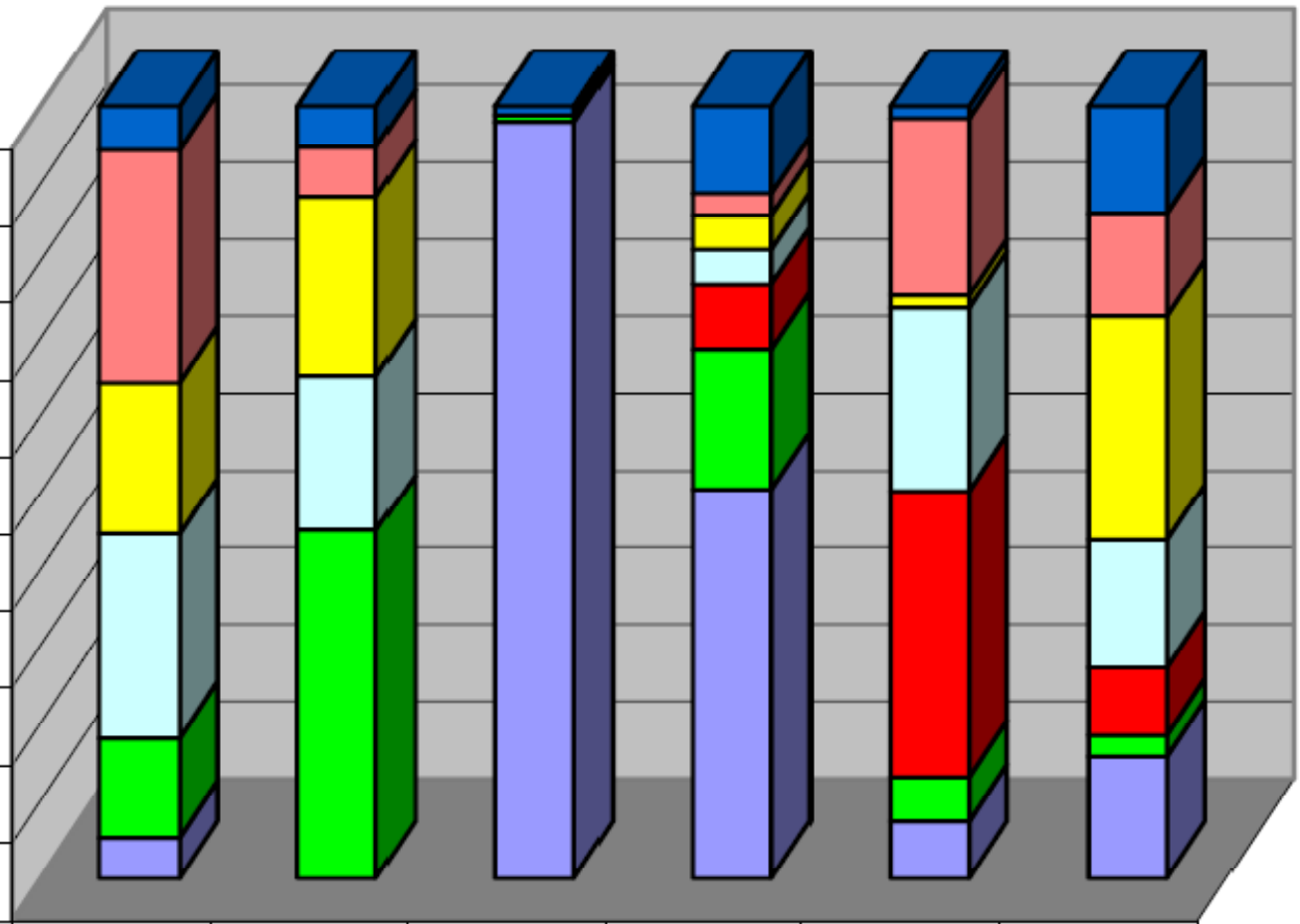


What can be done using HFBS?

Madhusudan Tyagi
NIST Center for Neutron Research

Beam Time

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%



	SANS	USANS	SPINS	DCS	HFBS	NSE
Instrument development	6%	5%	1%	11%	2%	14%
Biology	30%	6%	0%	3%	23%	13%
Complex fluids	20%	23%	0%	4%	2%	29%
Polymers	27%	20%	0%	4%	24%	17%
Small molecules	0%	0%	0%	8%	37%	9%
Materials science	13%	45%	1%	18%	6%	3%
Magnetism	5%	0%	98%	50%	7%	16%

Biology and Small Molecules....

2/5/2008

HFBS Tutorial

Center for Neutron Research

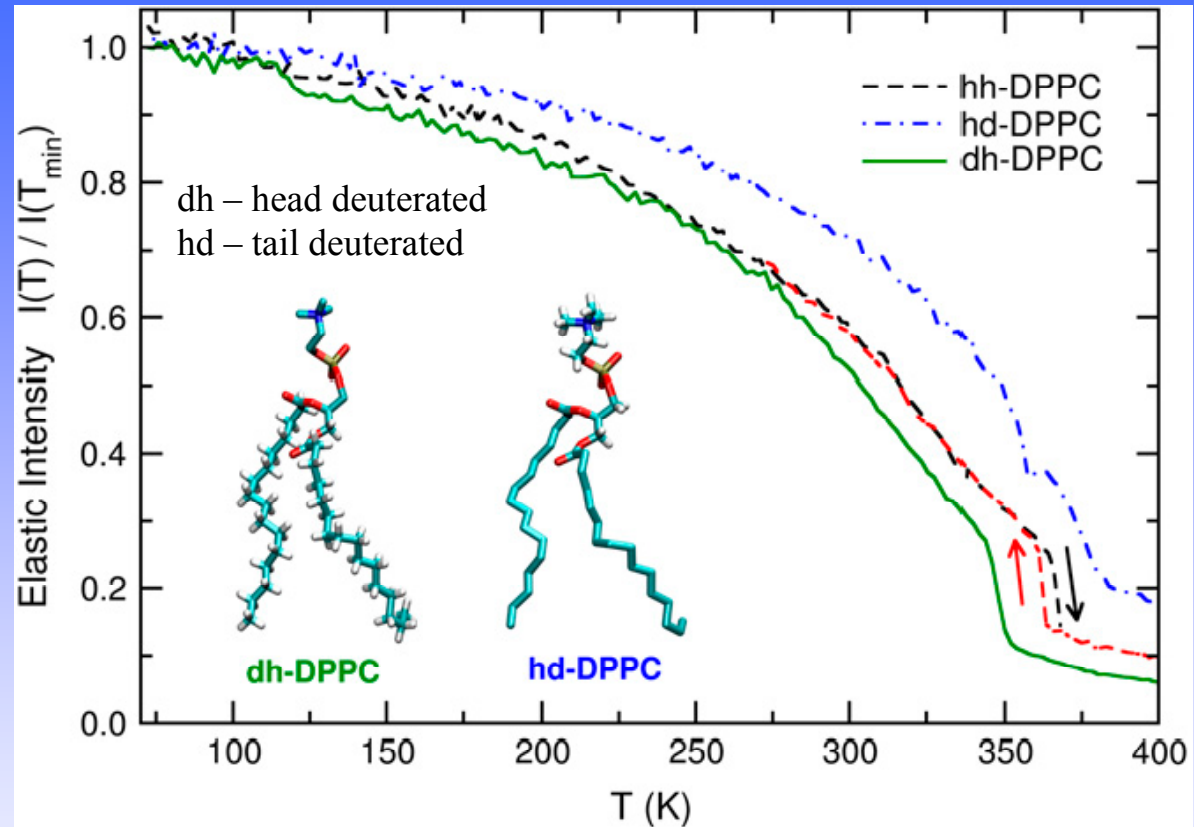


Melting in anhydrous lipid membranes

1,2-Dipalmitoyl-sn-glycero-3-phosphocholine (hh-DPPC)

Mechanism important as a wide variety of organisms can survive in anhydrous condition for a long period!

