The Influence of Environment on Polymer Mobility: Quasielastic Neutron Scattering on PEO/PMMA Blends

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Inma Peral, John Copley - time of flight at NIST
Jeff Lynn - Triple Axis at NIST

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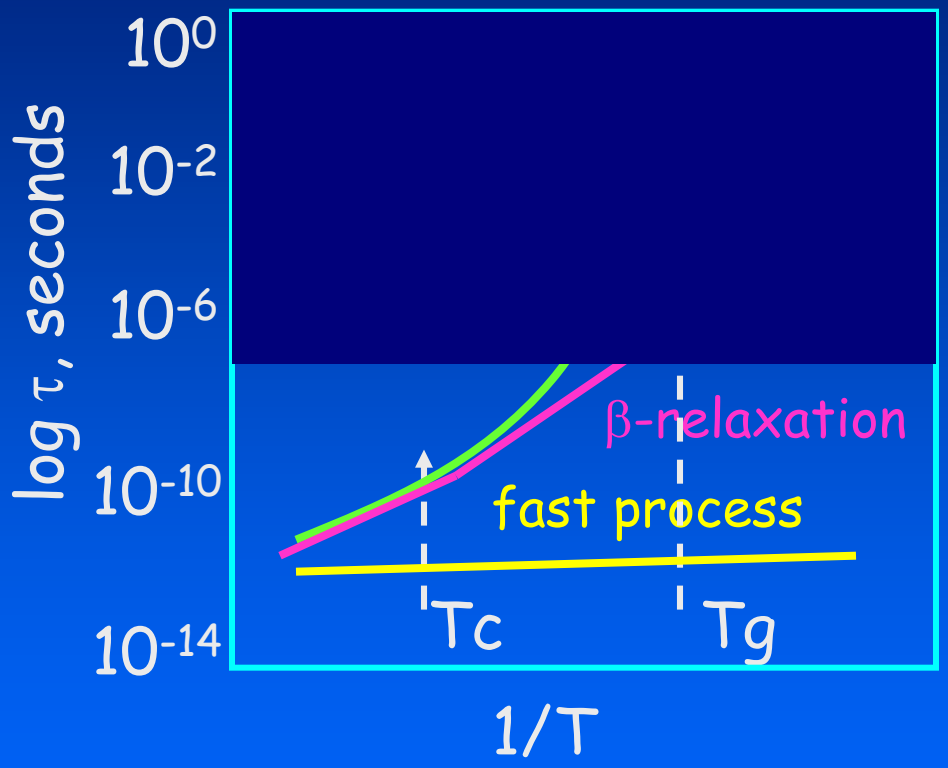
Structural dynamics of pure amorphous polymers

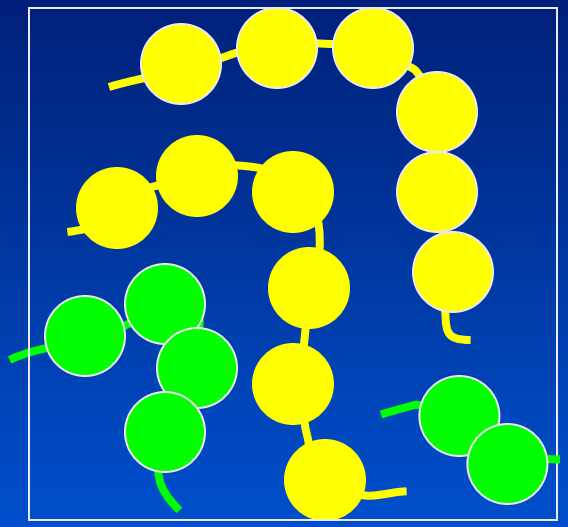


Important temperatures:
Tg: α-relaxation frozen;
Tc: α–β merge

Origin of distinct component mobility

Effective local concentration different from X_{bulk}

How does this arise?



$X_{bulk} = 0.5$

Concentration fluctuations

χ & MW, ΔTg

Length scale: varies ~10 nm?, different for high Tg, low Tg components.

Kumar, et al J. Chem. Phys. 105, 3777 (1996).

Chain connectivity

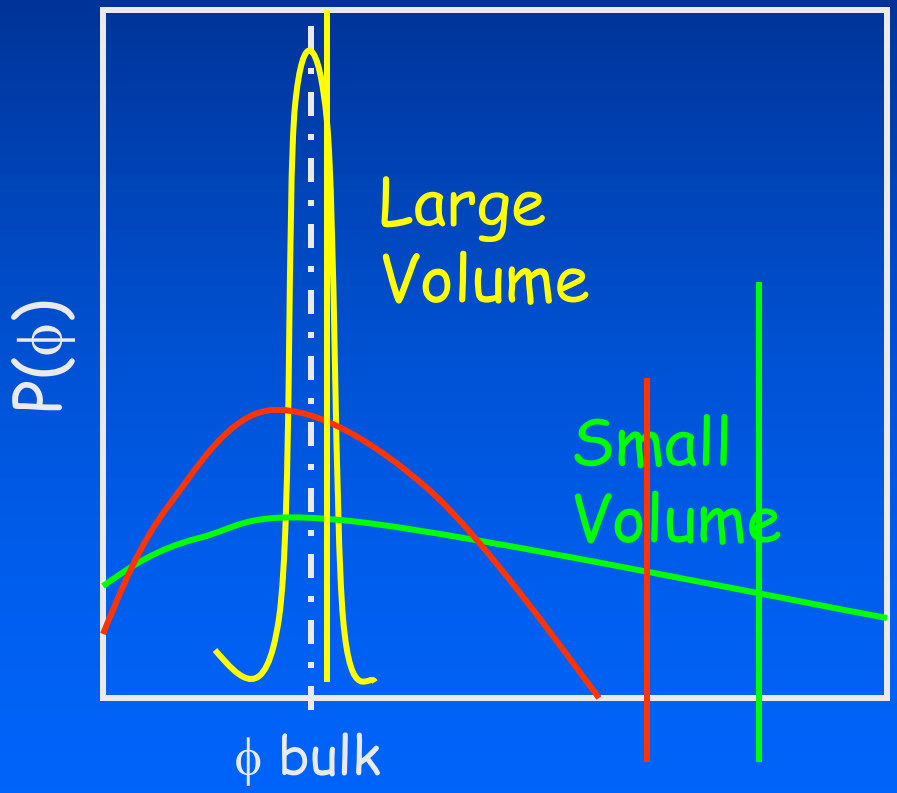
$\phi_{eff} = \phi_s + (1-\phi_s)X_{bulk}$

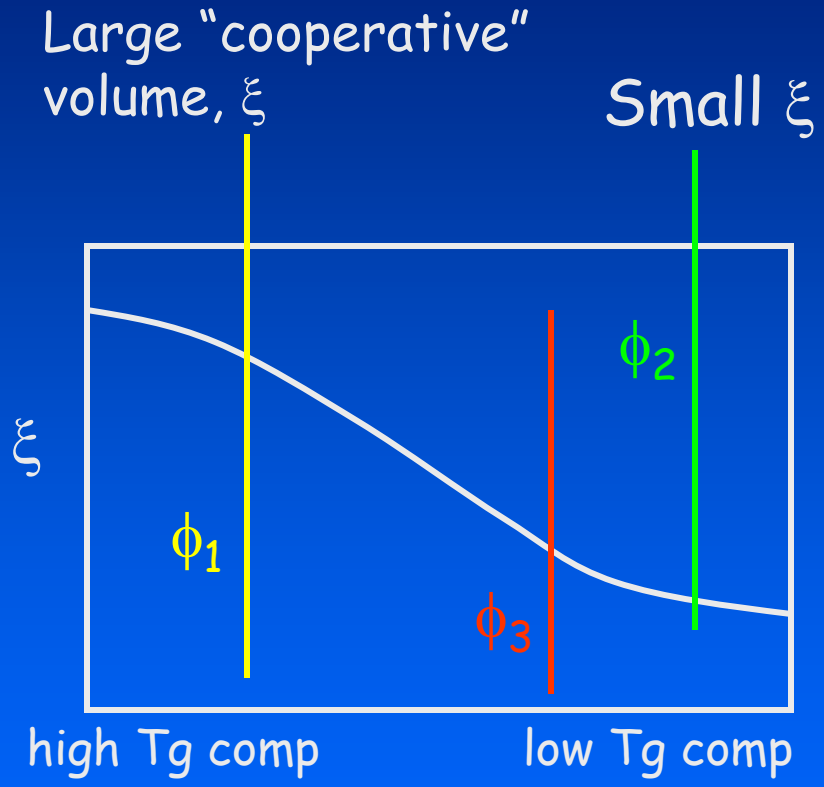
Length scale: Kuhn length temp & comp independent.

