

Local and Glassy Dynamics in Polymers

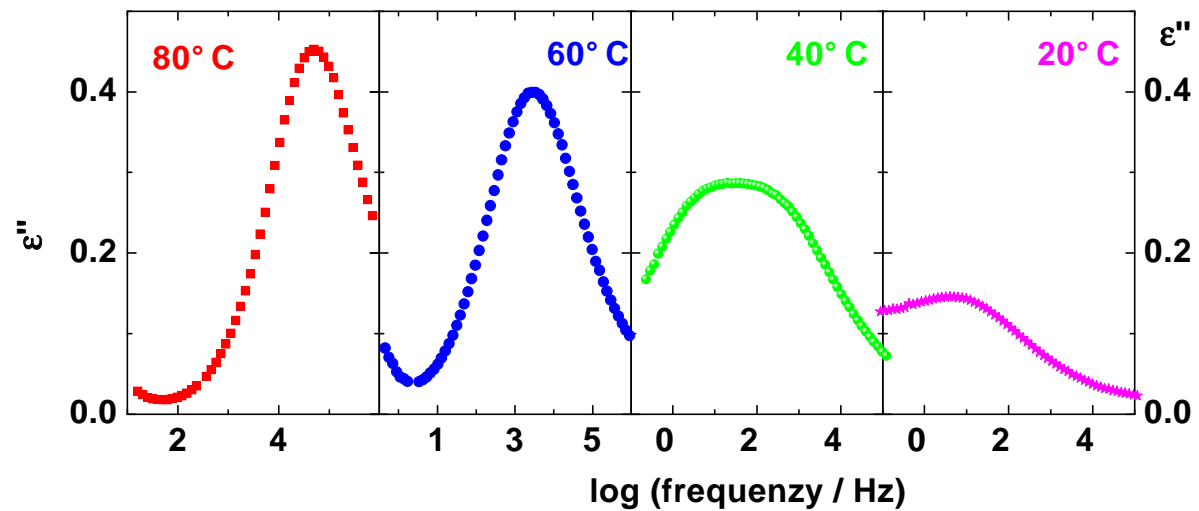
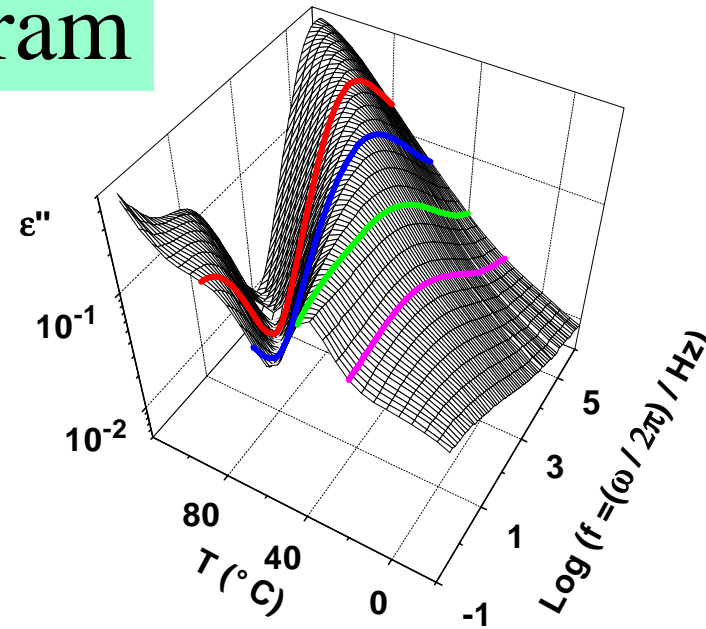
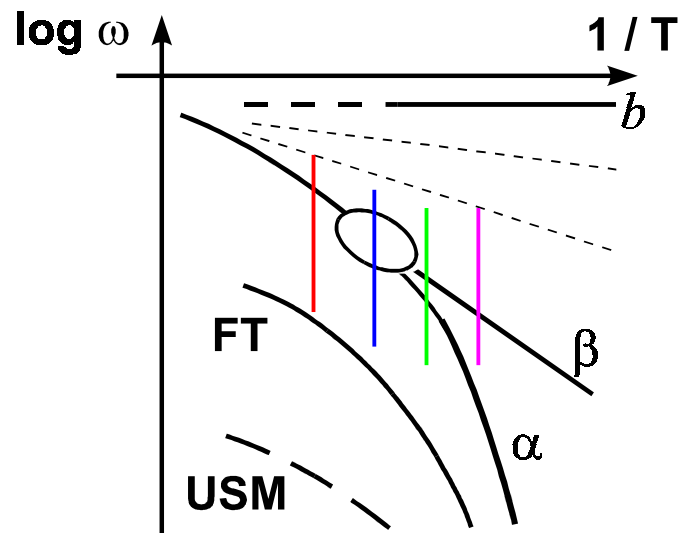
Trieste, June 27 2002

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- Introduction
- Scattering Functions and Cross Section
- Partial Deuteration
- Polybutadiene
- Polyisobutylene

Relaxation Processes

Typical Arrhenius Diagram



Inelastic Neutron Scattering

- Dielectrics and Rheology: No spatial information about the nature of the molecular motions
- However, inelastic neutron scattering experiments provide information in both space and time
- \Rightarrow we observe the geometry of the processes
- Further, neutron scattering provides information about the time evolution of the self (incoherent) and pair correlation (coherent scattering)

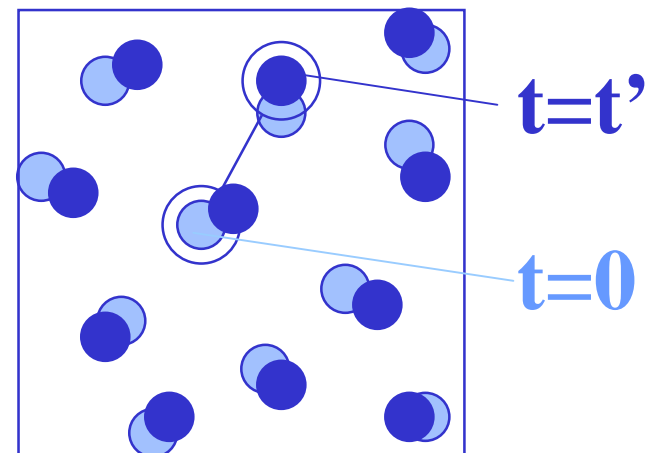
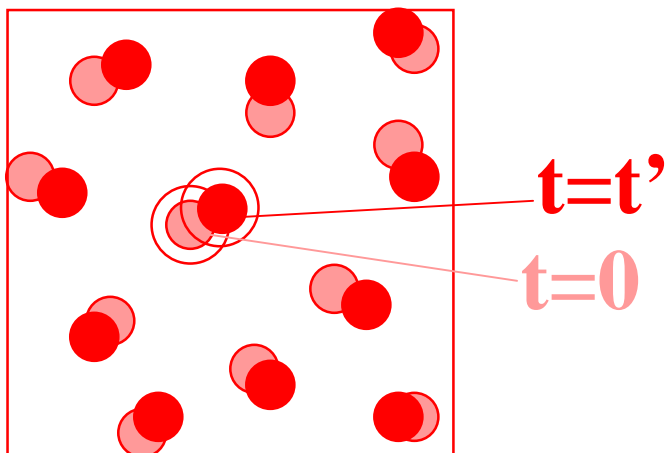
Scattering Functions

Incoherent scattering function (*Self correlation*)

$$S_{\text{inc}}(\vec{Q}, t) \equiv \frac{1}{N} \sum_i \langle \exp(i\vec{Q}(\vec{r}_i(t) - \vec{r}_i(0))) \rangle$$

Coherent scattering function (*Pair correlation*)

$$S_{\text{coh}}(\vec{Q}, t) \equiv \frac{1}{N} \sum_{i,j} \langle \exp(i\vec{Q}(\vec{r}_i(t) - \vec{r}_j(0))) \rangle$$



Selected Scattering Cross Sections

	σ_{coh}	σ_{inc}
H	1.76	80.26
D	5.59	2.05
C	5.55	0.00
O	4.23	0.00

$$|\bar{b}|^2 = \frac{\sigma_{coh}}{4\pi}$$

$$\overline{|b|^2} - |\bar{b}|^2 = \frac{\sigma_{inc}}{4\pi}$$

Hydrogen and deuterium have extremely different scattering characteristics!

