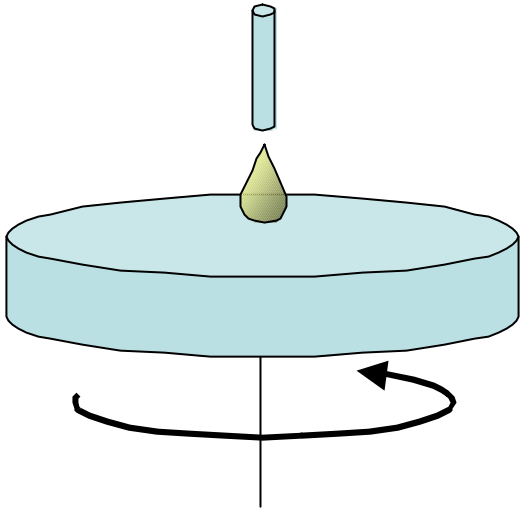
Ultrathin polymer films – how to prepare them ?

- **Spin coating**
- Physical vapour deposition
- Electro spraying
- Water transfer technique



Four key stages:

1. fluid dispense
2. spin-up
3. stable fluid outflow
4. evaporation dominated drying.

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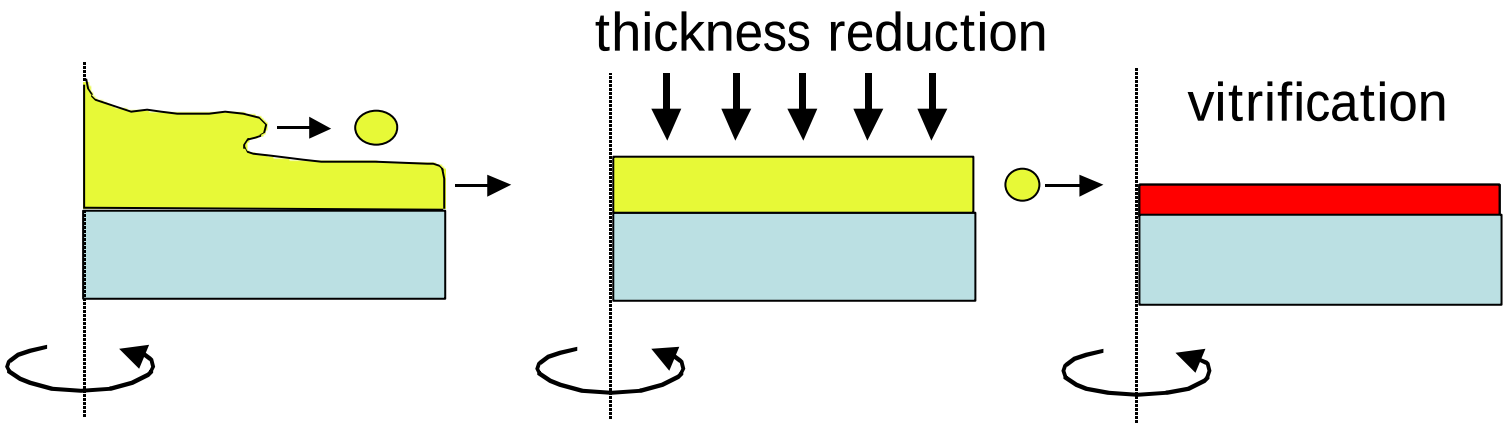
Ultrathin polymer films – preparation (2)

1. fluid dispense
2. spin-up
3. stable fluid outflow
4. evaporation dominated drying.

final thickness

$$h_f = c_0 \left(\frac{e}{2(1-c_0)} \frac{3h}{rw^2} \right)$$



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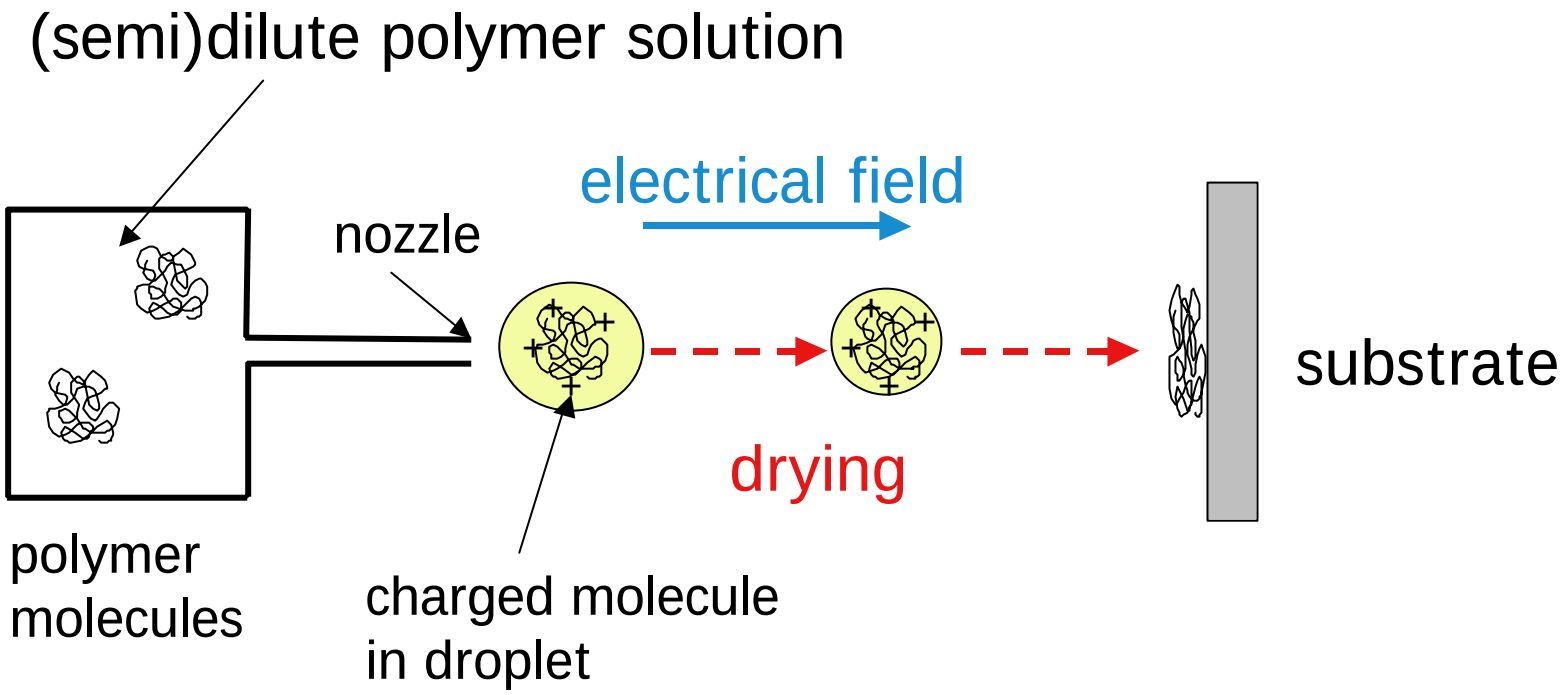
Ultrathin polymer films – preparation (3)

Electro-spraying:



→ deposition of unentangled single polymer molecules possible

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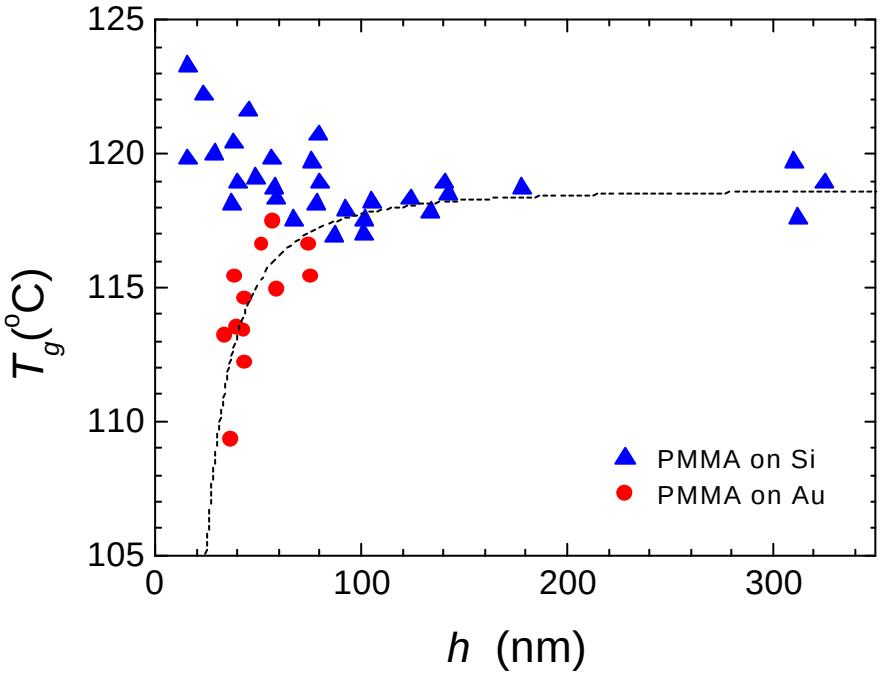
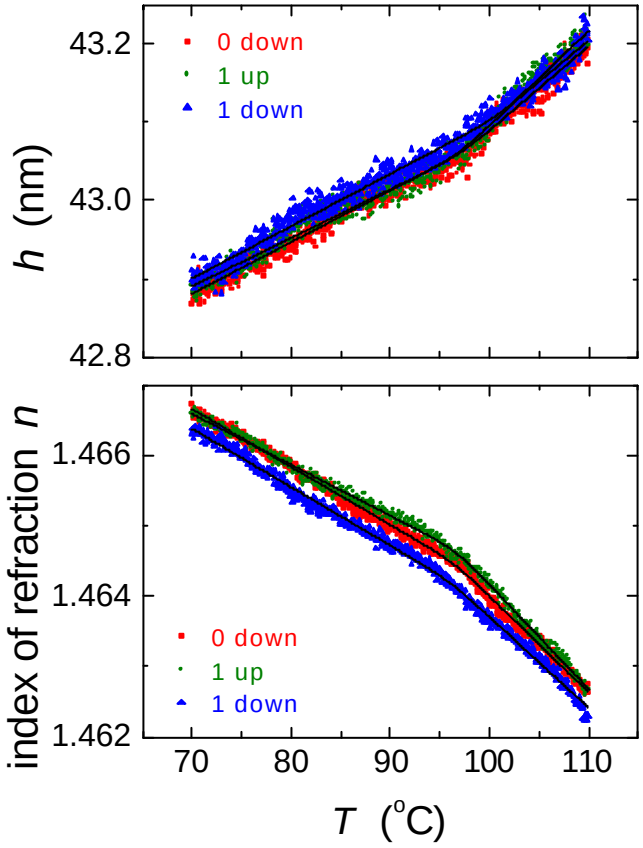
T_g-effects on ultra-thin polymer films

First results: [Keddie *et al.*, Faraday Discuss. **98**, 219 (1994)]





typical result from ellipsometry:
***h*(*T*), *n*(*T*)**

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T_g-effects on ultra-thin polymer films

Different techniques:

- Ellipsometry (refraction index, thickness)
- x-ray reflectivity (volume expansivity)
- PALS (free volume expansivity)
- Brillouin spectroscopy

In the following: T_g-effects on

- **different polymers:** PS, PMMA
- **different geometries:** supported, freely-standing films
- **different molecular mass**

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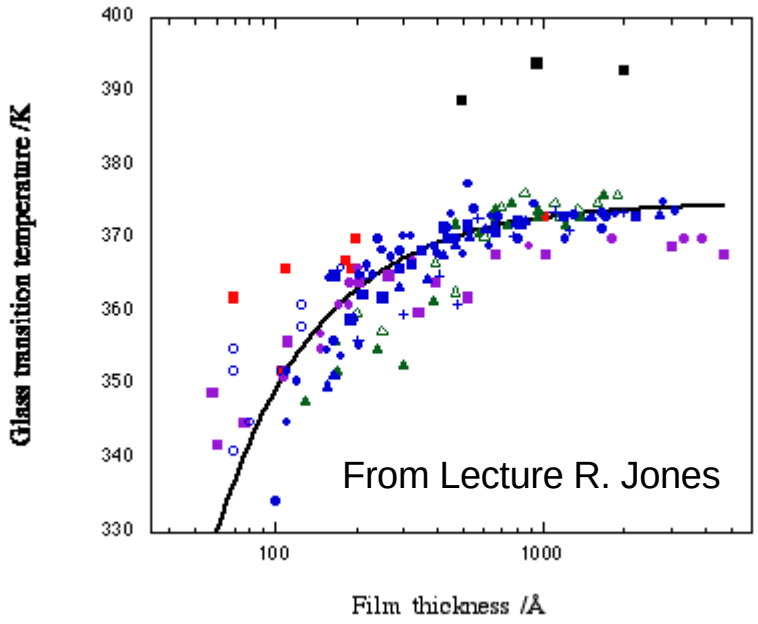
Supported PS films

PS supported on silicon



pretty universal behaviour

No M_w dependence between 120k and 2M

Different techniques:

- Ellipsometry
- Micro-DSC
- Dielectric Spectroscopy
- PALS

Substrates & conditions:

- HF-etched Si, vacuum
- HF etched Si, air
- SiOx
- Hexamethyl disilazane layer on silicon

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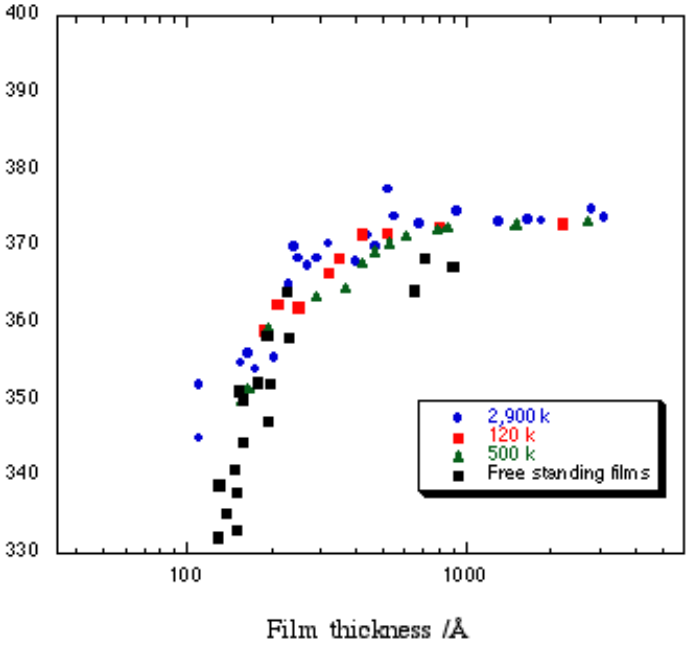
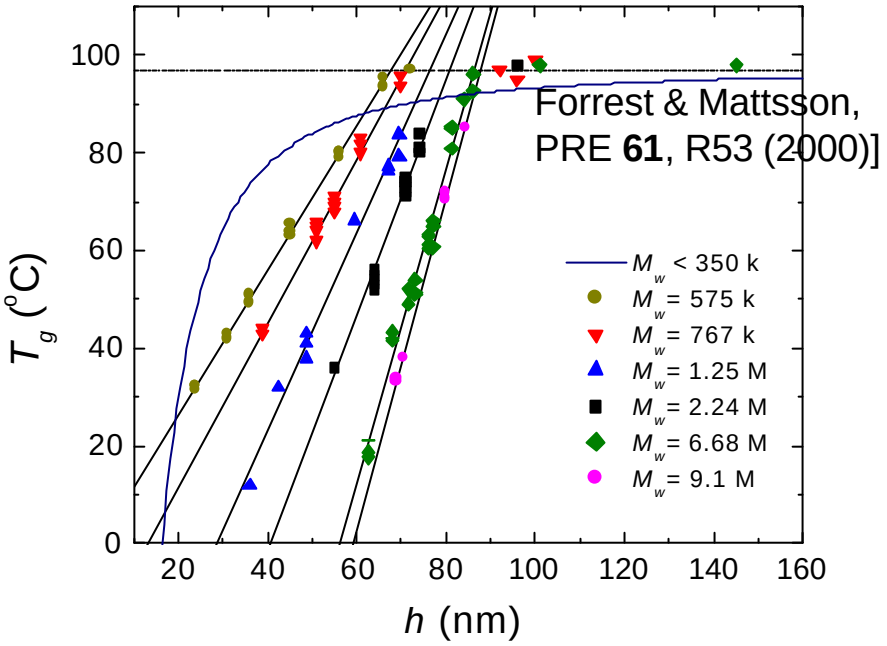
Supported PS films vs. freely-standing films

PS freely-standing, M_w < 347k



freely-standing films behave like supported films with half the thickness → **2 free surfaces**

high M_w (> 347k)



strong M_w dependence, but simple scaling:

$$T_g = T_g^* + b(h - h^*)\ln\left[M_w / M_w^*\right]$$

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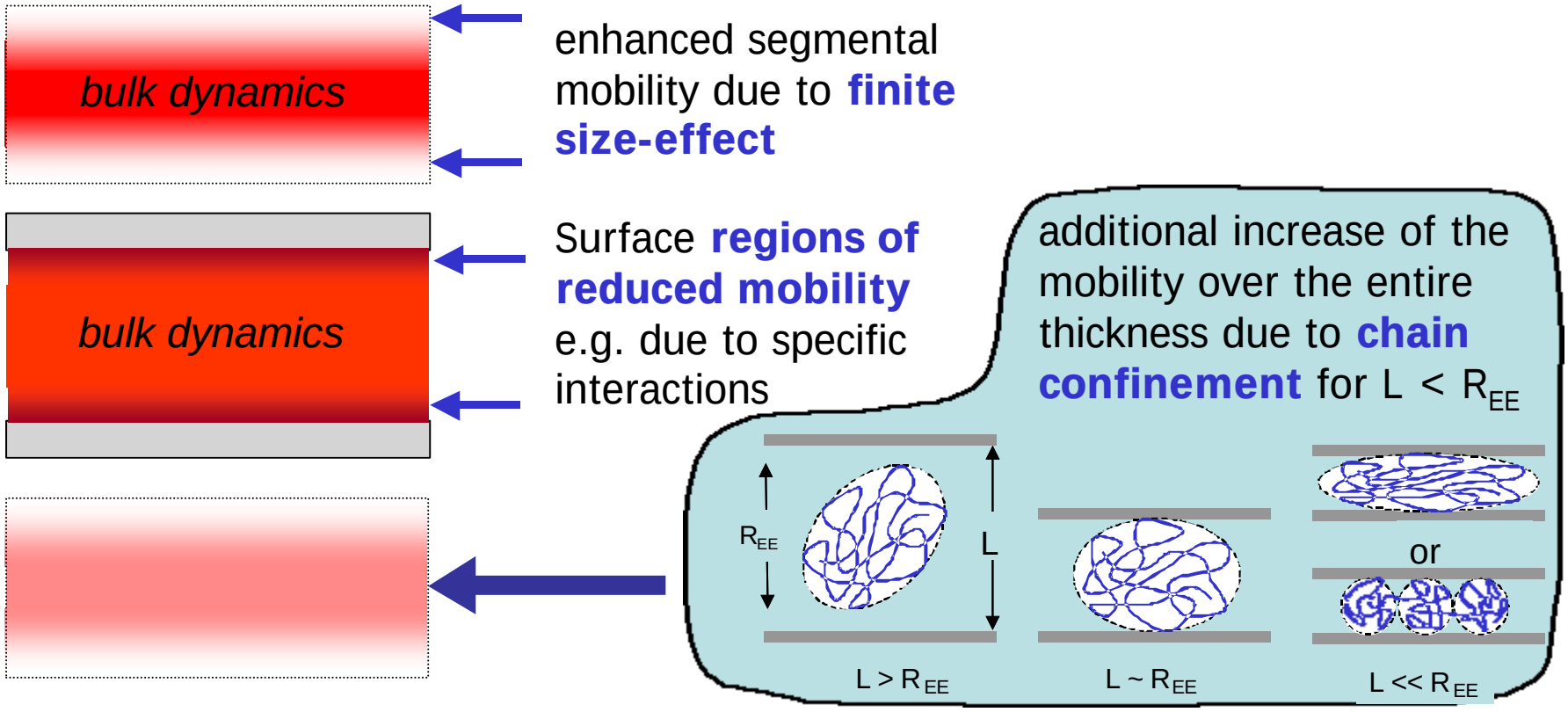
Three possible scenarios of changed segmental mobility in freely-standing or supported/capped polymer films:



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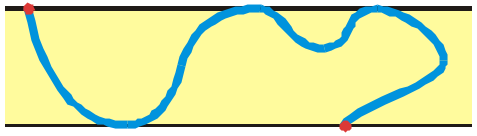
Some models that describe the T_g-depression in low-M_w PS films

segregation of chain ends to free surfaces

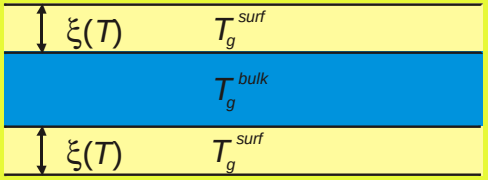
[Mayes, Macro. **27**, 3114 (1994)]

[Tanaka *et al*., Macro. **29**, 3040 (1996)]



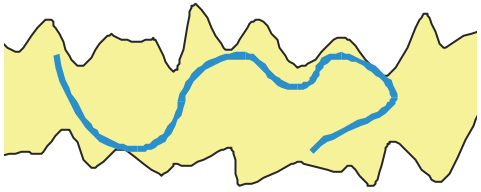
- near-surface cooperative motion

[Forrest & Mattson, PRE **61**, R53 (2000)]



coupling to capillary modes

[Herminghaus *et al*., EPJE **5**, 531 (2001)]



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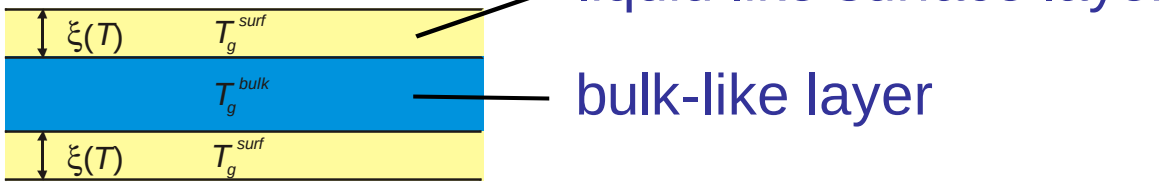
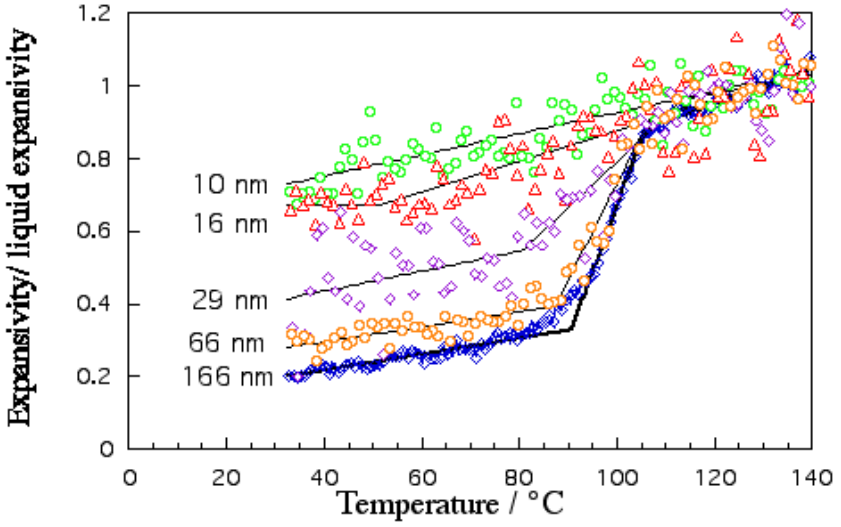
Implications from 2-layer model



- broadening of glass transition expected - **confirmed**
- Expansivity experiments average over mobility profile → film with 2 free surfaces has larger T_g-reduction - **confirmed**



Kawana and Jones 2001

Question 1: what is actual mobility profile?