Melting from gel-like solid phase to liquid phase

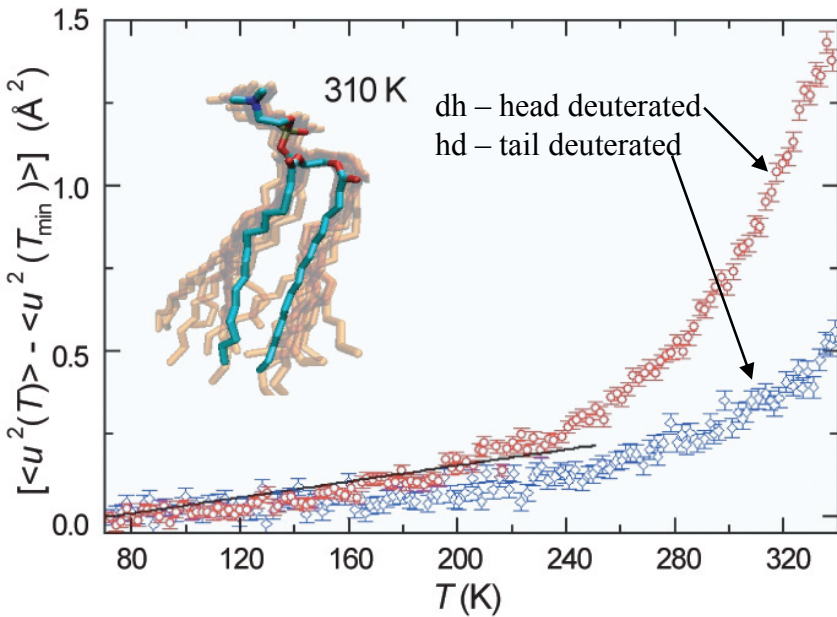


Note that scattering originates from protons depicted by white bonds.

Sharp portion of the transition only by lipid tails!!

Melting in anhydrous lipid membranes

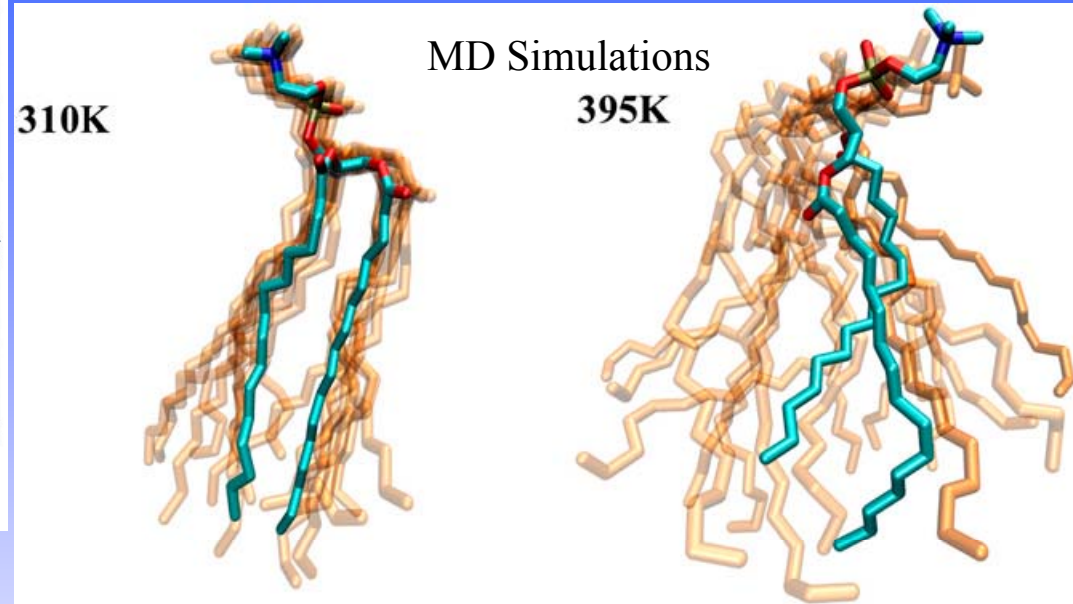
Summary through MDS snapshots



Below 220K, vibration regime is observed.

Above 300K, it is clear that a pronounced mobility is gained by protons in tail of lipid.

Sharp transition is dominated by contribution from lipid tails!



Very little mobility of head groups at low T while the tails show significant mobility!!

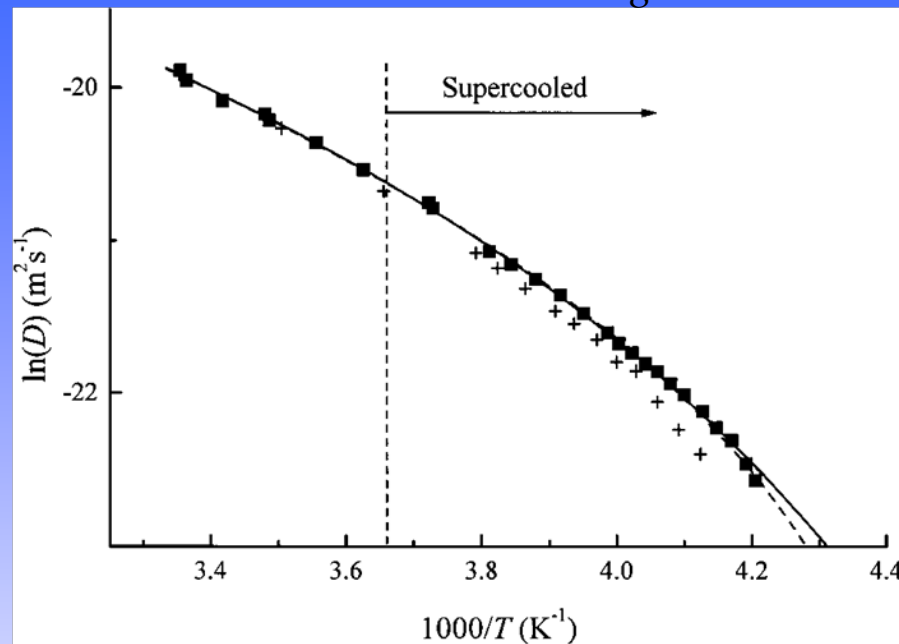
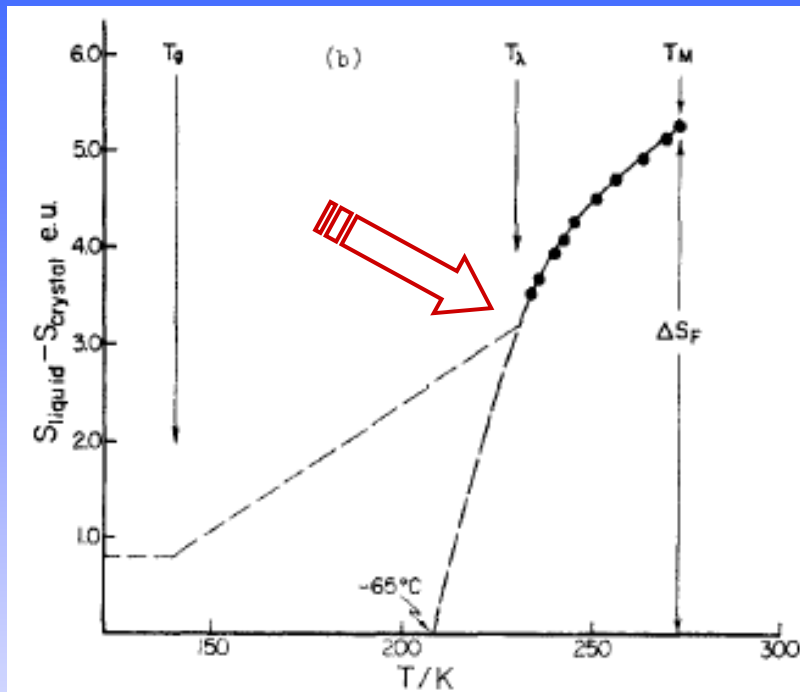
At high T, the head groups melt with no signature of distinct melting.