Lodge & McLeish, Macromolecules, 33, 5278 (2000)

Concentration fluctuations

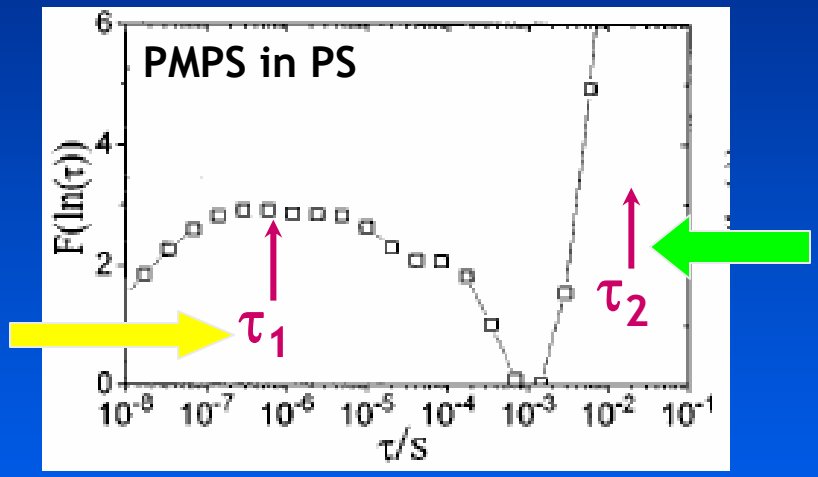
Probability distribution of local compositions





Bimodal distributions

eg. Dielectric Spectroscopy

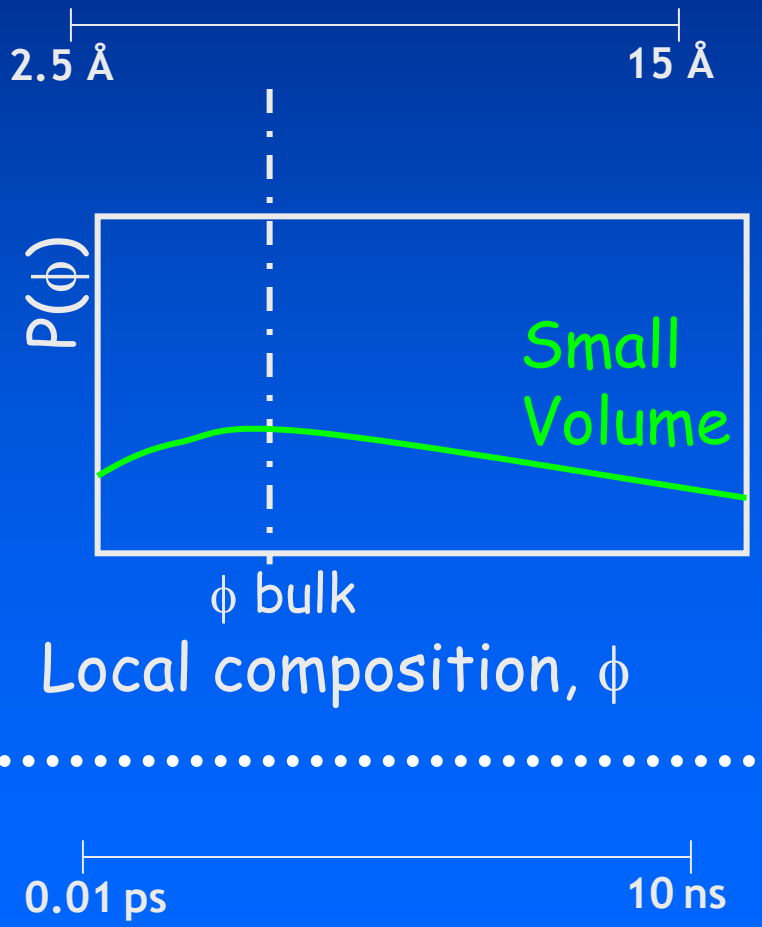


τ_1: low Tg component-rich regions, small P(ϕ), small ξ

τ_2: regions of $\phi \approx \phi_{bulk}$, high P(ϕ), large ξ

Kumar, et al J. Chem. Phys. 105, 3777 (1996).

Quasi-Elastic Neutron Scattering: "in the green"



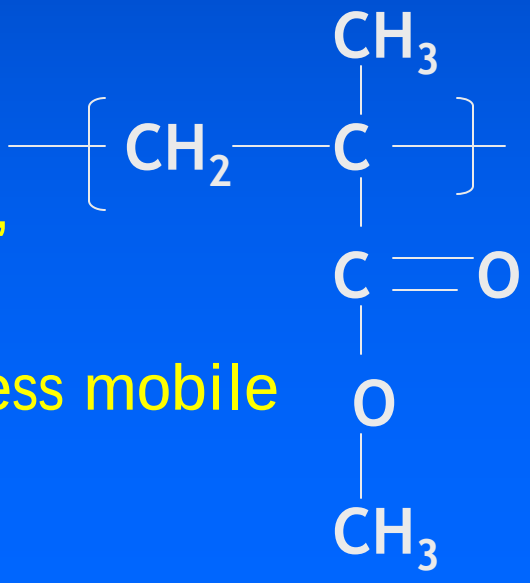
Target System: PEO/PMMA

PEO "poly ethylene oxide"

T_g ~ 220 K, more mobile

PMMA

"poly methyl methacrylate"



T_g ~ 400 K, less mobile

1. Large ΔTg and $\chi \approx 0$

Concentration fluctuations

2. Interactions independent of T

Distribution of local concentrations a constant

3. Different component behavior

Highlight concentration fluctuations

measurements

backscattering

- hPMMA – HFBS at NIST
  "self" motion of PMMA
- hPMMA/dPEO – HFBS at NIST
  self motion of PMMA in blend

Time-of-flight

- hPEO – DCS at NIST
  self motion of PEO
- dPMMA/hPEO – DCS at NIST
  self motion of PEO in blend

Neutron spin echo

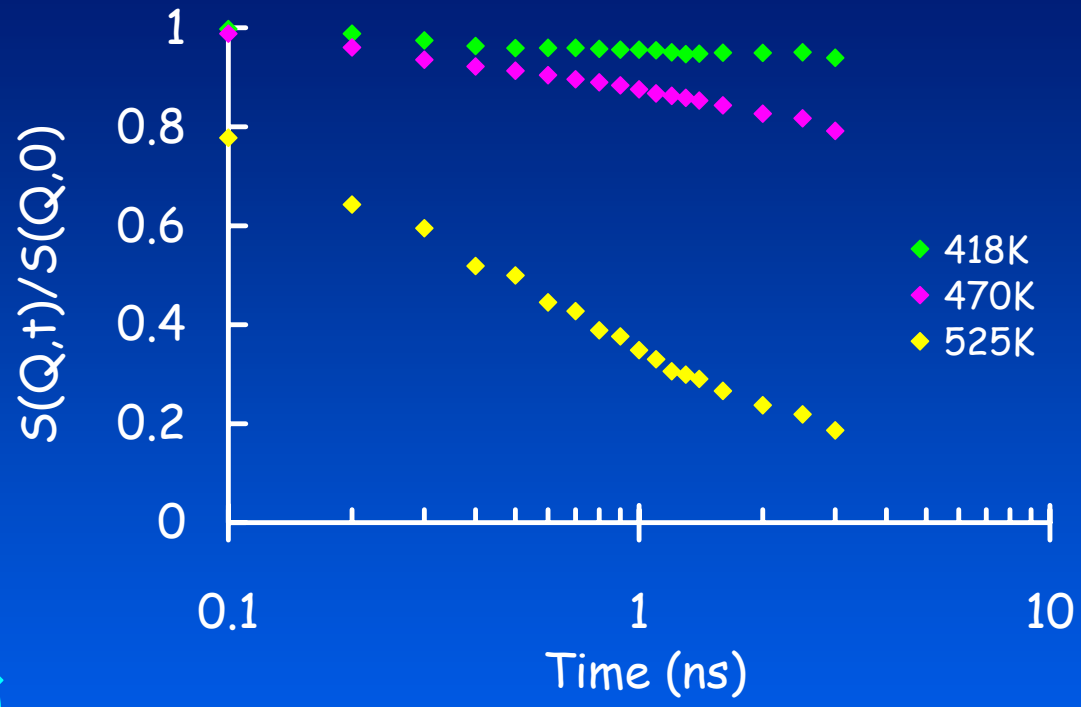
- dPMMA/DPEO – NSE at NIST
  collective motion of blend
- MD simulations – pure PEO, pure PMMA, blend underway…

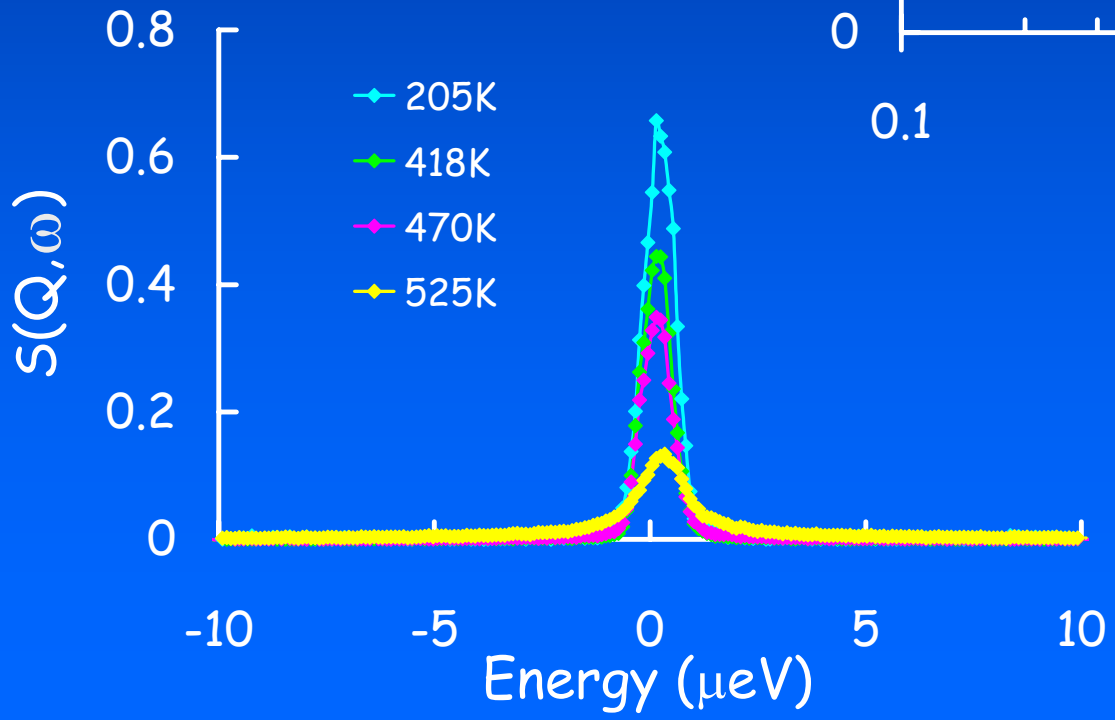
Data treatment

S(Q,t)

Fourier transform

S(Q,ω)