Neutron Scattering on Polymers (4 Informations)

deuterated polymer melt

collective (interchain) relaxation is observed

protonated polymer melt

self correlation (msd) is observed

protonated polymer chain in a deuterated matrix

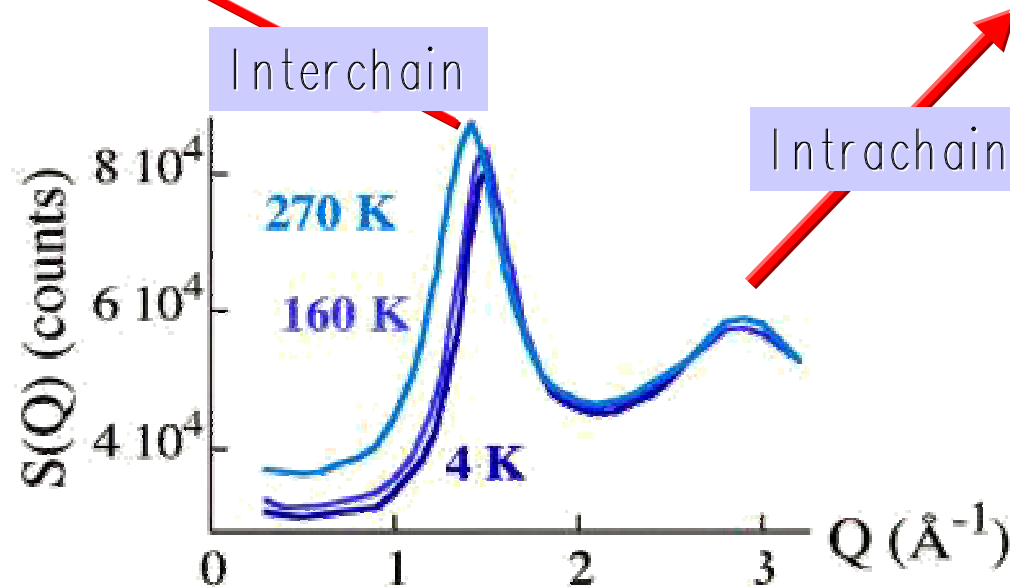
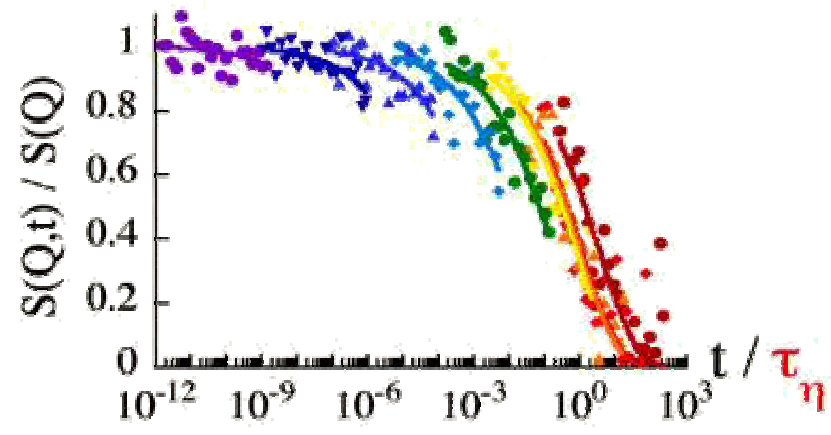
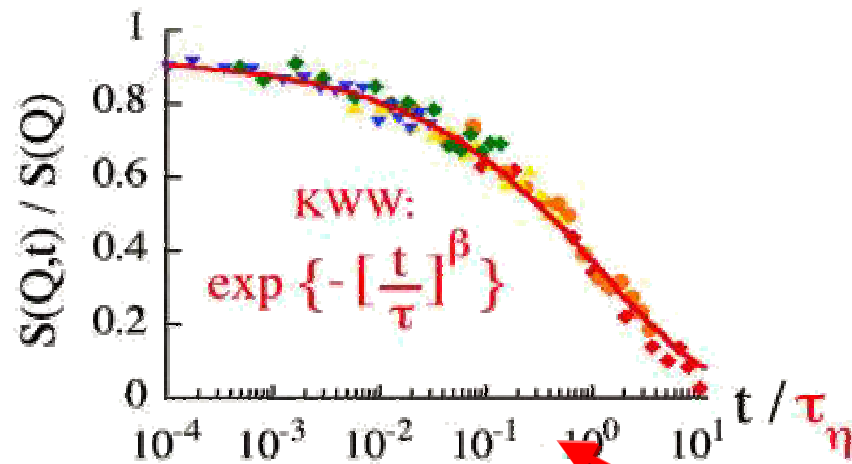
single chain dynamic is observed

partial deuterated polymer melt

intrachain correlation is observed

Glassy Dynamics in Polybutadiene

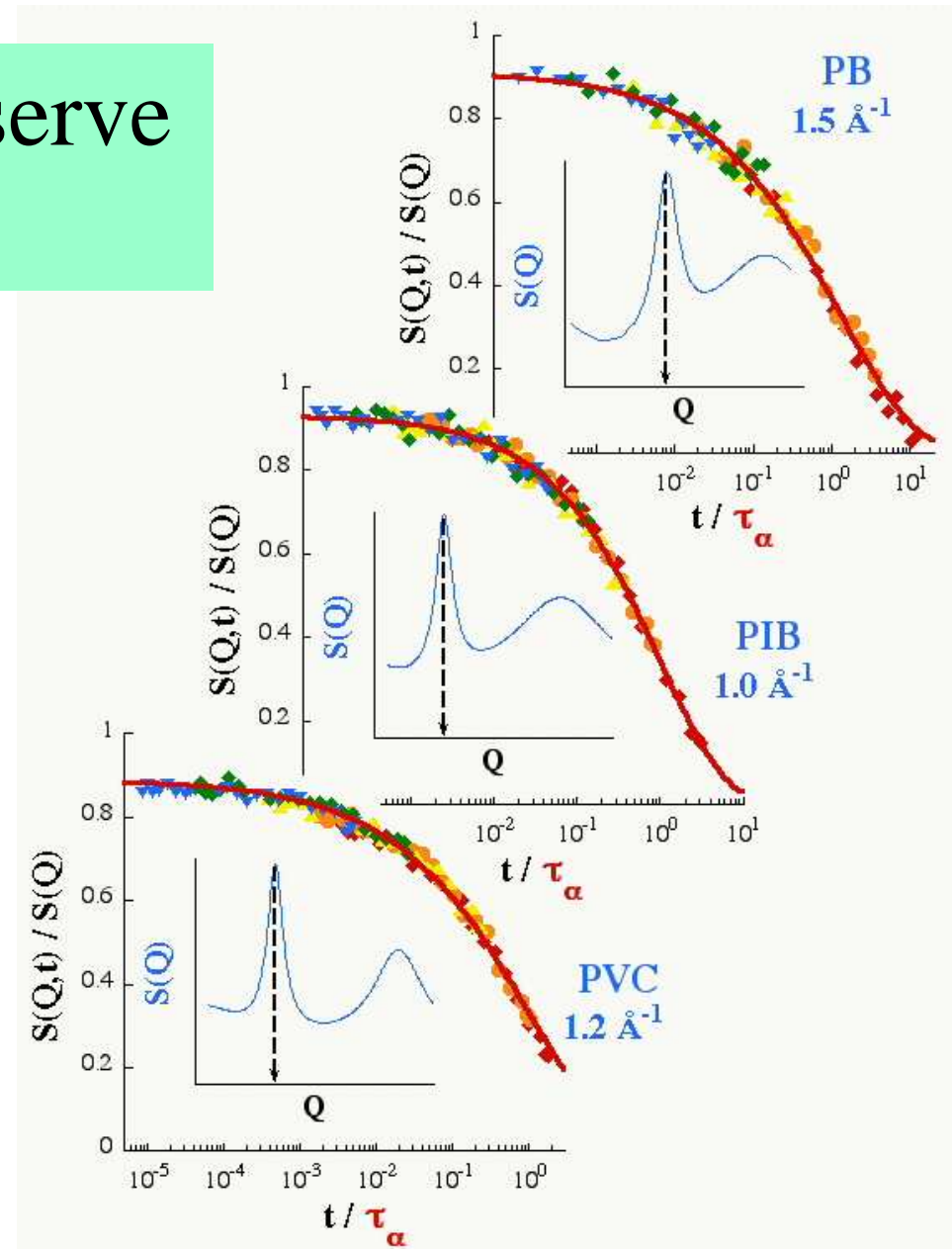
Pair Correlation (d6PB)



Glassy Dynamics in Polymers

At Q_{\max} Neutrons Observe
the α -relaxation

structural relaxation
 \Leftrightarrow **relaxation of short
range order underlies
mechanical relaxation
(shear flow)**



What is Known?

- It is established that (at least) two relaxation processes take place in all glass-forming polymers (α process and β process)
- The α relaxation results from inter-chain correlations, while the β relaxation mainly comes from intra-chain correlations

What is Unknown?