Doxastakis et al., BioPhys. J. 92, 147 (2007)

Thermodynamic transition in water

DSC

Pulse gradient NMR



Paradox in excess entropy!

Solution: A transition at 220K!

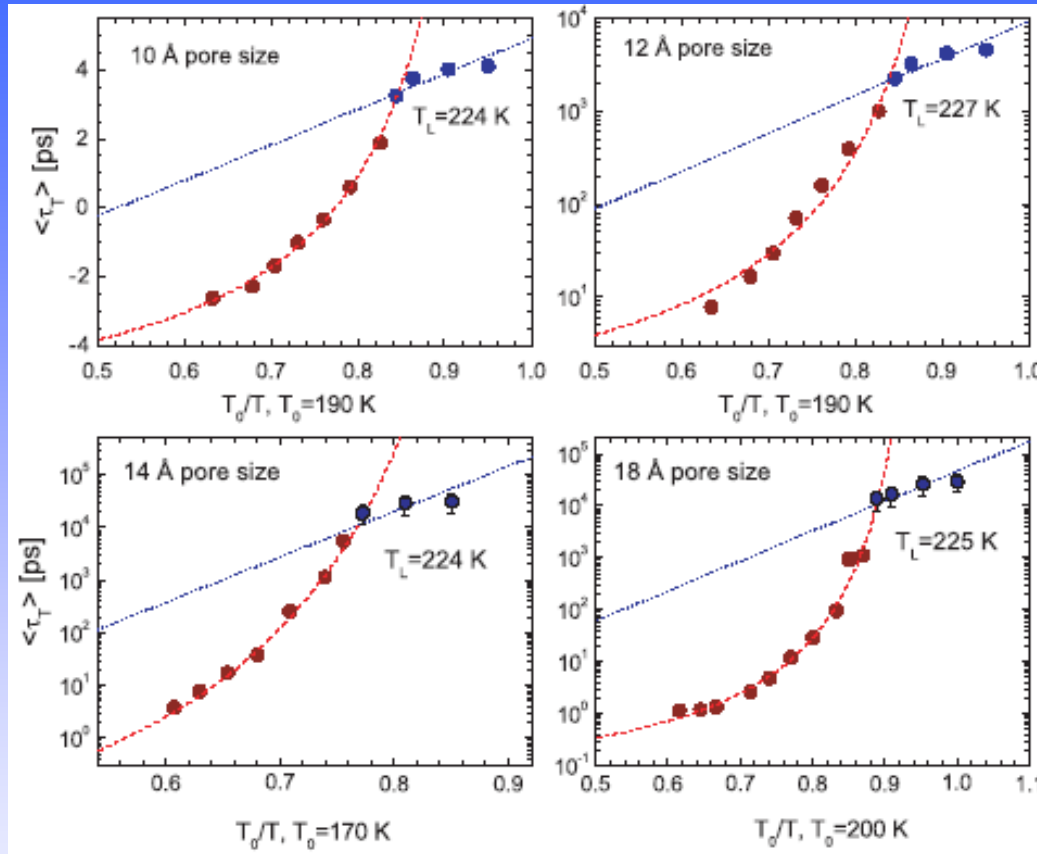
$$D = D_0 \exp\left(-\frac{B}{T - 170K}\right) \quad \text{good above 242K}$$

$$D = D_0 T^{1/2} \left(\frac{T}{220K} - 1\right)^{1.4} \quad \text{below 242K}$$

Angell, *J. Chem. Phys.* **77**, 3092 (1973)

Price, *J. Phys. Chem. A* **103**, 448 (1999)

Water in confined silica



fragile

VFT:

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

T ↑

crossover 222K

Arrhenius:

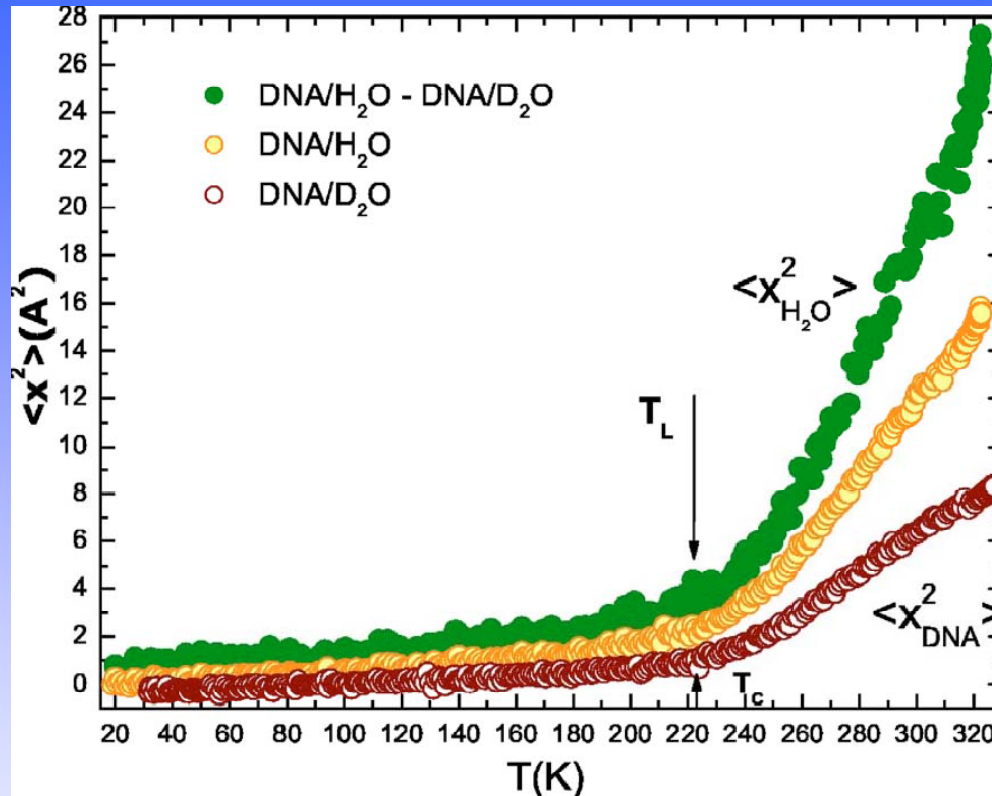
strong

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right)$$

Fragile-to-strong transition at around 222K in relaxation time of water!