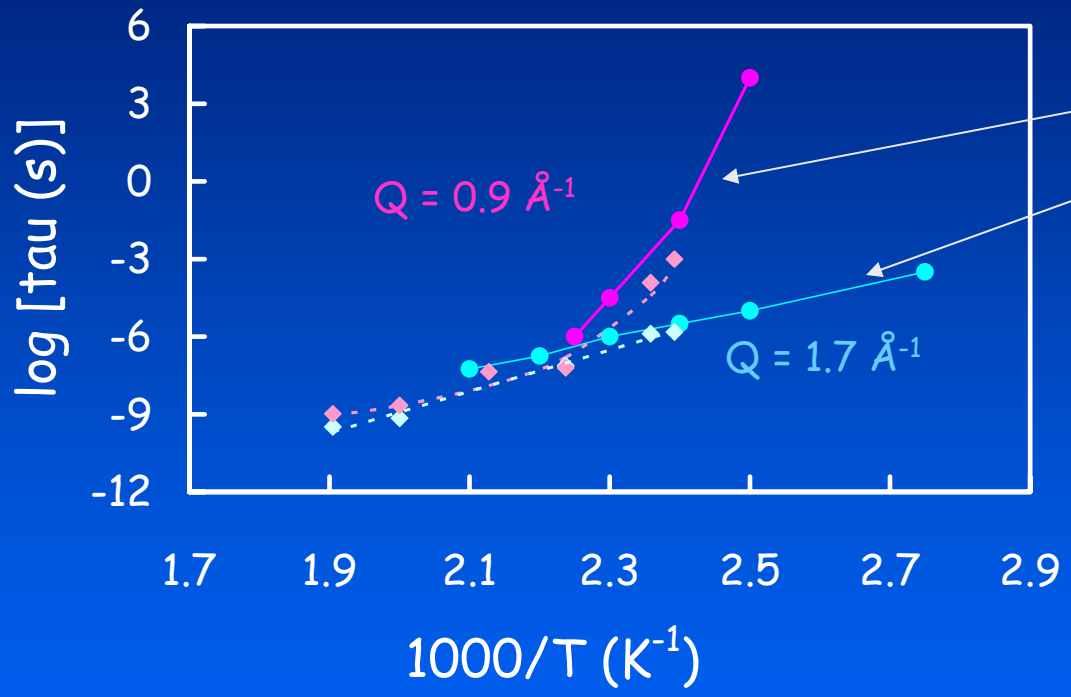


KWW Equation

$$\frac{S(Q,t)}{S(Q,0)} = A\exp\left(-\left(\frac{t}{\tau_{KWW}}\right)^{\beta}\right)$$

τ, β

Verification: PMMA

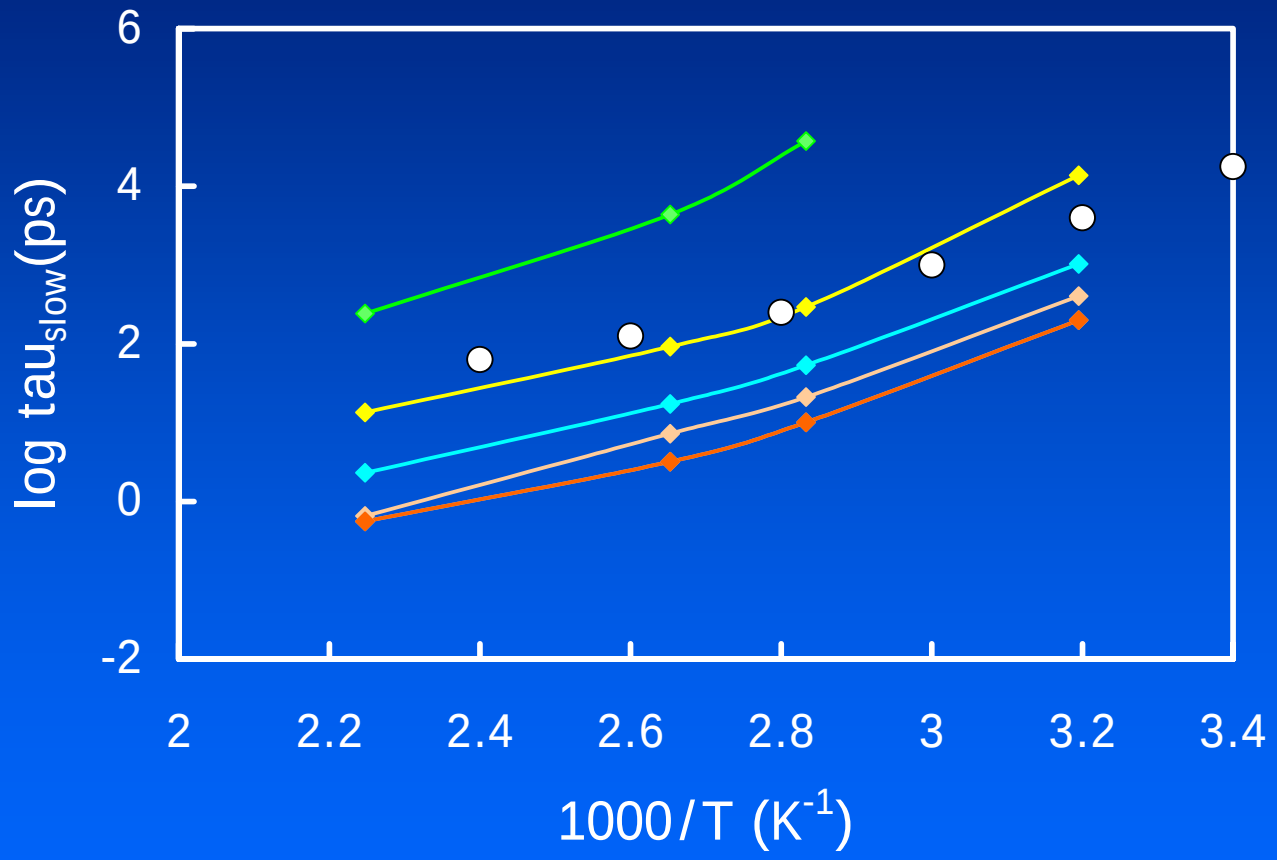


dielectric

Dielectric + neutrons for pure PMMA

PMMA in blend – no other measurements available.