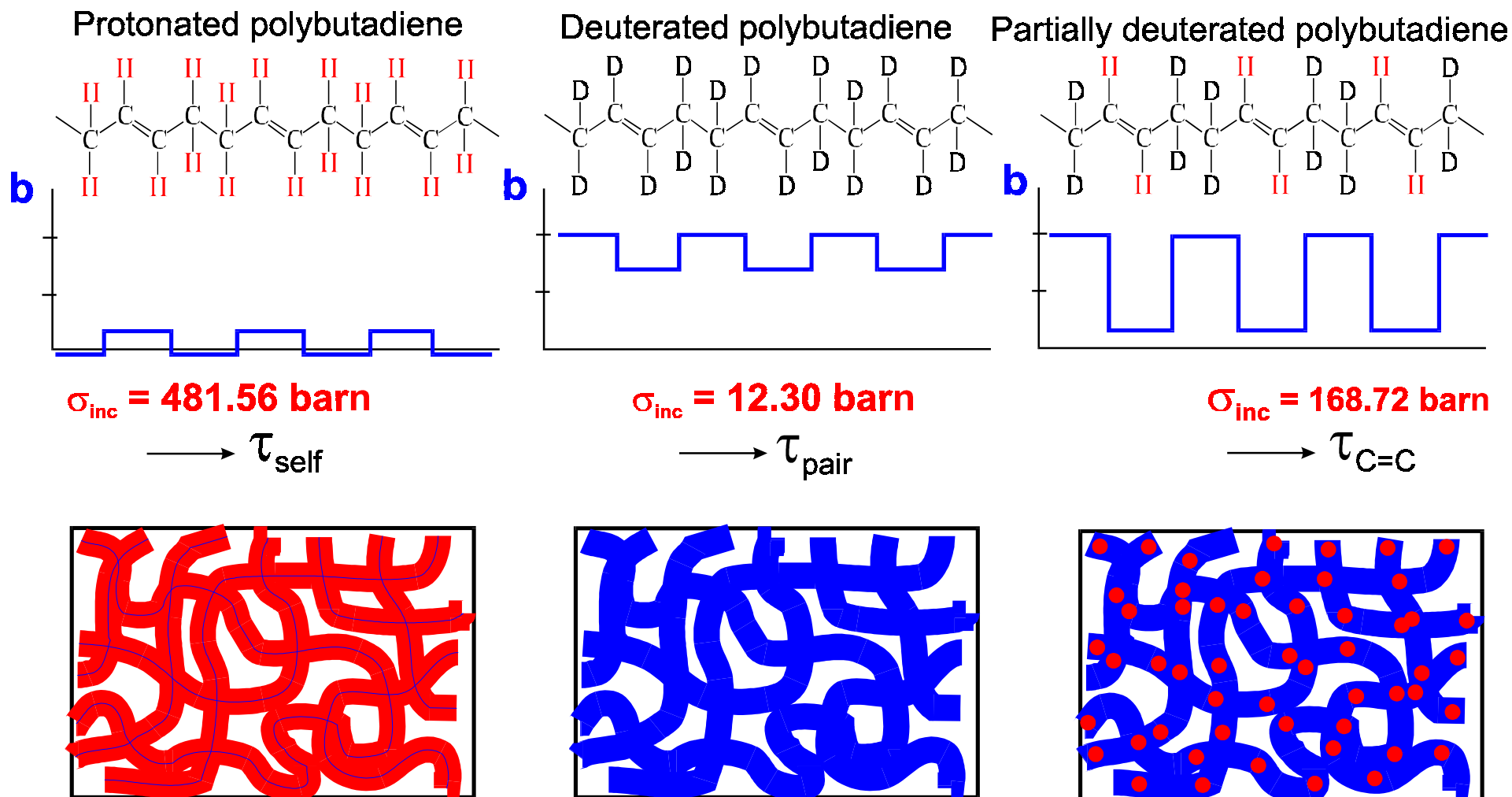
- What is the origin of the two relaxations?
- Are both processes correlated?

Partial Deuteration

- Deuterium and hydrogen have extremely different scattering characteristics
- Otherwise the deuterated (or partially deuterated) material has the same physical and chemical properties as the protonated one
- Therefore it is possible to highlight the time evolution of a given correlation

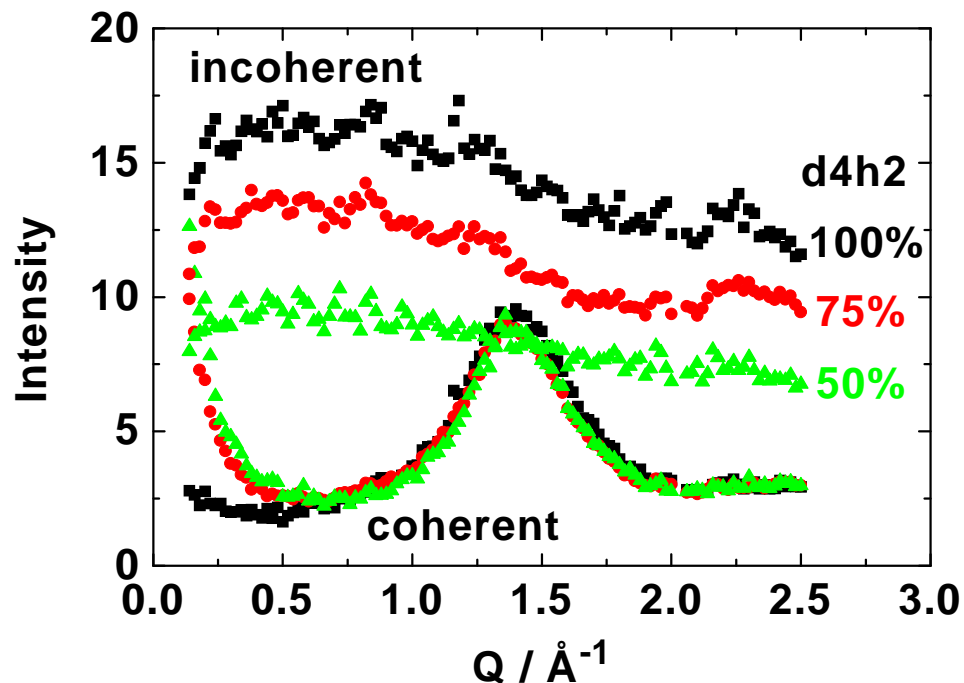
1,4 Polybutadiene with Different Deuteration

Different Correlations are Observed



Elastic Results: Diffuse Scattering

Polymer Blend (d4h2 and d6 1,4PB)

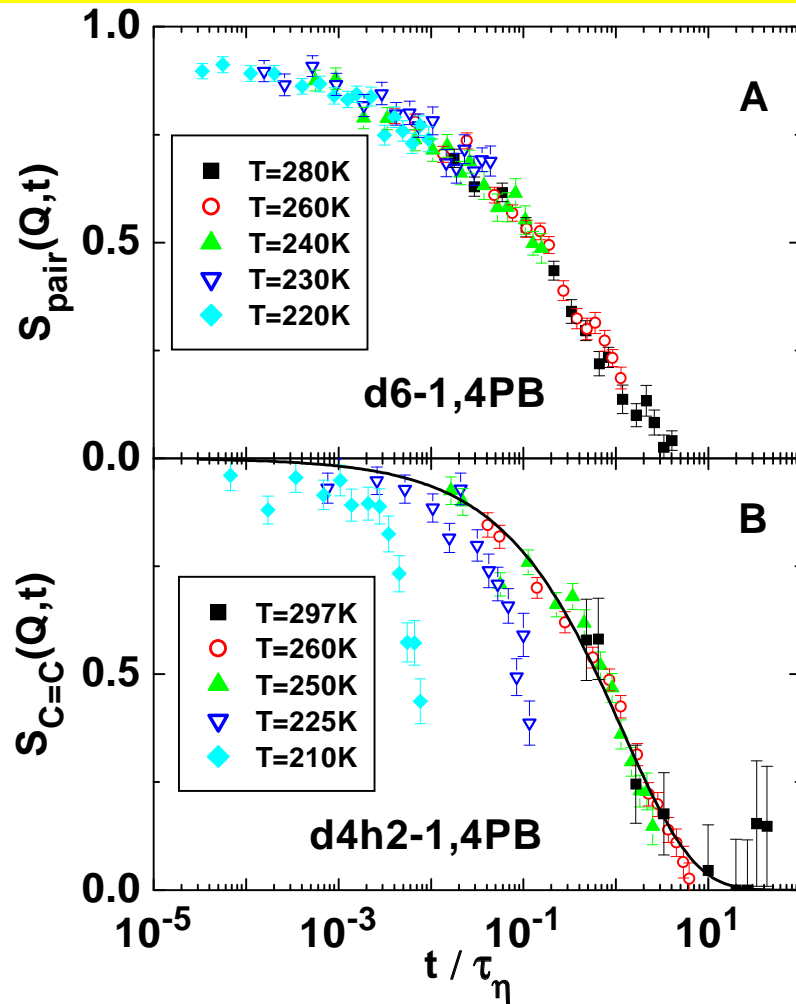


⇒ The peak maximum of the static structure factor is at the same position for both labelings

⇒ The static experiment can not distinguish the two different correlations

Inter-chain and intra-chain interference peak are at the same position!