Liu et al., *J. Phys: Cond. Matter* 18, S2261 (2006)

Relation with transition in DNA hydration water

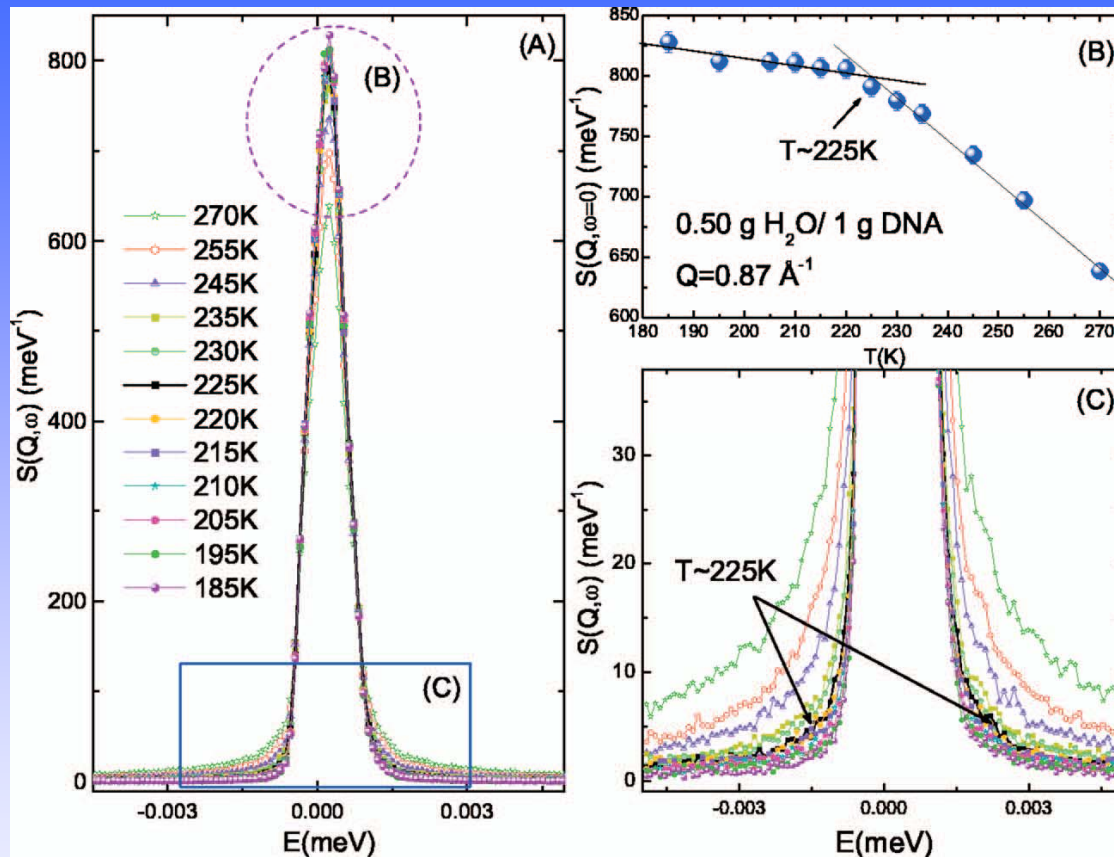


Smart use of isotope substitution provides the MSD for H of hydration water and of DNA.

The crossover in hydration water and DNA occurs at same temperature 222K!

Chen et al., J. Chem. Phys. 125, 171103 (2006)

Relation with transition in DNA hydration water



H₂O DNA – D₂O DNA

No data analysis! Visual analysis shows a change in dynamics at 225K!!

Chen et al., J. Chem. Phys. 125, 171103 (2006)

Relation with transition in DNA hydration water

Two temperature laws:

i) 270K – 230K VFT power law

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

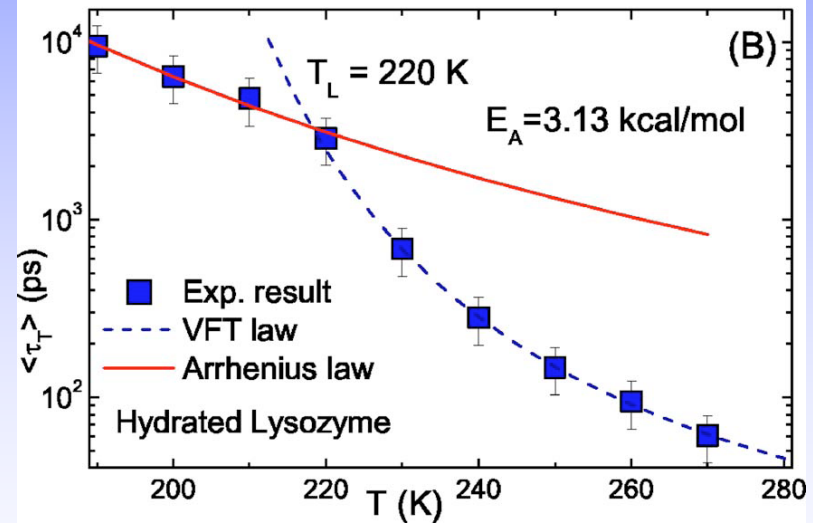
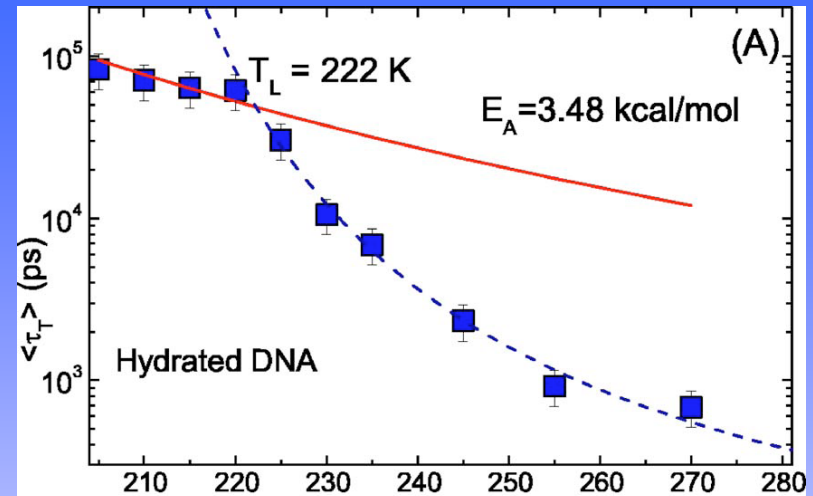
Fragile

ii) 220K and below Arrhenius law

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right)$$

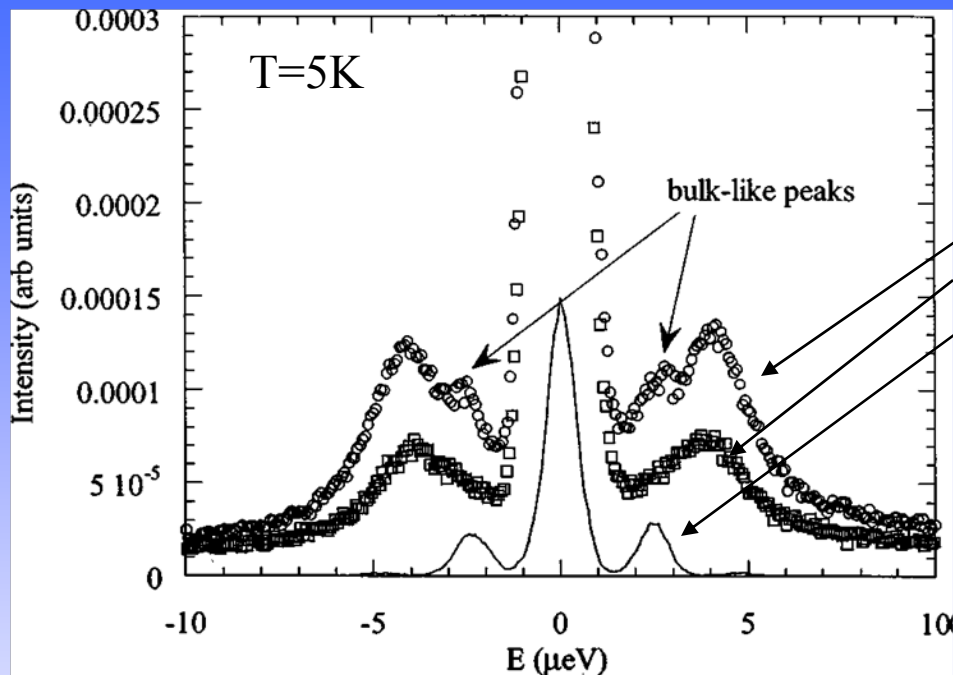
Strong

dynamic transition in DNA is driven by fragile-to-strong transition in water!

