Complementary Methods

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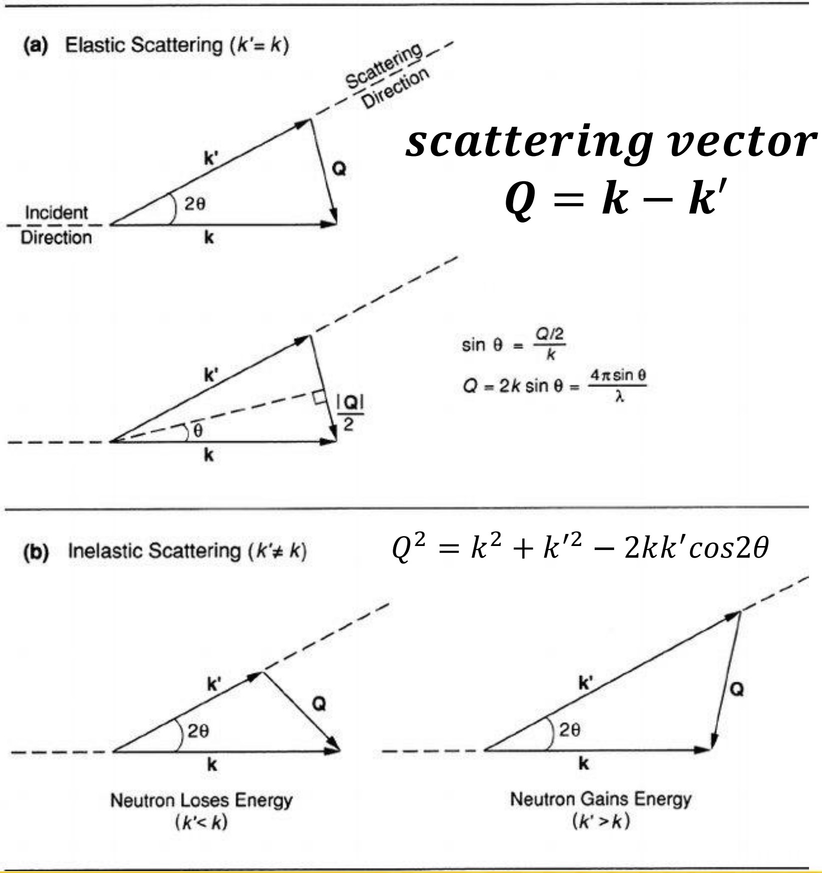
Scattering Concepts

Elastic Neutron Scattering

- No exchange of energy E_i-E_f=0
- Examines change in momentum or direction.

Inelastic Neutron Scattering

- Examines both energy and change in momentum or direction.



scattering vector

$$\boldsymbol{Q} = \boldsymbol{k} - \boldsymbol{k}'$$

$$Q^2 = k^2 + k'^2 - 2kk'cos2\theta$$

Pynn, Neutron Scattering: A Primer (1989)

Scattering Quantities

Measurable quantity in a NS experiment

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k_f}{k_i} \underbrace{\frac{1}{2\pi\hbar} \sum_{i,j} \langle b_i b_j \rangle \int_{-\infty}^{\infty} \left\langle e^{-i\vec{Q}\vec{r}_i(0)} e^{i\vec{Q}\vec{r}_j(t)} \right\rangle \cdot e^{-i\omega t} dt}$$

Dynamic Structure Factor $\boldsymbol{S(Q,\omega)}$

Coherent and incoherent

$$\sigma_{coh} = 4\pi \langle b \rangle^2 = 4\pi b_{coh}^2$$

$$\sigma_{inc} = 4\pi(\langle b^2 \rangle - \langle b \rangle^2) = 4\pi b_{inc}^2$$

coh and inc dynamic structure factors

$$S_{coh}(\vec{Q},\omega) = \frac{\sigma_{coh}}{N} \frac{1}{2\pi\hbar} \sum_{i,j} \int_{-\infty}^{\infty} \left\langle e^{-i\vec{Q}\vec{r}_i(0)} e^{i\vec{Q}\vec{r}_j(t)} \right\rangle \cdot e^{-i\omega t} dt$$

$$S_{inc}(\vec{Q},\omega) = \frac{\sigma_{inc}}{N} \frac{1}{2\pi\hbar} \sum_{i} \int_{-\infty}^{\infty} \left\langle e^{-i\vec{Q}\vec{r}_i(0)} e^{i\vec{Q}\vec{r}_i(t)} \right\rangle \cdot e^{-i\omega t} dt$$

Inverse Fourier Transform

Dynamic Structure Factors

$S_{inc}(Q,\omega)$ $\quad$ $S_{coh}(Q,\omega)$

Intermediate Scattering Functions

$S_{inc}(Q,t)$ $\quad$ $S_{coh}(Q,t)$

Correlation Functions

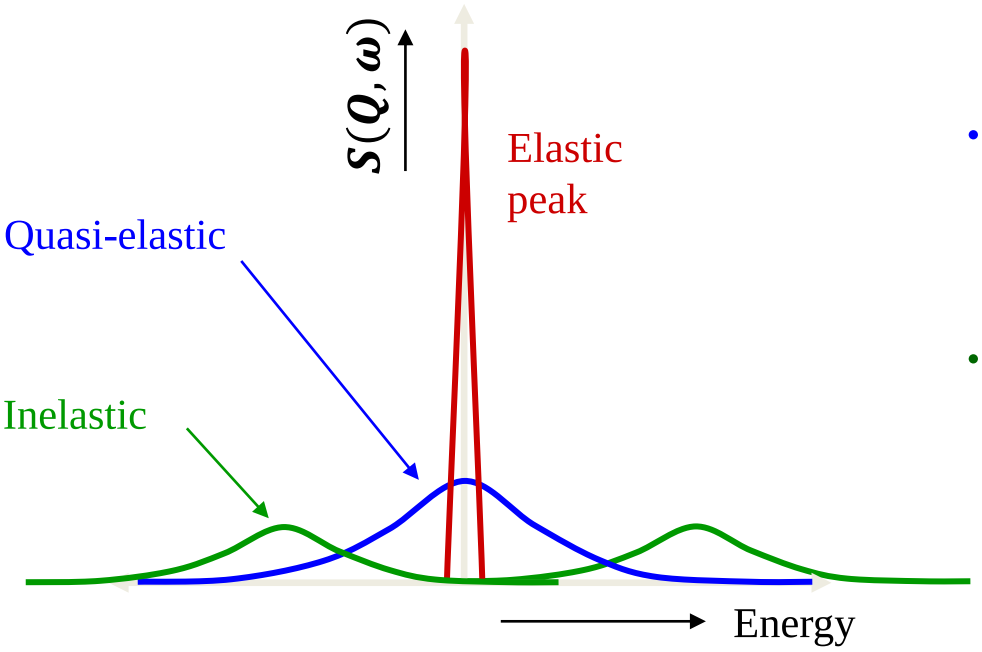
$G_{self}(r,t)$ $\quad$ $G_{pair}(r,t)$

Fourier Transform

$G_{self}(r,t)$ is the probability of finding a particle at position r after time t if **that same particle** was at position 0 at time t=0

$G_{pair}(r,t)$ is the probability of finding a particle at position r after time t if **there was a particle** at position 0 at time t=0

Types of Scattering and Motions



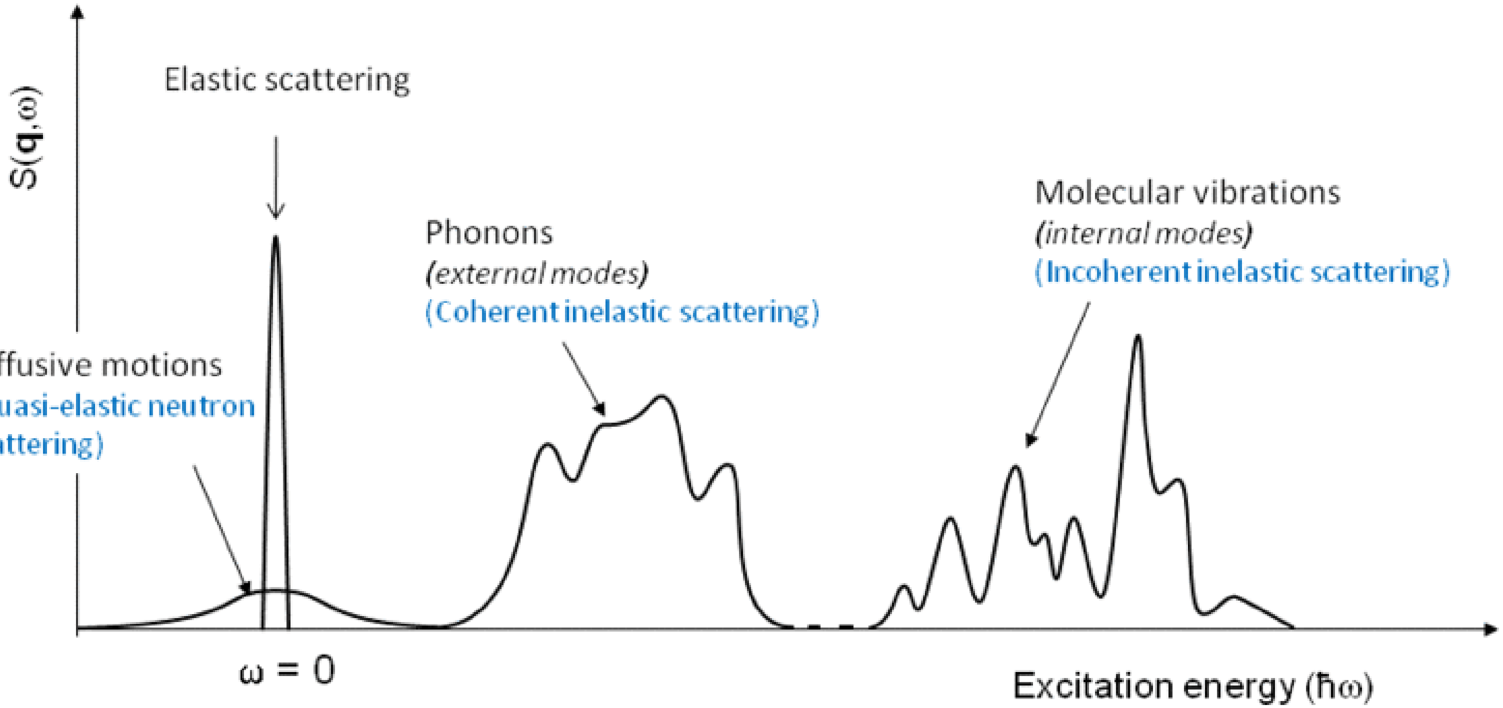
- Elastic neutron scattering:
  is the scattering for which the energy transfer is identically zero.