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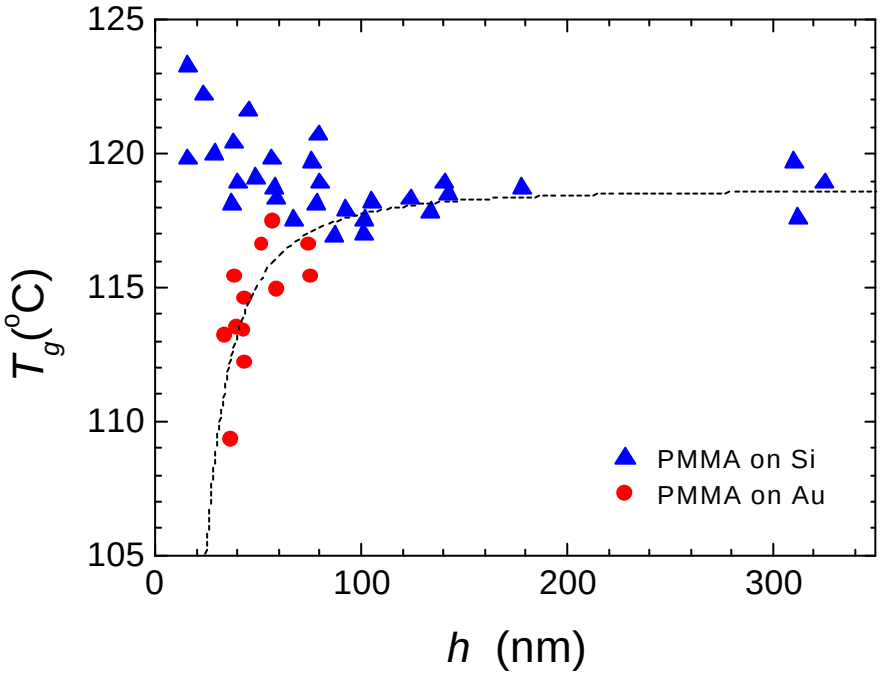
Supported PMMA films

PMMA supported on Si and Au



Substrate effects important for PMMA

- specific interactions (H-bonding) of PMMA with substrate
- also influence of tacticity on T_g-up/down shift !

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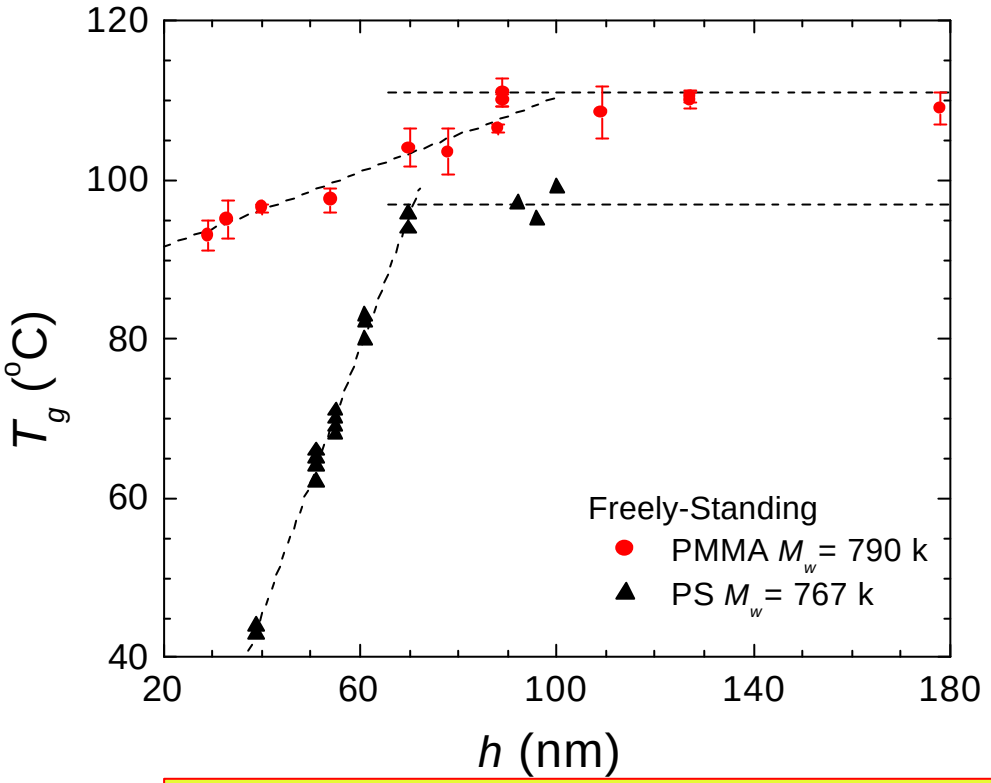
Comparison freely-standing PMMA – PS films



nearly equivalent molecular weights

Question 2:

Why do PS and PMMA behave so differently?

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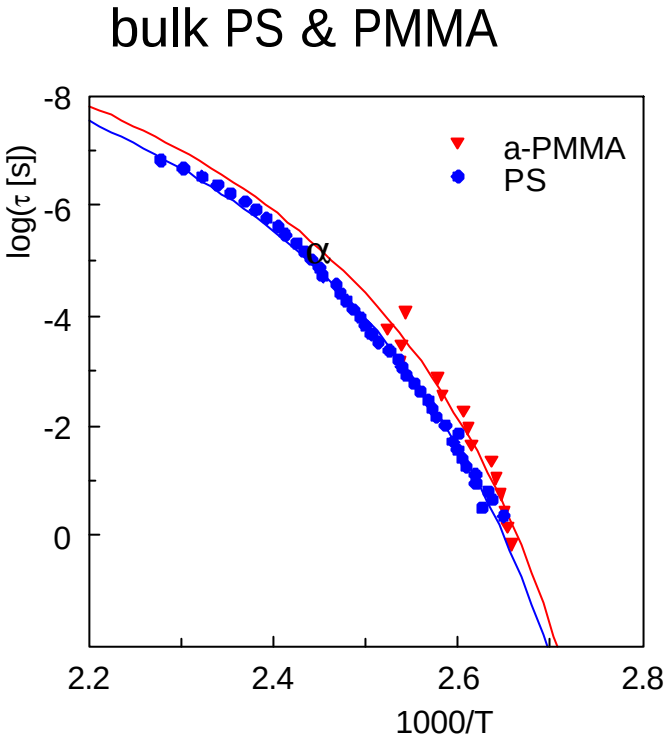
Why is T_g of PS more sensitive to thickness reduction than in PMMA ?

Both PS and PMMA have

- **similar T_g**
- **similar fragility index**

fragility index $\propto E_{a,local}(T=T_g)$ = measure for curvature of VFT curve



what else controls thickness sensitivity of T_g?

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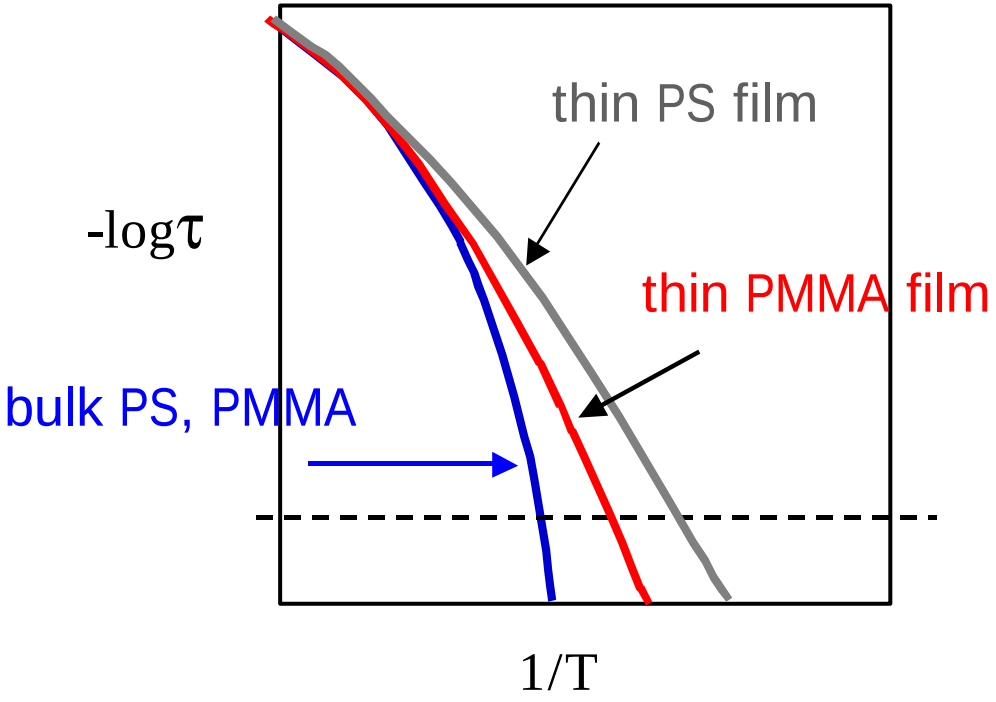
One possible answer:

In thin films, fragility might change differently for of PMMA and PS



Is there any evidence for this scenario?

broadband dynamic studies required → DRS

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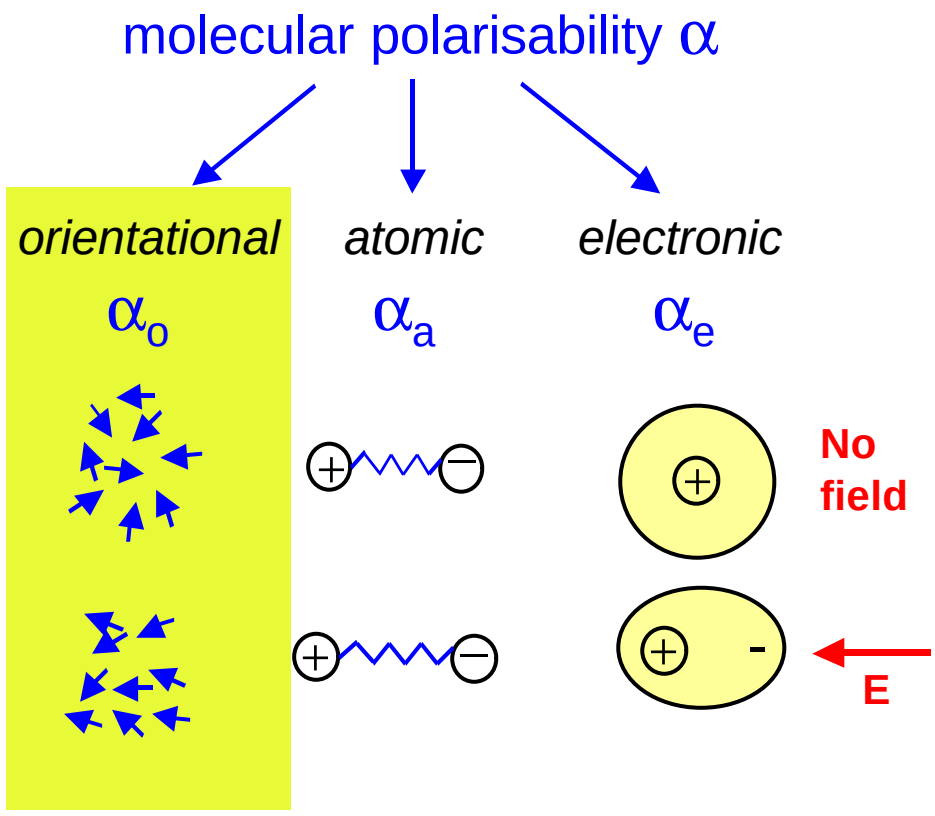
5. Dielectric relaxations in ultra-thin polymer films – basic issues



$$P = N_0 a E_L$$

N_0: concentration of dipoles

E_L: **local** electric field

$$P = N_0 (a_e + a_a + a_o) E_L$$

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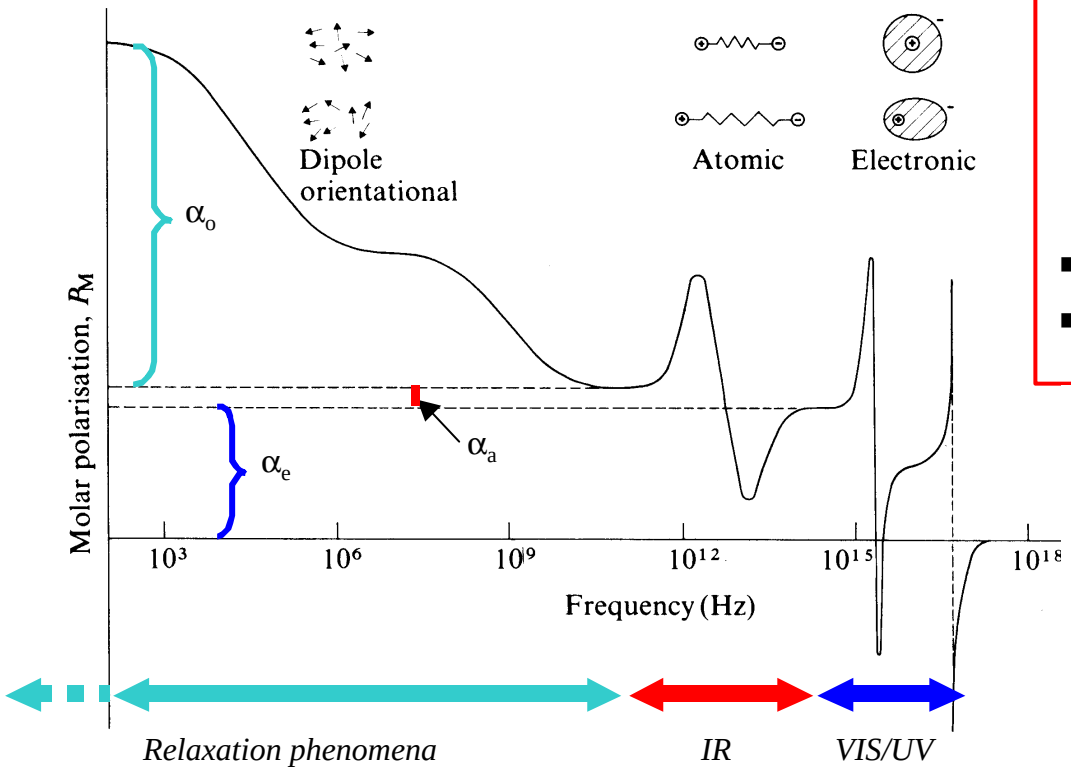
Dielectric relaxation spectroscopy – introduction

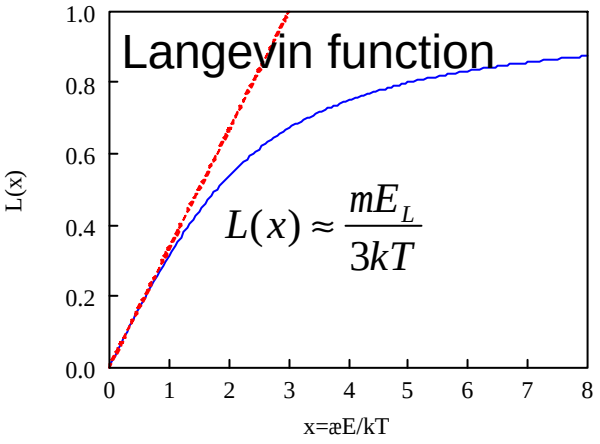


polar molecules:

orientational polarisability

$$a_o = \frac{m^2}{3kT}$$

- α_o depends on ***T*** und ***E***
- valid for weak fields



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Dielectric relaxation spectroscopy – introduction

From microscopic to macroscopic quantities:

Clausius-Mosotti relation

$$P_M = \frac{e-1}{e+2}\frac{M_W}{r} = \frac{N_A}{3e_0}\left(a_e + a_a + \frac{m^2}{3kT}\right)$$

M_W: molecular weight
r: density
N_A: Avogadro's number
e: dielectric constant

For polymers and other complex dielectrics:

Relation by **Onsager and Fröhlich**

$$\frac{(e-n^2)(2e+n^2)}{e(n^2+2)^2}\frac{M_w}{r} = \frac{N_A g m^2}{9e_0 kT}$$

new:

g: ***dipole-dipole correlation factor***

$$n^2 = e_\infty$$

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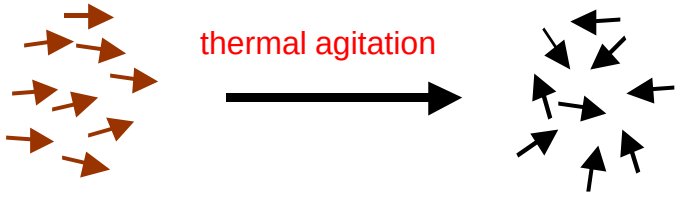
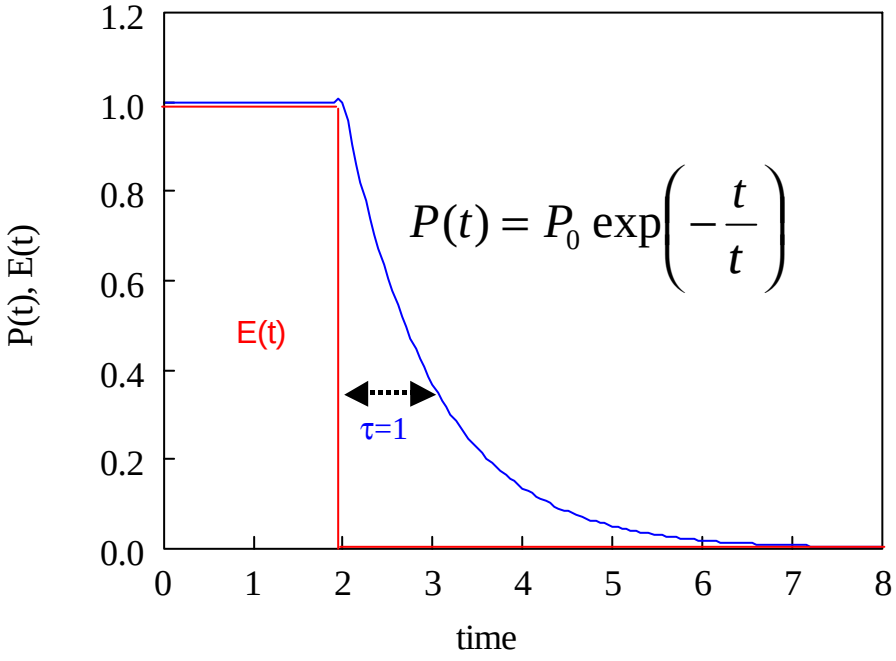
Dielectric relaxation spectroscopy – introduction

Dielectric relaxation:

Characteristic time to attain thermal equilibrium = τ





ac field, frequency *w*:

complex dielectric "constant"

$$e^*(w) = e'(w) - ie''(w)$$

Real part — *storage term*

Imaginary part — *loss term*

→ *actually 2 spectra*

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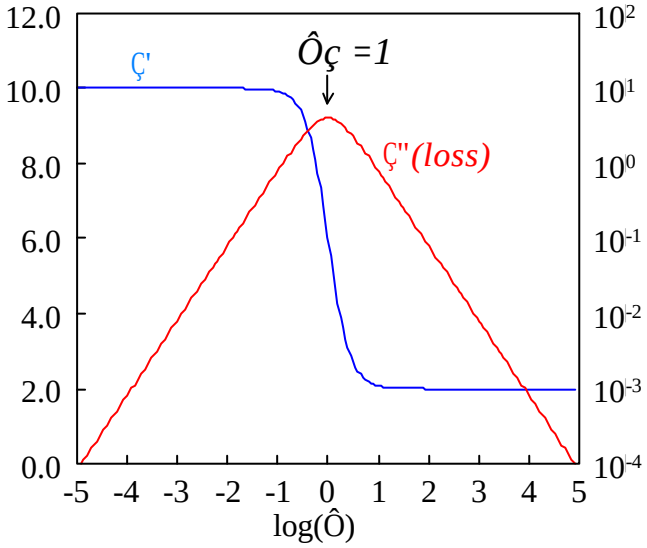
Dielectric relaxation spectroscopy – introduction