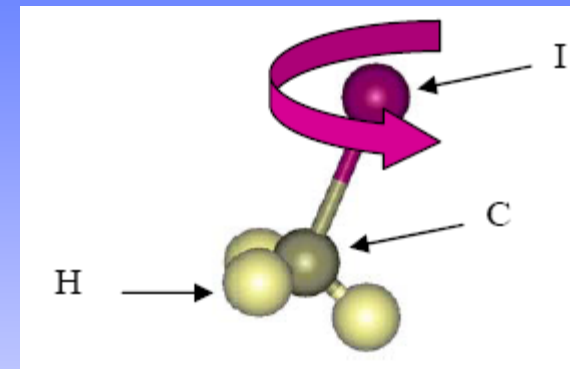


Chen et al., *J. Chem. Phys.* 125, 171103 (2006)

Low T dynamics of confined CH₃I molecule



pore diameter 58Å

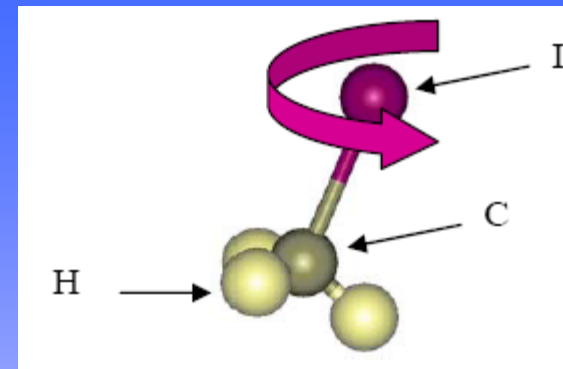
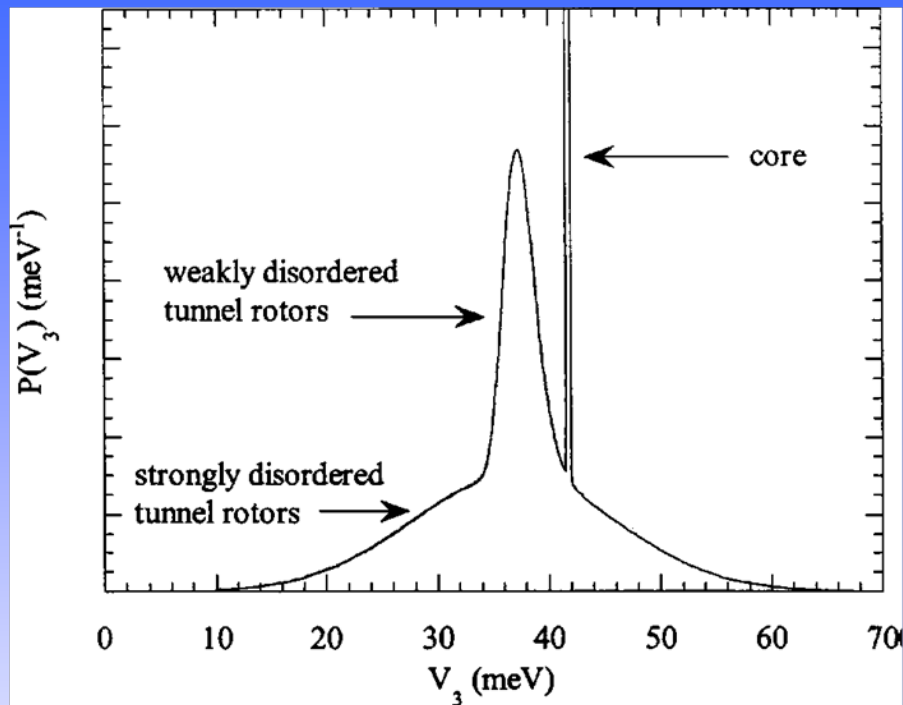


Full pore data shows peaks similar to bulk and additional peaks at $\pm 4\mu\text{eV}$, while the bulk-like peaks have disappeared in partially filled pore!

Origin: i) low energy peaks \rightarrow core ii) high energy peaks \rightarrow surface

Dimeo et al., Phys. Rev. B 63, 014301 (2000)

Low T dynamics of confined CH₃I molecule



Overall picture:

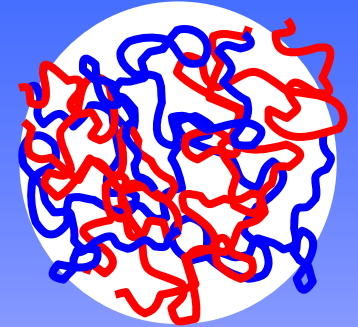
- 1) Core \rightarrow high degree of local order (5%)
- 2) Peaks at $4\mu\text{eV}$: surface molecules
 - i) strongly disordered 70%
 - ii) weakly disordered 25%

probability distribution of barrier height
extracted from the full pore spectra

Dimeo et al., Phys. Rev. B 63, 014301 (2000)

Polymers....

“Thermodynamically Miscible Polymer Blend”:
two-component system molecularly mixed