- Quasi-elastic neutron scattering:
  peaks at zero energy transfer, but is broadened compared to the instrumental resolution. It arises from diffusive or diffusive-like processes.

- Inelastic neutron scattering:
  peaks at non-zero energy transfer. This scattering reflects the vibrational or fast modes of the system.

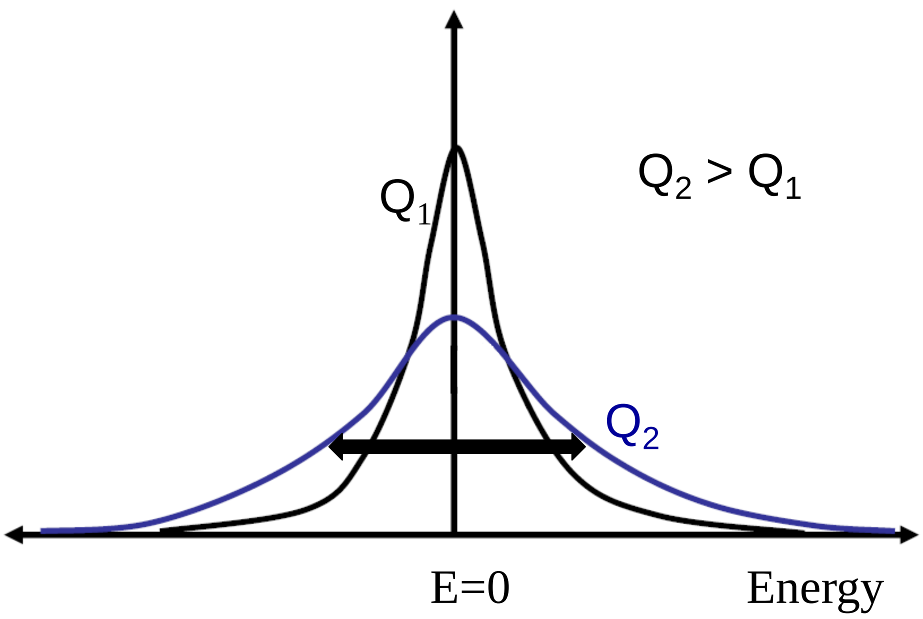
Courtesy of C. Brown

Scattering Types in Broad Picture



Broadening - What Can We Learn?

Fick's Law $D\nabla^2 G_s(r,t) = \frac{\partial G_s(r,t)}{\partial t}$ $G_s(r,t)$ is the solution



$$G_s(r,t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

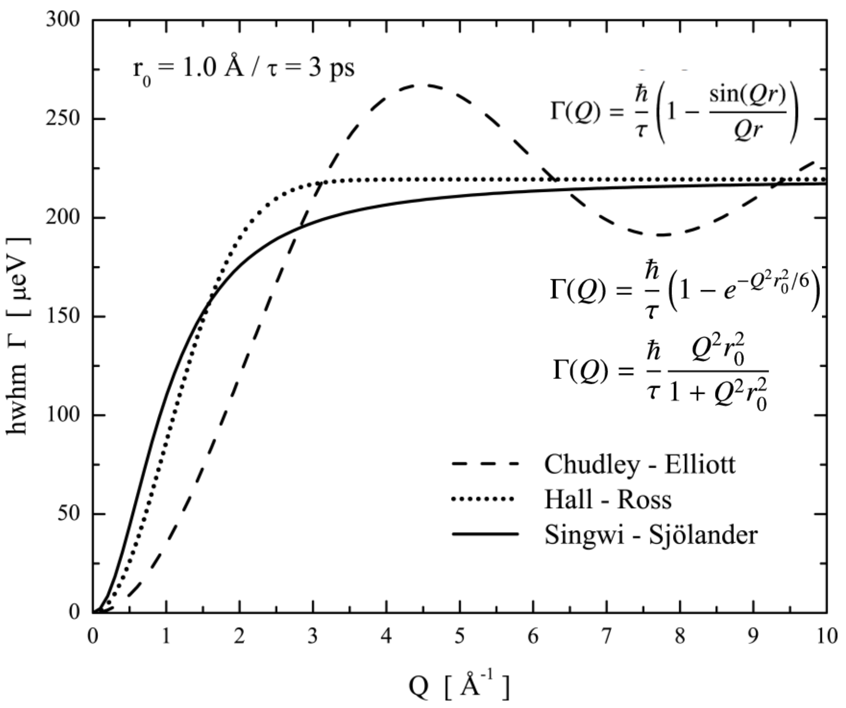
$$S(q,t) = \exp(-Q^2 Dt)$$

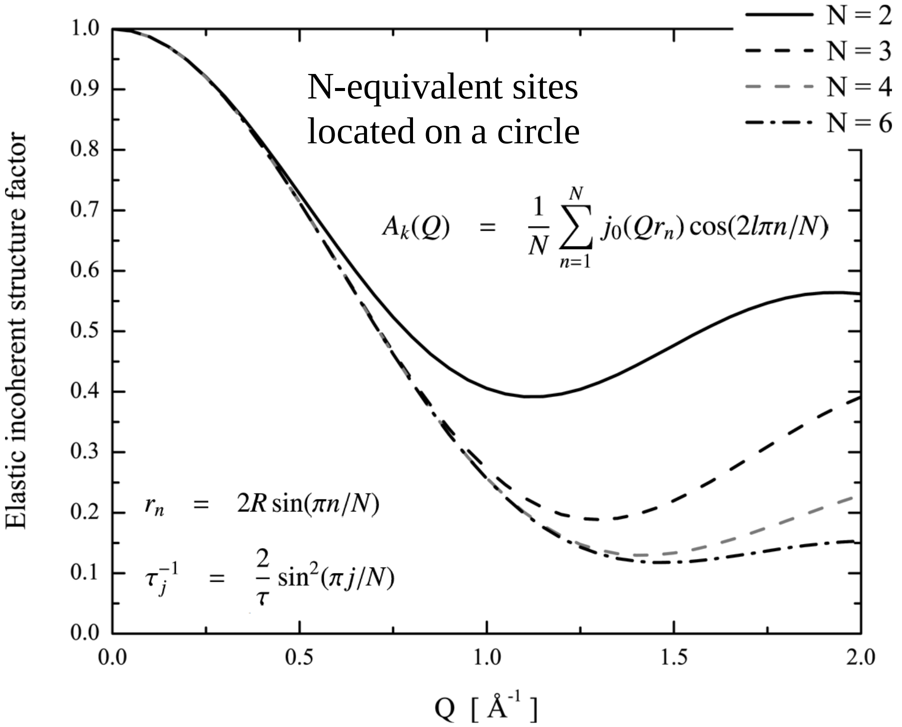
$$S(q,\omega) = \frac{1}{\pi}\frac{\Gamma(q)}{\Gamma^2 + \omega^2}$$ $\Gamma(q) \sim DQ^2$

Lorentzian function

Broadening - What Can We Learn?