Inelastic Results: Neutron Spin Echo

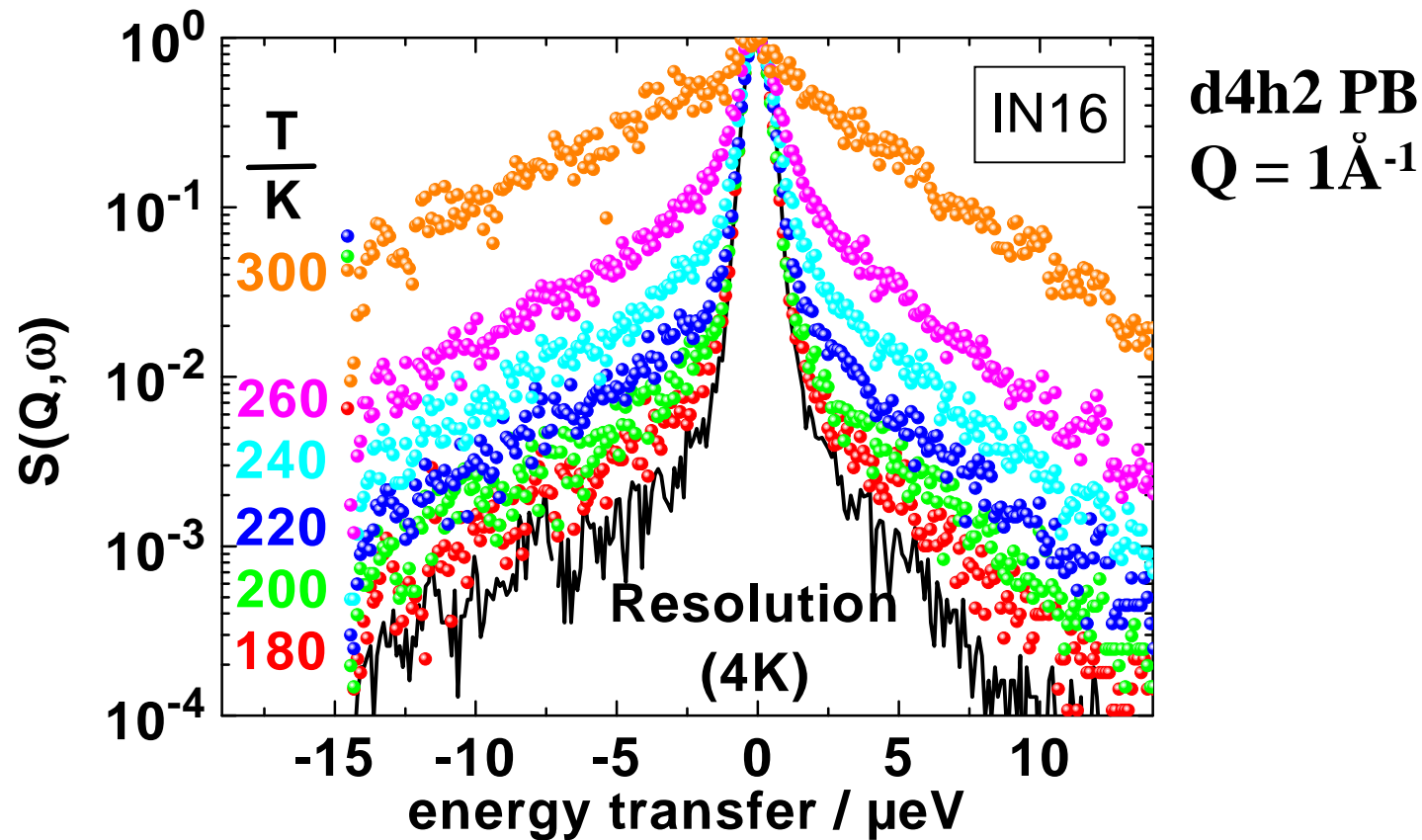


\Rightarrow The pair correlation **at Q_{max}** scales with the viscosity (α process)

\Rightarrow The C=C-C=C correlation **at Q_{max}** does not scale with the viscosity (β process?)

In the inelastic experiment we observe two different processes in the same sample at different labeling !

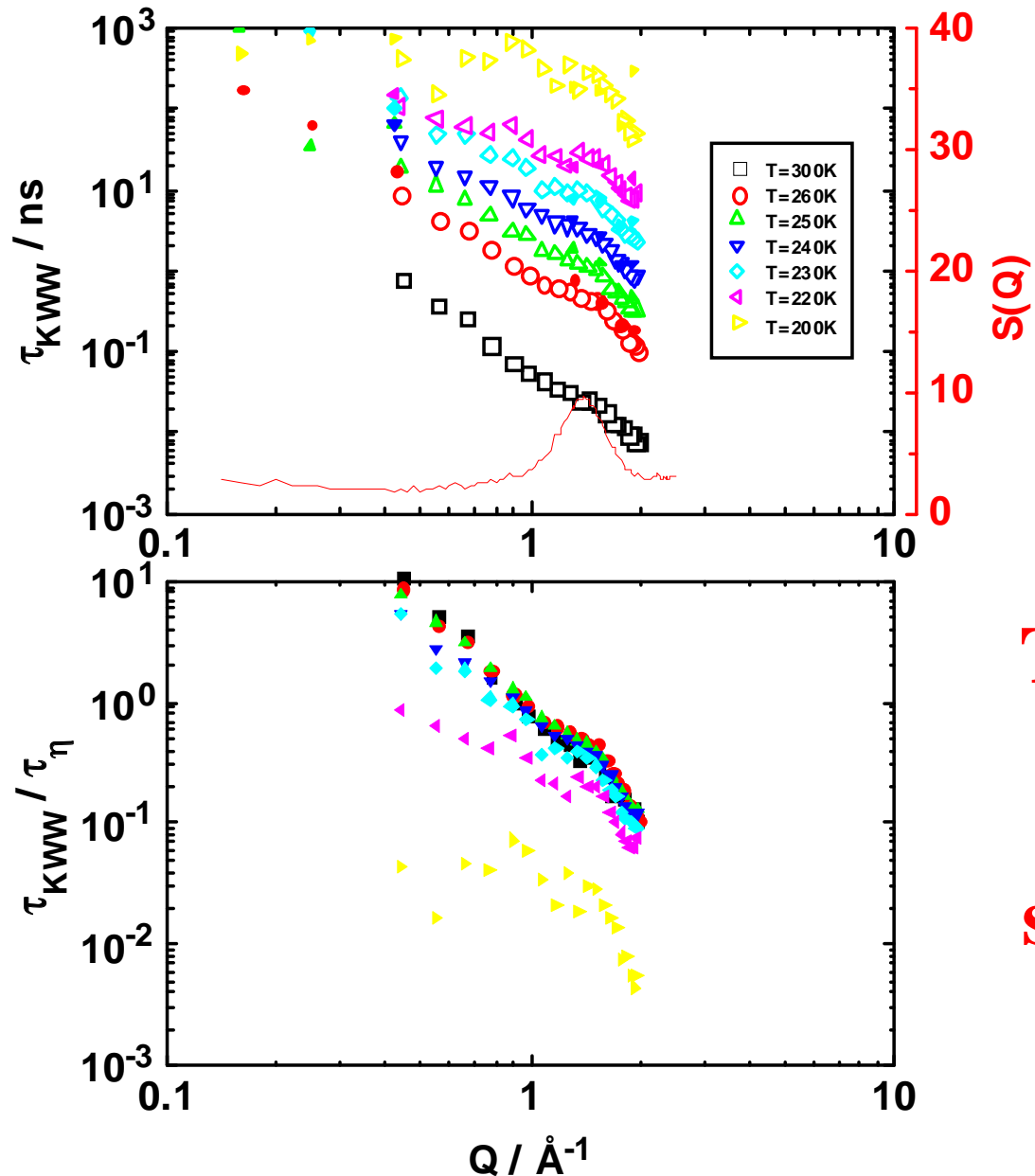
Inelastic Results: Neutron Backscattering



Backscattering data were fitted with ($\beta=0.4$):

$$S(Q, \omega) = FT \left\{ A \cdot \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \right\} * R(Q, \omega)$$

Inelastic Results: Neutron Backscattering



The Backscattering experiment shows qualitatively the same result like the NSE experiment!