Relaxation functions:

Single relaxation time process

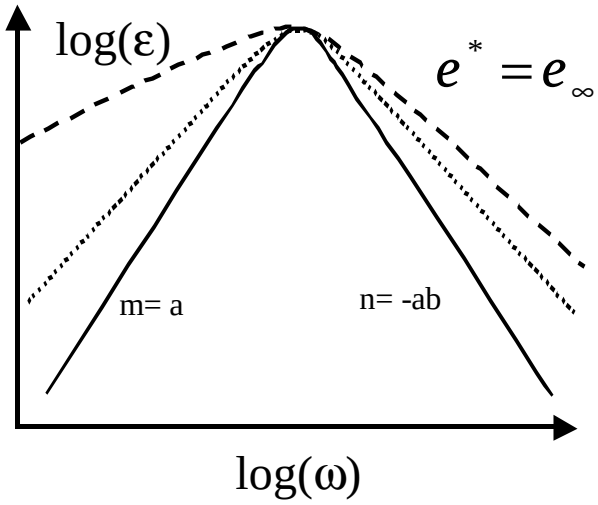


$$e'(w) = e_\infty + \frac{e_s - e_\infty}{1 + w^2 t^2}$$

$$e''(w) = \frac{e_s - e_\infty}{1 + w^2 t^2} wt$$

Distribution in relaxation times

→ *Havriliak-Negami (HN) function:*



$$e^* = e_\infty + \frac{\Delta e}{\left[1 + (iwt)^a\right]^b}$$

→ 2 independent shape parameters

- relaxation strength $\Delta\varepsilon$
- mean relaxation time τ

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DRS on ultrathin films

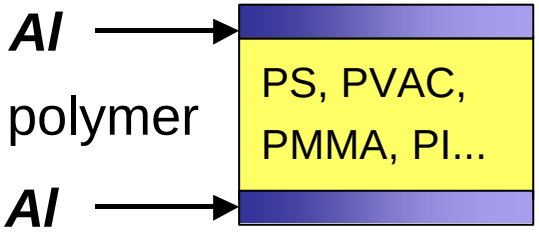
advantages:

+ sensitivity (C*) increases with 1/L
+ very wide dynamic range
+ robust sample preparation

drawbacks:

freely standing geometry hard to achieve

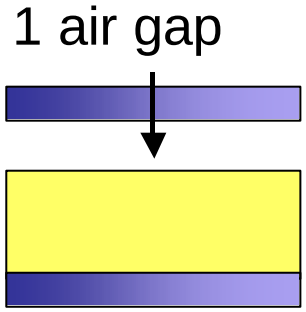
DRS restricted to polar polymers



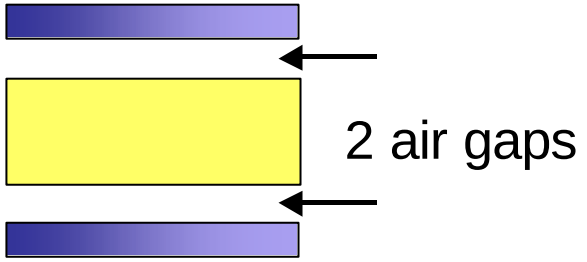
Fukao, first studies

Hartmann, Kremers group

Wübbenhorst (coop. with *Dutcher*)



Sharp, Forrest 2002



?

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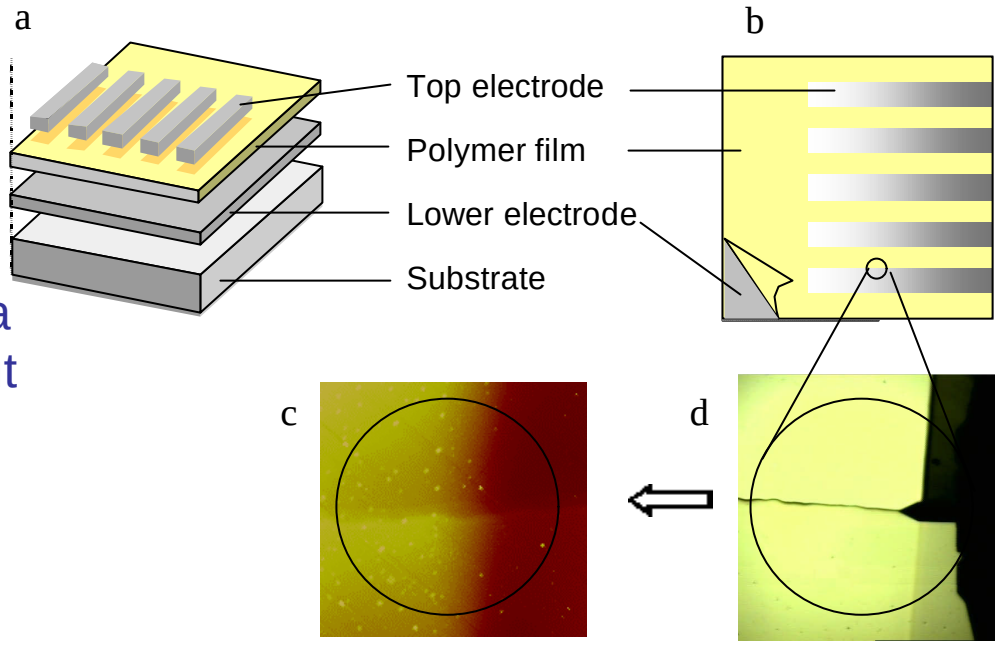
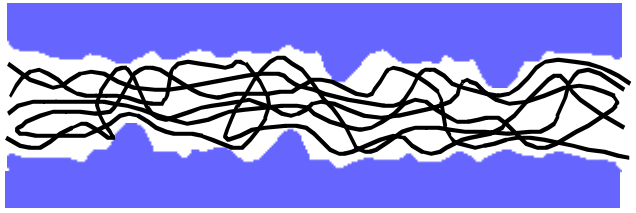
Preparation of ultrathin film "capacitors"

1. **spincoating of very dilute solutions** on Al-coated glass substrates.
2. evaporation of **patterned top electrode**



optical microscopy & AFM image

→ well defined DRS samples with a thickness as low as **4nm** without shorts !



4nm → 10-15 atomic layers !

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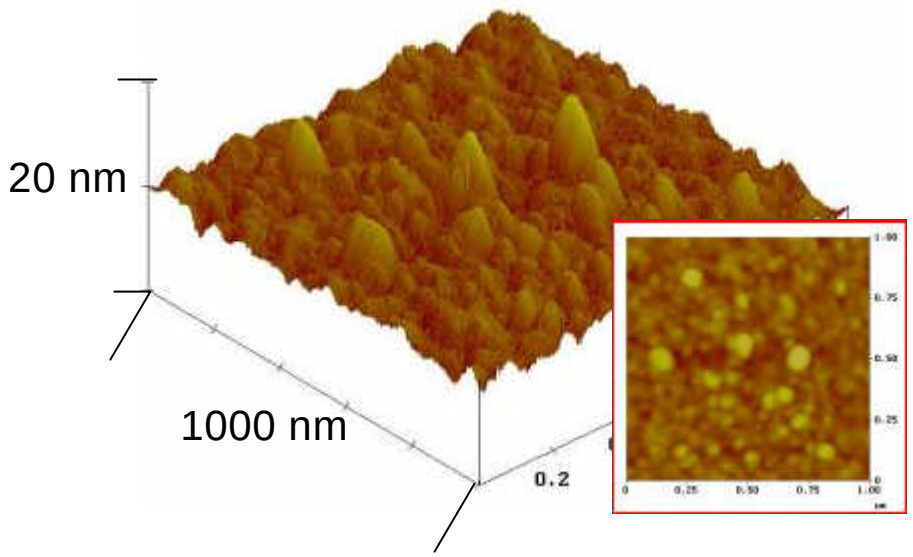
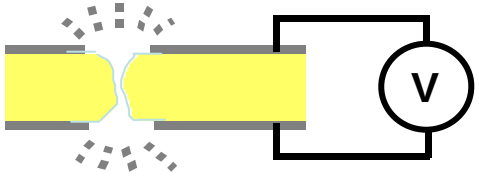
Why does it work?

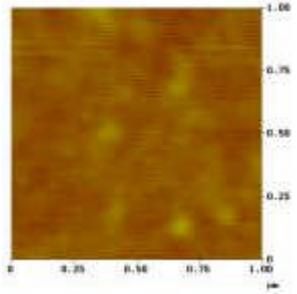
1. **excellent film forming** behaviour of polymers → smooth and close polymer films
2. "**self-healing**" in case of local shorts

Al coated glass substrate





smooth surface of PMMA on Al, height-range 10nm



Sometimes: It does not work

permanently shorted samples
samples with high parasitary losses

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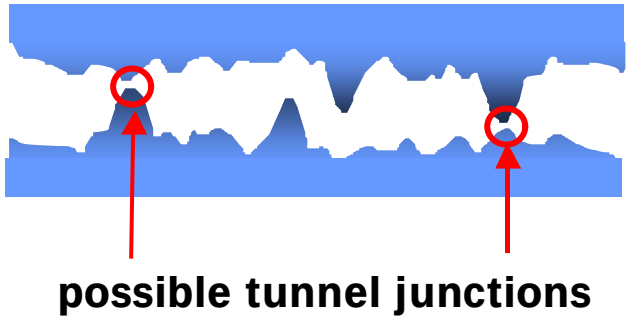
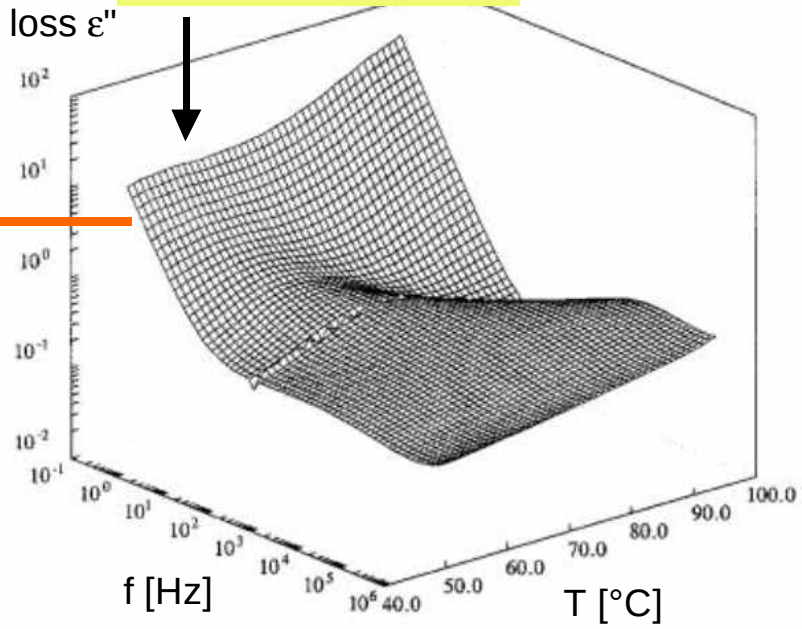
Origin of parasitary losses: tunnel junctions



possible tunnel junctions

unusual loss



‘proper’ spectrum of i-PMMA

i-PMMA spectra with weakly T-dependend low-frequency loss

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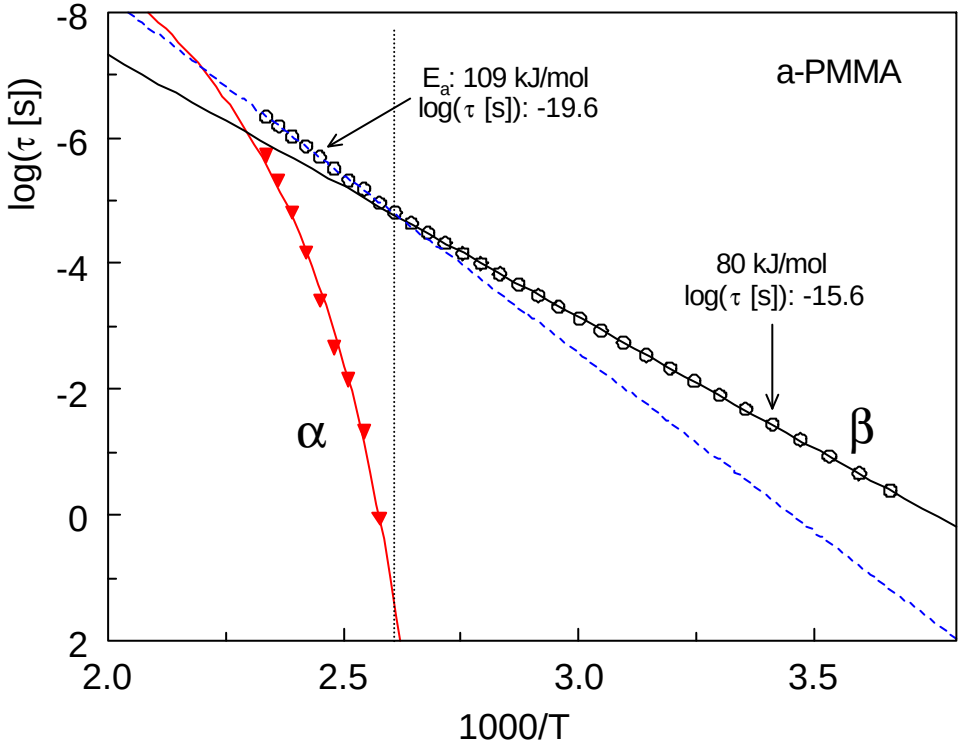
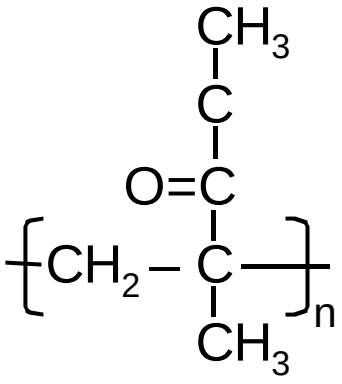
Outline

1. Introduction
2. Phenomenology of the glass transition
3. Polymer chains in nano-scale geometry – general issues
4. Glass transitions effects in ultra-thin polymer films – main findings and models
5. Dielectric relaxations in ultra-thin polymer films – basic issues
6. DRS results on ultra-thin PMMA films
7. Liquid-like surface mobility in supported PS-films
8. Summary and Future work

6. DRS results on ultra-thin PMMA films

Poly(methyl methacrylate), PMMA





dielectric b-process

	E_a [kJ/mol]	$\log(\tau_0)$
β	80	-15.6

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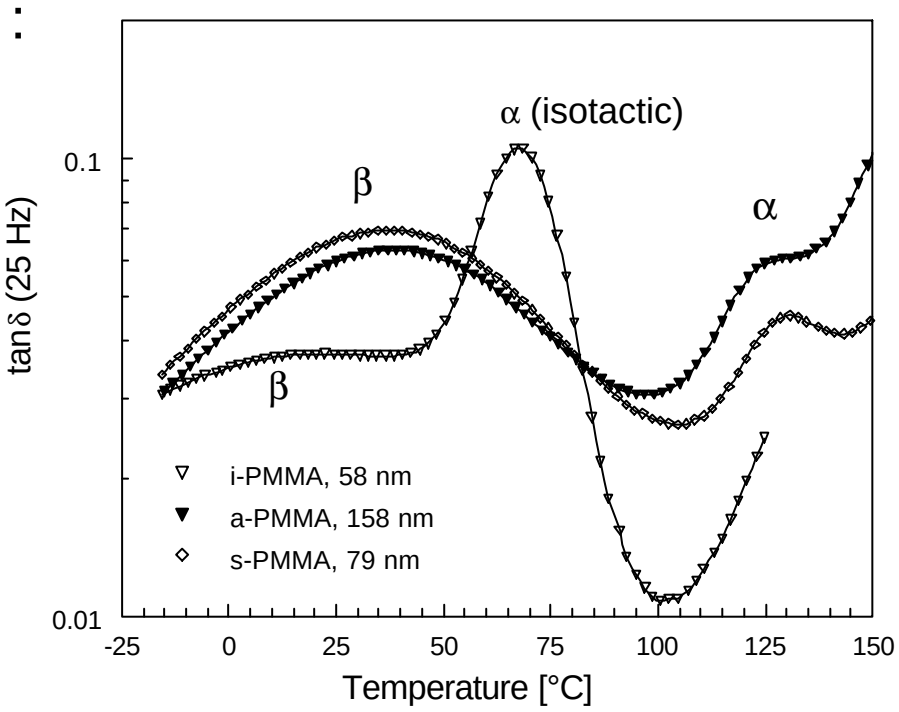
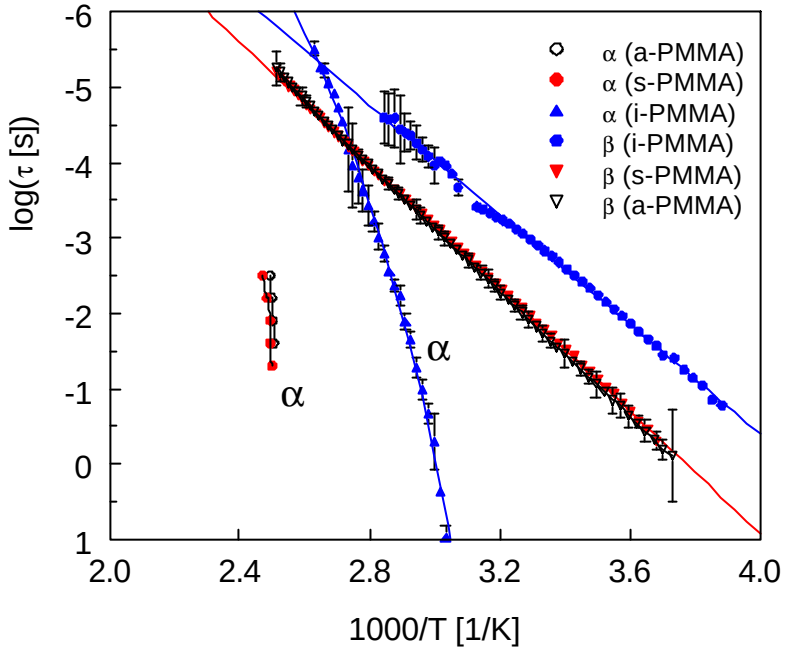
"Bulk" PMMA – large influence of stereoregularity





i-PMMA: E_a ~ 70kJ/mol

	E_β [kJ/mol]	T_g [°C]
i-PMMA	70	56
s-PMMA	80	120

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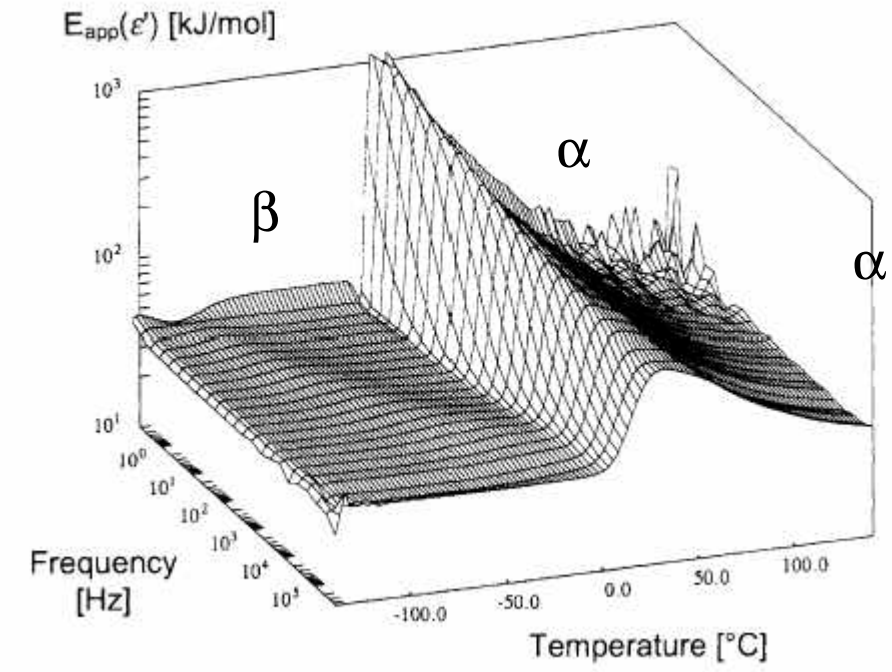
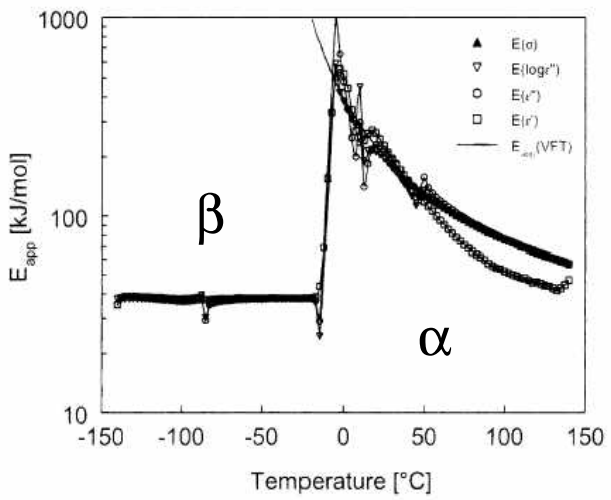
"Bulk" dynamics of stereoregular PMMA

Determination of the glass transition temperature by local activation energy analysis:



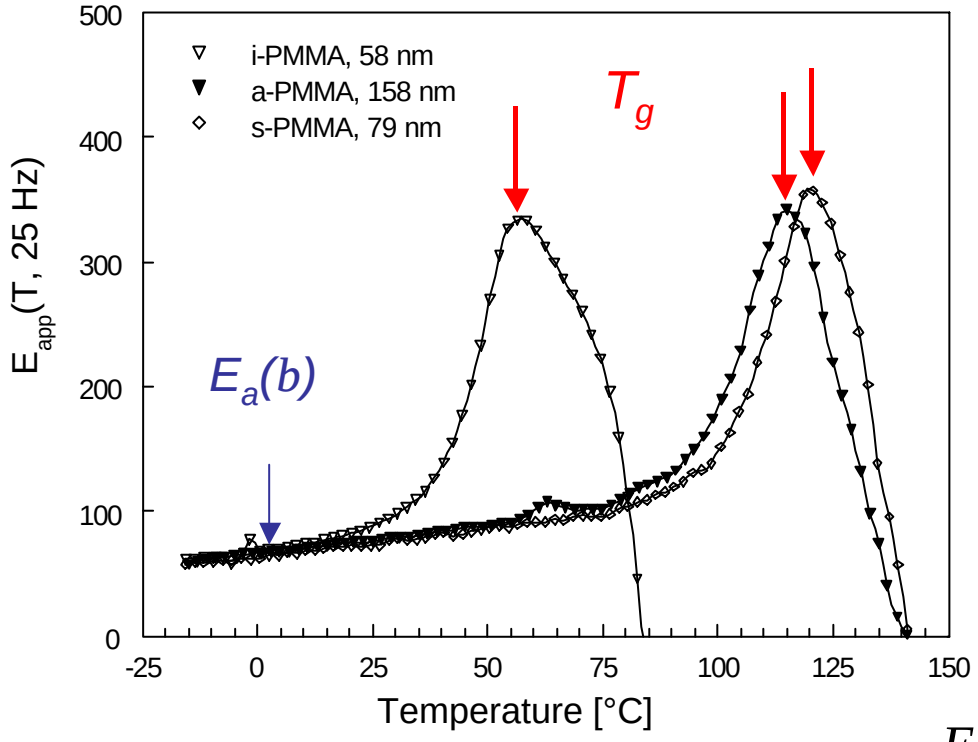
$$E_{app}\left(w_0, T_0\right) = -RT^2 \left.\frac{\partial e'/\partial T}{\partial e'/\partial \ln w}\right|_{w_0, T_0}$$



Maximum in E_{app} at T where VFT-law breaks down

"Bulk" dynamics of stereoregular PMMA

Local activation energy analysis for PMMA:



$$E_{app}\left(w_0, T_0\right) = -RT^2 \left.\frac{\partial e'/\partial T}{\partial e'/\partial \ln w}\right|_{w_0, T_0}$$

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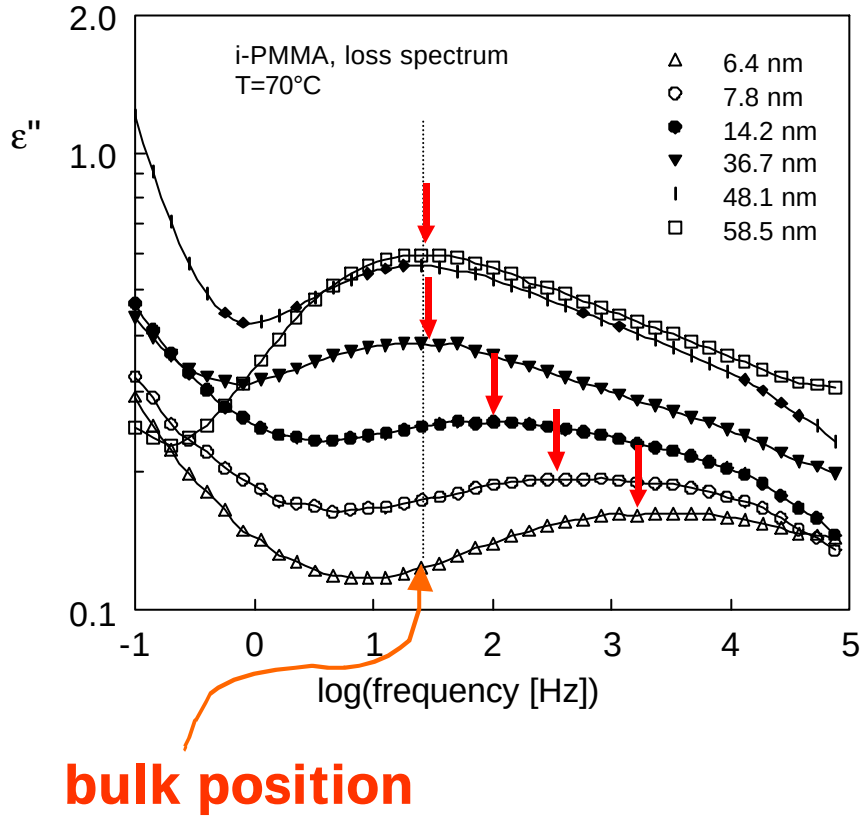
Thickness effects on the a-relaxation

Isotactic PMMA



- **Shift** of relaxation spectrum
- **Broadening** in α-process
- **Reduction** in relaxation strength

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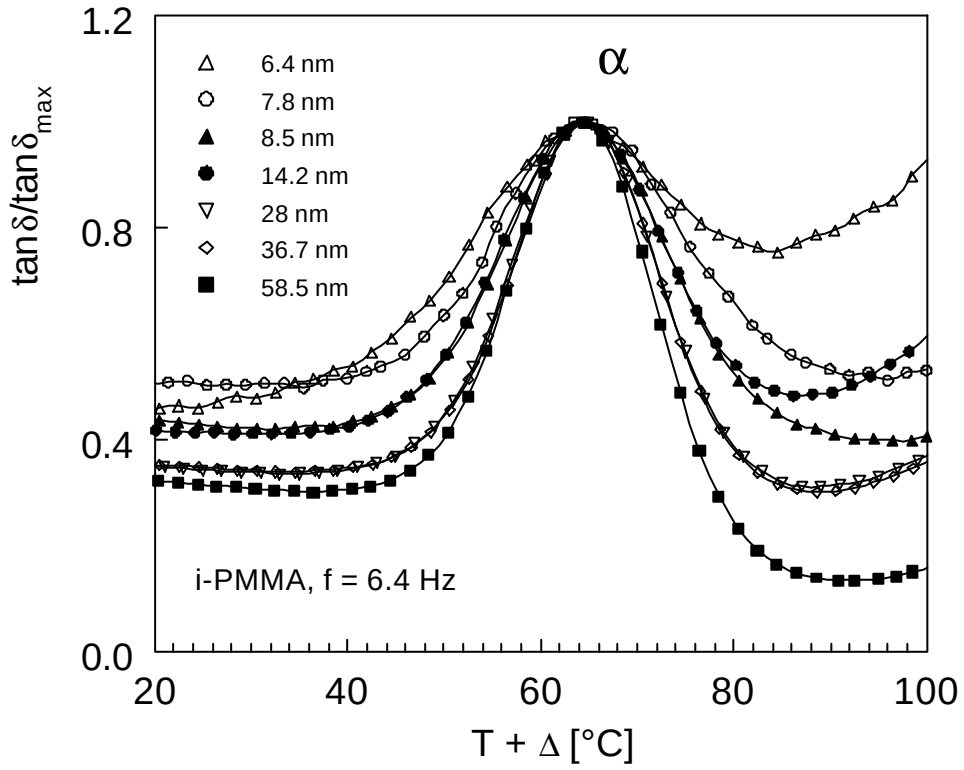
Thickness effects on the a-relaxation

normalized and shifted loss tangent vs. temperature



Clear broadening of α-process at low & high temperature (frequency)

general broadening favours existence of **mobility profile t(L)**

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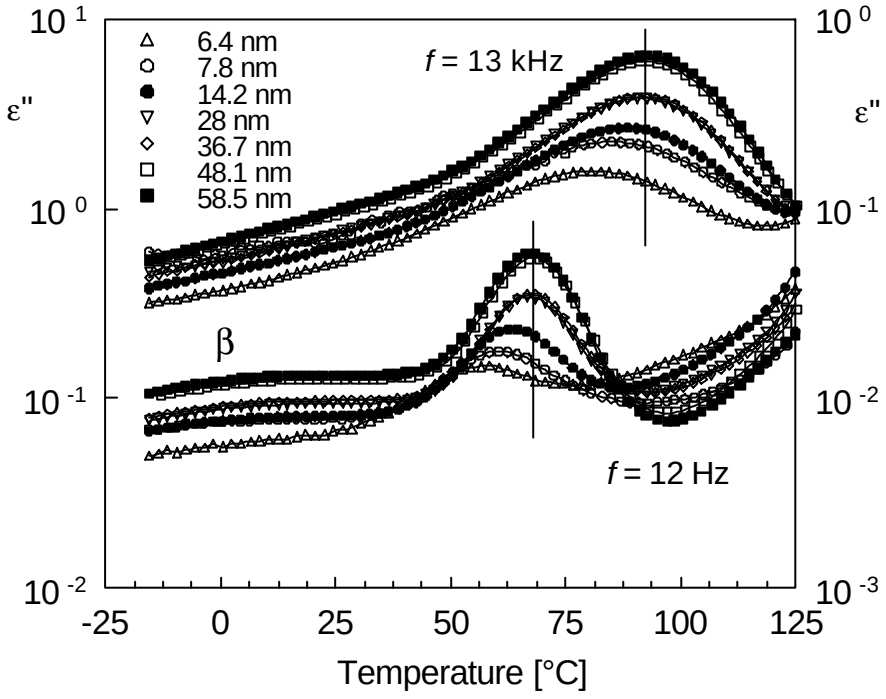
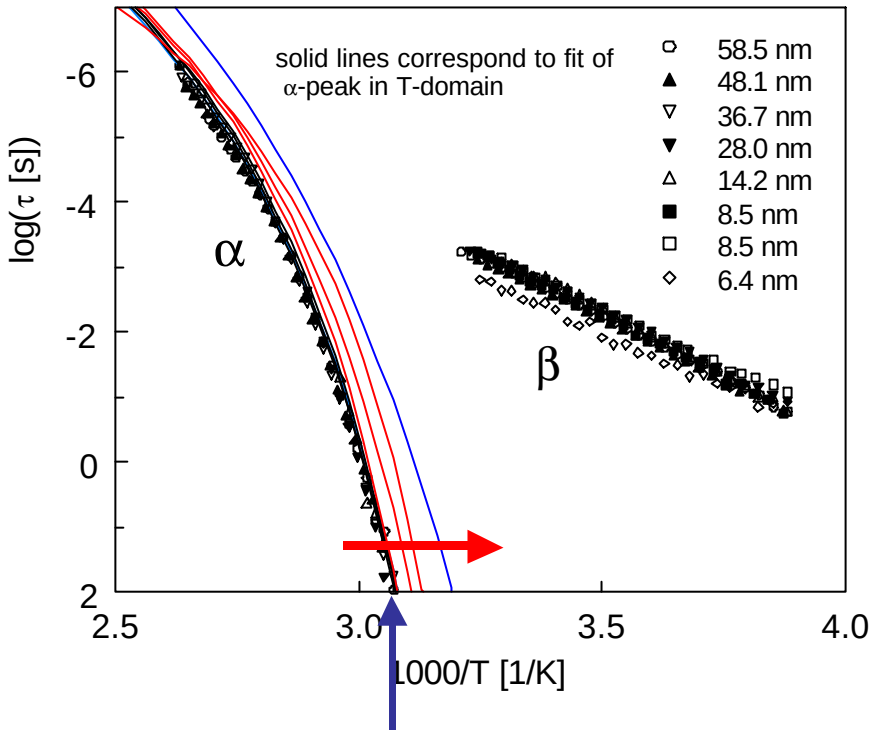
Thickness effects on the a-relaxation

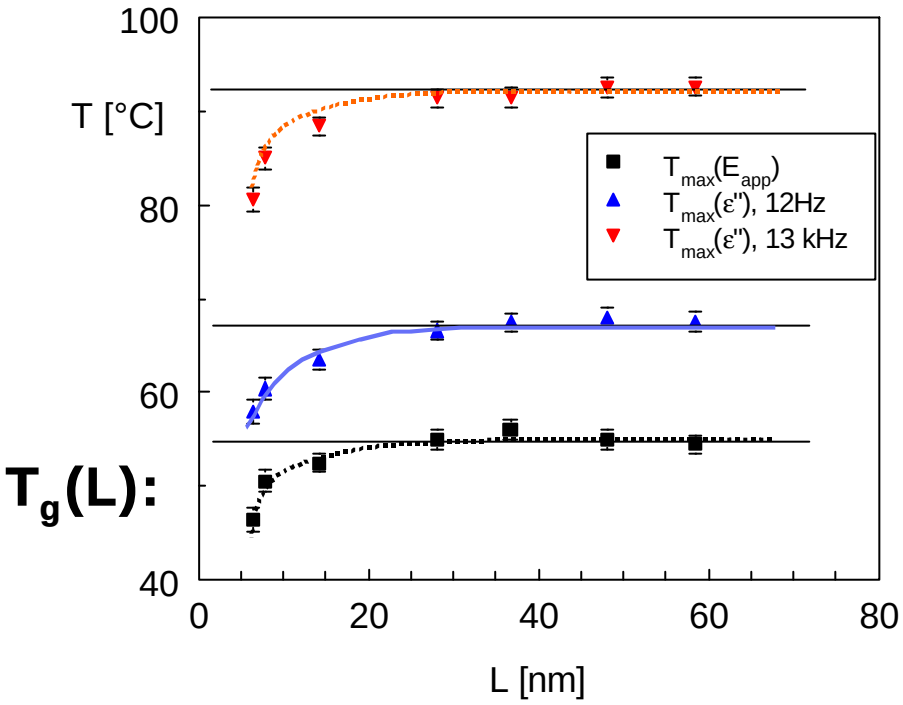




T_g (t=100s)

→ Shift of a-peak both at low and high frequencies

Determination of T_g from VFT-fit of a-process



→ **Same thickness dependence of T(a) at very different frequencies:**
0.01, 10, 10^4 Hz

entire speed-up of glass transition dynamics

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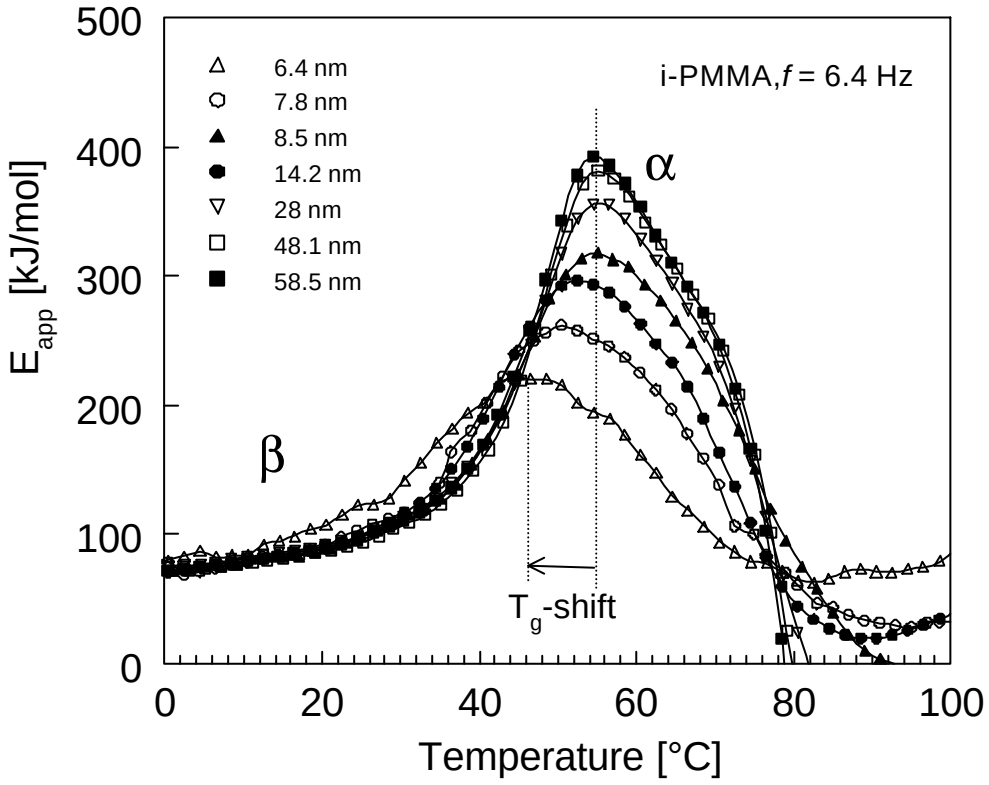
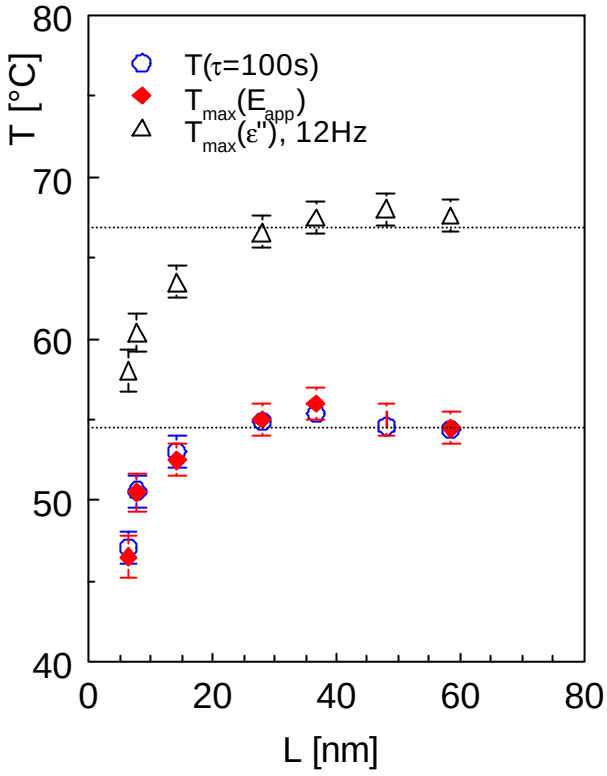
Determination of T_g from peak in local activation energy $E_a(T)$:





→**excellent agreement between two ways of T_g evaluation**

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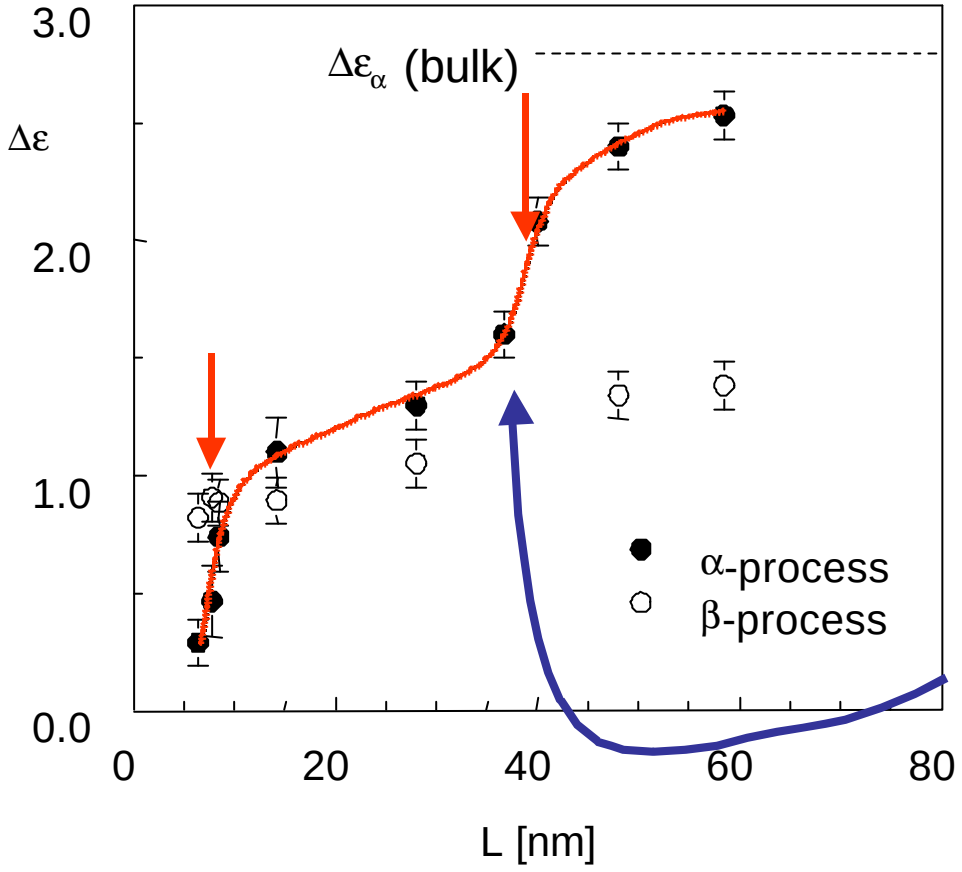
a-process of i-PMMA: relaxation strength $De_a(L)$