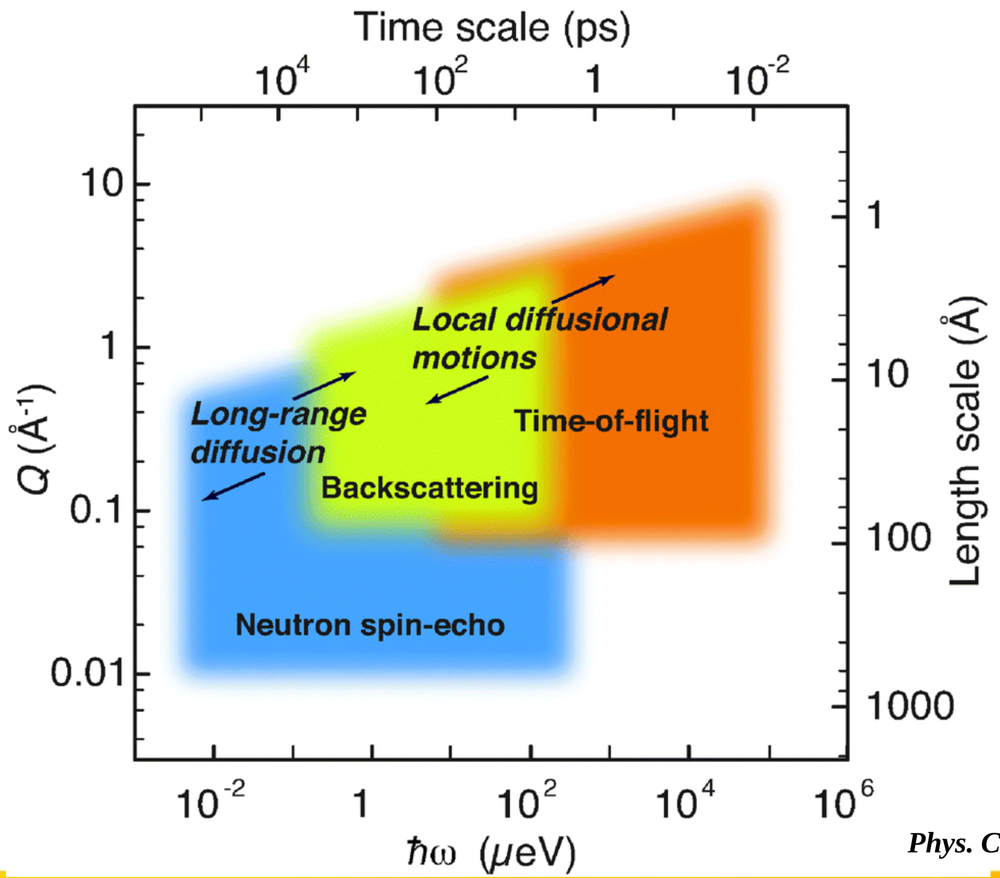
$$EISF = \frac{I_{elastic}(Q)}{I_{elastic}(Q) + I_{QENS}(Q)}$$





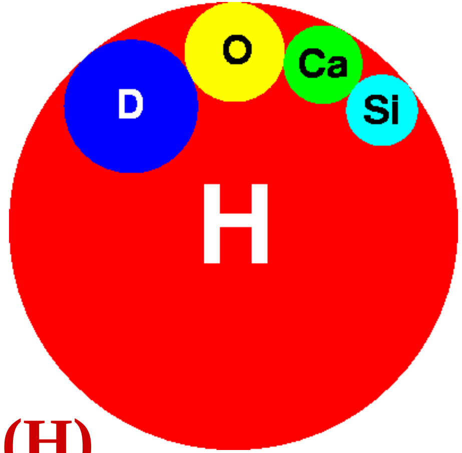
Z. Phys. Chem. 224 (2010) 5-32

NSE and Complementary Neutron Techniques

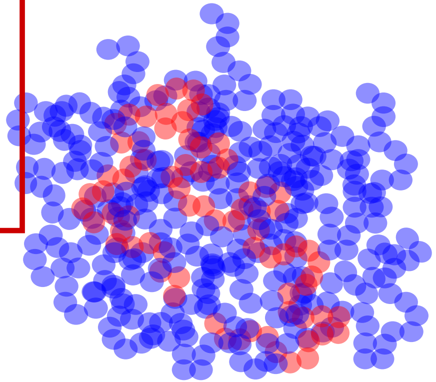


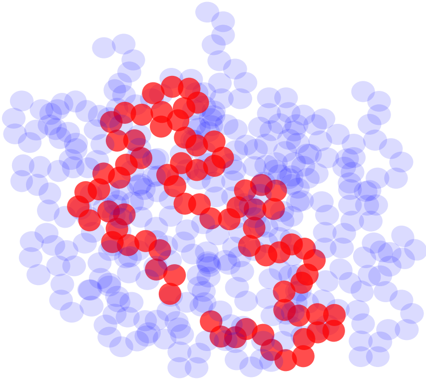
Phys. Chem. Chem. Phys., 2015, 17, 26-38

Advantage of Hydrogen

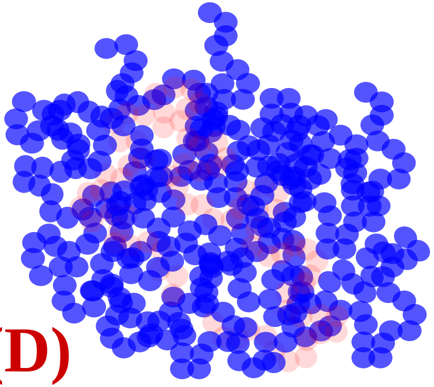


elements		Incoherent	coherent
σ (H)	~	82	2
σ (D)	~	2	5
σ (C)	~	0	5
σ (O)	~	0	4



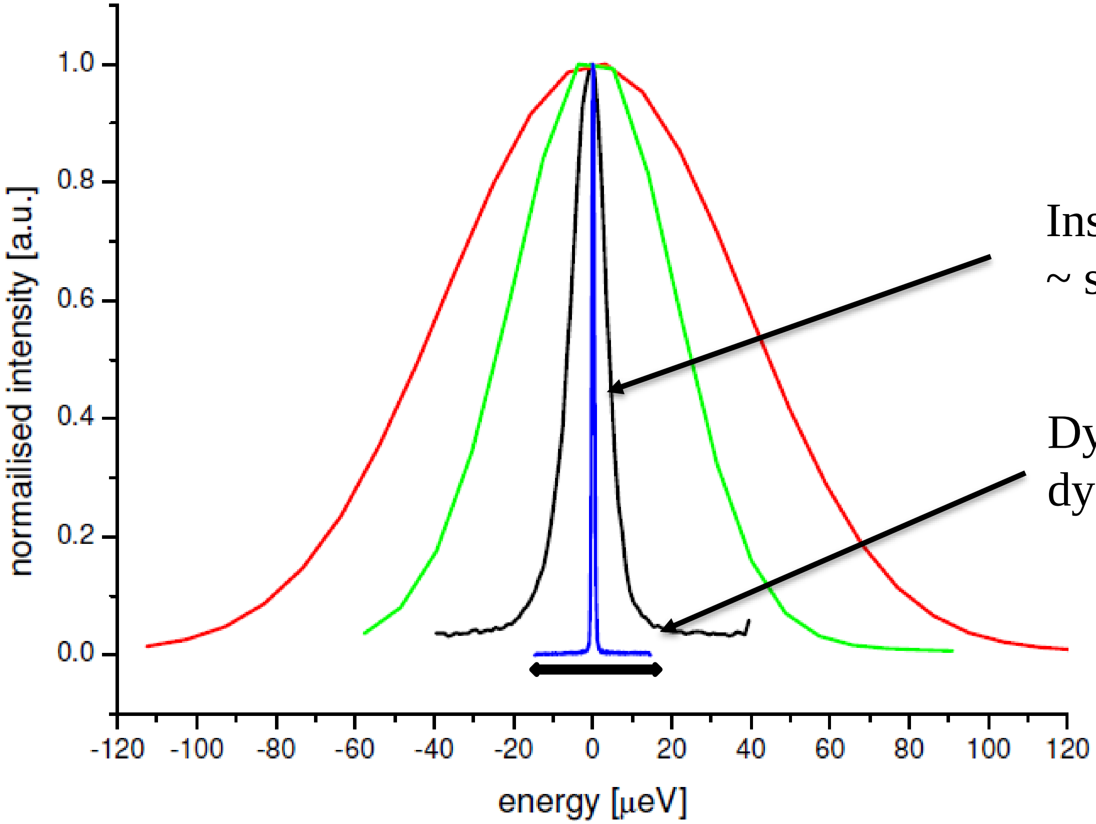


A(D)/B(H)



A(H)/B(D)

Resolution: Why is it Important?