Verification: PEO



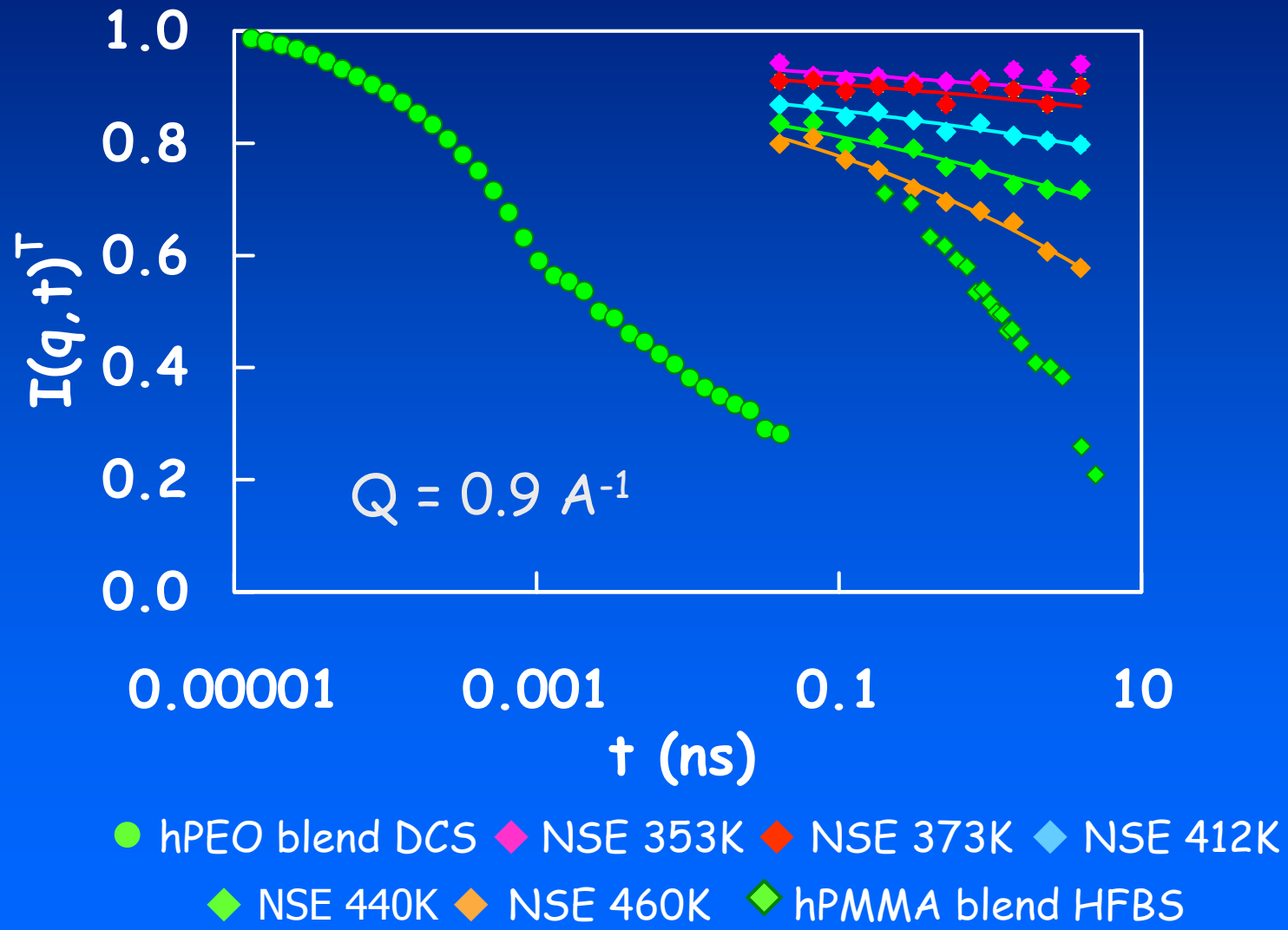
NMR + neutrons for PEO in blend

- NMR data

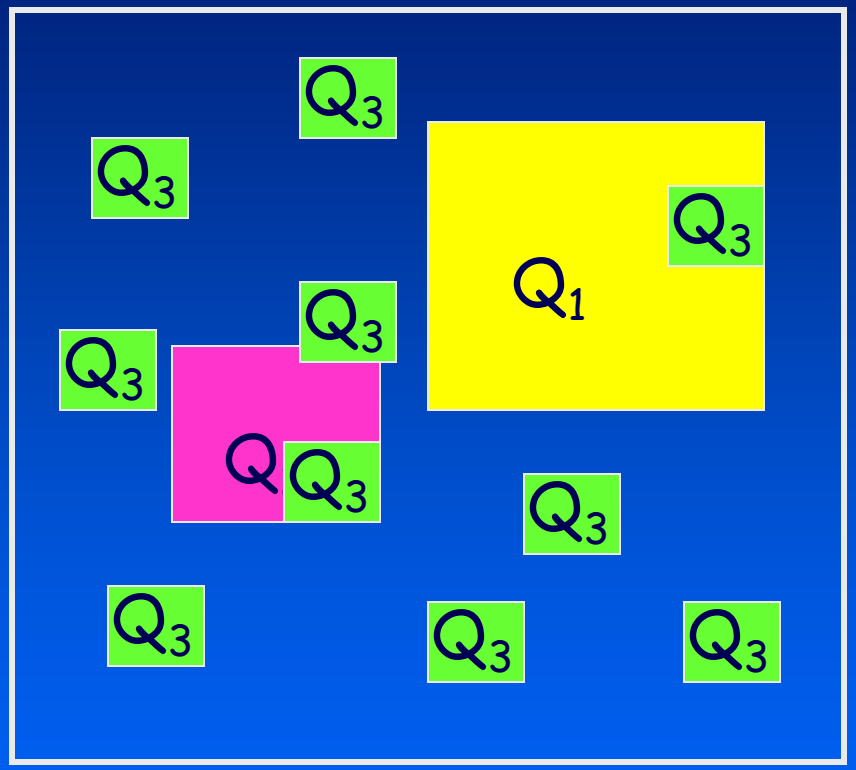
Q=0.724 Å^{-1}
Q=1.050 Å^{-1}
Q=1.354 Å^{-1}
Q=1.655 Å^{-1}
Q=1.955 Å^{-1}

Lutz et al., Macromolecules (2003)

Comparison of component mobilities



Potential advantages of neutrons for this problem



Macroscopic sample

Controllable selection

↓

"local composition" length scale

"Relevant length scale…."

NS Length scales

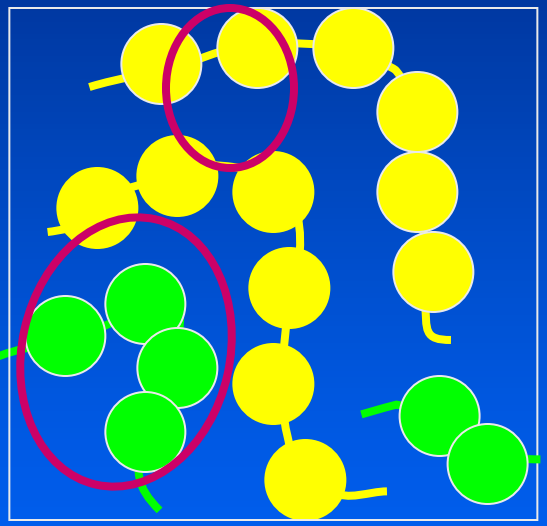
↓

Large range of local ϕ

"Importance of concentration fluctuations"

Mobility of a "local" volume

1. *CONCENTRATION FLUCTUATIONS:*
   different local compositions ϕ
   - ⇨ $\phi \approx \phi_{bulk}$
   - ⇨ $\phi \approx 1$
   - ⇨ **distribution = f(Q)**
2. *DYNAMIC HETEROGENEITY*:
   same ϕ - different mobility



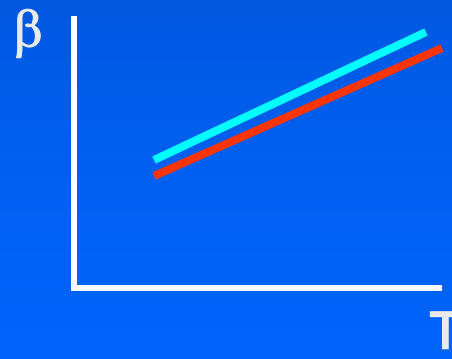
Only local compositions mobile within the QENS timescale contribute to the average!

Impact of Concentration Fluctuations

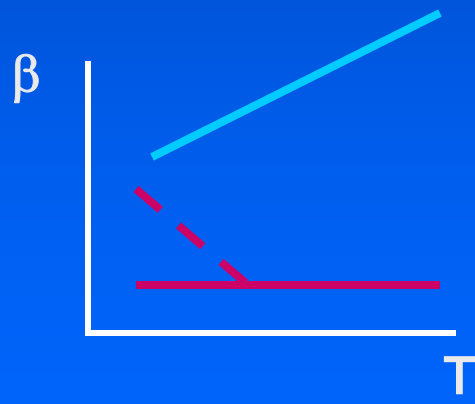
$$I(q,t) = \exp[-(t/\tau)^{\beta}] = \int_{-\infty}^{+\infty} f(\ln\tau)\exp(-t/\tau)d(\ln\tau)$$

Stretching exponent from KWW equation

Dynamic heterogeneity



Concentration fluctuations

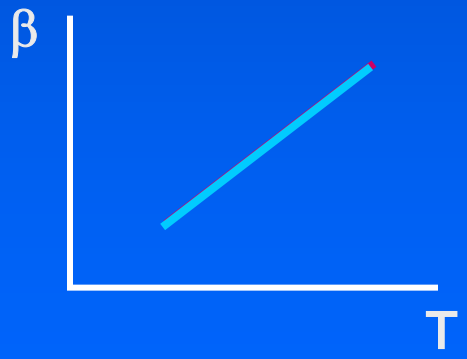


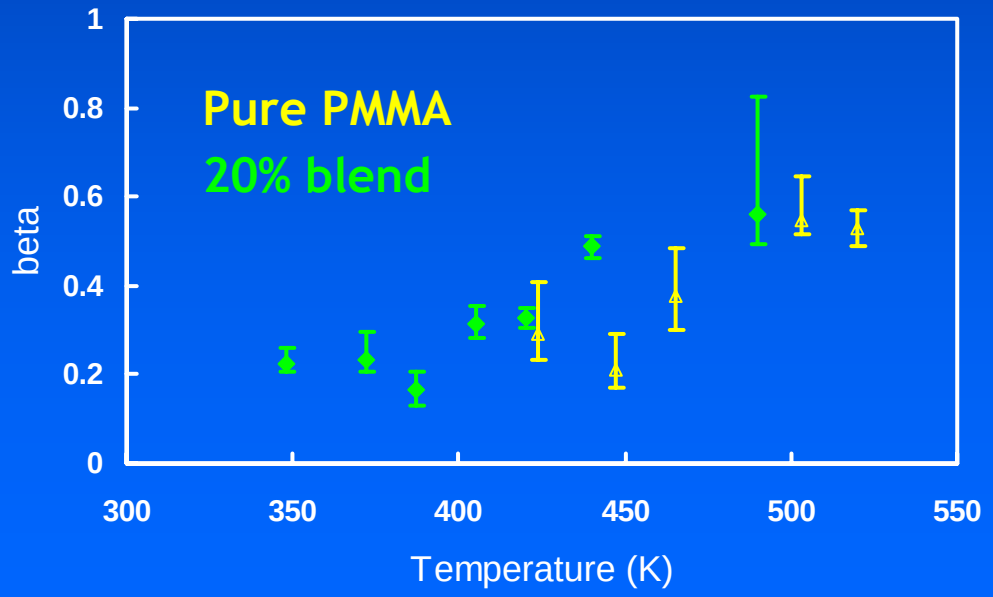
"Slow" component - PMMA

$$I(q,t) = \exp[-(t/\tau)^{\beta}] = \int_{-\infty}^{+\infty} f(\ln\tau)\exp(-t/\tau)d(\ln\tau)$$