2-stage behaviour in relaxation strength of cooperative dynamics

→ 2 characteristic length scales involved

L = 30 - 40nm close to R_{EE}

→ **effect of chain confinement**

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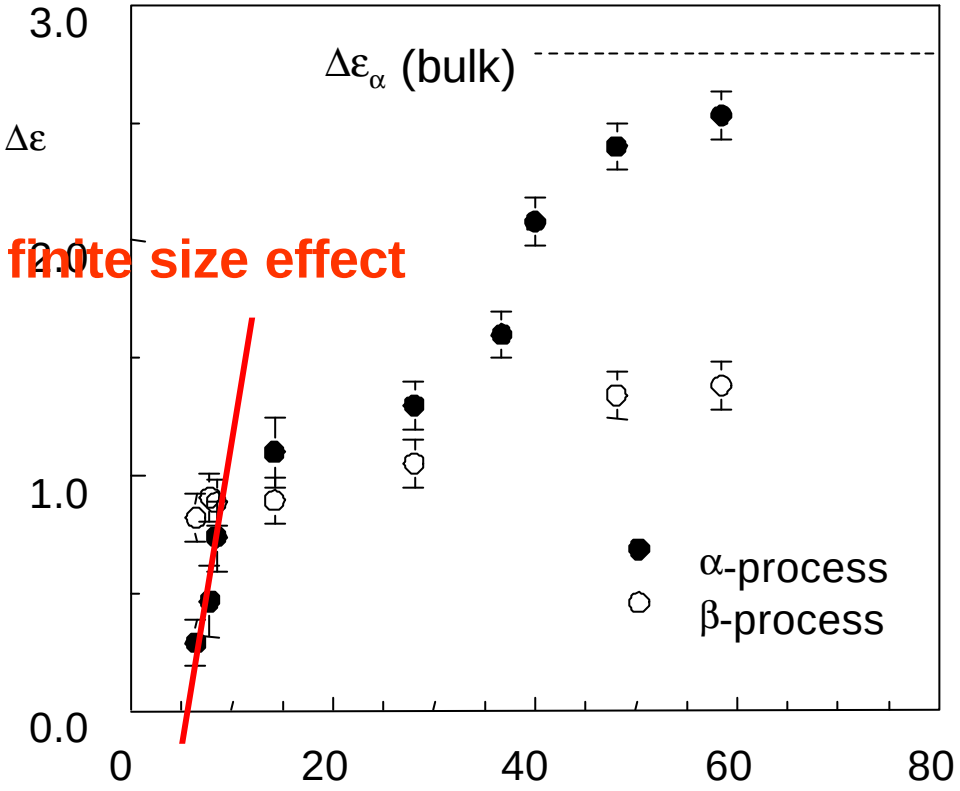
a-process of i-PMMA: relaxation strength $De_a(L)$



2-stage behaviour in relaxation strength of cooperative dynamics

→ 2 characteristic length scales involved

Extrapolation of De_a to zero → x ~ 5nm

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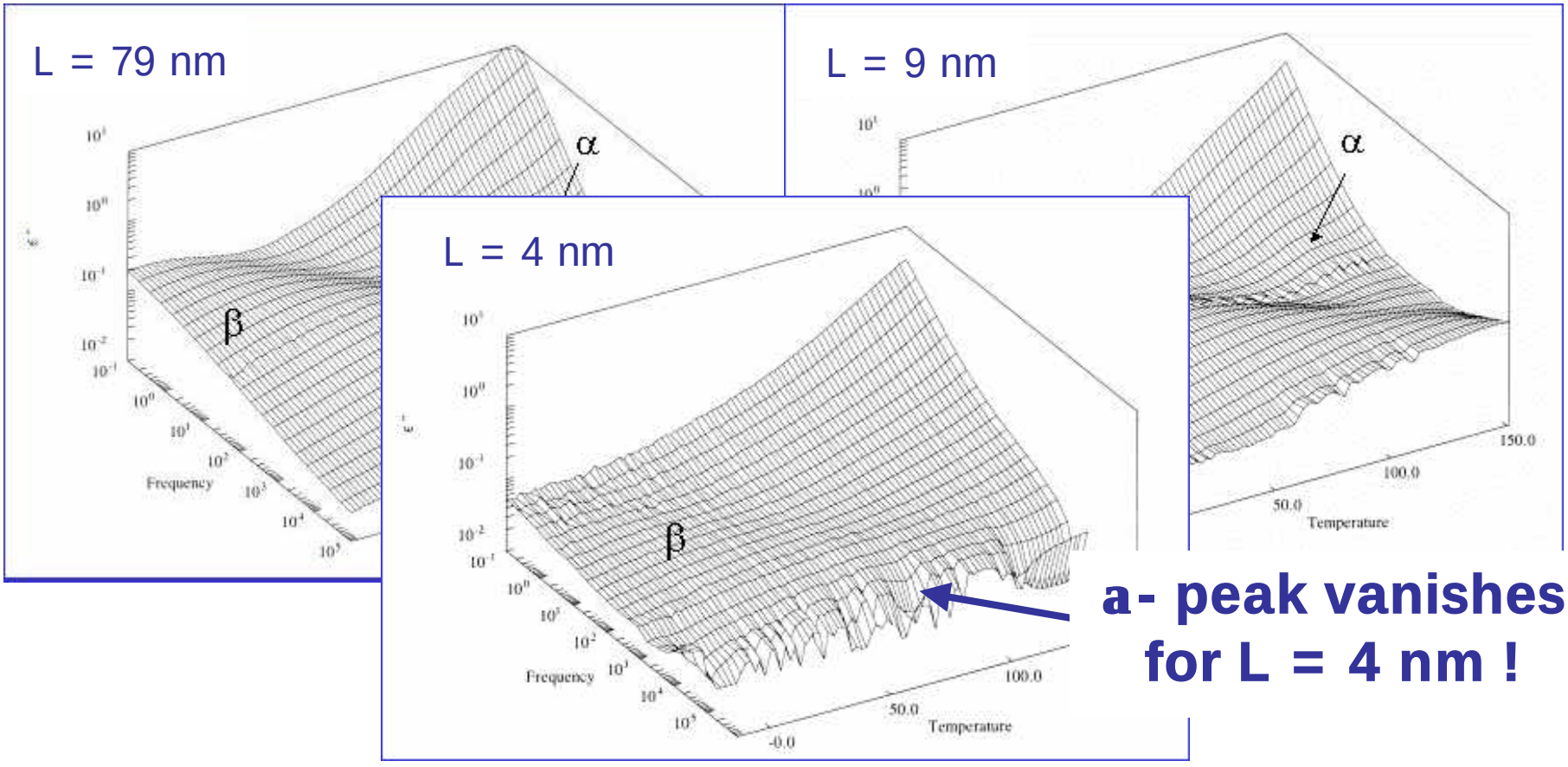
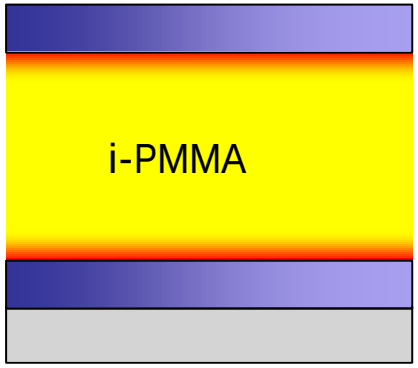
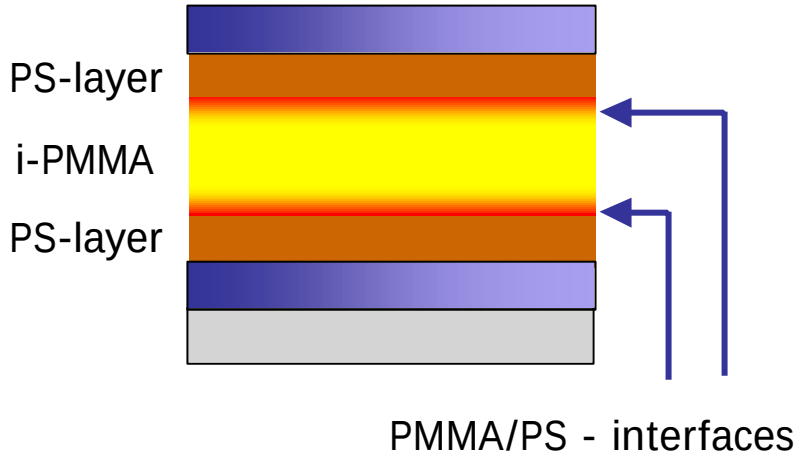
More evidence for critical length of a-process from syndiotactic PMMA



PS-PMMA-PS Tri-layer samples

- Alternatively, replacement of metal-polymer interface by **polymer-polymer** interface → 3-layer film **PS | PMMA | PS**





preparation:

spin-coating → floating PMMA → floating PS-2 → Al-deposition

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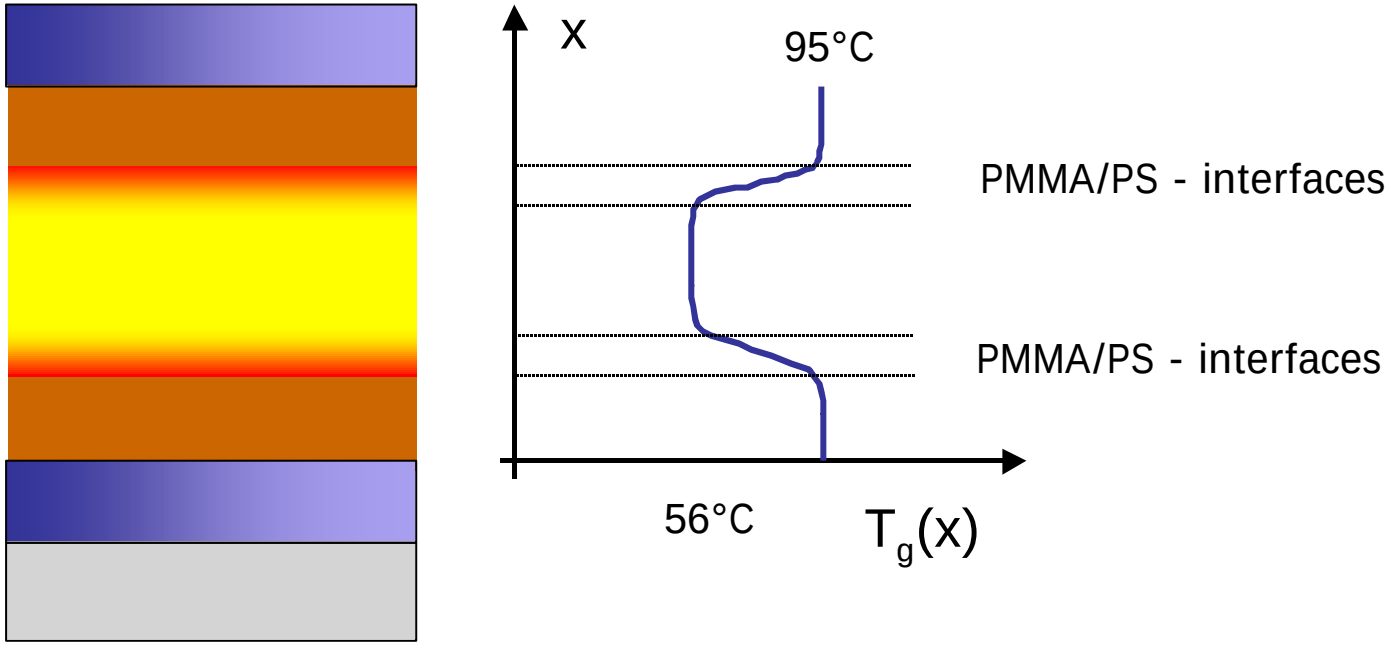
PS-PMMA-PS Tri-layer samples (2)

expected mobility profile:



Dielectric response dominated by PMMA (PS almost apolar)

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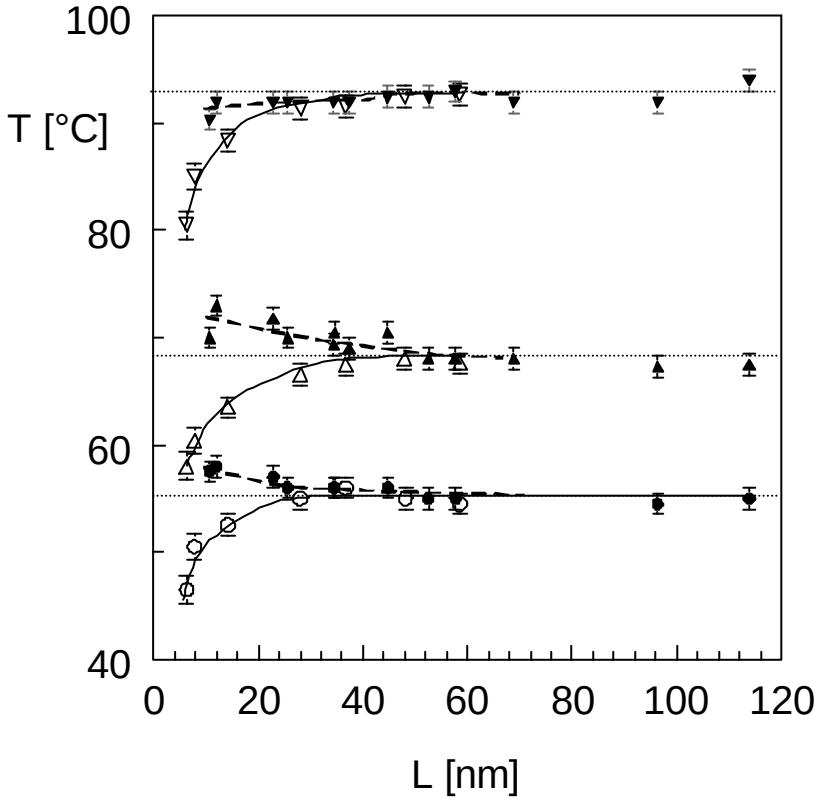
PS-PMMA-PS Tri-layer samples

Shifts in the relaxation time t_a – T_g-effects



- slight up-shift in T_g in tri-layer films instead of T_g-depressions
- higher T_g of interdiffusion layer PS/PMMA likely dominates the average glass transition dynamics for ultra-thin films

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Now discussion of b-process in PMMA

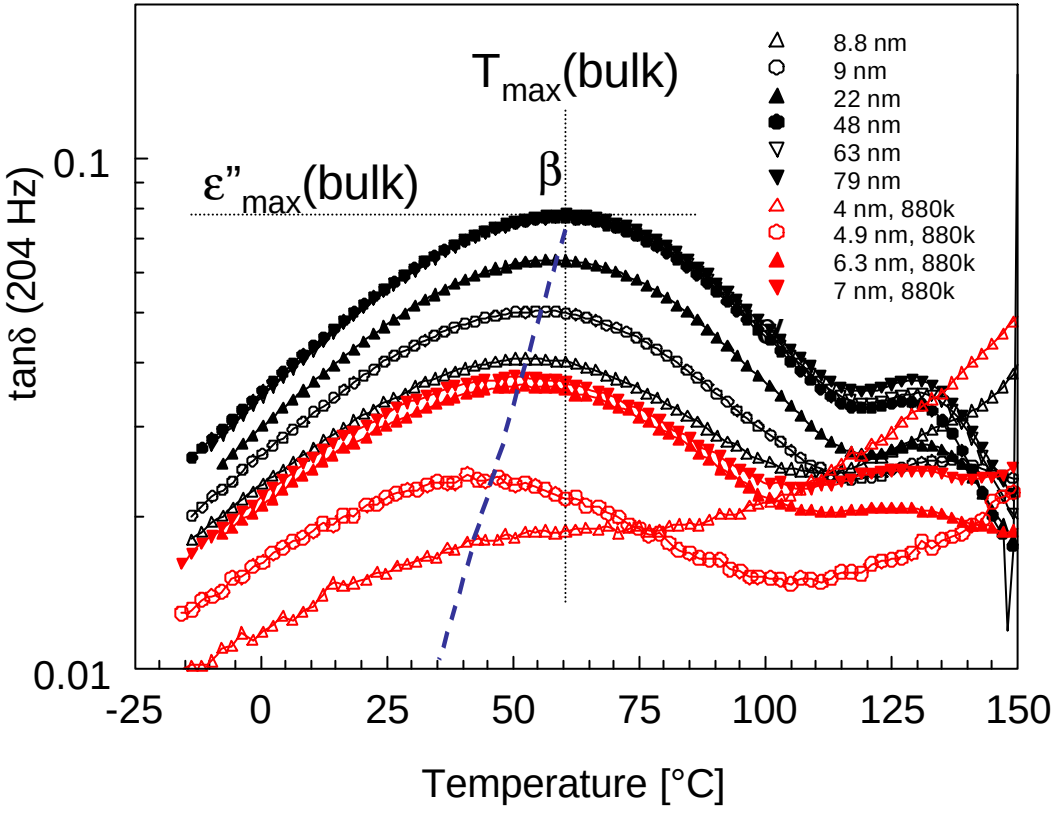
2 diff. molecular weights:

- *145´10³ g/mol*
- *880´10³ g/mol*

- Below critical thickness $L_c \sim 1 - 1.5\ R_{EE}$:

→ Maximum of β-peak shifts to lower T

- Continuous decrease of peak intensity toward lower L



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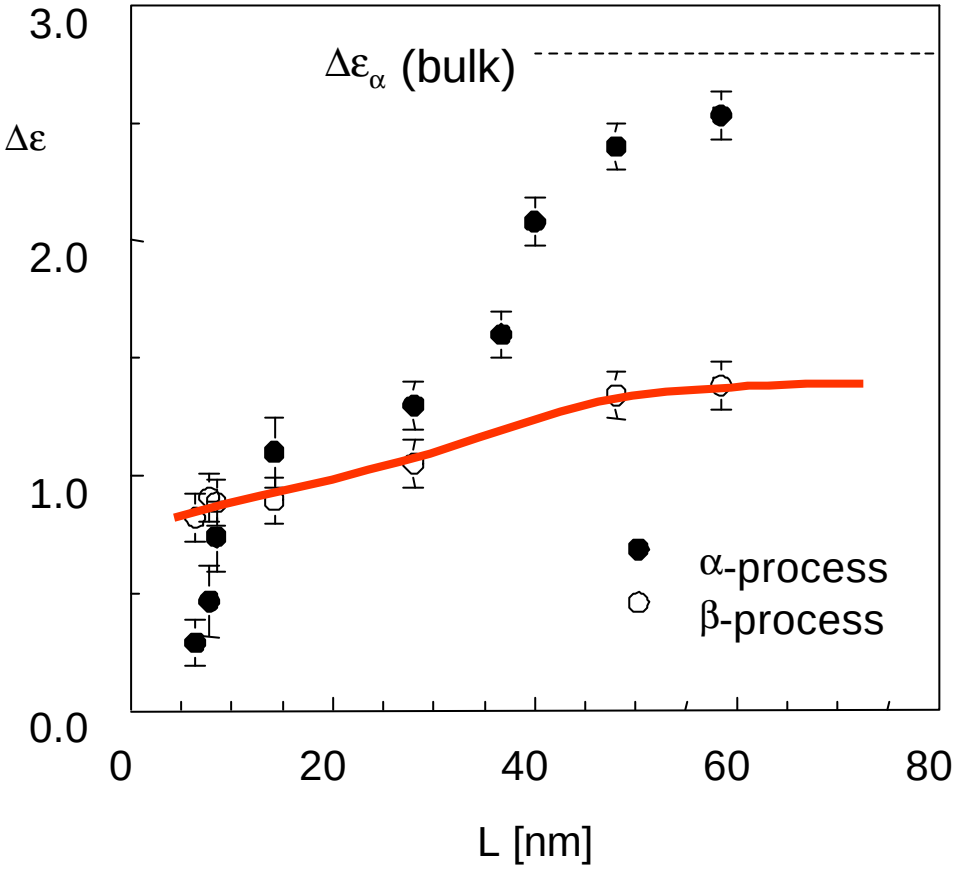
Again, isotactic PMMA, b-process



- Below critical thickness $L_c \sim 1 - 1.5\ R_{EE}$:
- Continuous decrease of $\Delta\varepsilon_\beta$ toward lower L

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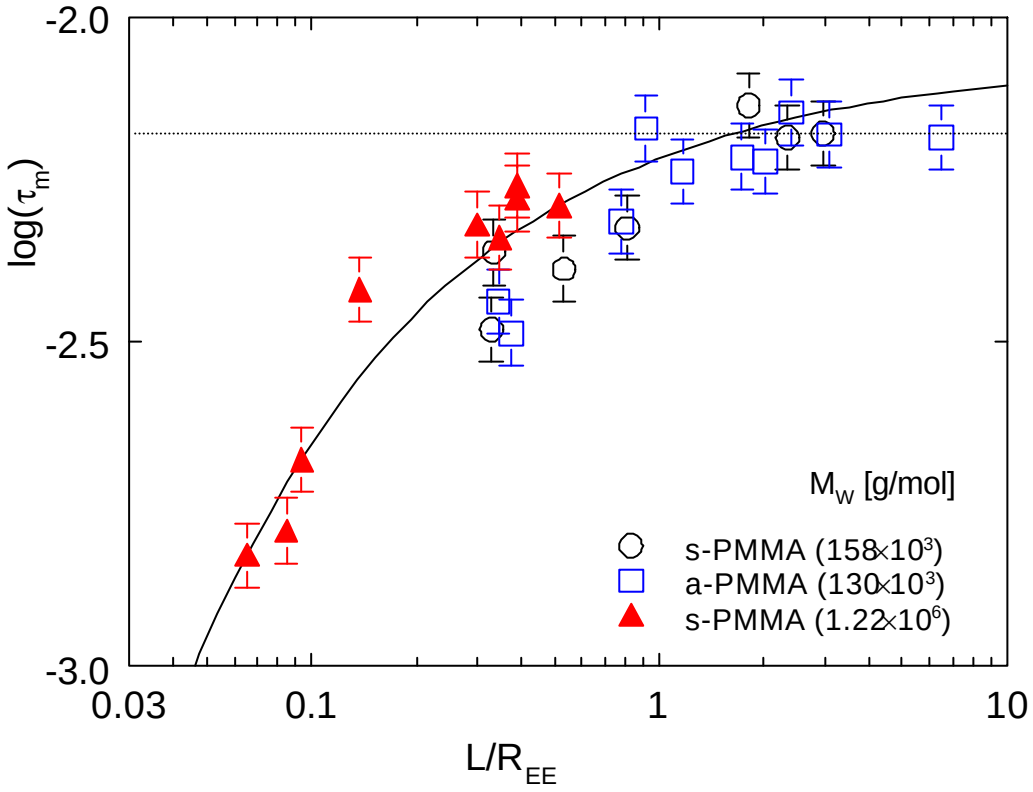
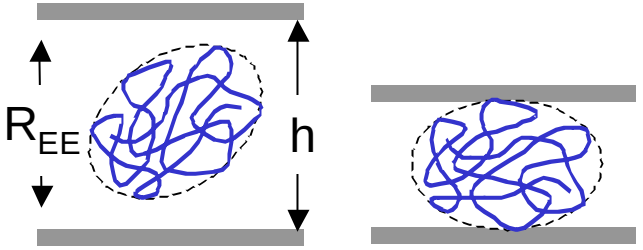
b-process, relaxation time at 35°C