Instrument resolution
~ slower dynamics that can be resolved

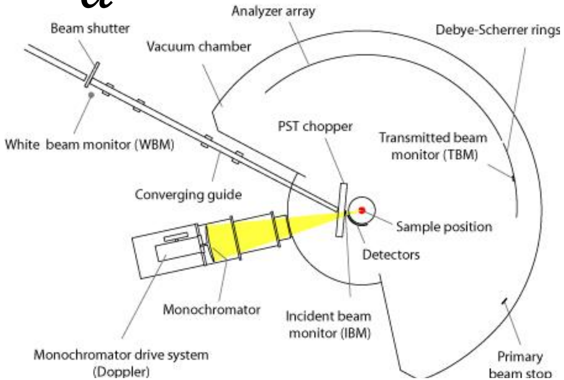
Dynamic range ~ faster
dynamics that can be analyzed

Backscattering Spectrometers

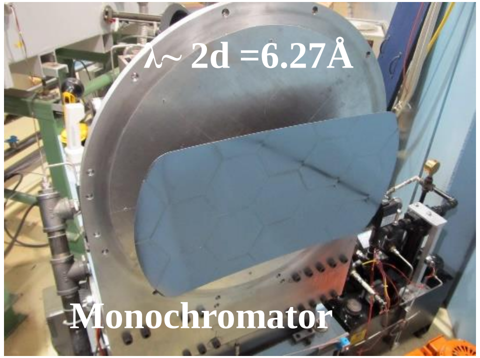
$$\frac{\Delta\lambda}{\lambda} = \cancel{\frac{\Delta\theta}{tan\theta}} + \frac{\Delta d}{d}$$

IF $2\theta \approx 180°$

Reactor based

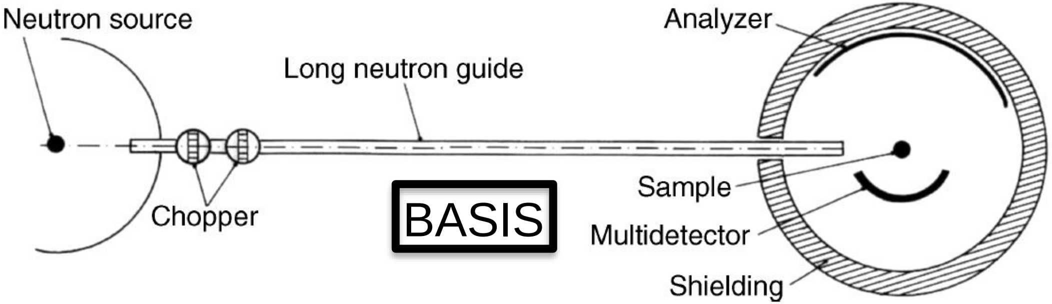


HFBS



$$\textit{Instrument resolution} \sim 0.8\mu eV$$

$$\textit{Dynamic range} \sim \pm 36\mu eV$$



BASIS

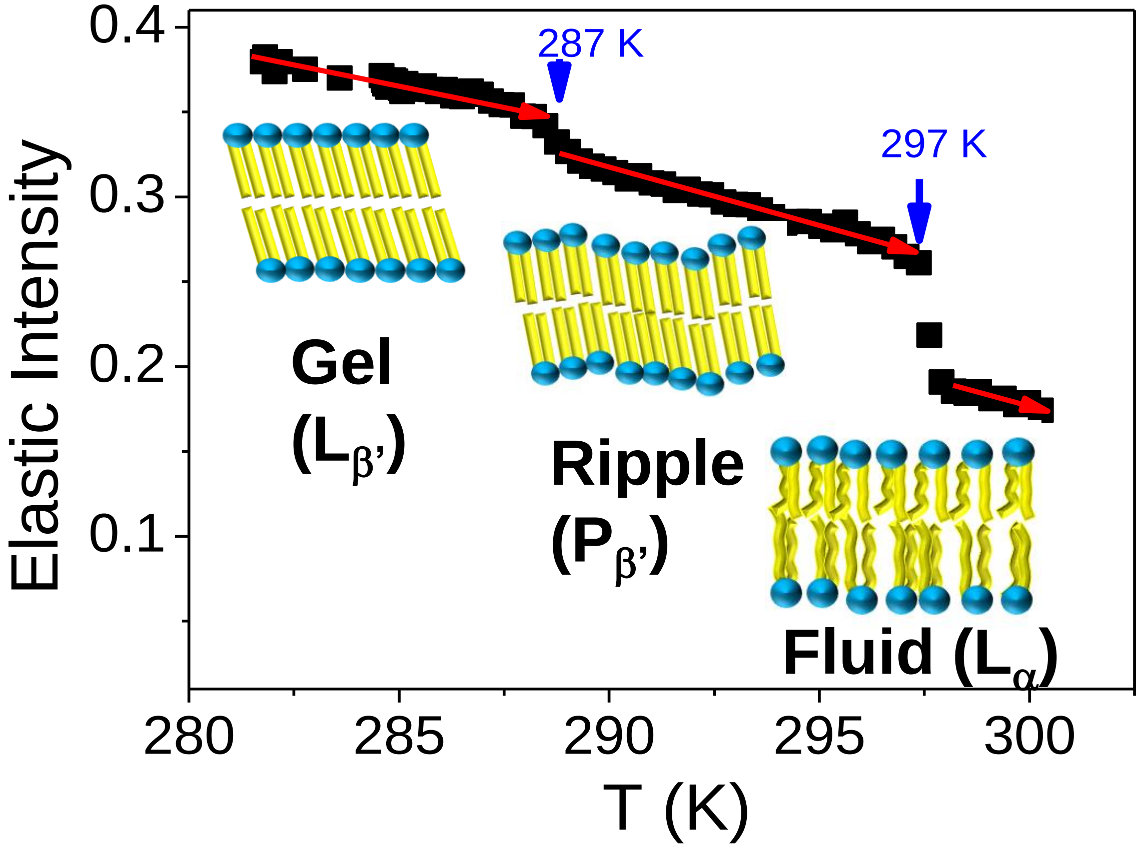
Spallation source based

$$\delta E \sim 2E\left(\frac{\Delta t_p}{t_0}\right)$$

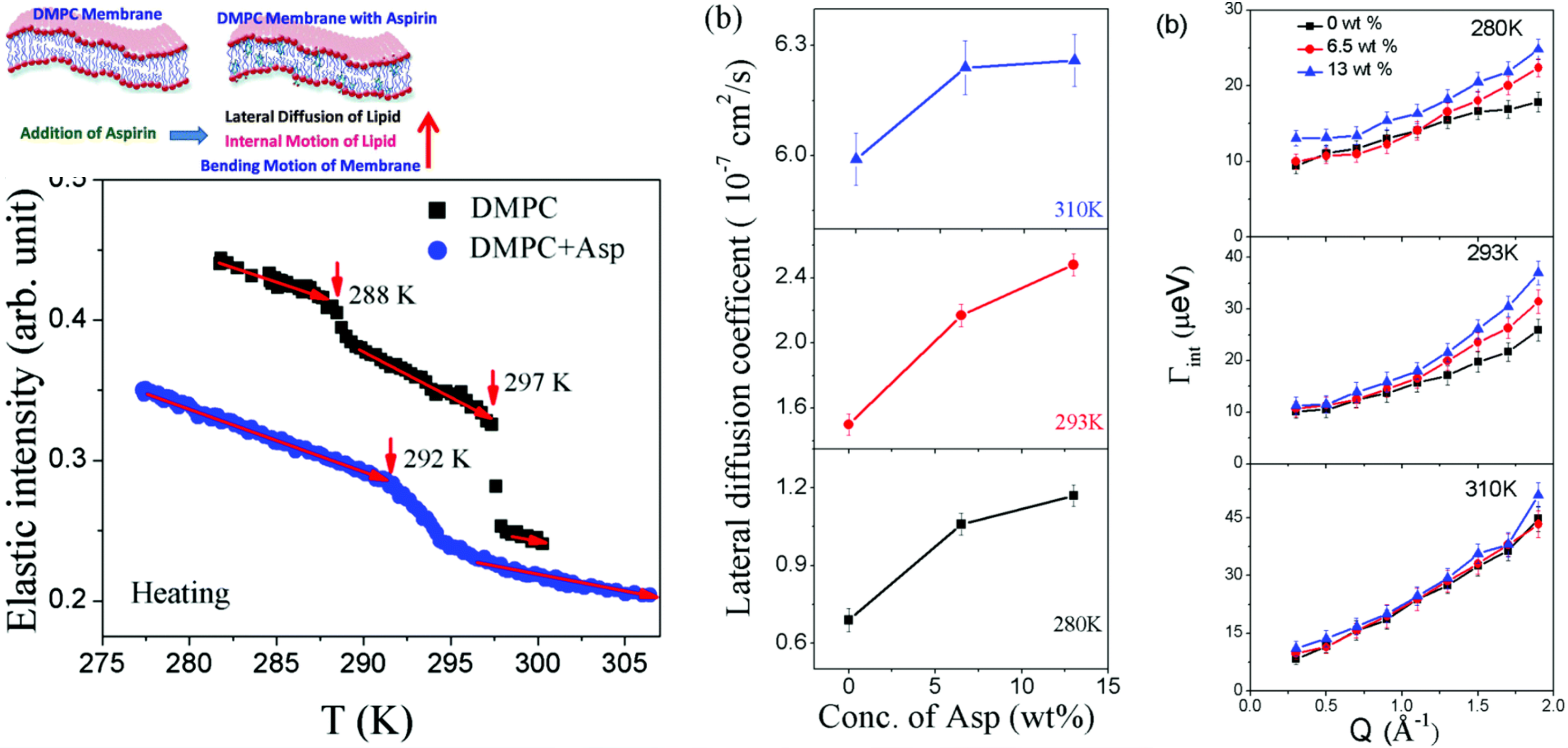
$$\textit{Instrument resolution} \sim 3.4\mu eV$$