Stretching exponent from KWW equation

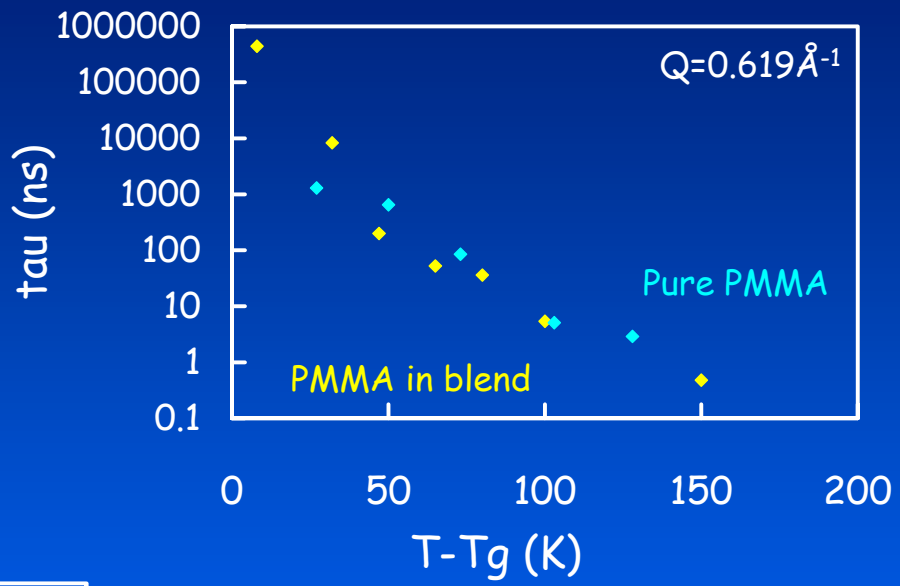
Dynamic heterogeneity

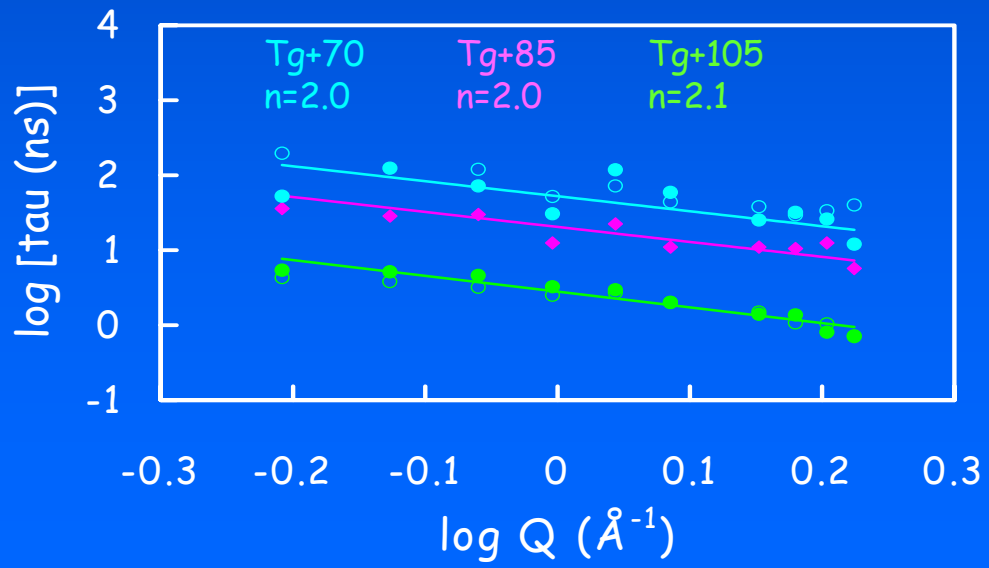




Temperature dependence

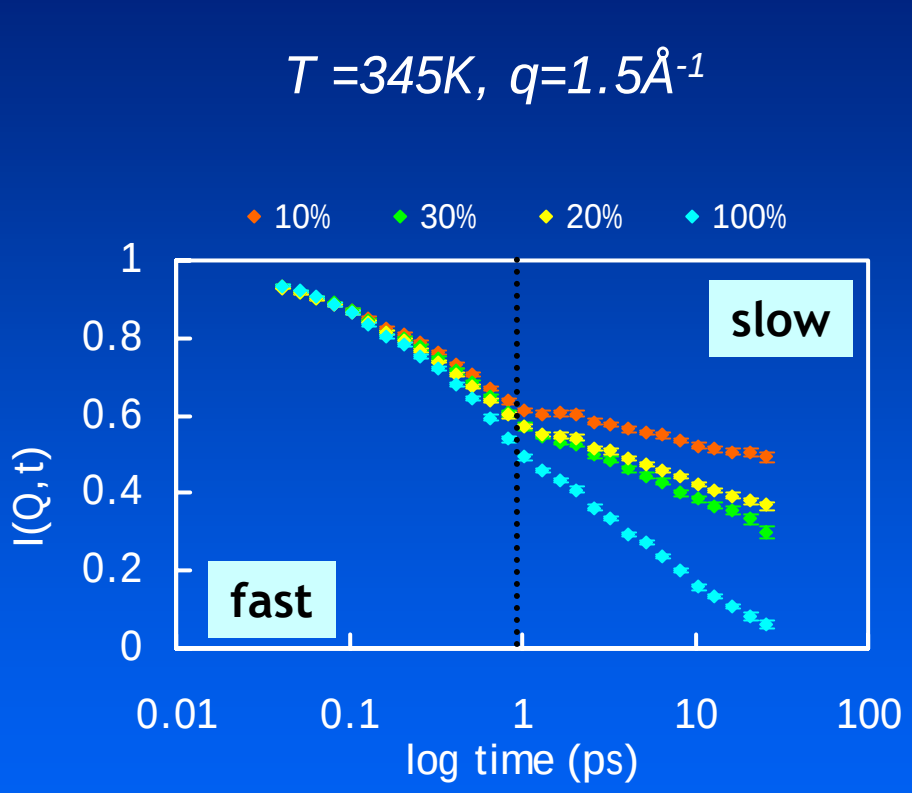
Result is a simple temperature scaling……



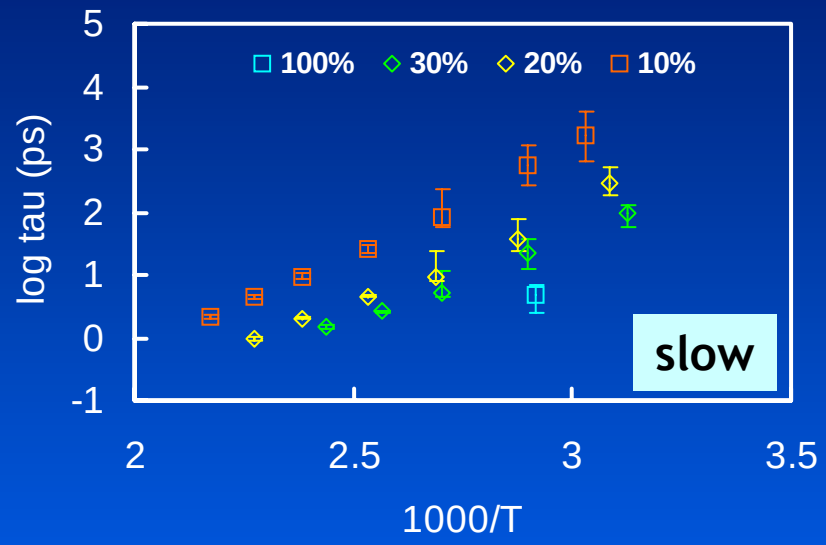


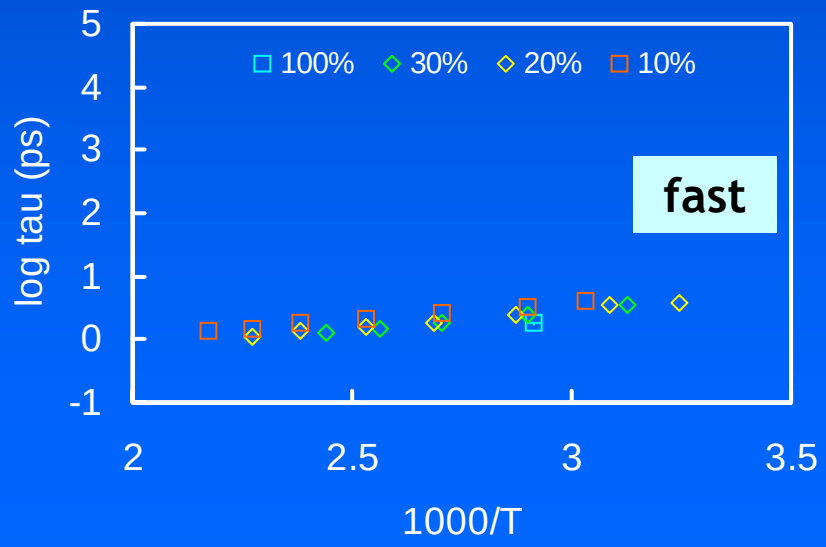
Same behavior at same distance above Tg…..

"Fast" component - PEO

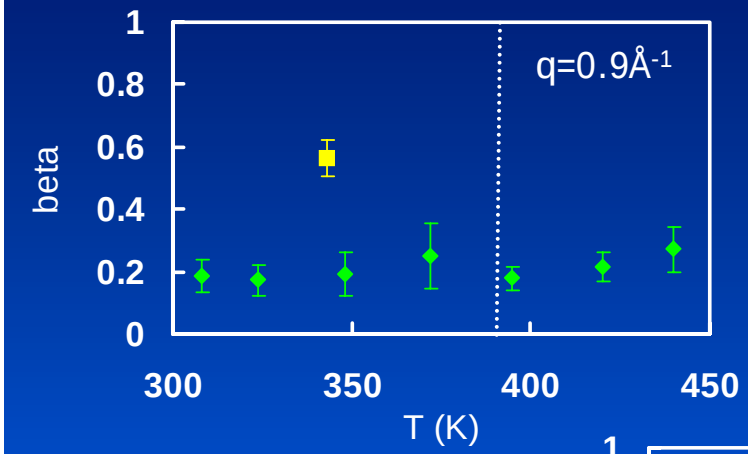


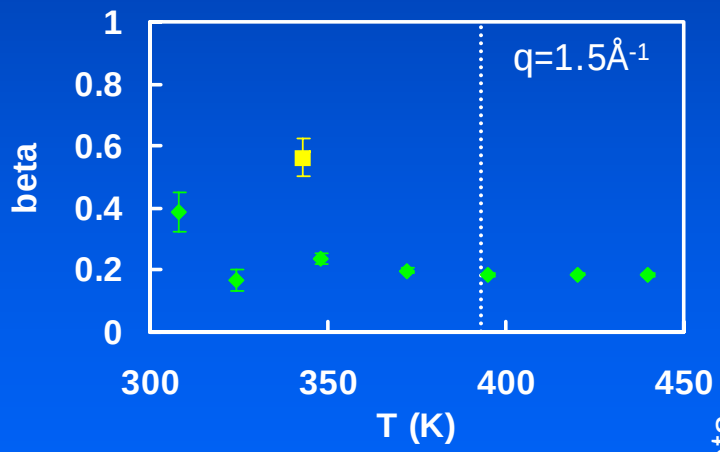
Bimodal?