Extract Parameters for Self and Pair correlation

$$S_{NSE}(Q, t) = I_{coh}(Q, t) - 1/3 I_{inc}(Q, t)$$

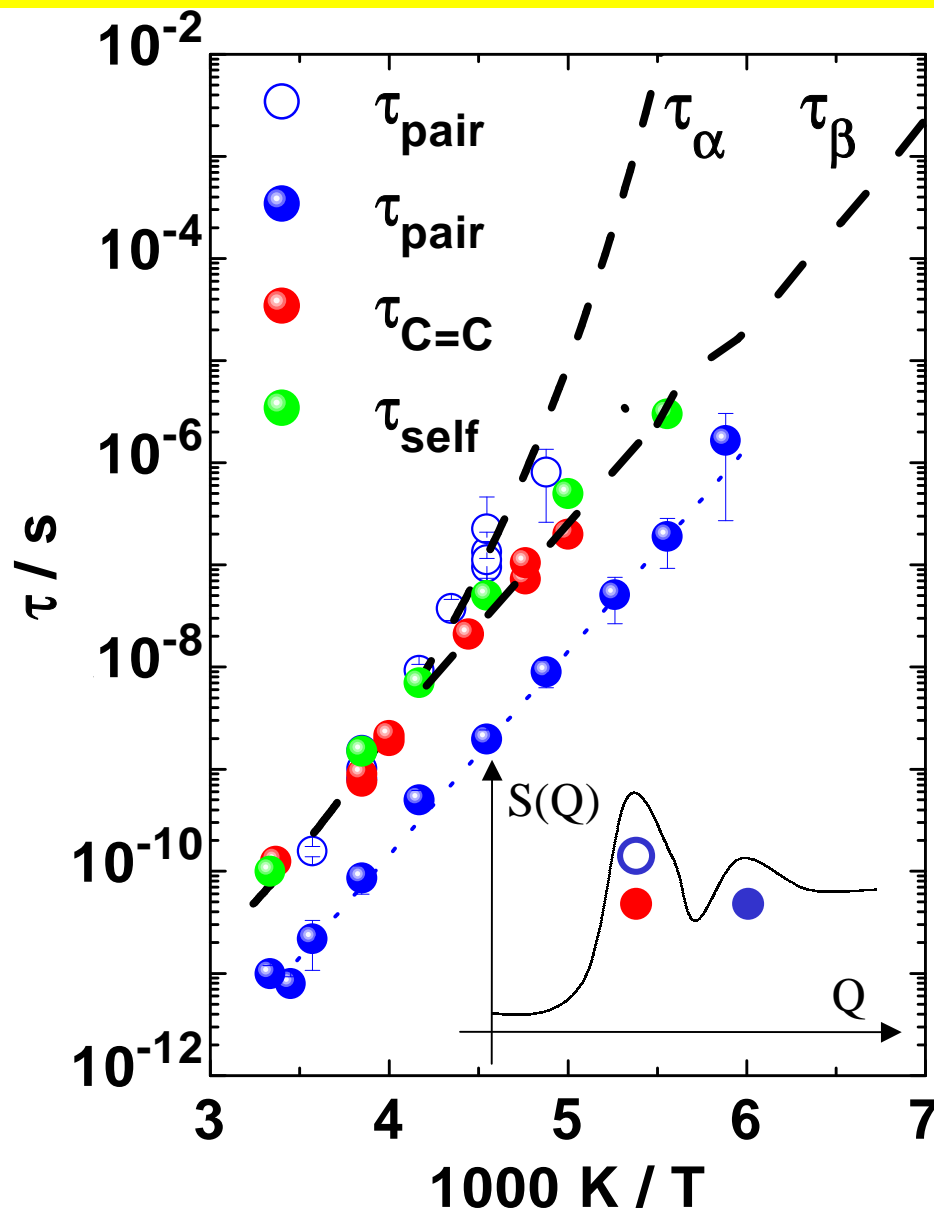
$$S_{BS}(Q, t) = I_{coh}(Q, t) + I_{inc}(Q, t)$$

with: $S_{BS}(Q, t) = FT\{S_{BS}(Q, \omega)\}$

Assumption: $I_{coh}(Q, t)$ and $I_{inc}(Q, t)$ are KWW functions

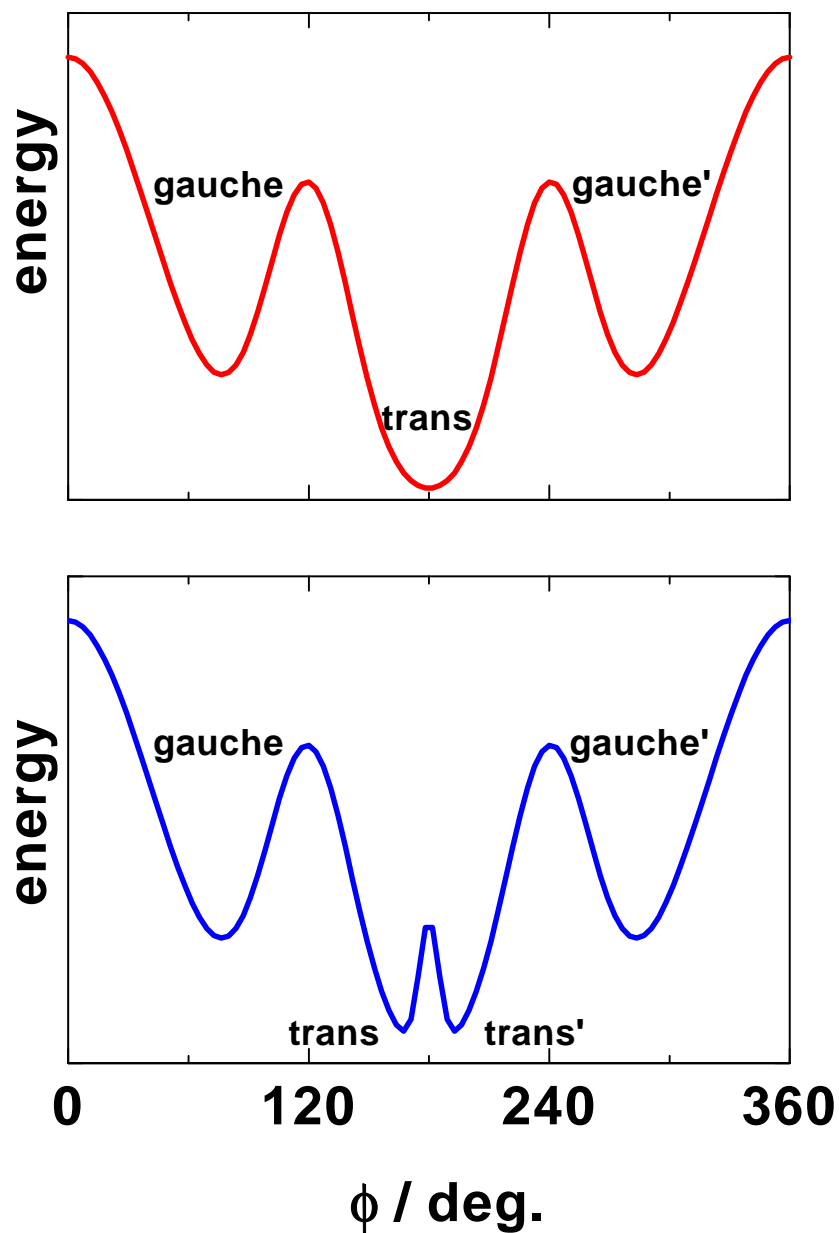
$$I(Q, t) = A(Q, T) \exp\left[-\left(\frac{t}{\tau_{KWW}(Q, T)}\right)^\beta\right]$$

Activation Plot – Conclusion



- The pair correlation at the first peak follow the glass transition, and at the second peak the β relaxation.
- Above α - β crossover temperature, T_{cr} , the C=C-C=C-correlation shows the temperature dependence of the α relaxation, and below the temperature dependence of the β relaxation.
- The self correlation of the double bond hydrogens shows also the temperature dependence of the β relaxation.
- **Conclusion:** β process corresponds to a motion of the double bond and decouple at T_{cr} from the α process

Intra-chain Potential

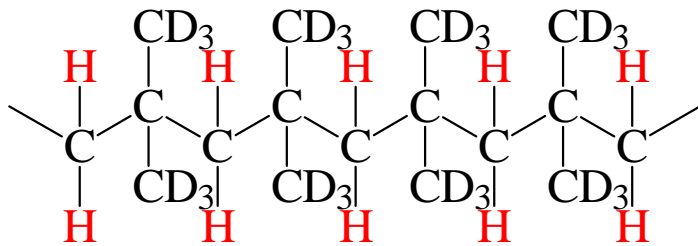


Typical for Polymers

Peculiarity in
Polyisobutylene

Polyisobutylene

Aim: Investigation of the t-t jump process

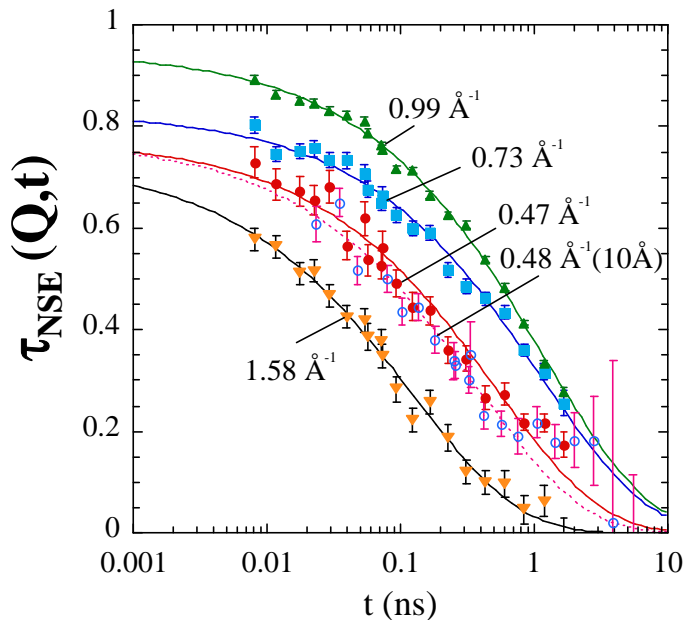
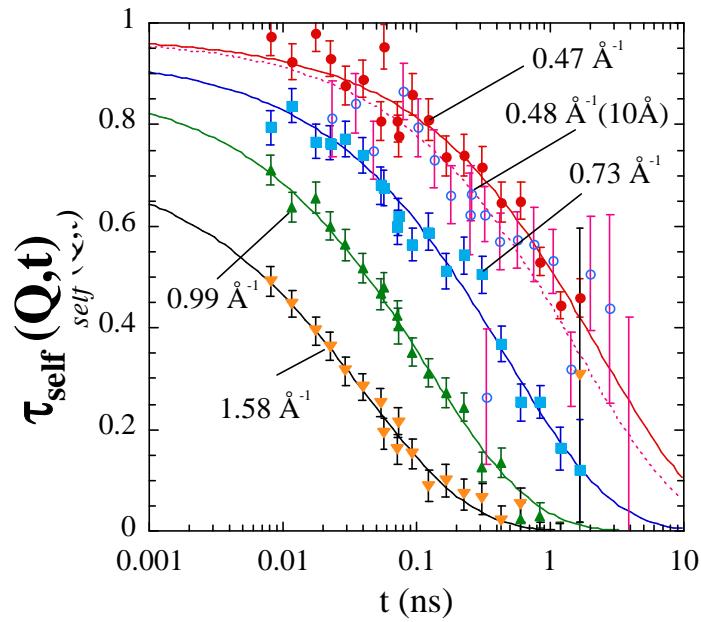