$$\textit{Dynamic range} \sim \pm 100\mu eV$$

Phase transitions in DMPC



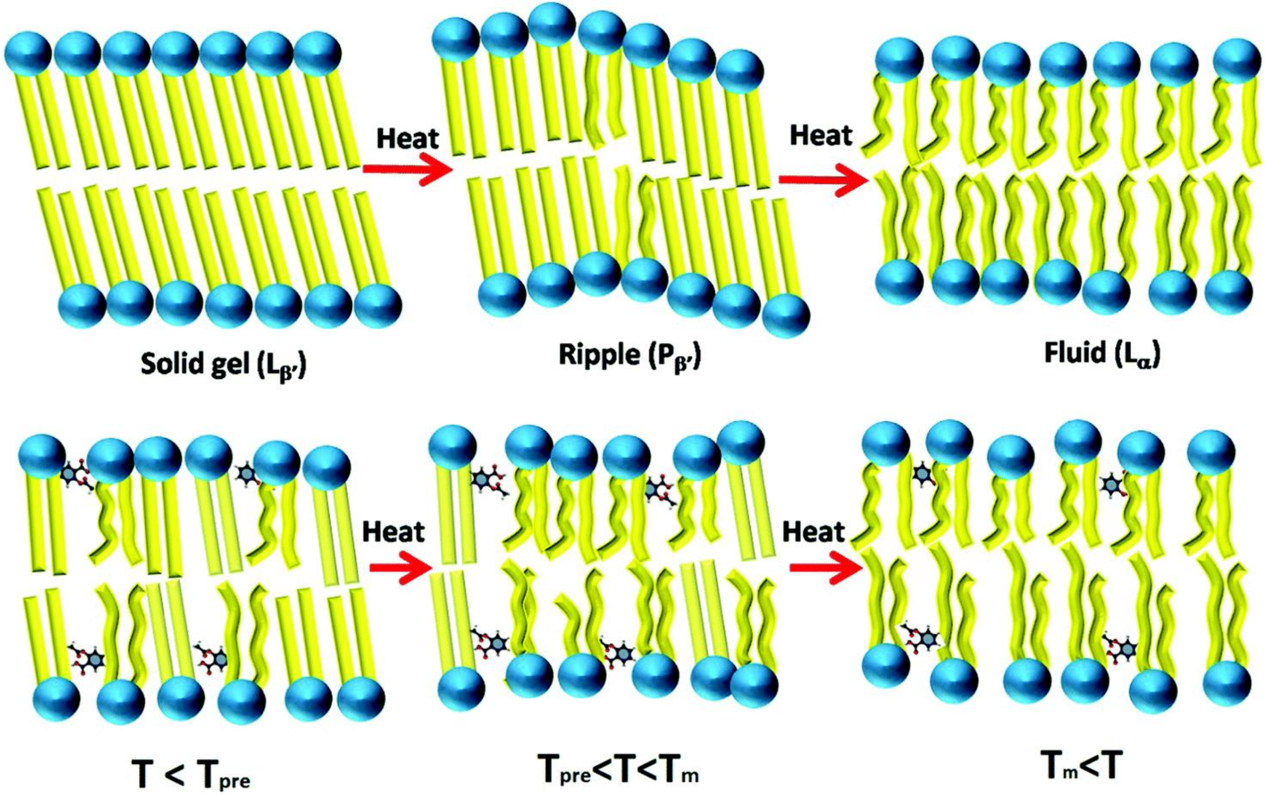
Incorporation of Aspirin into the DMPC and its Effects



Incorporation of Aspirin into the DMPC and its Effects

Neat DMPC

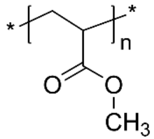
DMPC/Aspirin

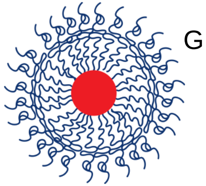


Phys. Chem. Chem. Phys., *2017, 19, 2514*

Gas Diffusivity in Grafted Nano-Particles & Local Polymer Dynamics

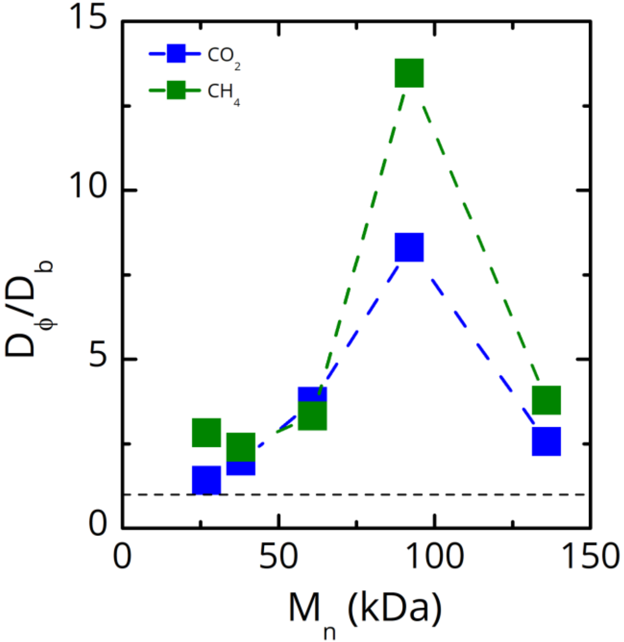
Polymethyl acrylate

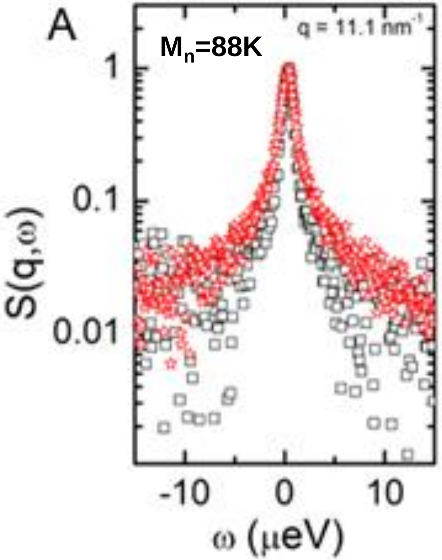


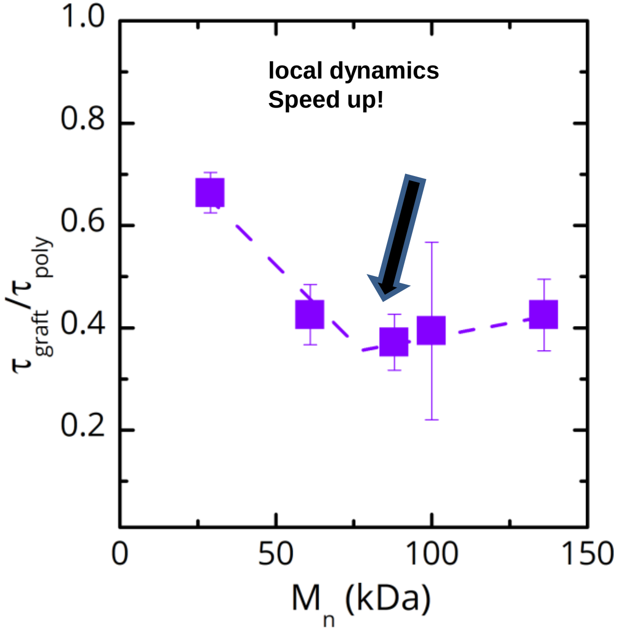


GNPs

Faster dynamics of grafted in comparison to bulk polymer!