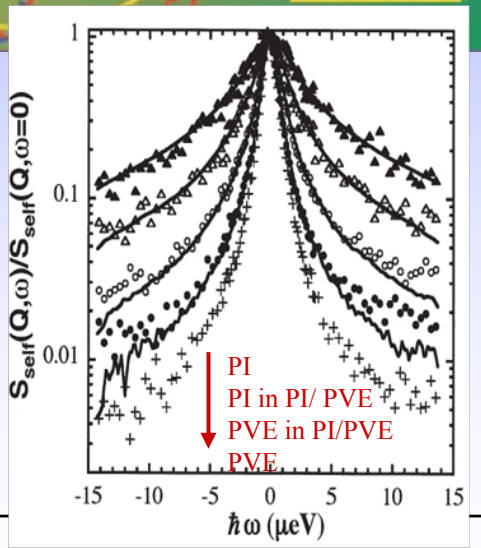
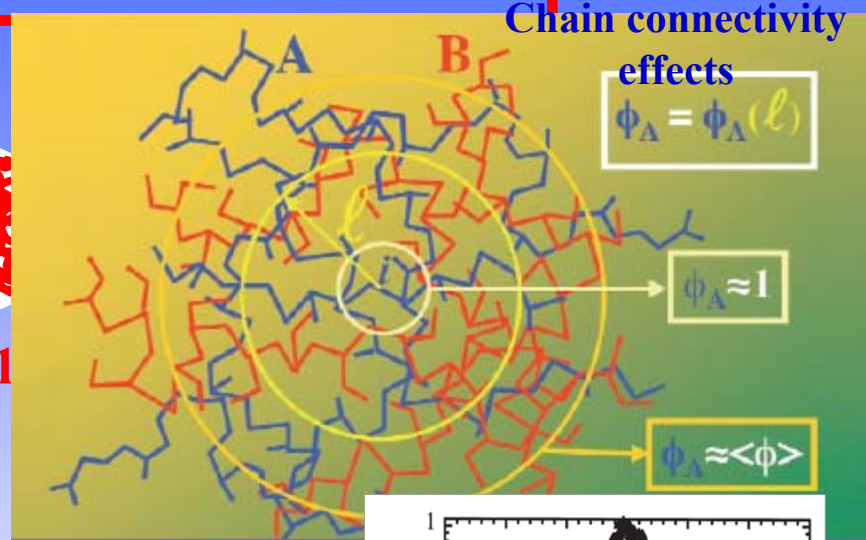
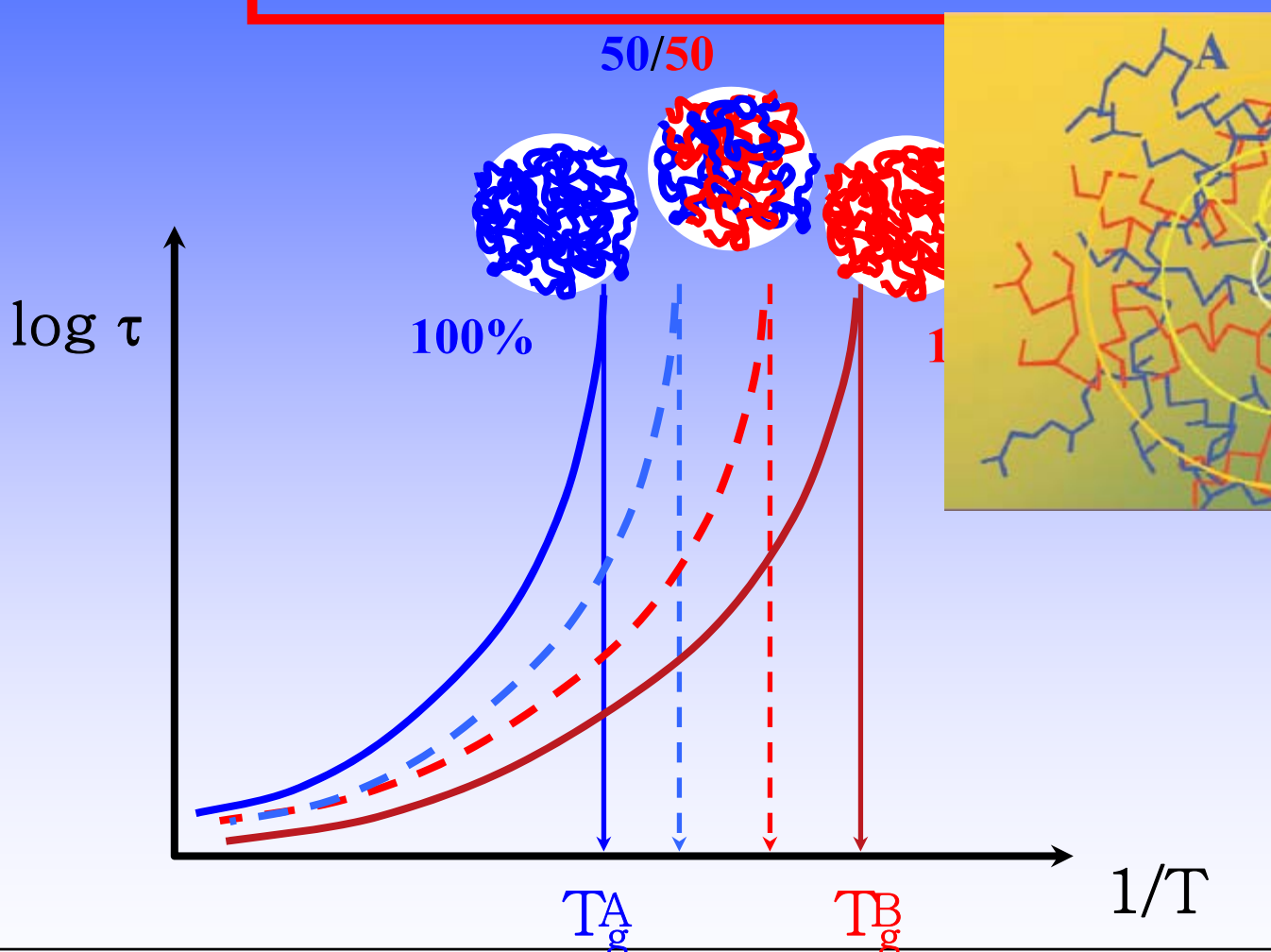
Technological importance:
new materials, mechanical properties, rheology, etc

Fundamental questions:
dynamic miscibility, length scales, etc

KEY QUESTION:

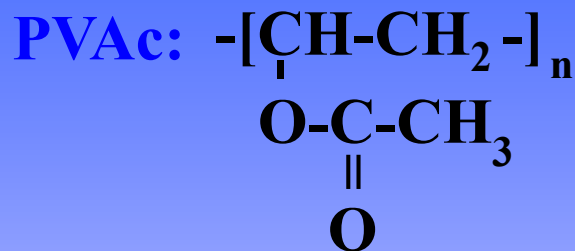
How is the dynamics of **one component
modified by **blending**?**