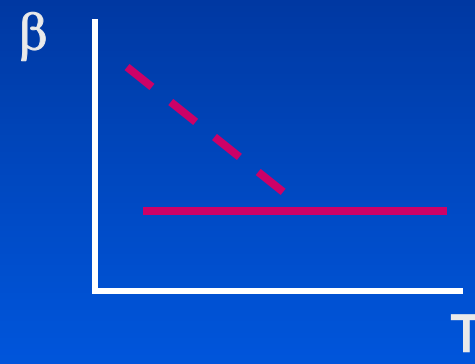


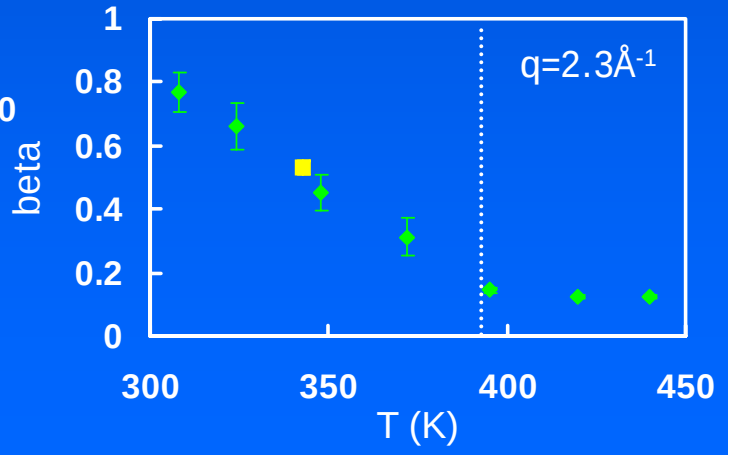
Mobility distribution - PEO





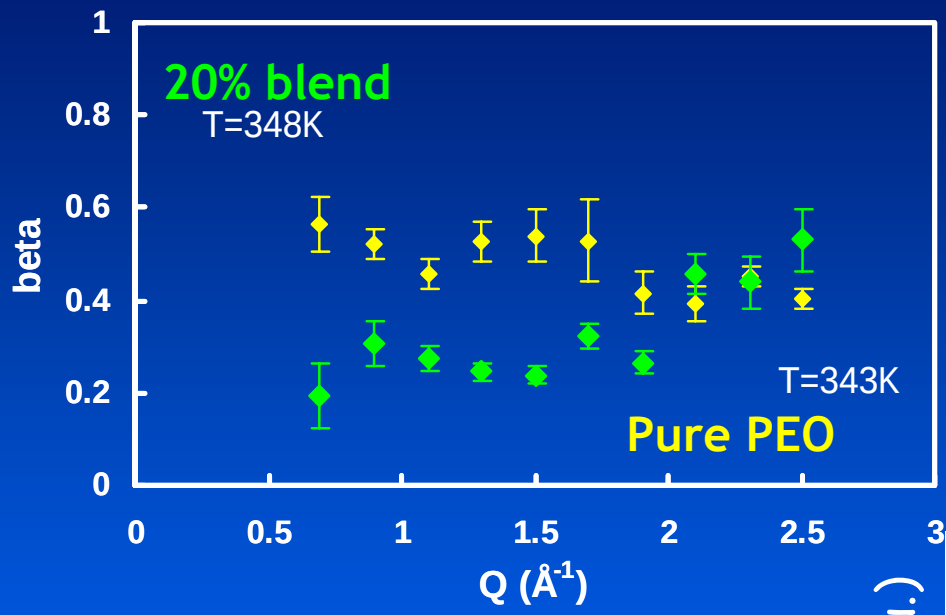
✓ concentration fluctuation driven dynamics



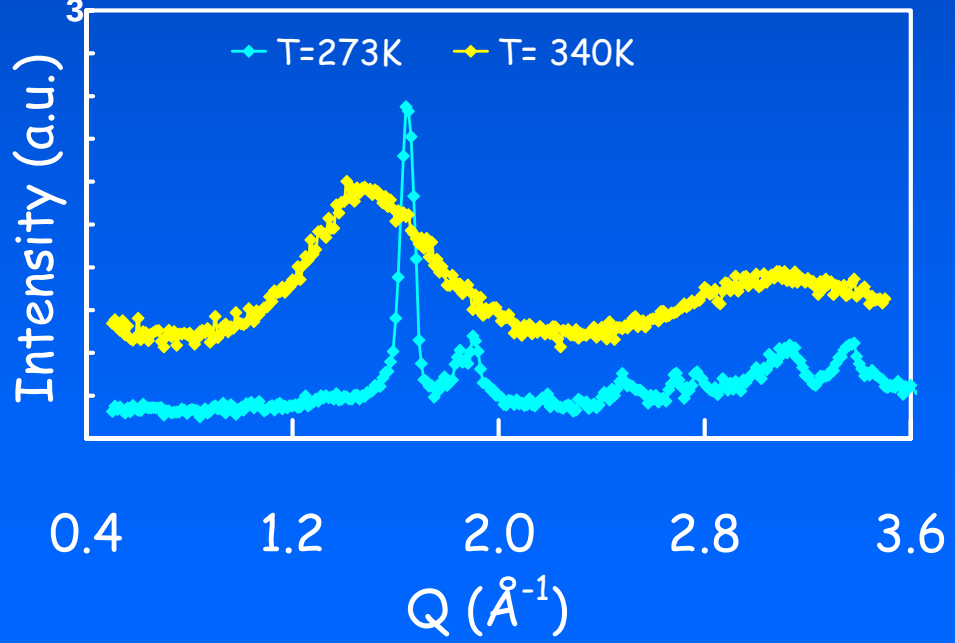


- Pure PEO
- 20% blend

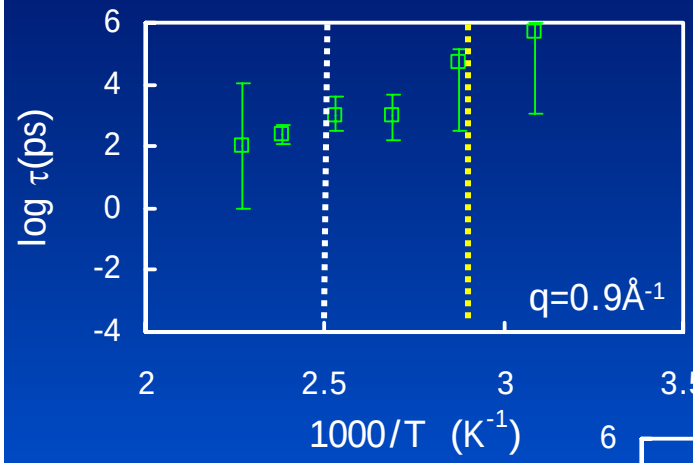
Relevant length scale for local compositions

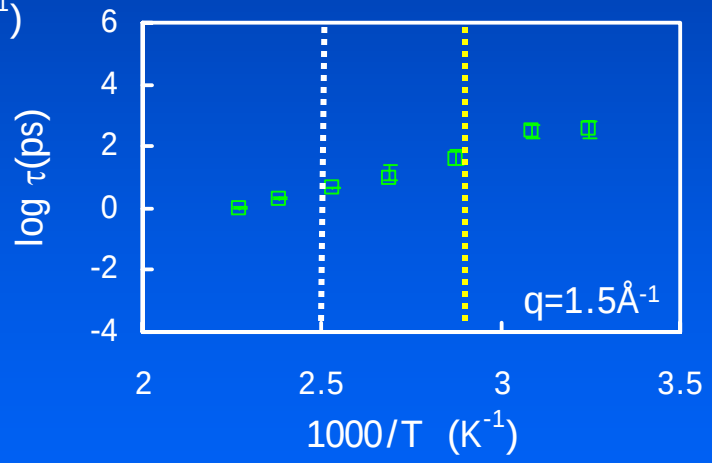


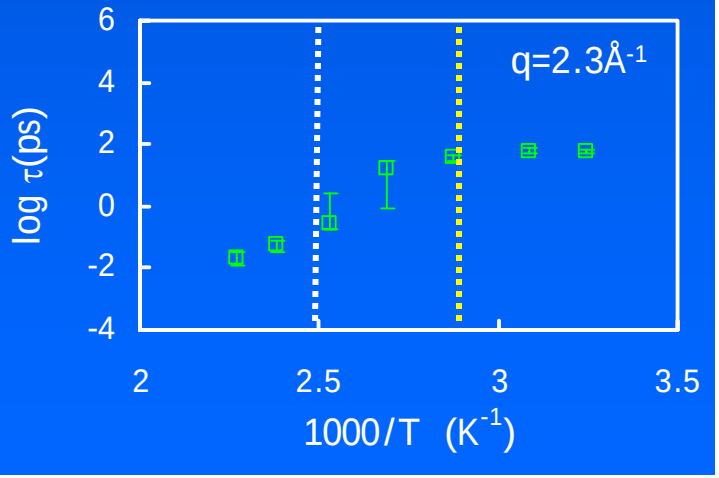
More local environments in blend through peak in S(Q)