→*speed-up of local dynamics in very thin films*

→*scaling with reduced thickness L/R_{EE}*



h > R_{EE}

h ~ R_{EE}

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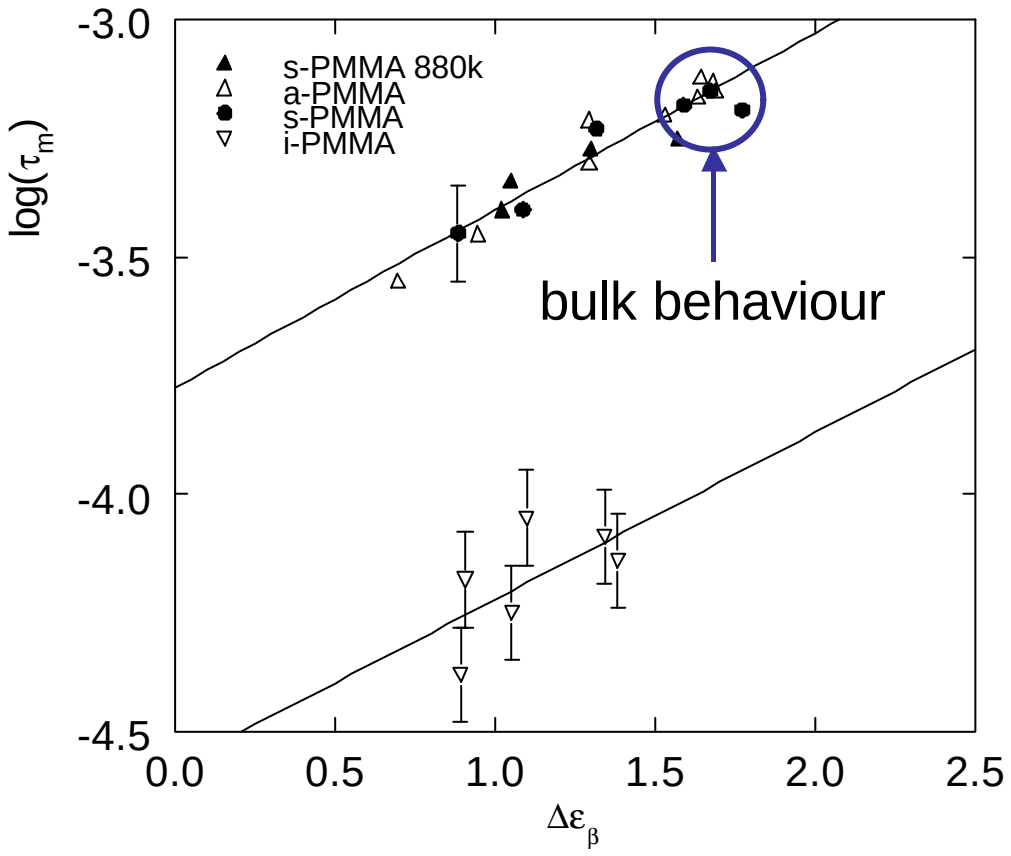
Correlation between relaxation strength and relaxation rate



simultaneous changes of De_b and $\log(t_b)$:

Reduction of amplitude (mean jump angle) of molecular fluctuation → speed-up of dynamics

Reason:

changes in the conformation statistics induced by chain confinement

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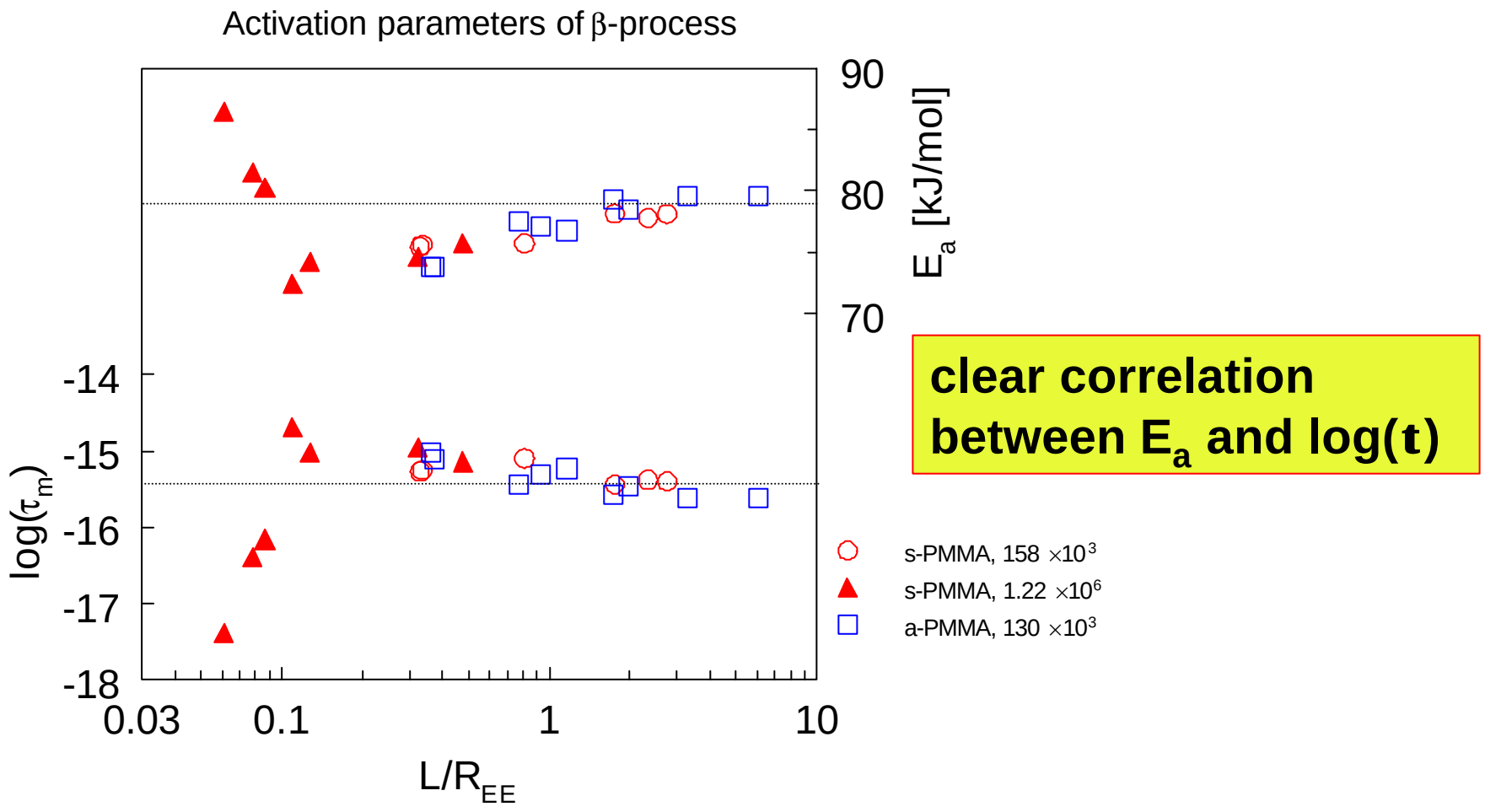
b-process, activation parameters



clear correlation between E_a and log(t)

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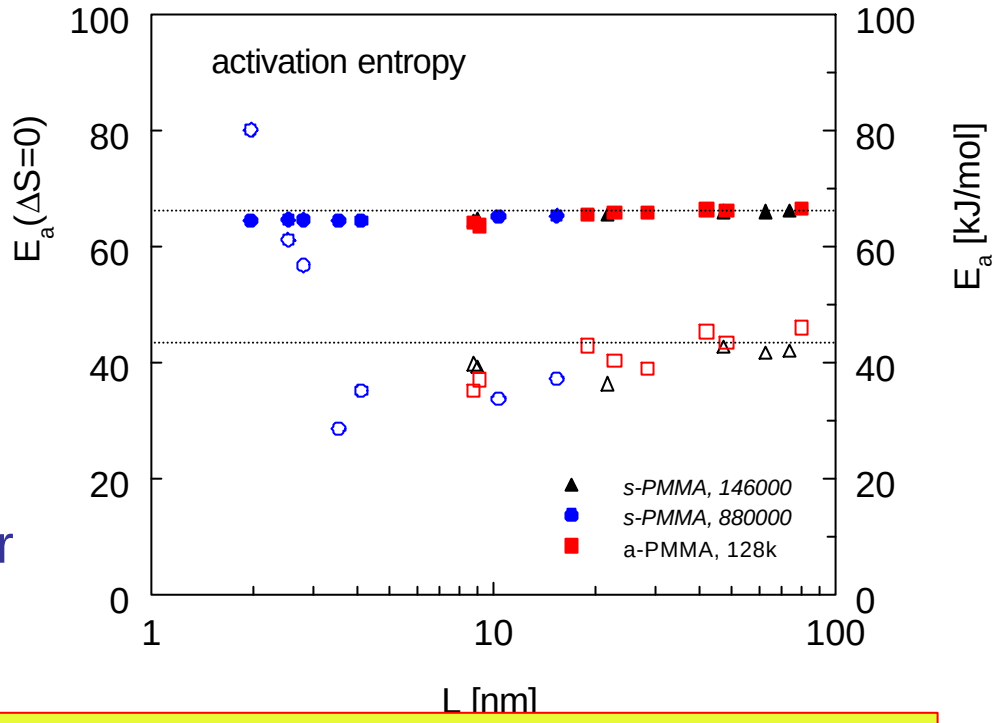
b-process, quantifying cooperativity

Starkweather analysis: activation entropy

$$f(T) = \frac{k_B T}{2\pi h} e^{-\Delta H/RT} e^{\Delta S/R}$$

$$E_A = RT\left(1 + \ln\frac{k_B}{2\pi h} + \ln\frac{T}{f}\right) + T\Delta S$$

→ Separation of activation entropy from E_a as a measure for degree of cooperativity



→ dominant role of the activation entropy in thickness effects on the β-process.

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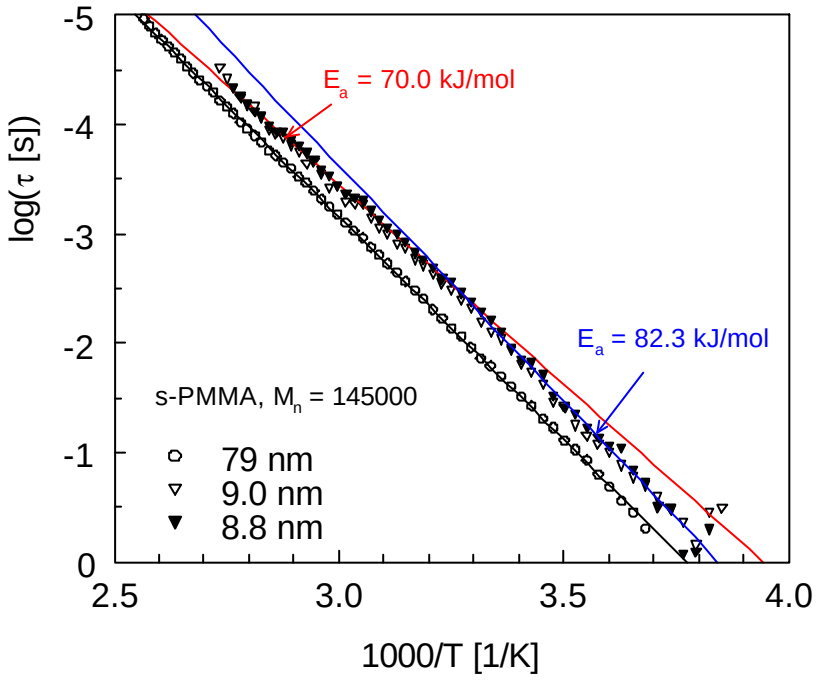
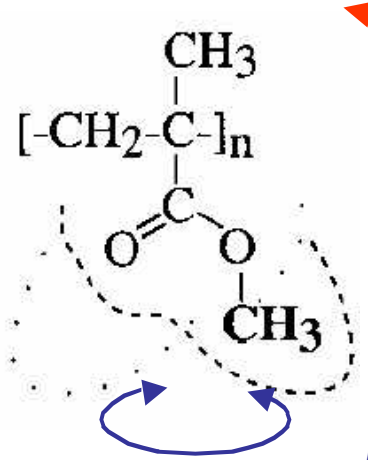
A refined analysis of the dielectric b-process



Kulik et al., (multidim. NMR)

Bonagamba et al., (CODEX-NMR)



b_2: cooperative process involving the backbone

b_1: noncooperative process

Chain confinement ($L < R_{EE}$):

Suppression of (large scale) cooperative component of dielectric b-process

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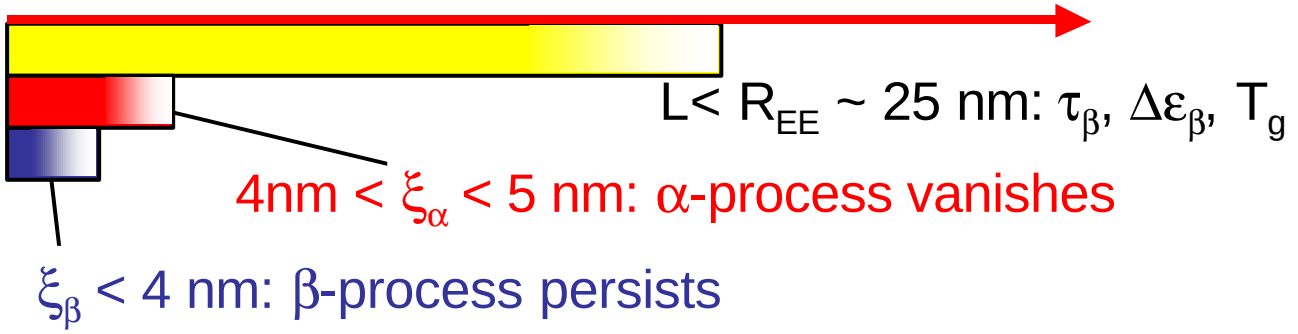
Summary dielectric results on PMMA

- DRS study on PMMA reveales two mechanisms that affect the glass transition temperature in supported PMMA-films:
  - **chain confinement** which speeds-up the β-process together with the α-process
  - a "true" **finite size effect** which is related to the cooperativity length of the glass transition

- DRS results revealed three characteristic length scales:



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b-process of PMMA: further considerations

changes in b-process ←→ changes in conformational statistics

What does the b-process senses?

stretching of polymer chains →increase of trans conformations

coiling of chains → increase of gauche conformations

Polymer theory:

hardly any change in conformational and orientational statistics expected as long $L > L_p$ (persistence length)

However, hold only for thermal equilibrium!

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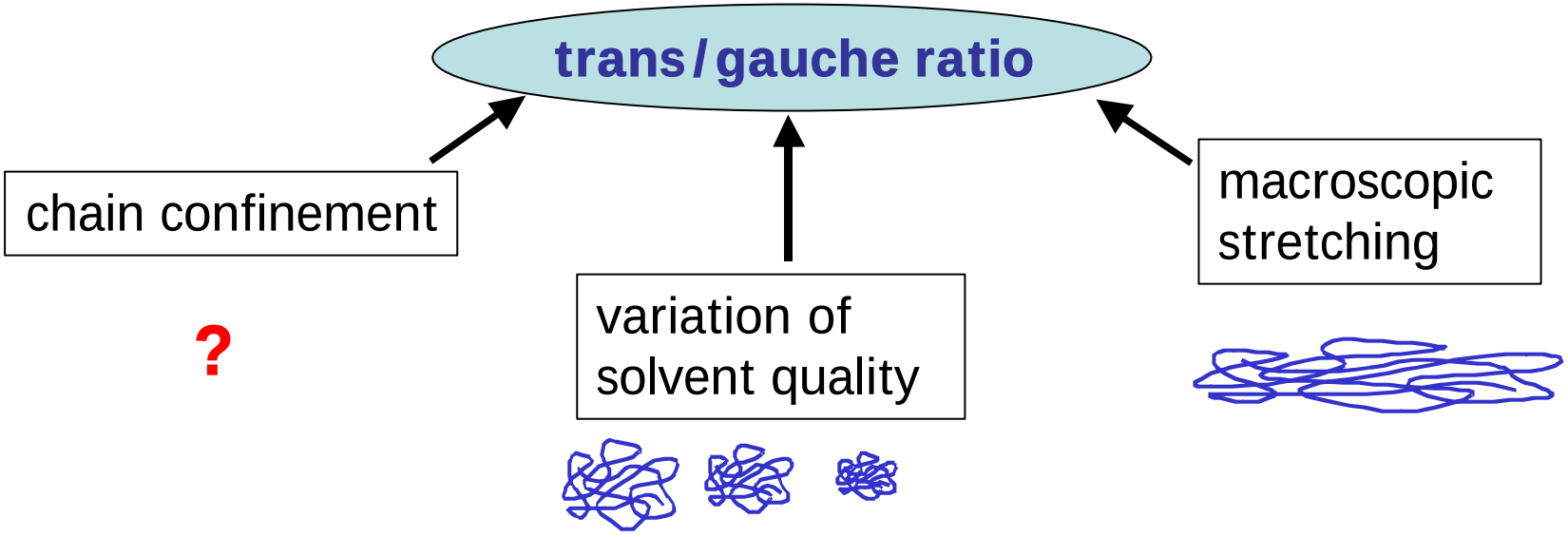
b-process of PMMA: further considerations

→ **additional experiments required** to establish relation between dielectric β-relaxation and conformational statistics



Very recent experiments on i-PMMA/cloisite nanocomposites

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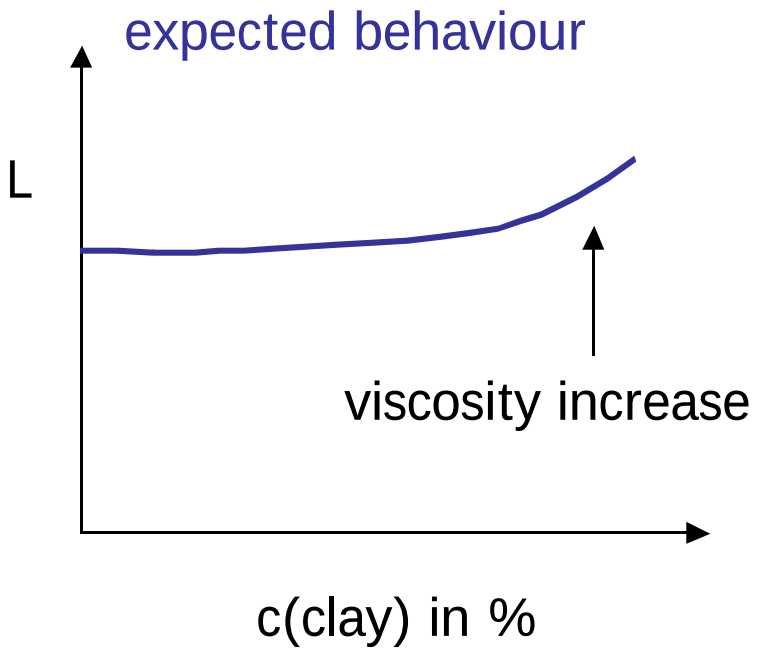
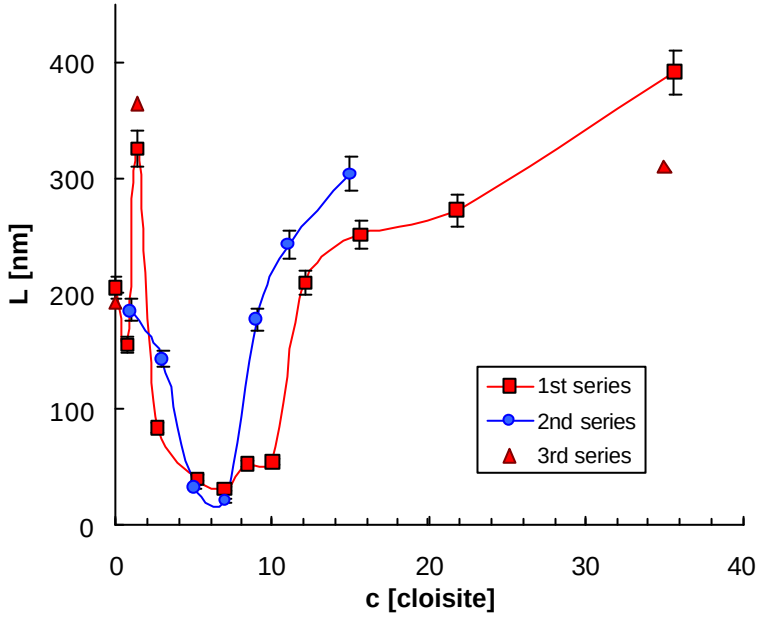
i-PMMA/clay nanocomposites

- Solutions of i-PMMA and cloisite in chloroform
- varying content of clay: 0 – 35wt%
- spin-coating of solutions, envisaged film thickness ~ 250 nm