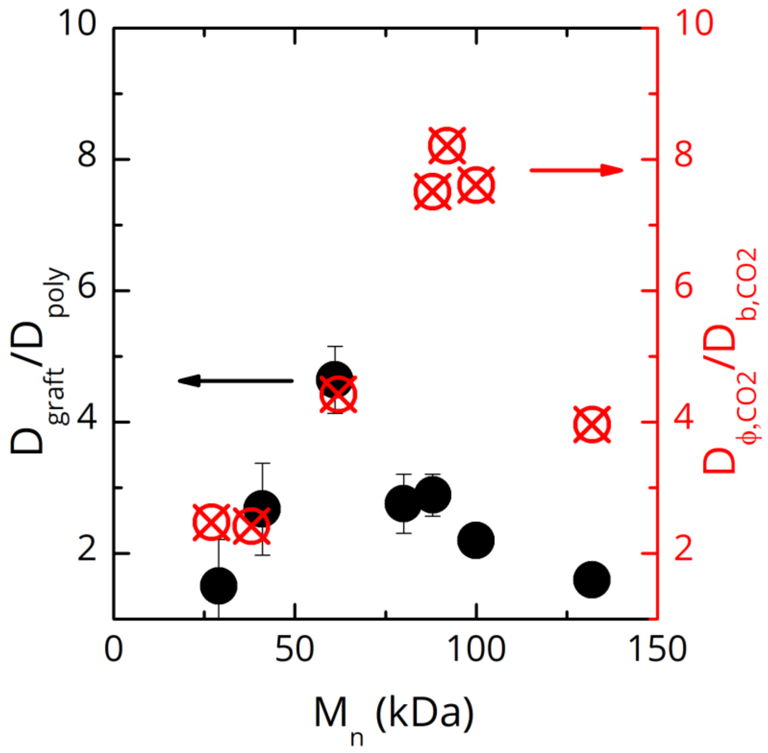


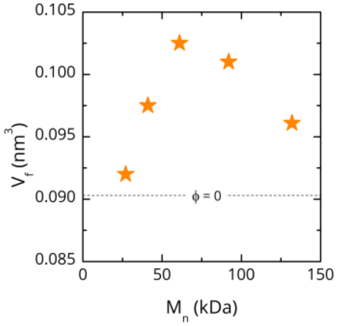


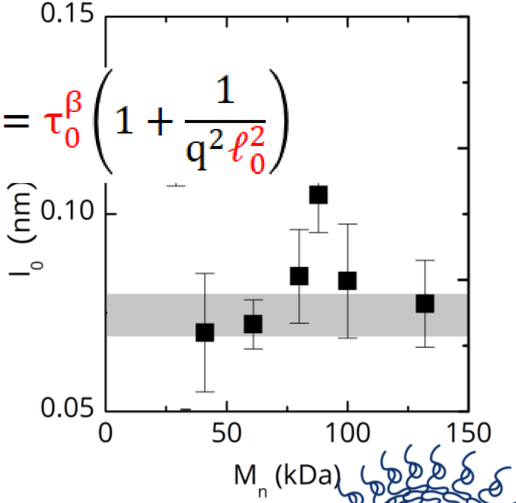


Gas Diffusivity in Grafted Nano-Particles & Local Polymer Dynamics

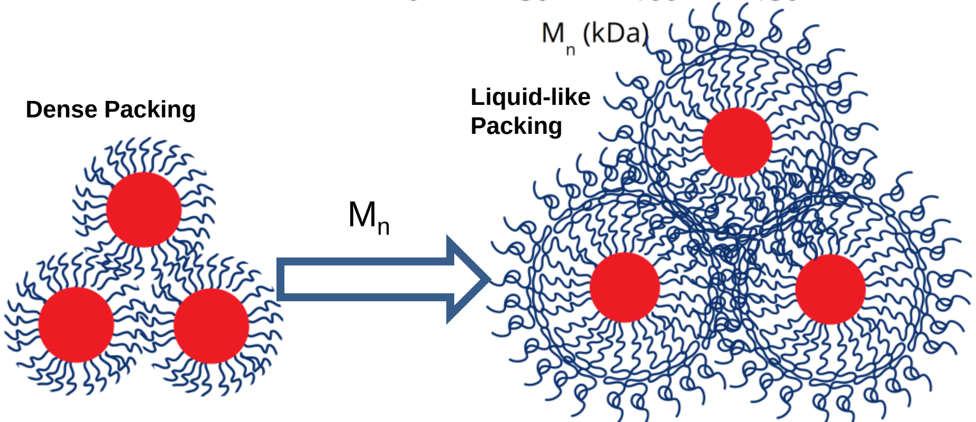
Diffusivity of gases, local free volume and polymer local dynamics – Strongly correlated!







$$\tau^{\beta} = \tau_0^{\beta}\left(1 + \frac{1}{q^2 \ell_0^2}\right)$$



Phys. Rev. Lett. 123, 158003 (2019), Macromolecules 54, 6968 (2021)

Time of Flight: Basic Concepts

Energy of a neutron $E = \frac{1}{2}mv^2 = \frac{\hbar^2 k^2}{2m}, \qquad k = \frac{2\pi}{\lambda}$

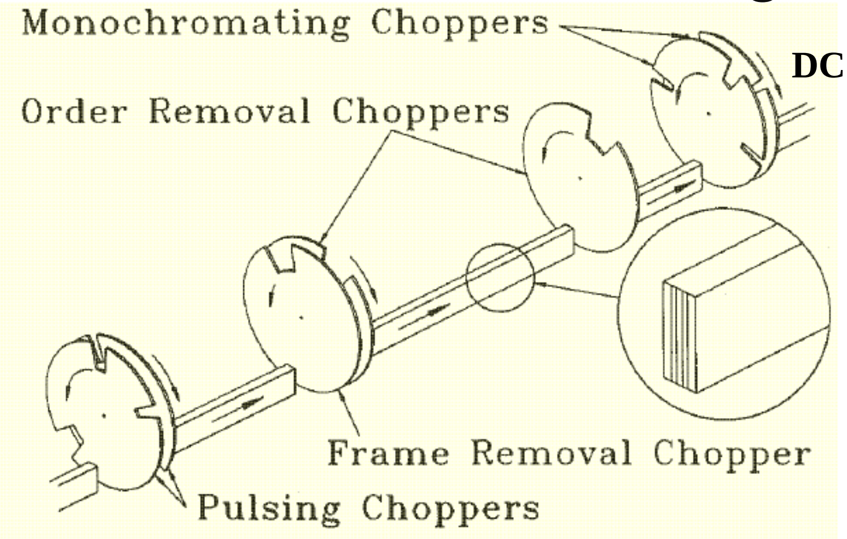
Velocity of that neutron $v = \frac{\hbar k}{m} = \frac{h}{m\lambda} = \frac{6.6261 \cdot 10^{-34}\mathrm{Js}}{1.6749 \cdot 10^{-27}\mathrm{kg}} = \frac{3956\frac{\mathrm{m}}{\mathrm{s}}}{\lambda[\text{Å}]}$

Time of flight of that neutron $t = \alpha L \lambda\ , \ \alpha = m_{\mathrm{n}}/h = 252.77\mu\mathrm{s}/(\text{Å}\mathrm{m})$

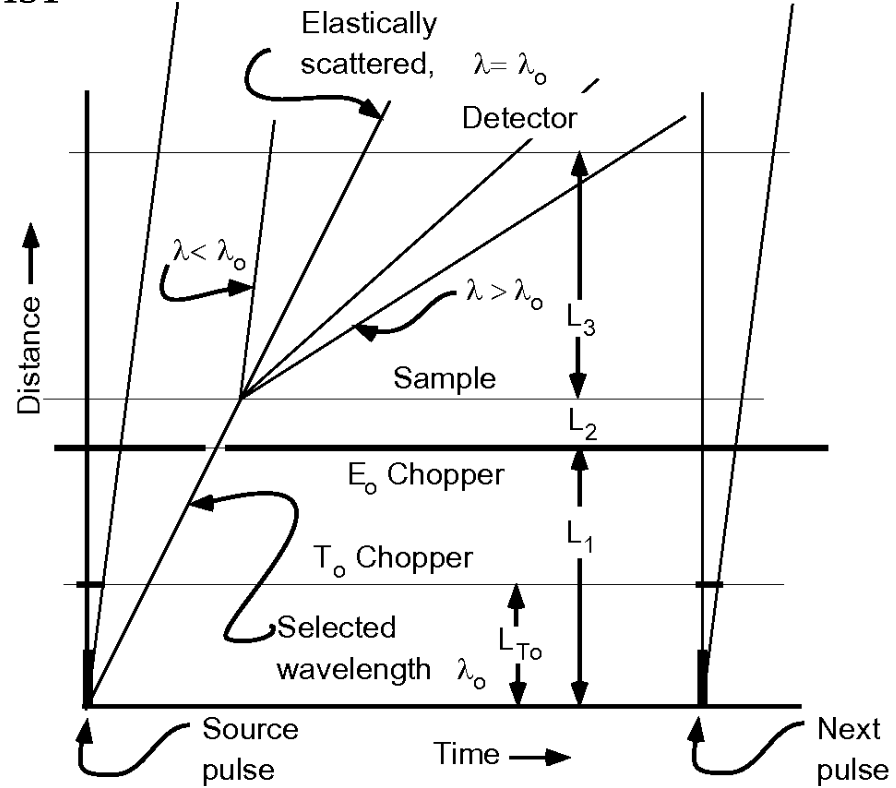
Wavelength spread of a pulsed beam $\frac{\Delta\lambda}{\lambda} = \frac{\tau}{t}$