Relaxation Times





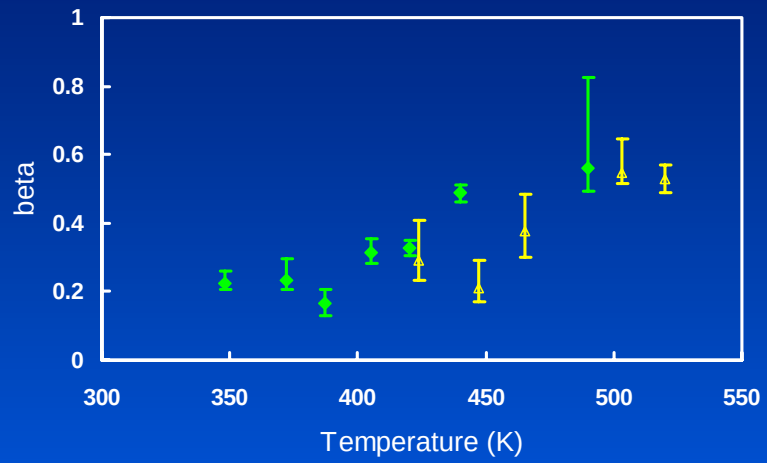


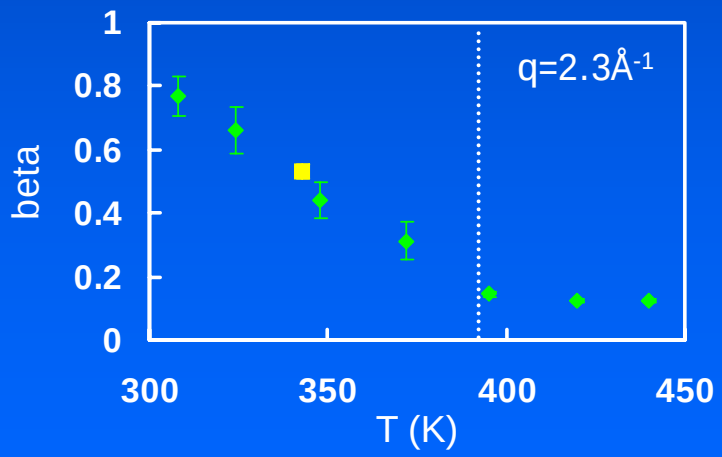
Tg PMMA

Tg blend

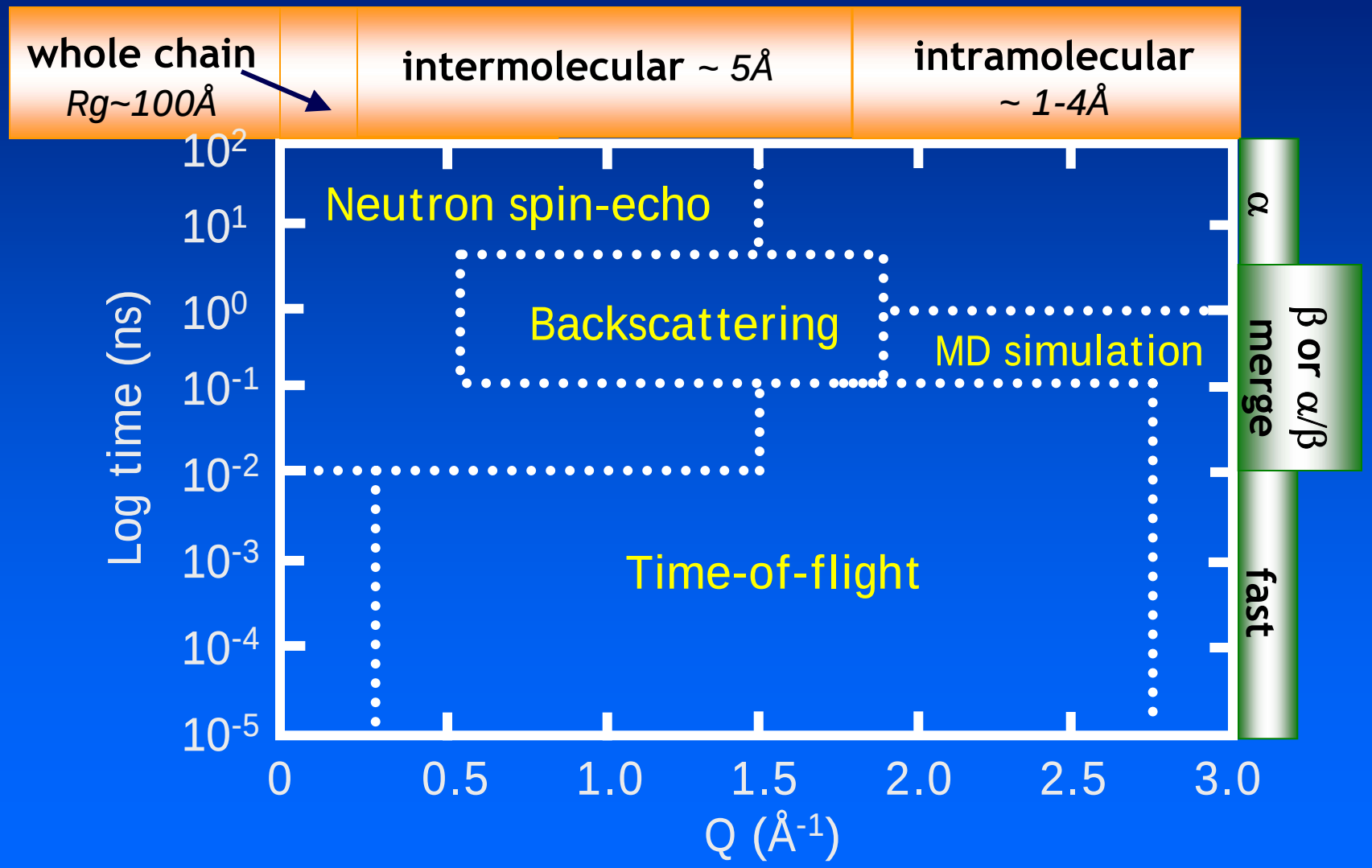
Summary

- PMMA: dynamics not sensitive to variations in local composition.
- PEO: concentration fluctuations important.
- Spatial scales less than peak in S(Q) bias towards PEO.





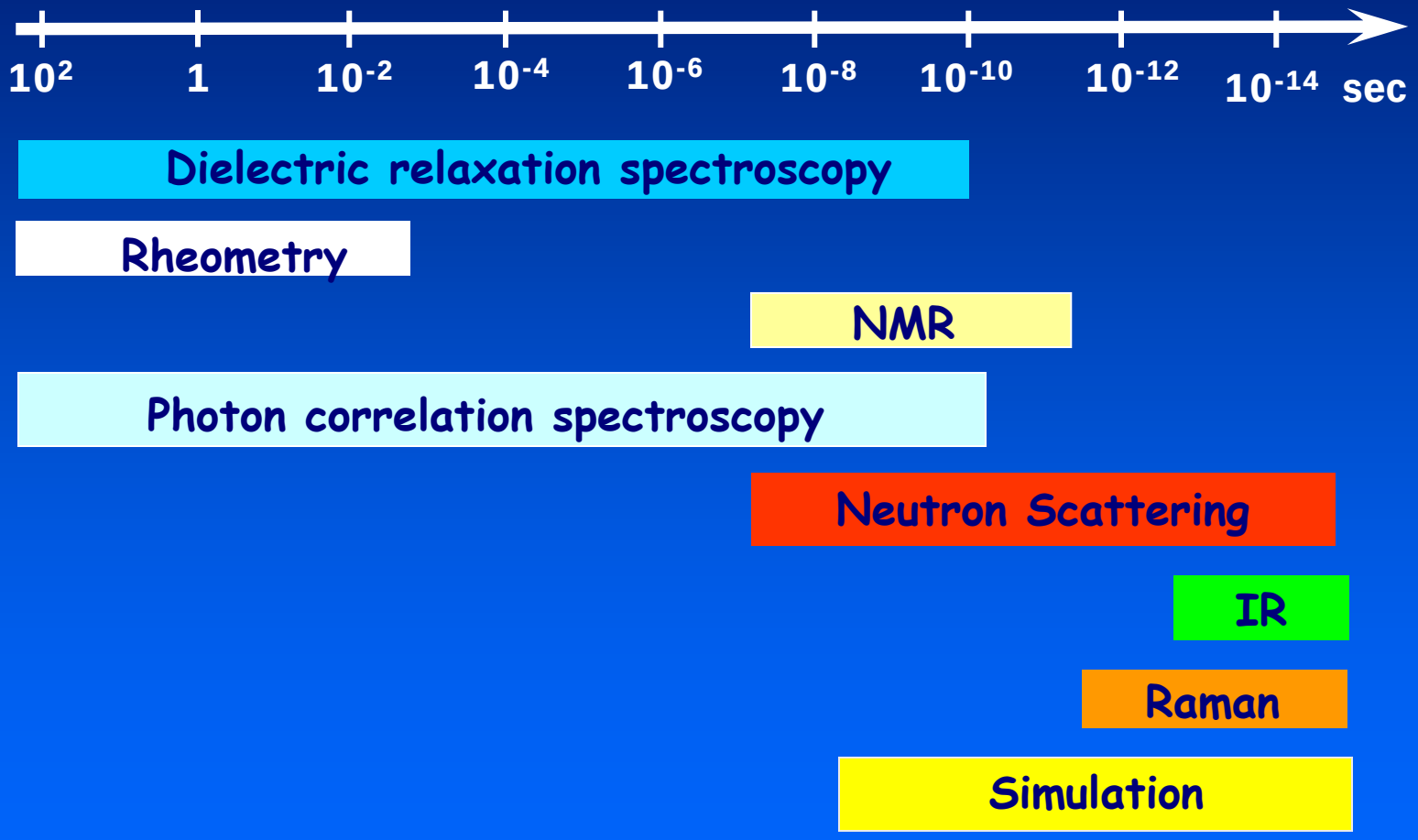
Time & Spatial Scales of Neutrons



Issues in miscible blend dynamics

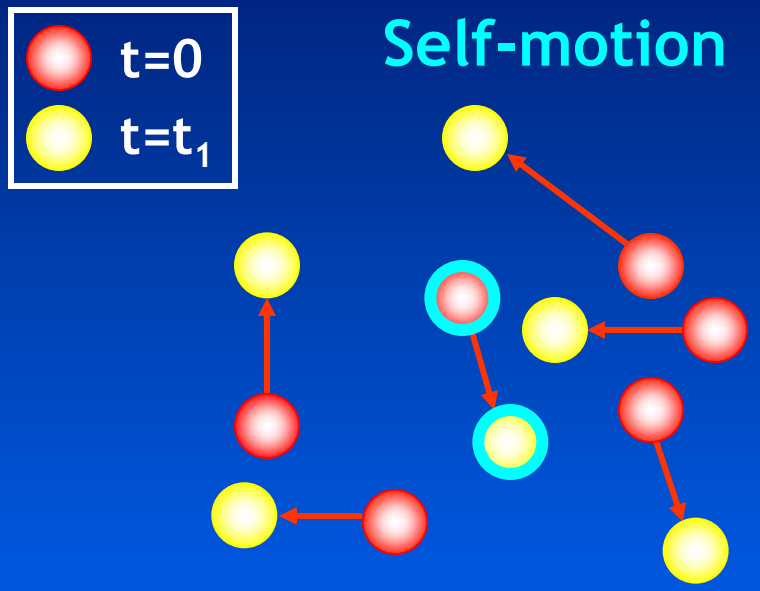
- Importance of concentration fluctuations….
- Relevant length scale for local compositions…
- Asymmetry of changes…
- Other contributions to local compositions….
- Temperature dependence….