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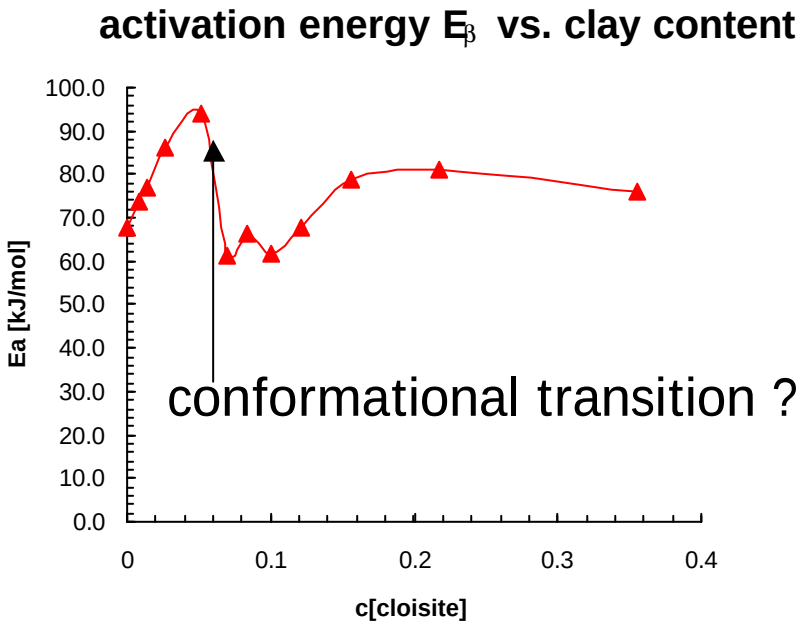
i-PMMA/clay nanocomposites

DRS results:

- slow down of β-process at thinnest films
- transition in activation energy



conformational transition induced by shear induced alignment of clay platelets

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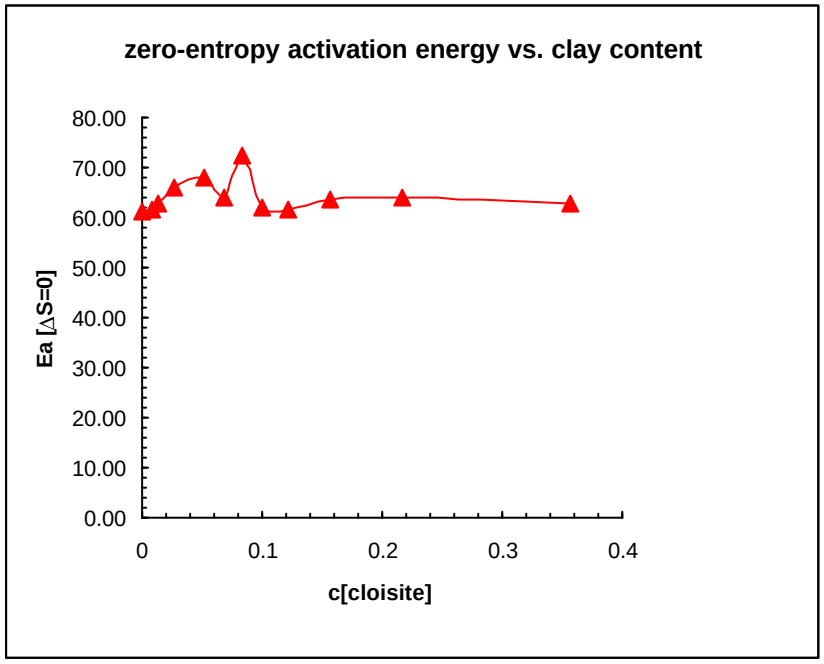
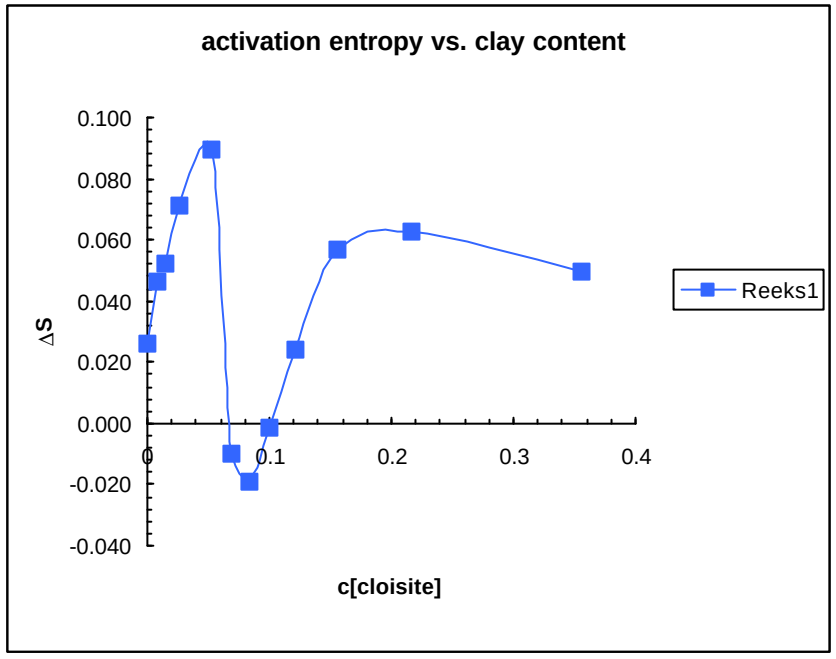
i-PMMA/clay nanocomposites

Activation entropy:





β-process makes transition from **increasingly cooperative** relaxation to **non-cooperative** relaxation

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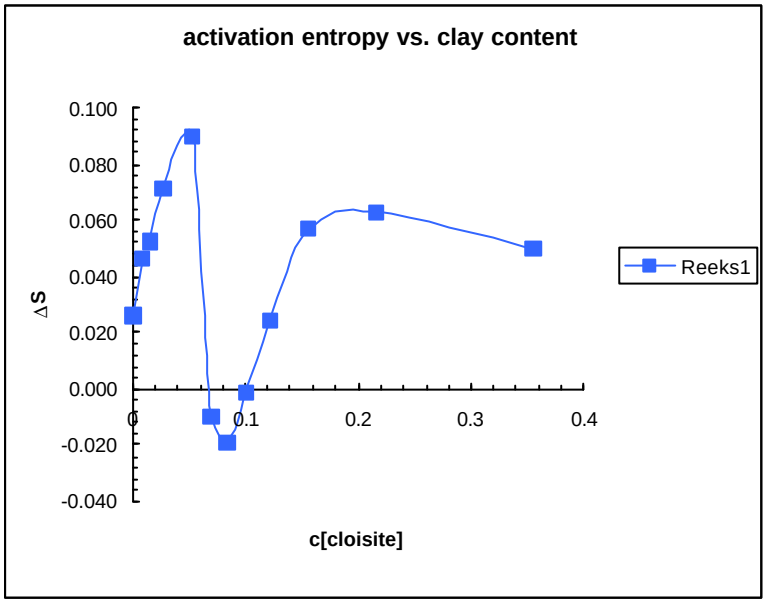
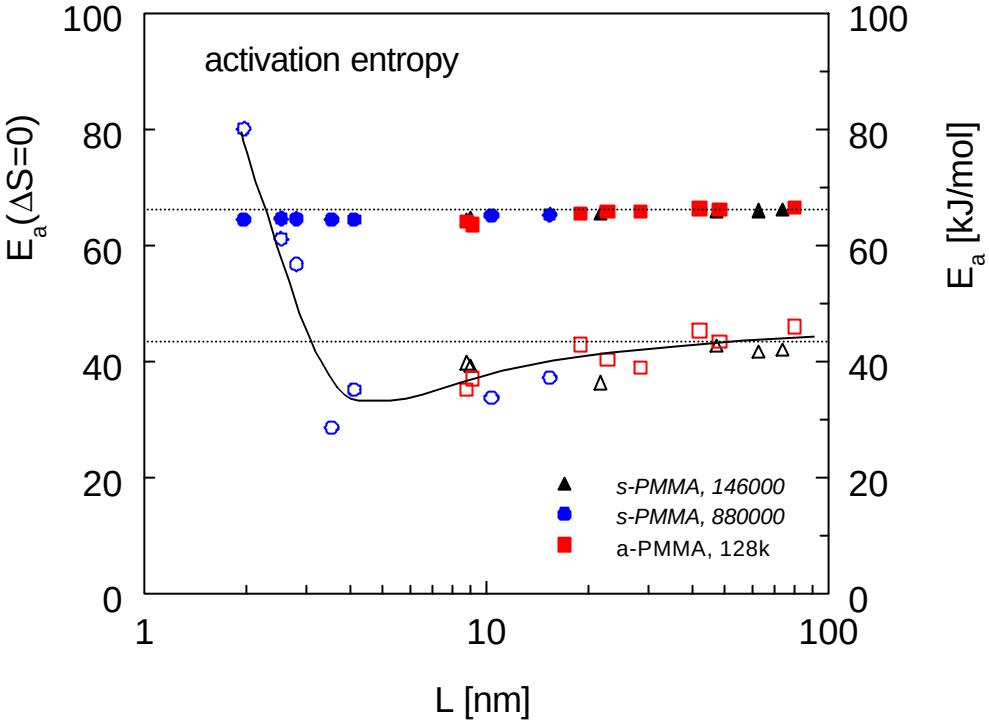
i-PMMA/clay nanocomposites





Conclusions:

- chain stretching causes increase of ΔS_β (gauche → trans)
- thin film confinement decreases ΔS_β (trans → gauche)

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i-PMMA/clay nanocomposites

What do we really see?

stretching of polymer chains	increase of trans conf.
coiling of chains	increase of gauche conf.

Reason:

drying of spin-coated polymer films in vitrified state causes chain collapse

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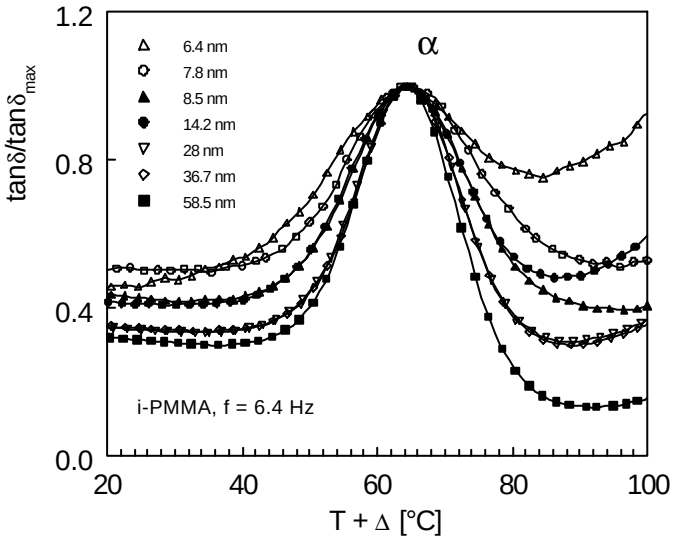
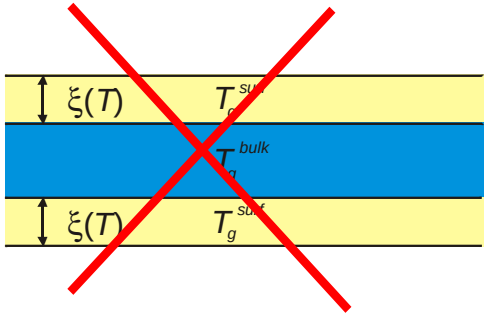
Back to initial questions

Q1: mobility profile in thin PMMA films

DRS results on ultrathin PMMA films (6.4 < L < 100 nm):



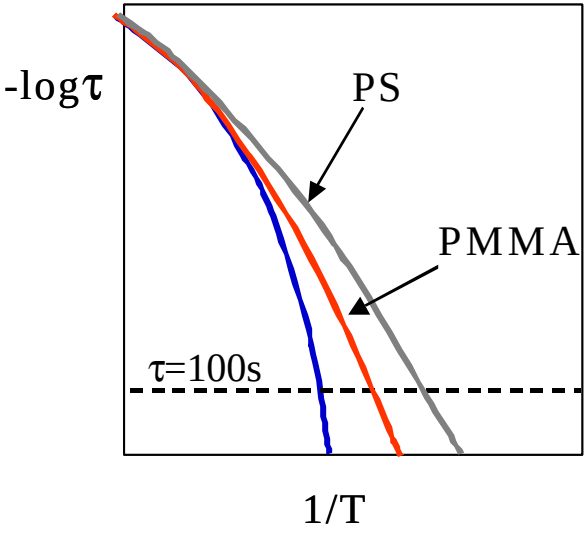
- continuous α-peak broadening implies gradual enhancement of mobility towards film surface
- no hint for sharp 2-layer scenario



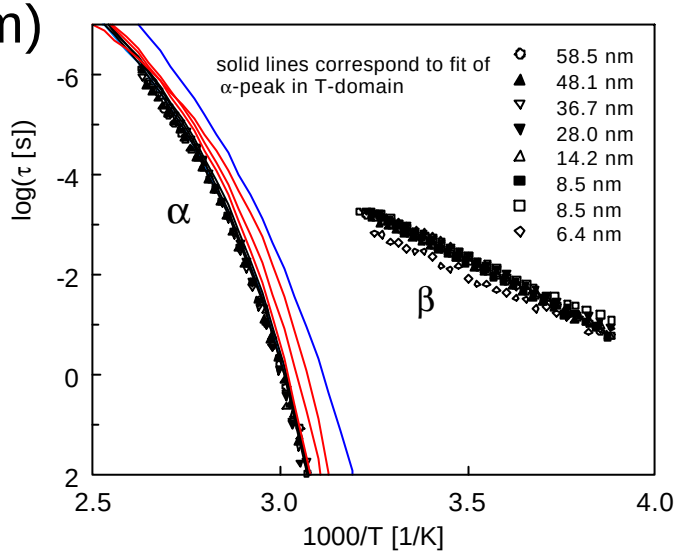
Back to initial questions

Q2: "fragility" hypothesis:

Our initial assumption:



DRS results on ultrathin PMMA films (>6.4nm)



For PMMA, no substantial change in fragility found

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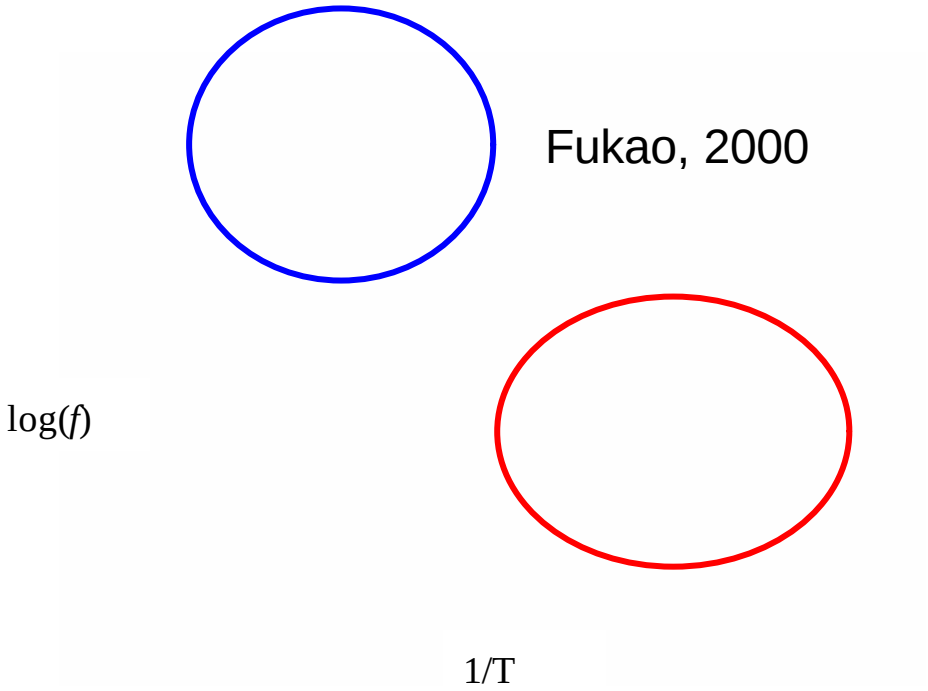
What happens with PS?



Fukao, 2000

Results from Fukao apparently confirm decrease in fragility for ultra-thin PS films

Problem:
relaxation data originate from two different techniques

thermal expansion spectroscopy

dielectric spectroscopy

Equivalence of dielectric relaxation data and volume expansion assumed !

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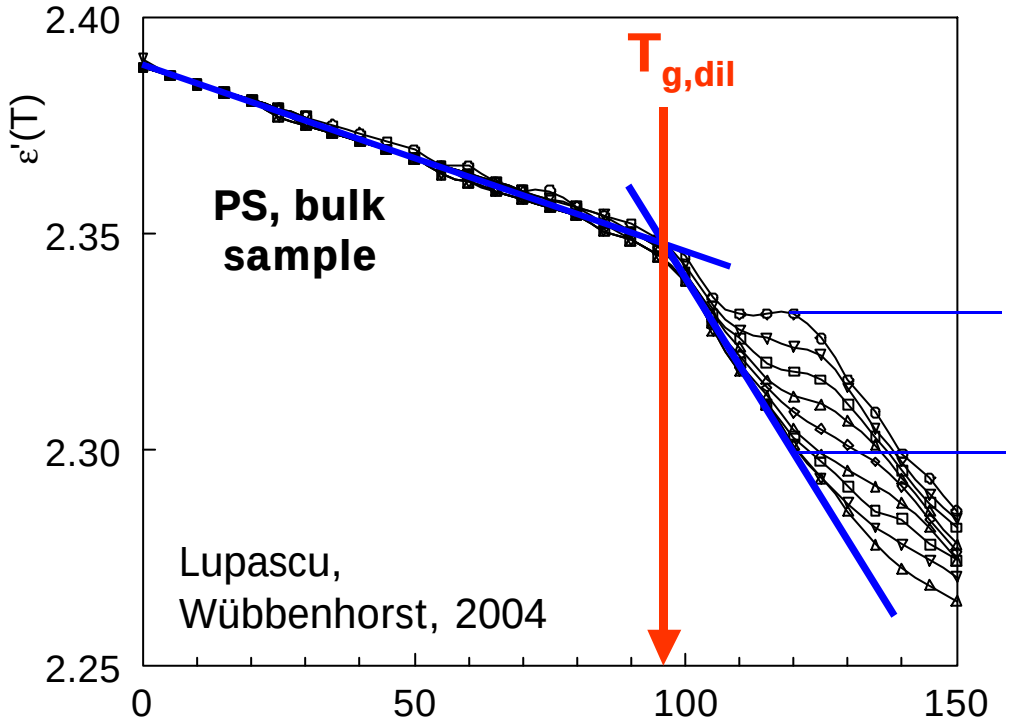
Dielectric measurements on PS thin films:

2 experiments in one:



Kink in ε'(T) marks change from liquid expansivity to expansivity of the glass → $T_{g,\,dil}$

Step in ε'(T) at $T>T_g$ due to dielectric α-relaxation

→ frequency dependent

- **Capacitive dilatometry → $a_v(T)$**
- **Dielectric spectroscopy → $t_a(f,T)$**

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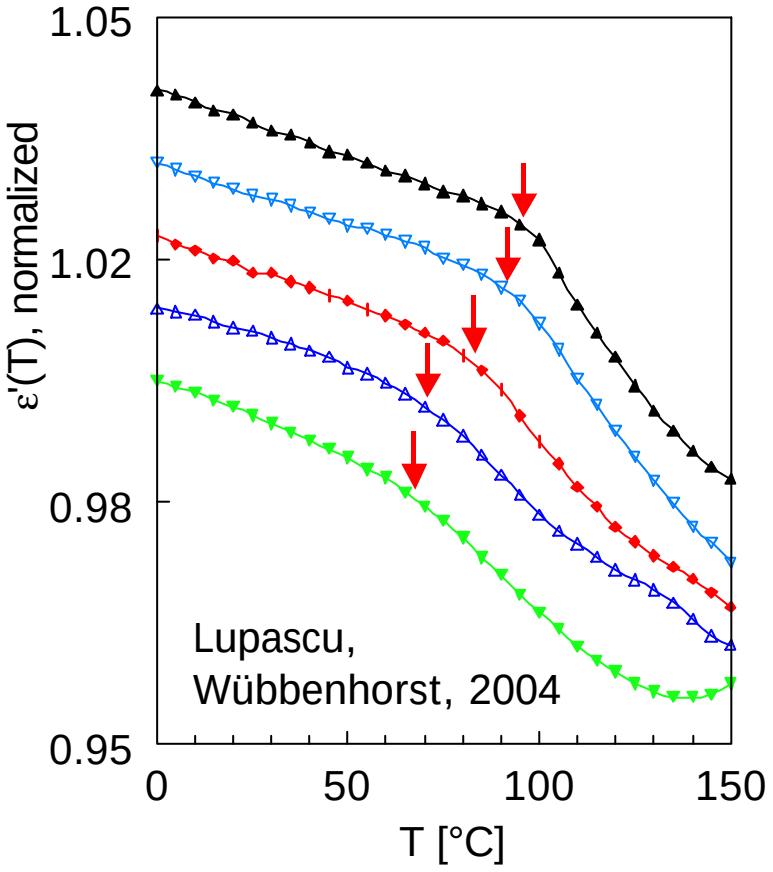
Capacitive dilatometry on ultra-thin PS films



- **Systematic reduction of $T_{g,dil}$** with lower film thickness
- **Broadening** of volumetric glass transition at lowest film thicknesses

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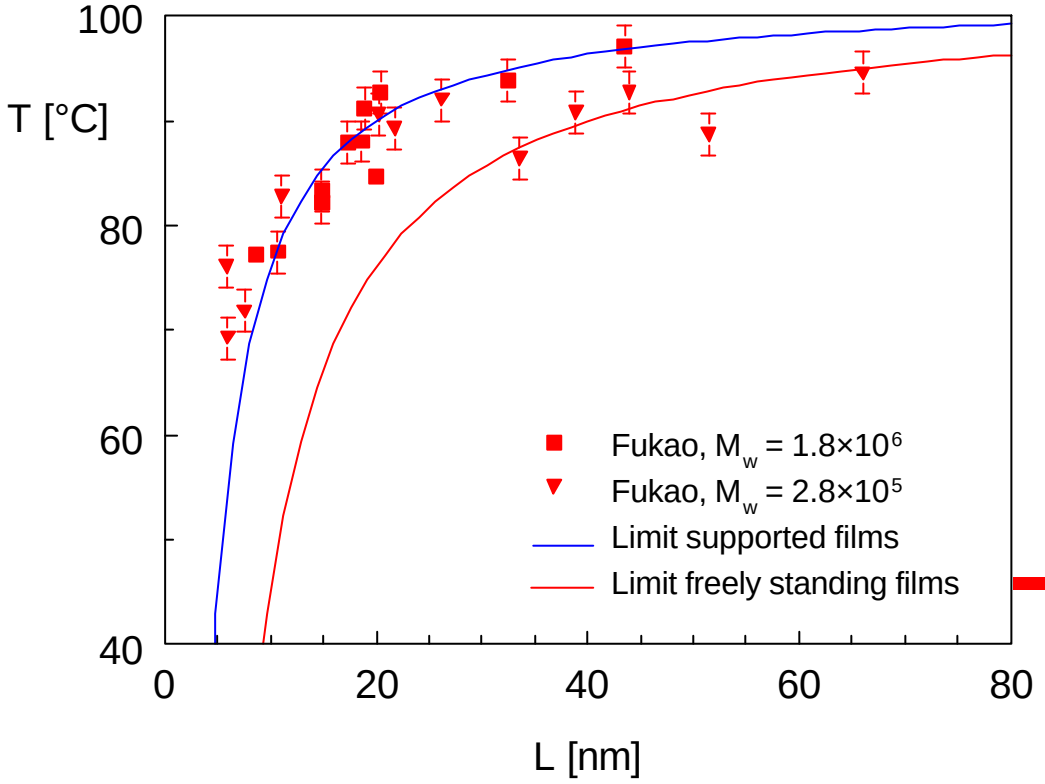
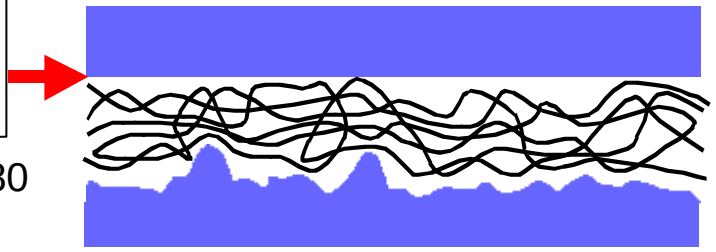
Capacitive dilatometry on ultra-thin PS films

Fukao's results (PRE 2000)



T_g reductions from capacitive dilatometry in good agreement with typical literature data (blue line)

→Al/polymer/Al sandwich samples behaves like films having 1 free surface.