Different segmental dynamics (α -relaxation) for each component in the blend



Dynamics of Both Components in a blend

20% PEO / 80% PVAc BLEND



$$T_g = 314 \text{ K}$$



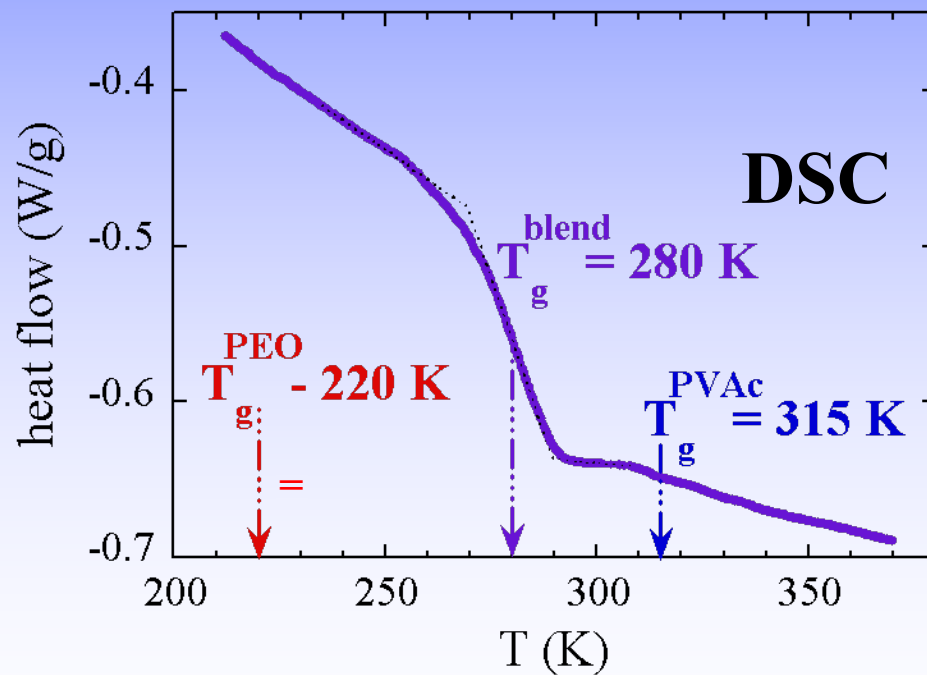
$$T_g \approx 220 \text{ K}$$

$$\Delta T_g \approx 100 \text{ K}$$

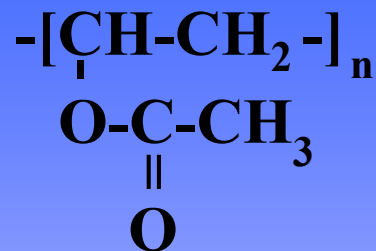
wt % PEO $\lesssim 25$



MISCIBLE
AMORPHOUS
BLENDS



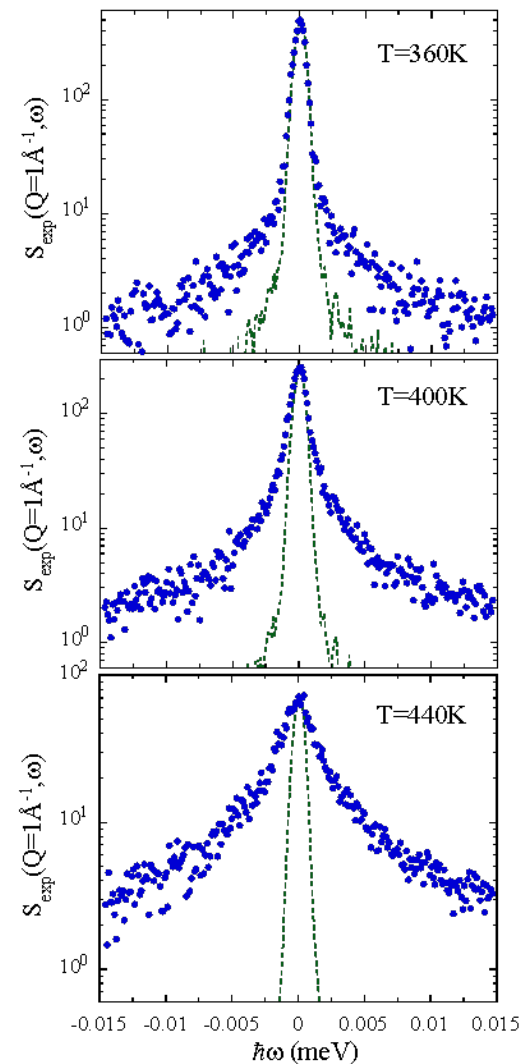
PVAc in BLEND



Description of the NS data:

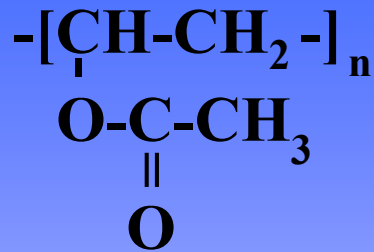
FT of a KWW function

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



Backscattering Measurements: PVAc in blend

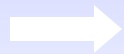
PVAc in BLEND



Description of the NS data:

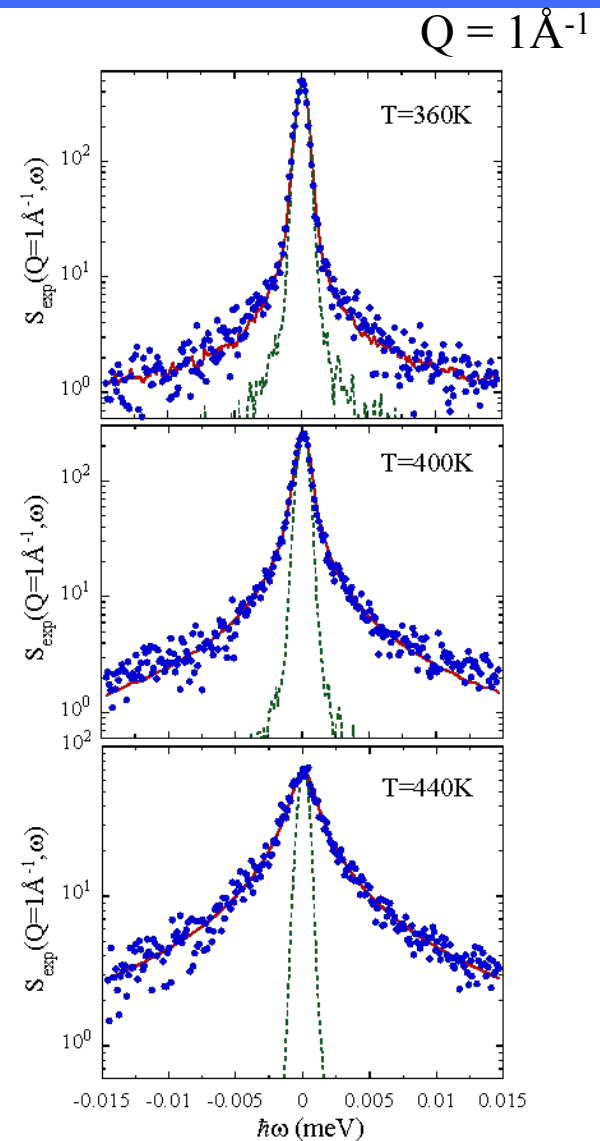
FT of a KWW function

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



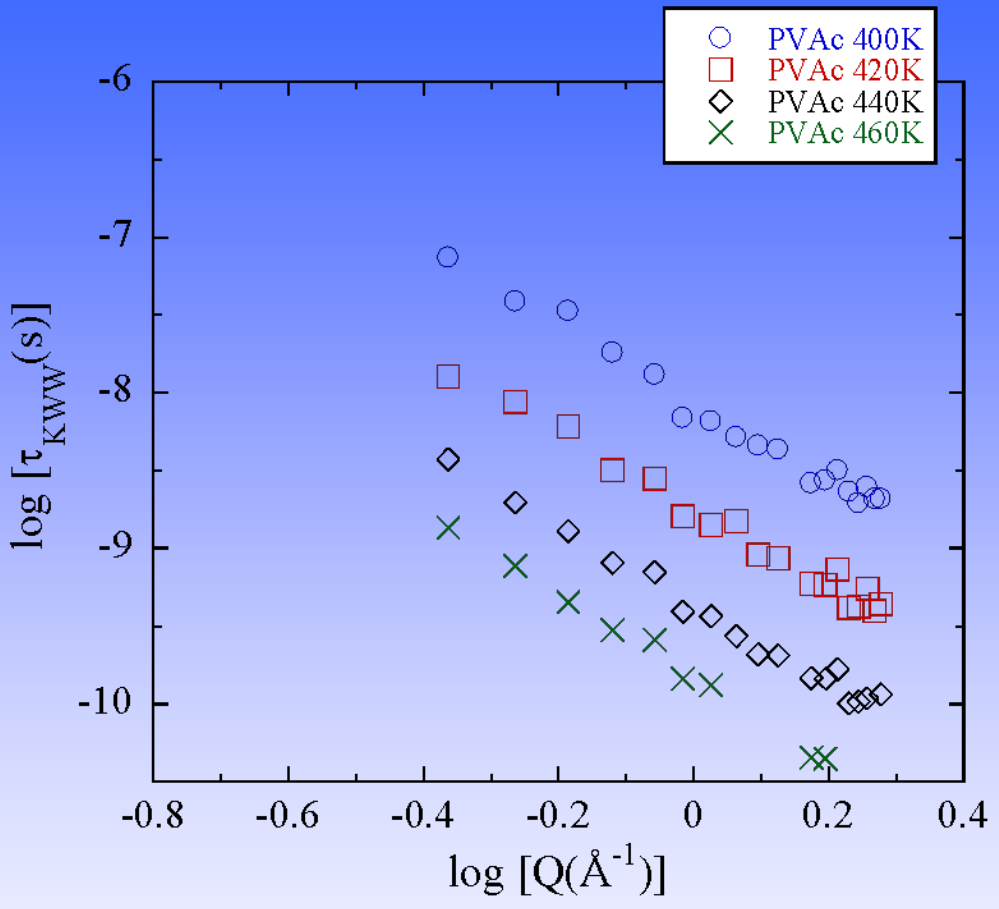
$$\beta = 0.50$$

Shape of the spectra seems to be unchanged by blending!