Techniques to Explore Dynamics



Experimental Probe: QENS

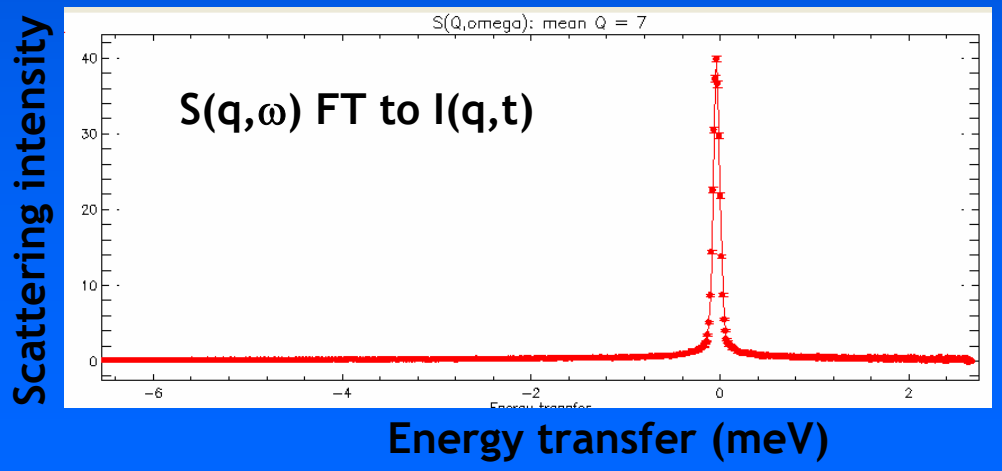
DCS, NG-4 at NIST



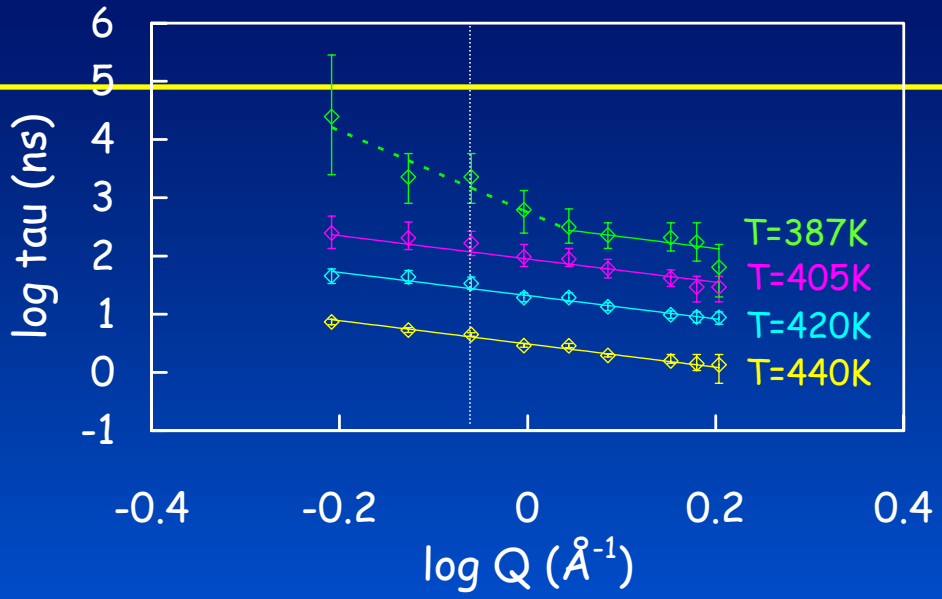
hPEO

+

dPMMA



KWW fit parameters - Q dependence of $\tau \propto Q^{-n}$

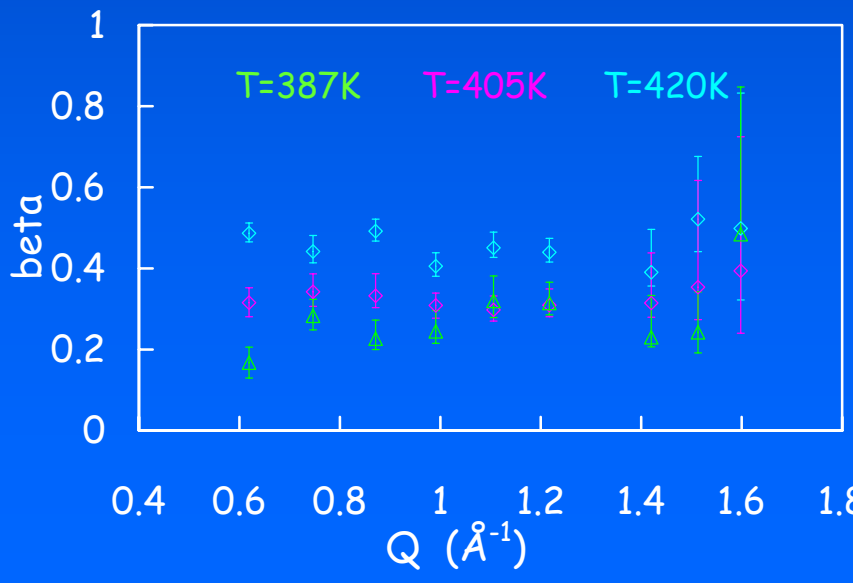


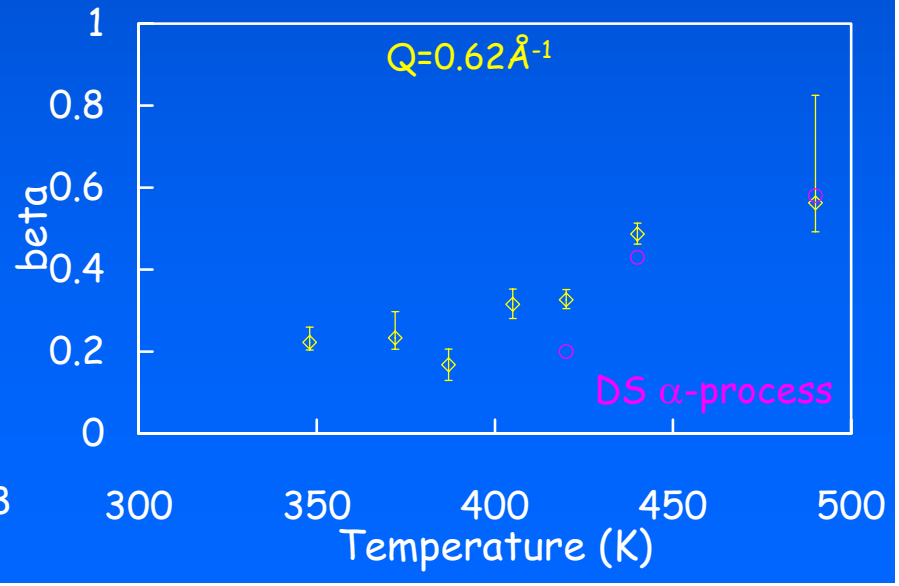
- At T ≥ 1.17 Tg : n = 2 (non-Gaussian*, heterogeneous**)
- At T < 1.17 Tg : n = 2/β (Gaussian*, homogeneous**)

* Colmenero et al., Phys.Rev.Lett. 1992

** Colmenero et al., J.Phys.:Cond. Matt. 1999

Stretching Exponent, β



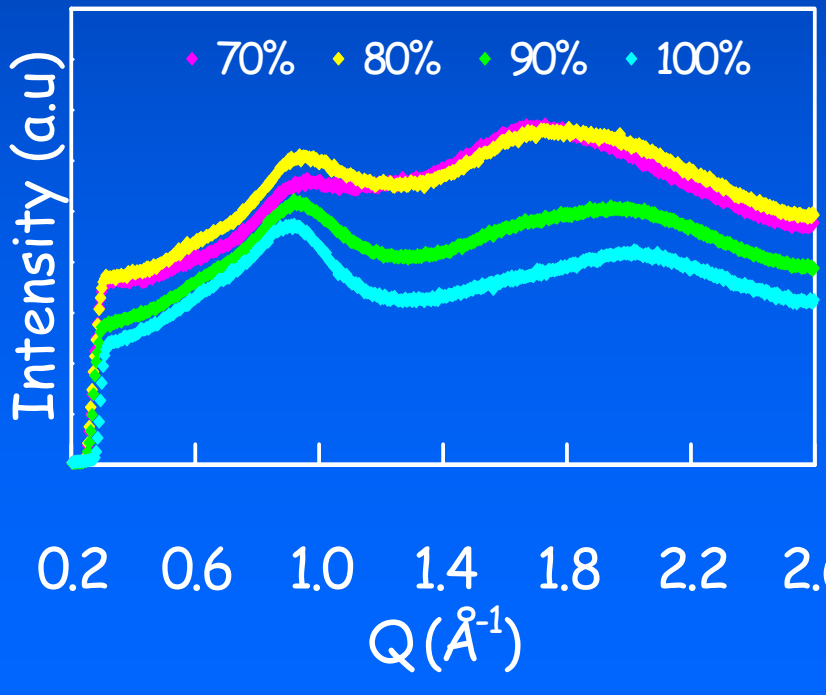


Static Structure

- Triple-axis spectrometer BT7 at NIST
  - **Ein = Eout measures S(Q,0)**
  - **accessible Q-range= 0.5-4.0 Å^{-1}**

→ **Preferred packing distances**

d_8PMMA and d_8PMMA/ d_4PEO blends



d_4PEO