Asymmetric electrode system – interface between top electrode and polymer film mimics free surface

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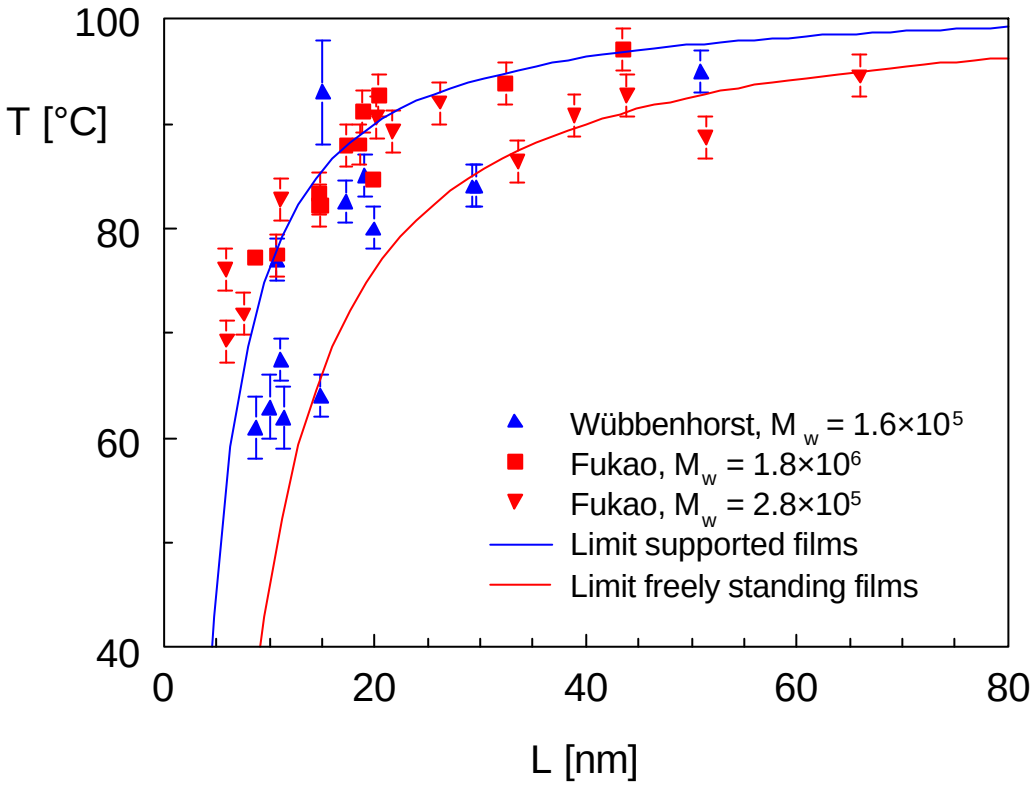
Capacitive dilatometry on ultra-thin PS films

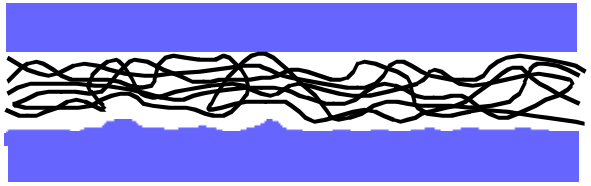
Comparison of recent own data with Fukao's results



Larger T_g- reductions found for same film thickness than Fukao

→ T_g-reductions partially close to values known for freely standing PS films

Possible reason:



Our Al-polymer-Al sandwich films mimics freely standing geometry to some extent (reduced surface roughness of lower Al-layer)

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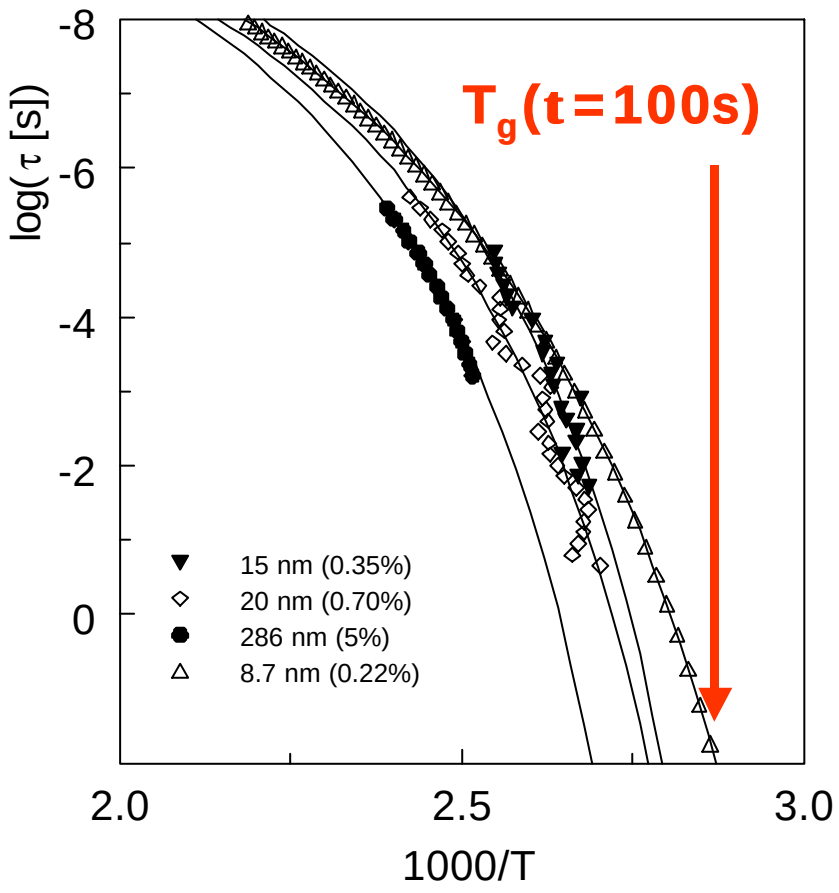
Glass transition temperature from a-process



T_g determination from relaxation time of structural relaxation:

- dielectric α-process found in PS films as thin as 8.7 nm
- systematic speed-up of α-process towards lower L

no substantial changes in fragility !

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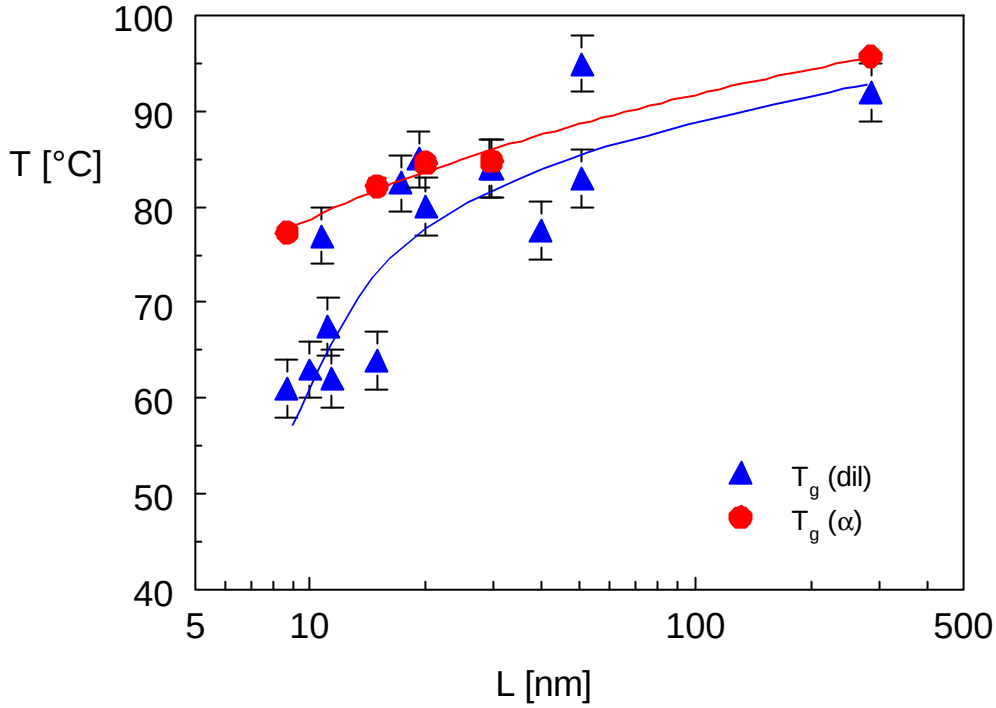
Glass transition temperature from a-process

Comparison of volumetric T_g with T_g(a)

PS-film 8.7 nm:

dilatom. T_g = 61°C

T_g from α-process:
77.3°C



Increasing discrepancy between T_g(dil) and T_g(α) for thin PS films

→ decoupling of volume expansivity from structural relaxation as seen by DRS?

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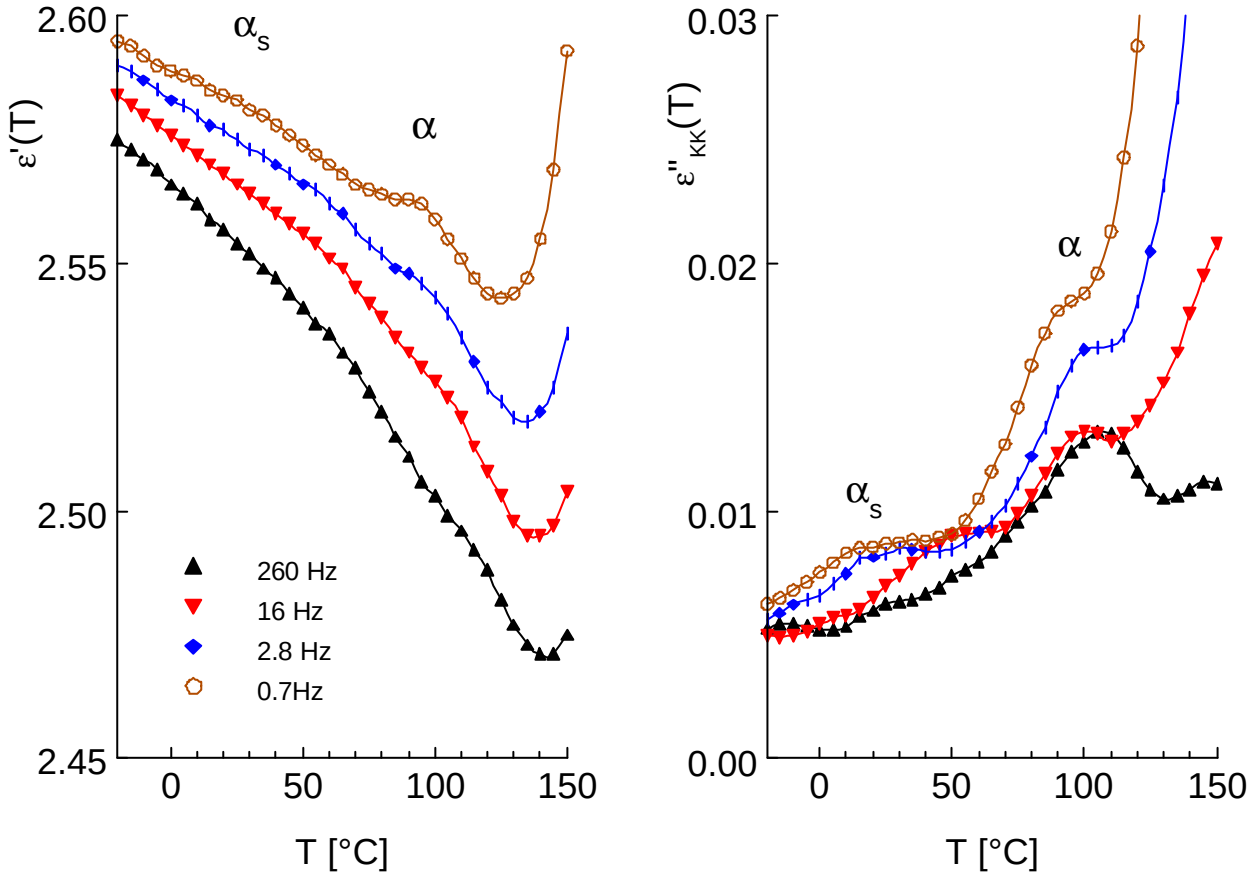
Recent DRS results from ultra-thin PS films

An additional relaxation process in PS-films with L<15 nm

PS film L=8nm:

2nd dielectric process



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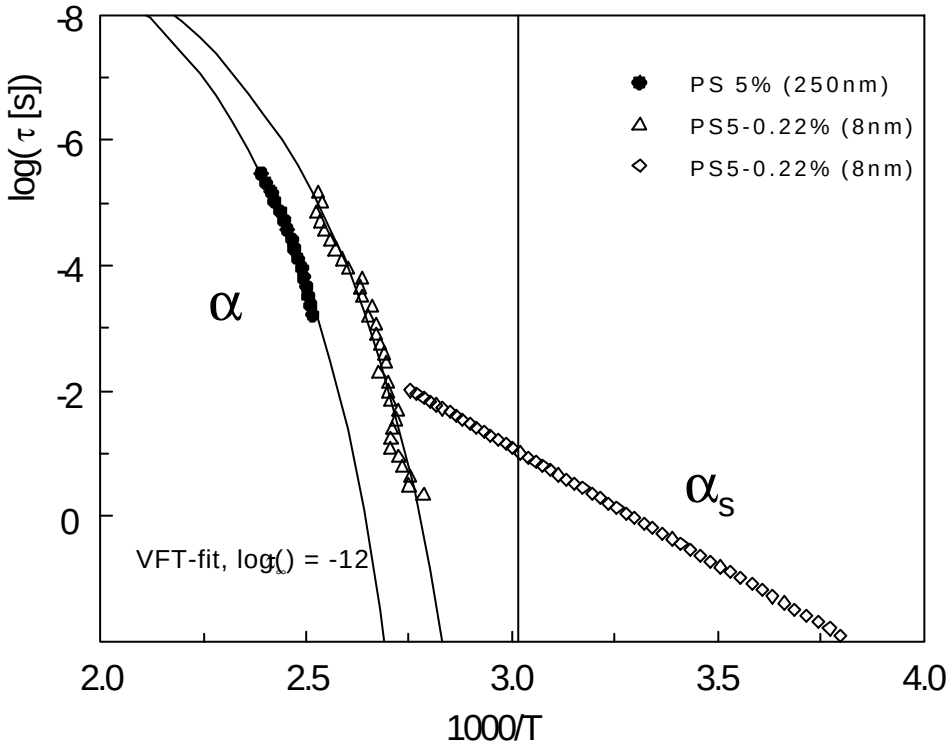
Recent DRS results from ultra-thin PS films



2nd dielectric process: α_s

- thermally activated process, E_a = 71 kJ/mol
- non-cooperative (τ_∞ ~ 10^{-12}s

a_s process most likely related to dynamics in surface layer

direct evidence for 2-layer model (?)

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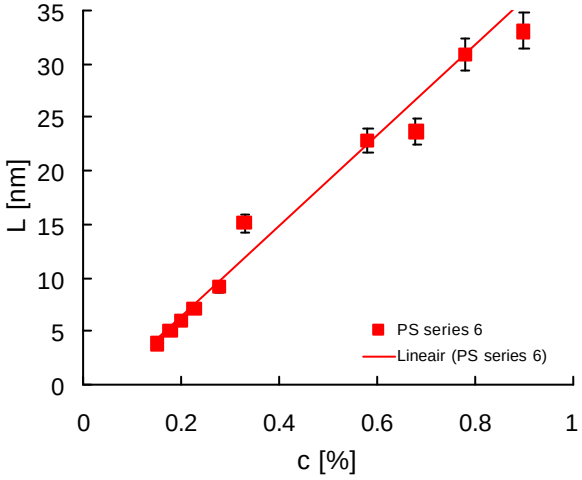
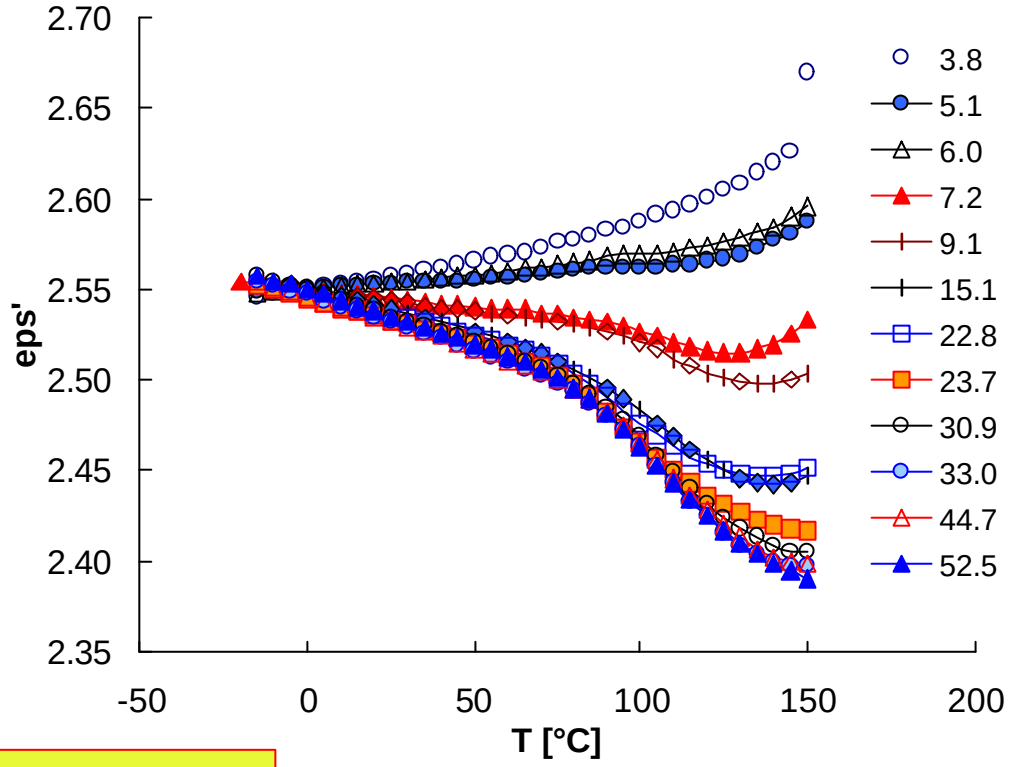
Recent DRS results from ultra-thin PS films

New series of PS films: thickness as low as 3.7 nm





kink in ε'(T) vanishes for L < 5nm

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Conclusions

Dielectric spectroscopy on ultra-thin films of PMMA and PS revealed

- T_g reductions due to finite size effect
- disapperance of the α-relaxation at films below 5nm
- T_g effects and changes in local β-relaxation due to **chain confinement**
- PMMA films: changes in the β-relaxation proof existence of **"undersized" polymer coils** in ultra-thin films

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Conclusions (2)

There are clear differences in thin film dynamics between PS and PMMA:

- Apparent T_g-reductions are much larger for PS than for PMMA
- Finite size effect manifests in different way:
  - PMMA: deviation from bulk-VFT behaviour
  - PS: separate relaxations related to core and surface dynamics

  → layer-like mobility profile confirmed

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PME

Polymer Materials & Engineering