Due to the high incoherent cross section of the hydrogen atoms with the partial deuteration the motion of the methyl group is almost invisible (about 10% of the signal)

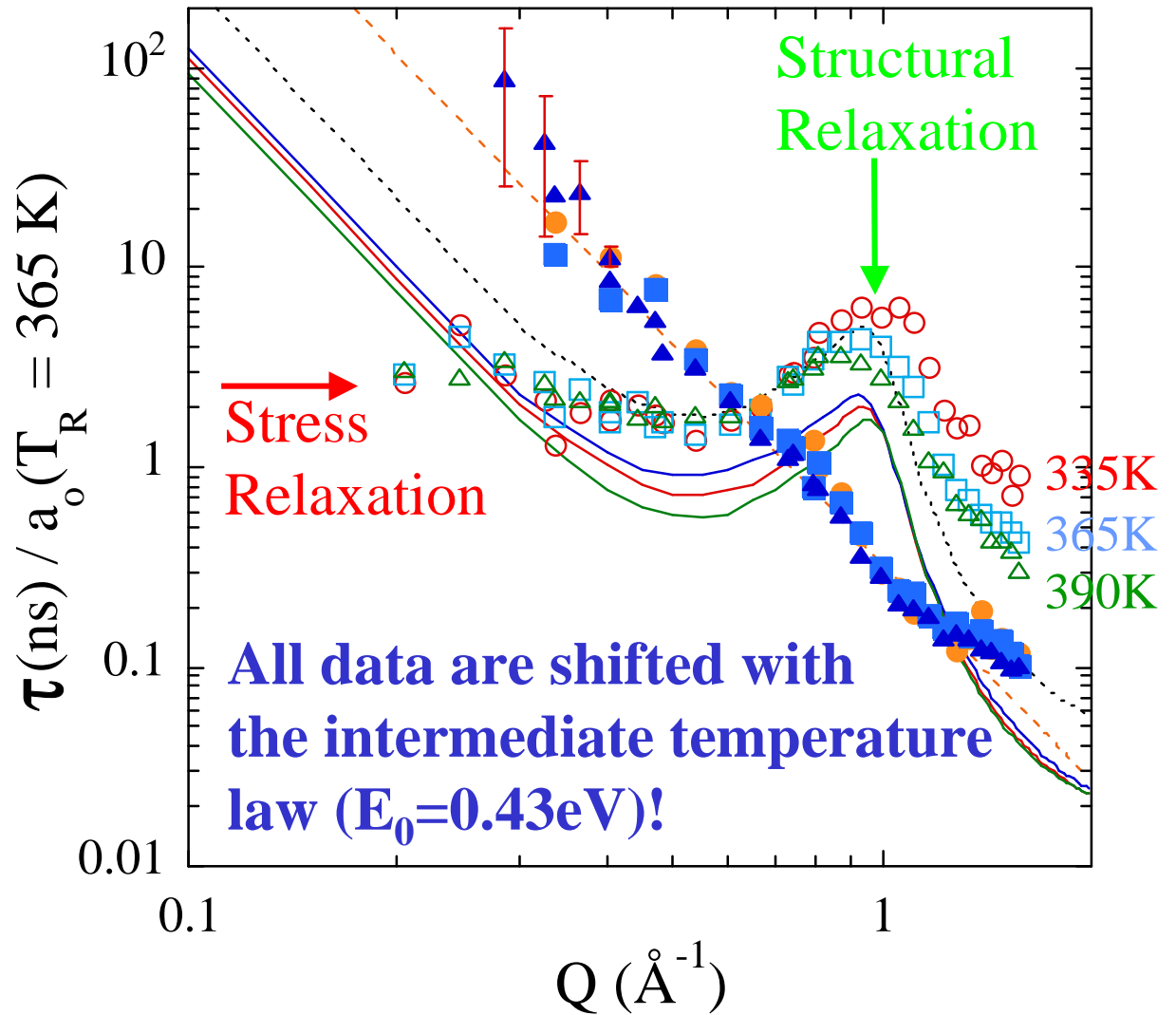
Therefore, the signal reflects the motion of the methylene hydrogens

Data were compared with results from MD simulations and a simple diffusion model

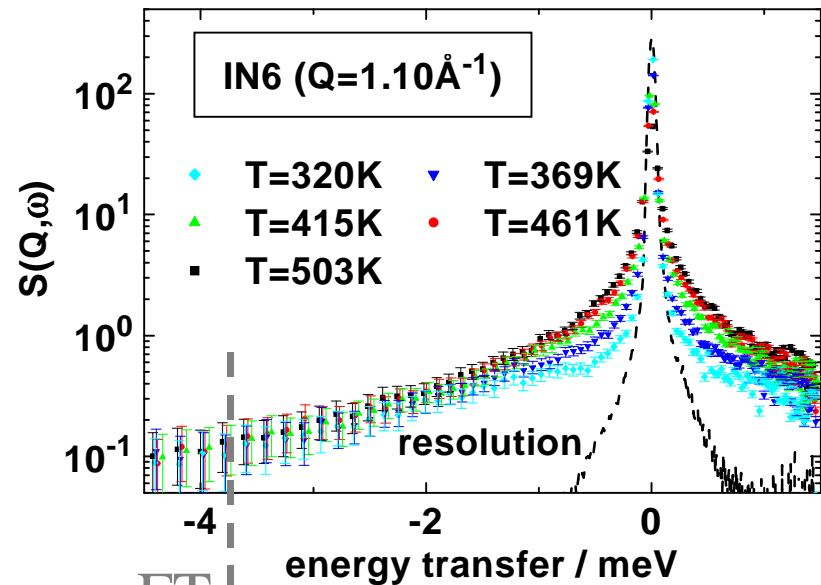
Glassy Dynamics in Polyisobutylene



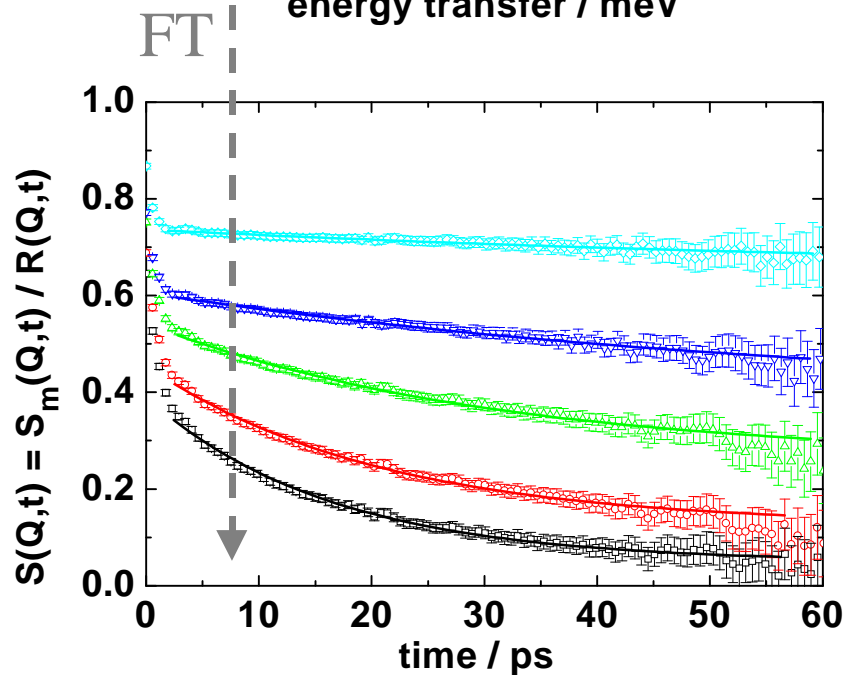
B. Farago e.a. *PRE* **65**, n.n. (2002) in press