Example: L=10m, v=1000m/s, $\Delta\lambda \sim 0.01$ $\tau \sim 100\mu s$

Time of Flight: Basic Concepts



DCS at NIST

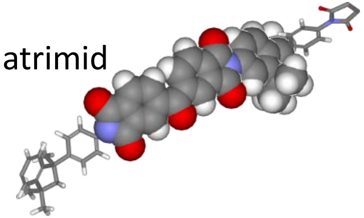


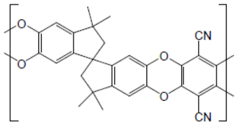
Energy Resolution:

$$\Delta E = \frac{h^3}{m^2 \lambda^3} \frac{\Delta t}{L}$$

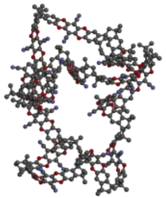
A New Polymer for Gas Separation PIM-1

Matrimid

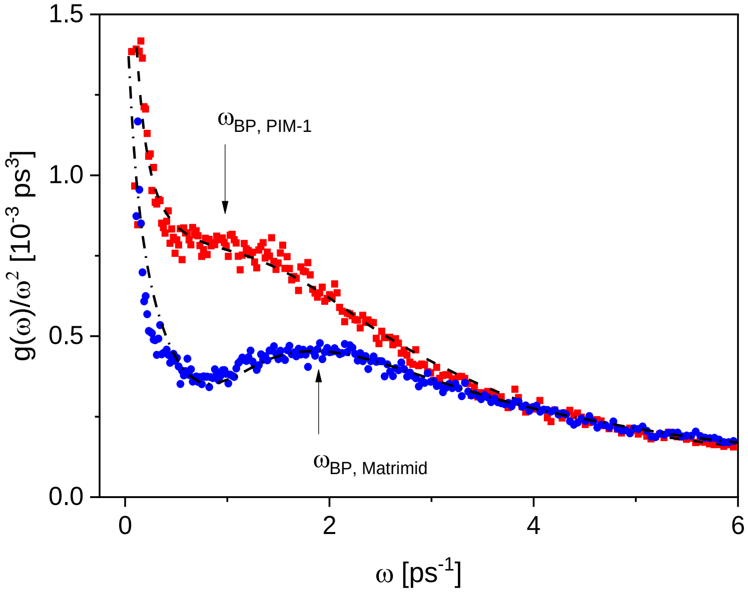


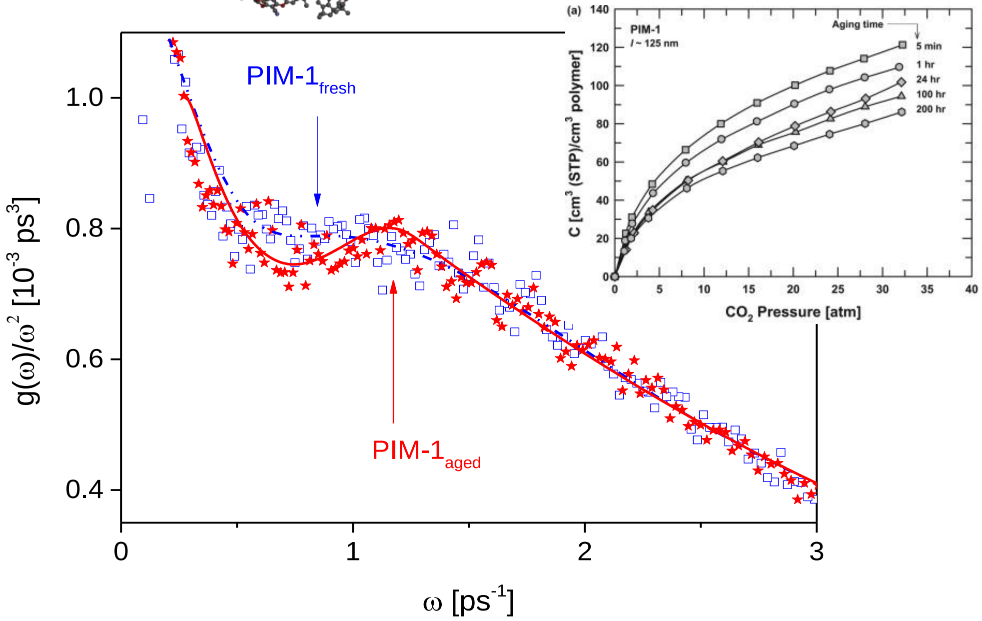


Novel Polymer **PIM-1**



Stiff PIM chains cause early solidification which leads to sponge-like structure that allows higher compressibility

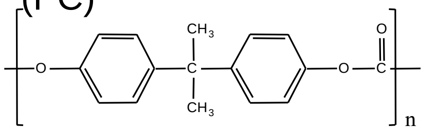




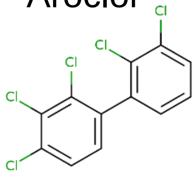
Phys. Chem. Chem. Phys 20, 1355 (2018), J. Mem. Sci. 537, 362 (2017), submitted

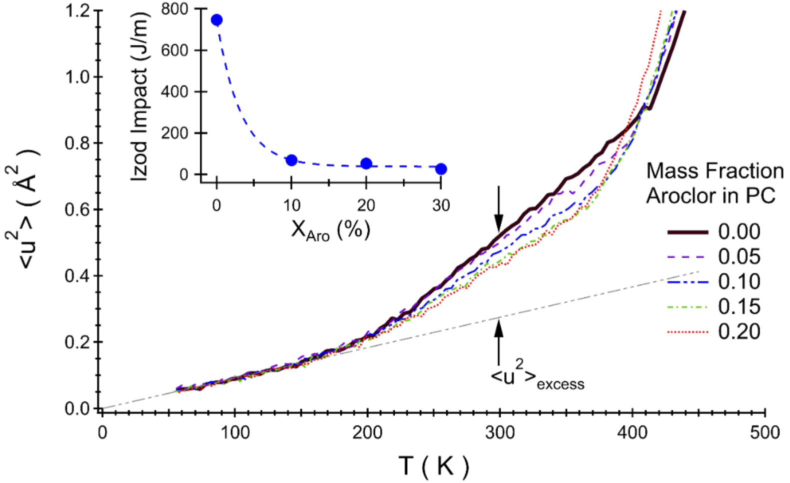
Sub-nano Relaxations and Toughness in Polymer Glasses

Polycarbonate (PC)

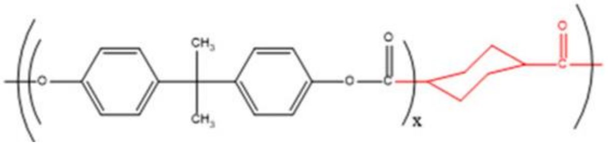


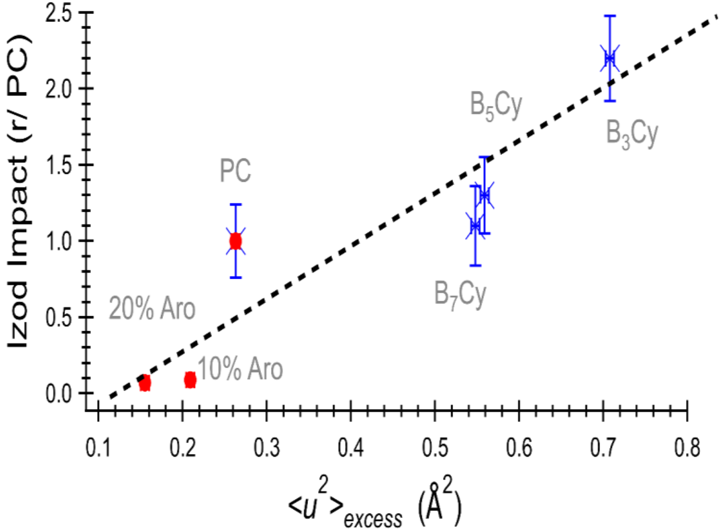
Aroclor





B_xCy: incorporate 1,4-cyclohexyl (Cy) links





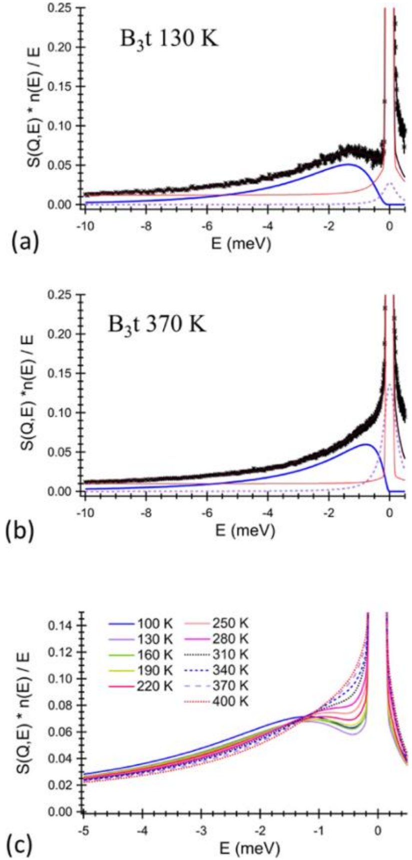
Mean Squared Displacement $<u^2>$

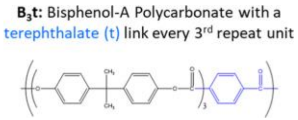
$$\frac{I(T)}{T(T=0)} = exp\left(-\frac{Q^2 < u^2 >}{3}\right)$$

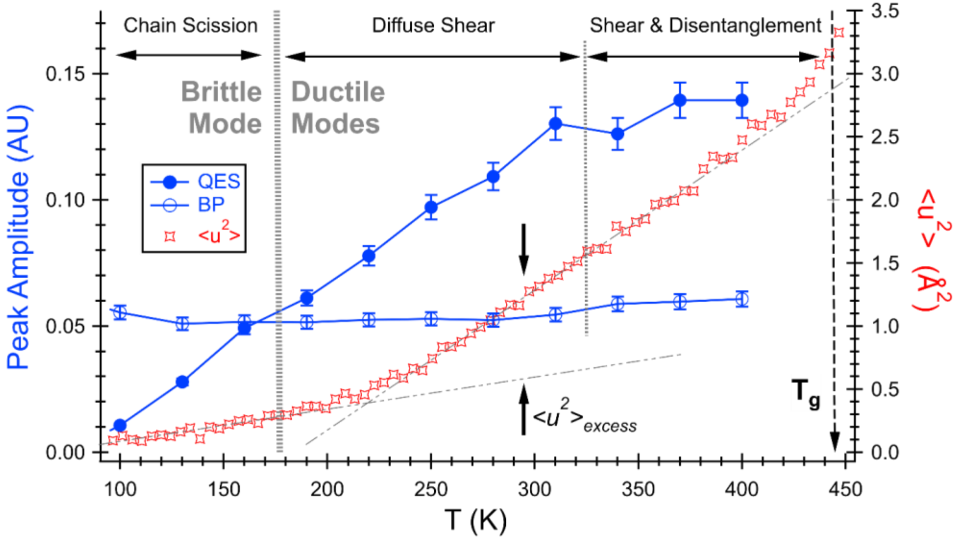
Excess MSD is a critical, nanoscale indicator of macroscopic toughness in PC glasses.