Local Dynamics in Polyisobutylene



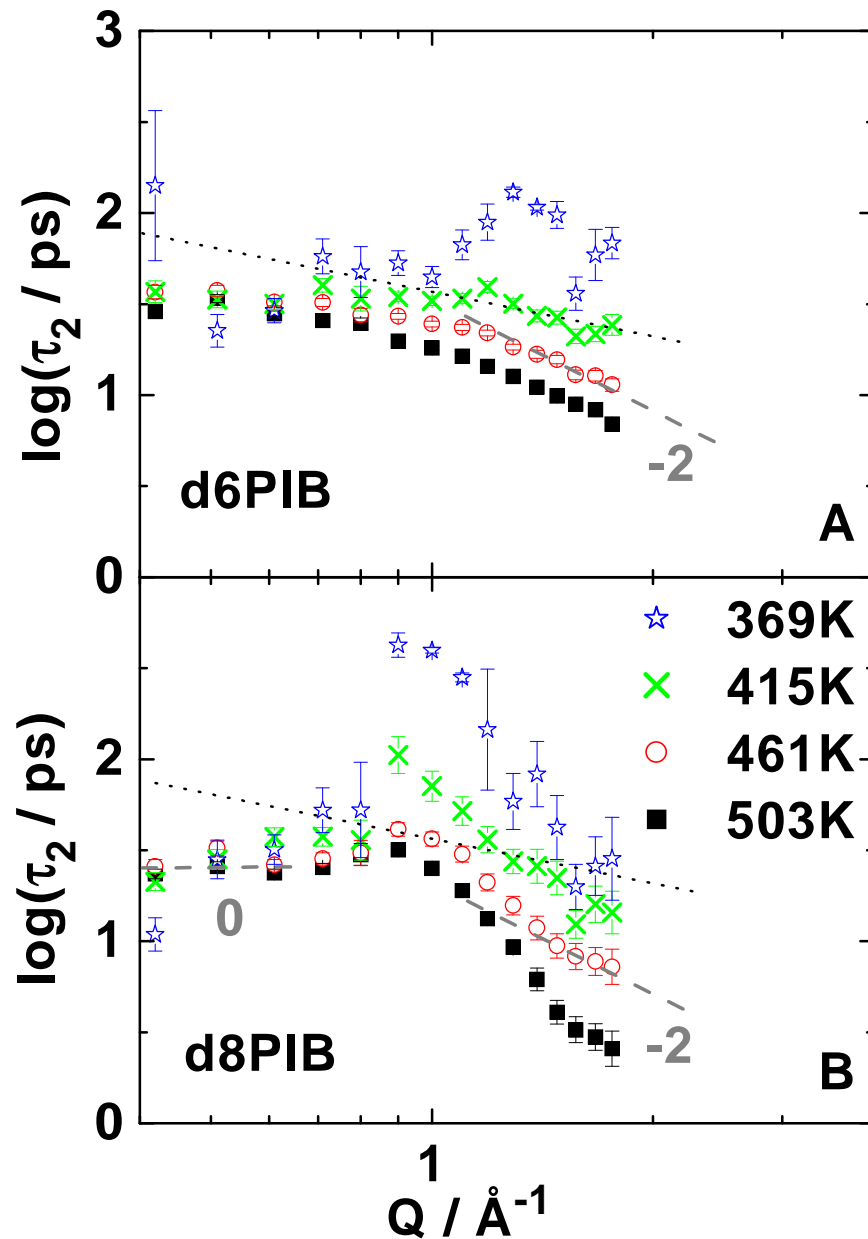
Data in frequency domain, $S(Q, \omega)$, were Fourier-transformed into the time domain with consideration of the instrument resolution $R(Q, \omega)$



Data in time domain were fitted with:

$$S(Q, t) = A(Q) \cdot S_{Phonons}(Q, t) \cdot (F_2(Q) + (1 - F_2(Q)) \cdot \exp[t / \tau_2])$$

Fit Results: The Correlation Times

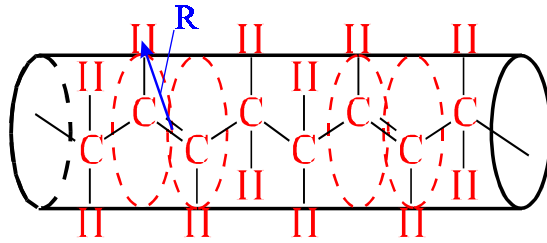
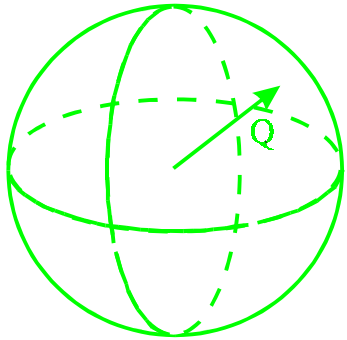


The Q -dependence of τ_2 shows clearly two regions:

$$\tau_2 \sim \text{const}$$

$$\tau_2 \sim Q^{-2}$$

Scattering Function for Diffusion on a Circle



Diffusion Equation:

$$D\Delta P(\vec{r}, t) = \frac{\partial}{\partial t} P(\vec{r}, t)$$

Boundary Conditions: $P(\varphi, t = 0) = \delta(\varphi, \varphi_0)$, $P(\varphi, t \rightarrow \infty) = \frac{1}{2\pi}$

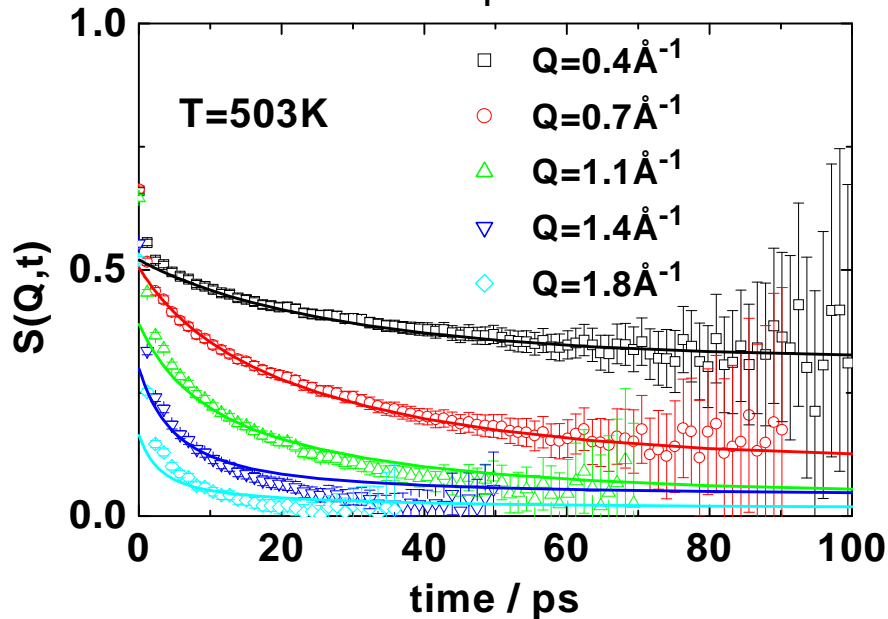
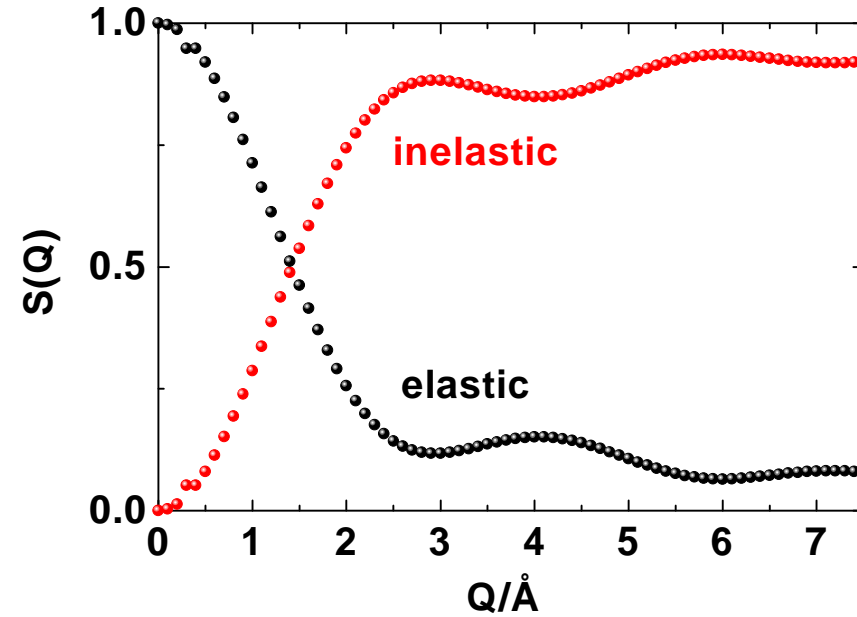
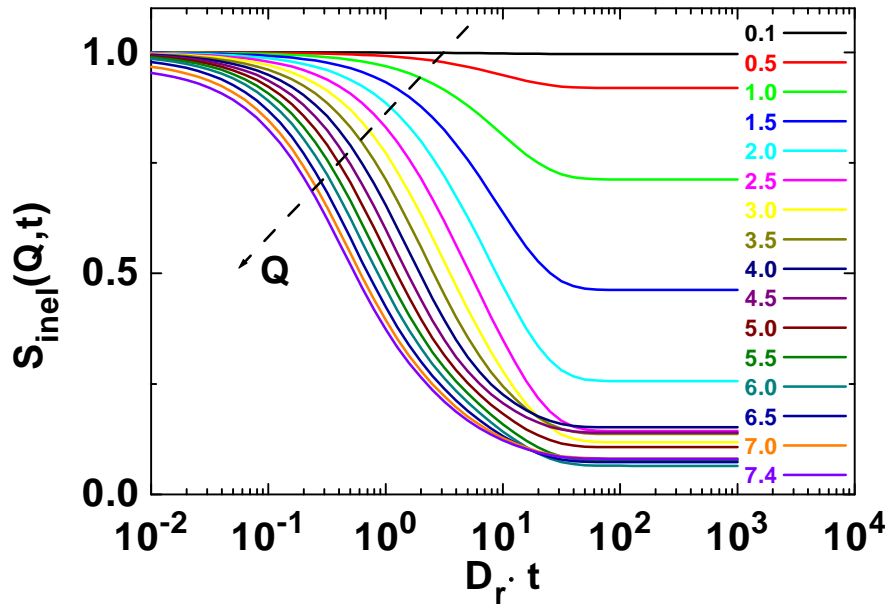
$$\text{Solution: } P(\varphi, \varphi_0, t) = \frac{1}{2\pi} \left\{ 1 + \sum_{k=1}^{\infty} \cos(k(\varphi - \varphi_0)) \exp(-D_r k^2 t) \right\}$$