Macromolecules 2020, 53, 15, 6672

Sub-nano Relaxations and Toughness in Polymer Glasses





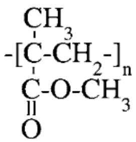


Onset of Excess MSD coincides both with crossover between the observed BP and QES dominated regions as well as the onset of Ductility and toughness above Brittle to Ductile transition.

Macromolecules 2021, 54, 5, 2518

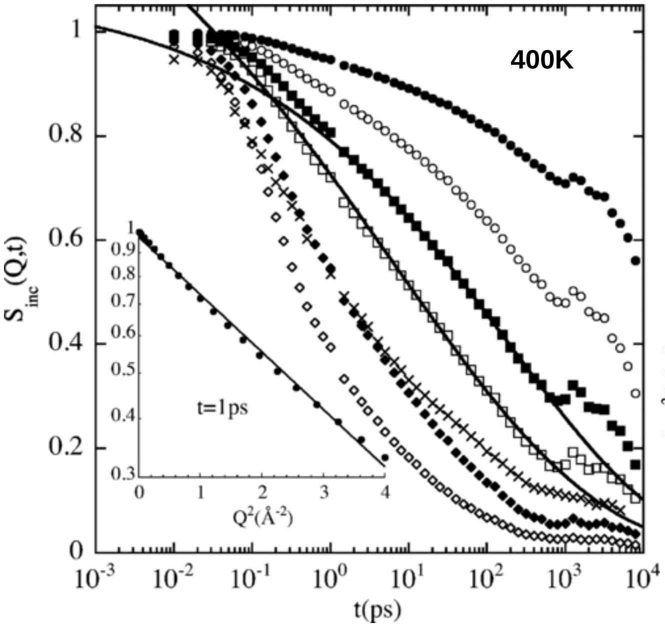
MD Simulations and NS

PMMA: Tg~400K

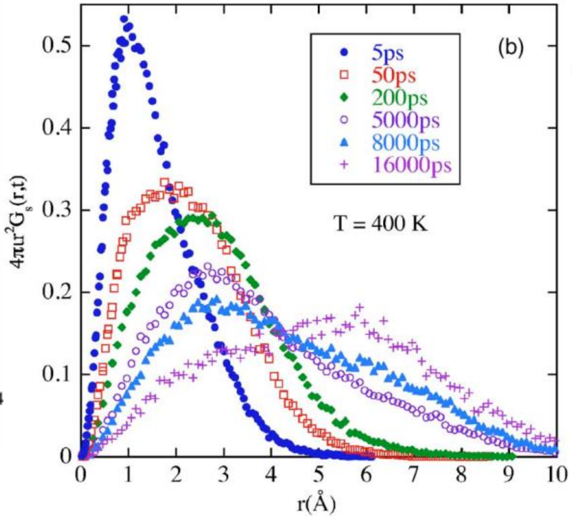


PEO: Tg~ 200K

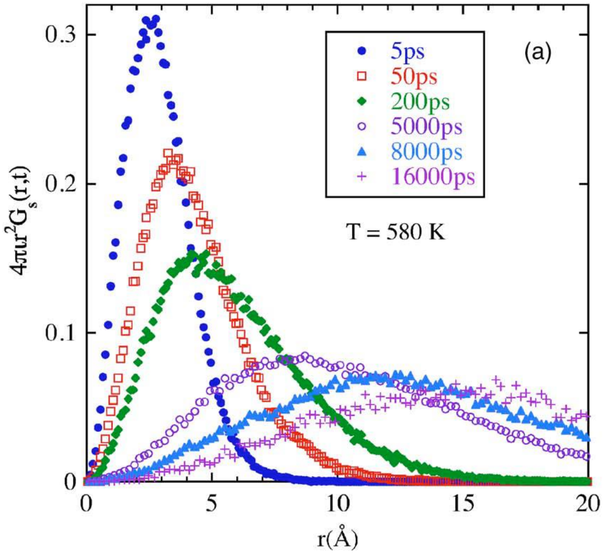
$-[CH_2-CH_2-O-]_n$



Relaxation of PEO chains –
extremely stretched

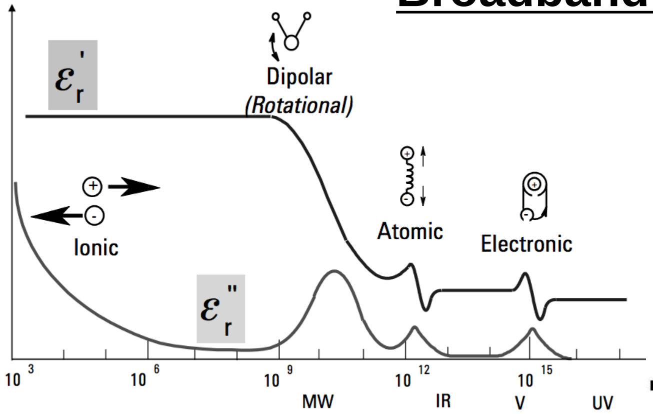


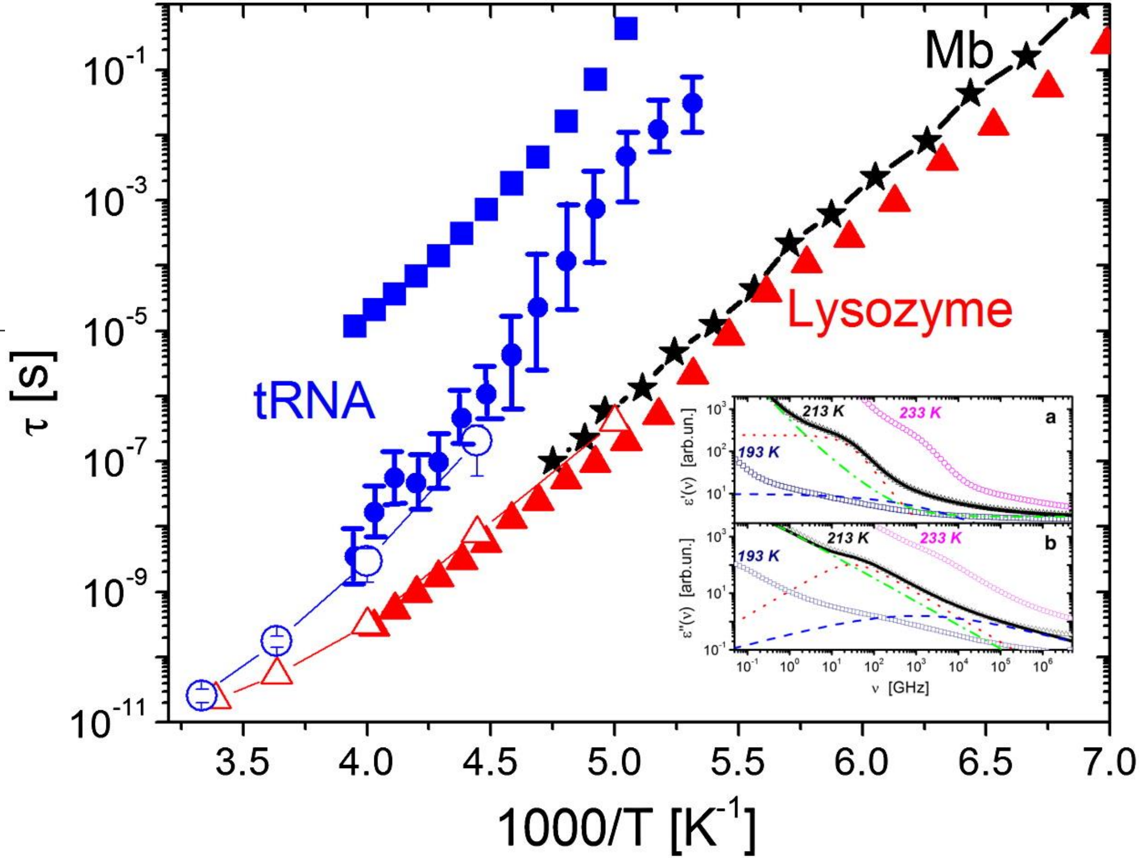
Additional peak –
PEO chains caged by PMMA



*PHYSICAL REVIEW E **72**, 031808 2005*

Broadband Dielectric Spectroscopy and NS





Biophysical Journal Volume 98 2010 1321–1326

Thank You!