$$S(Q, t) = \frac{1}{4\pi} \int d\Omega \int d\Omega_0 P(\varphi, \varphi_0) \exp[iQ(R(\Omega) - R(\Omega_0))]$$

$$S_{elast}(Q) = \frac{1}{2} \int_0^{\pi} \sin \vartheta d\vartheta \cdot J_0^2(QR \sin \vartheta)$$

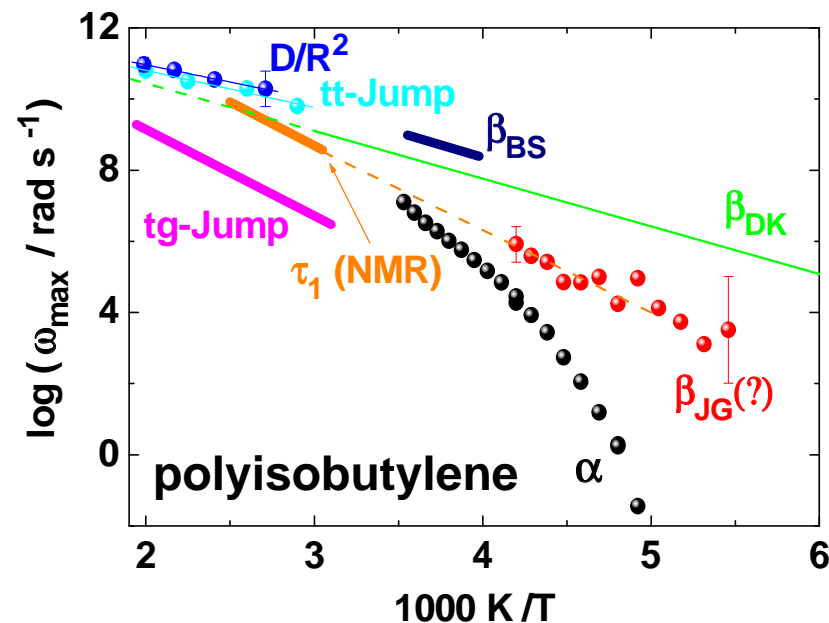
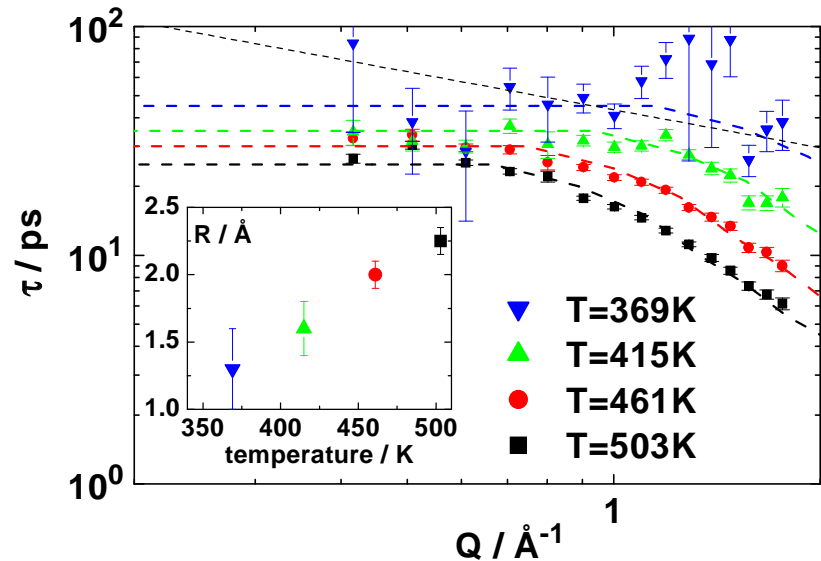
$$S_{inel}(Q, t) = 2 \sum_{k=1}^{\infty} \exp\left[-\frac{D}{R^2} k^2 t\right] \int_0^{\pi} \sin \vartheta d\vartheta \cdot J_k^2(QR \sin \vartheta)$$

Comparison with Data



- At lower Q a good agreement between model and data is observed.
- At higher Q the differences increase in both spectral form and elastic intensity
- We have estimated $R \approx 2.3\text{\AA}$

Relaxation Times versus Q and Relaxation Map



- Model and data shows qualitatively the same Q- dependence of the correlation times

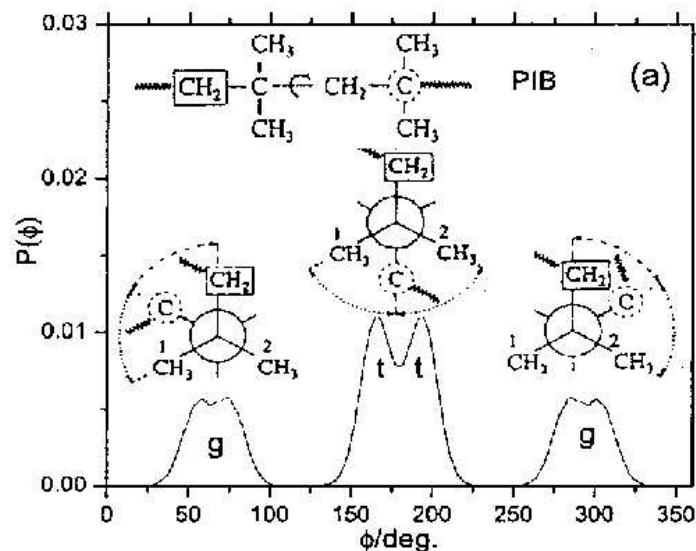
- R depends on temperature

Open Question: Is the local relaxation a diffusion process in a spatial restricted area?

- tt-jump process and data of the d6PIB sample shows almost the same correlation times

- **Note:** tt-jump distance is much smaller than evaluated by the data

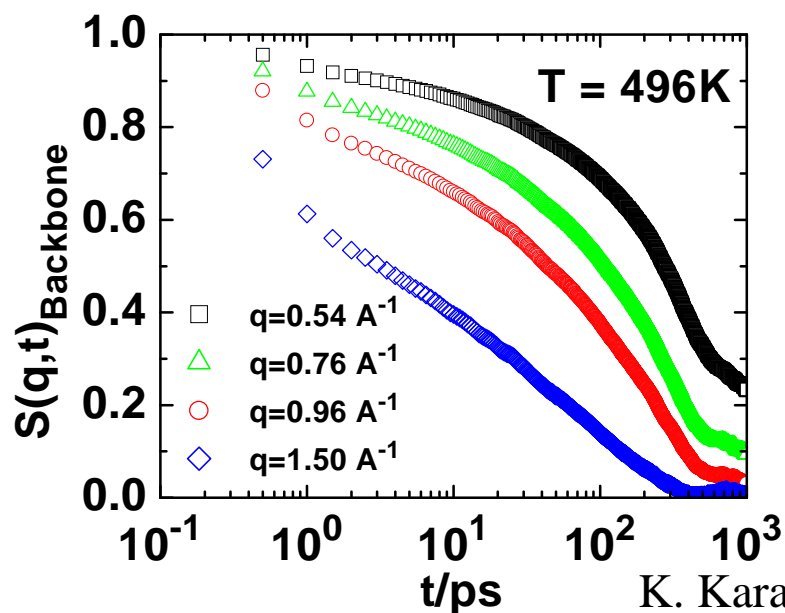
Molecular Dynamic Simulation



Polymer melt with 5 chains of 25 monomers in a cubic box with periodic boundary conditions was simulated under constant pressure and temperature conditions.

Analysing the incoherent scattering function $S(Q,t)$ three distinct processes were identified.

The slow and intermediat processes could be related to trans-trans and trans-gauche jumps.



K. Karatassos e.a. *MM* 35, 1451 (2002)

Collaborators

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Thank you for your attention!