Q and T-dependence of characteristic times

PVAc

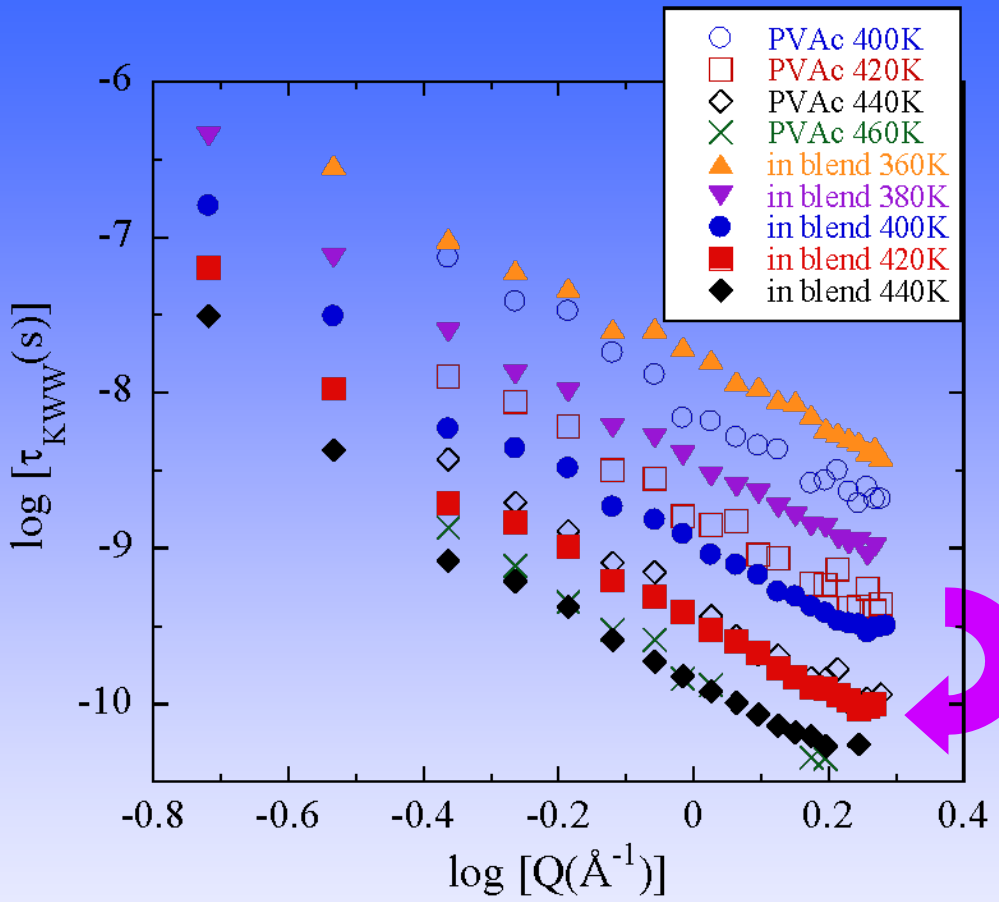


Q and T-dependence of characteristic times

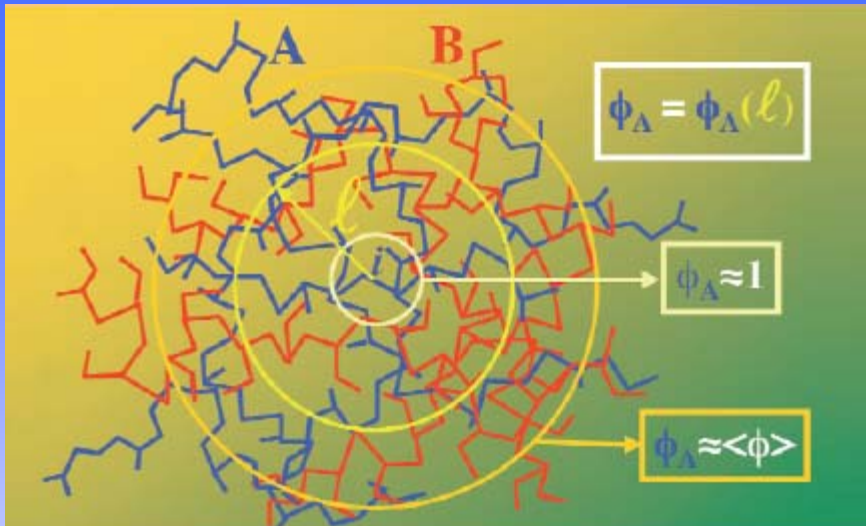
PVAc in BLEND

• At the same temperature, **faster** dynamics of PVAc in blend.

• No apparent change in Q-dependence after blending!

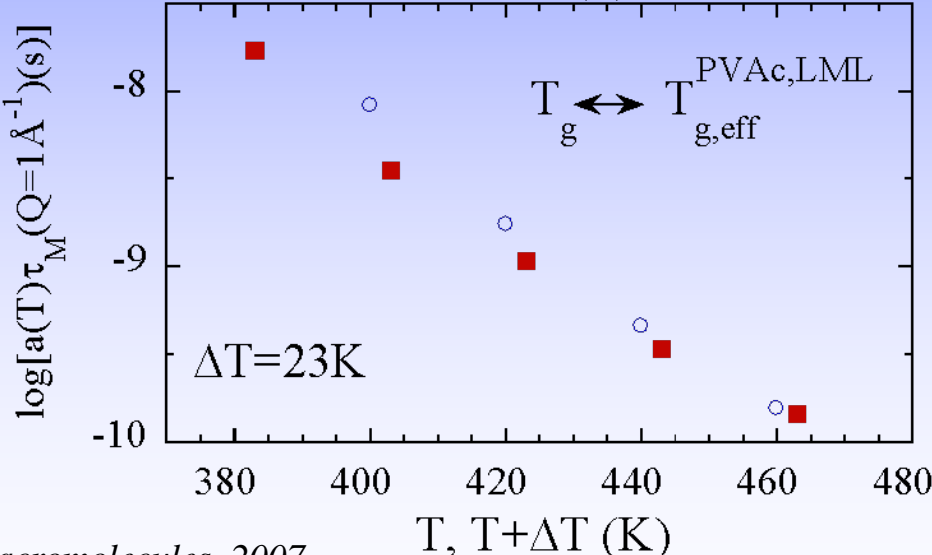
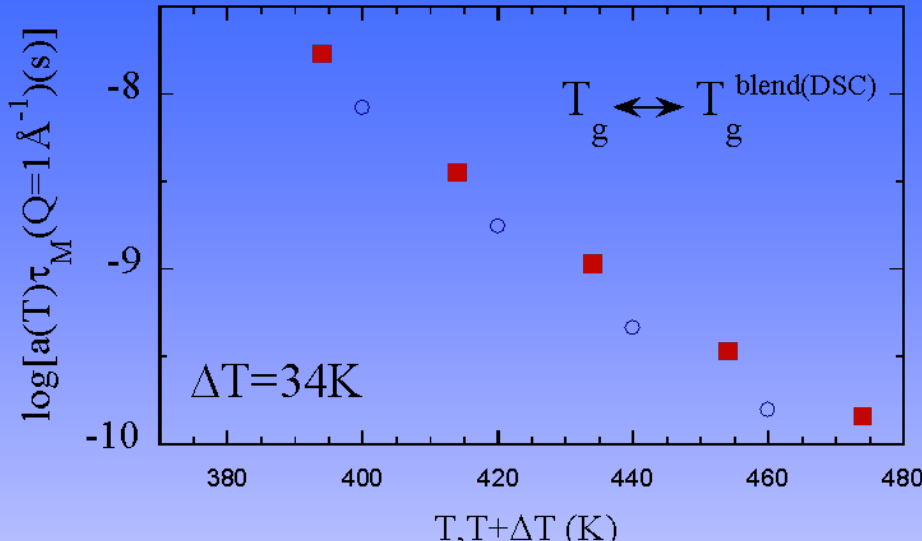


Q and T-dependence of characteristic times



A shift in glass transition temperature or equivalently, concentration effects can be used to explain the dynamics of high-T_g component.

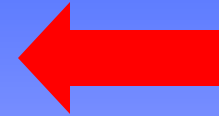
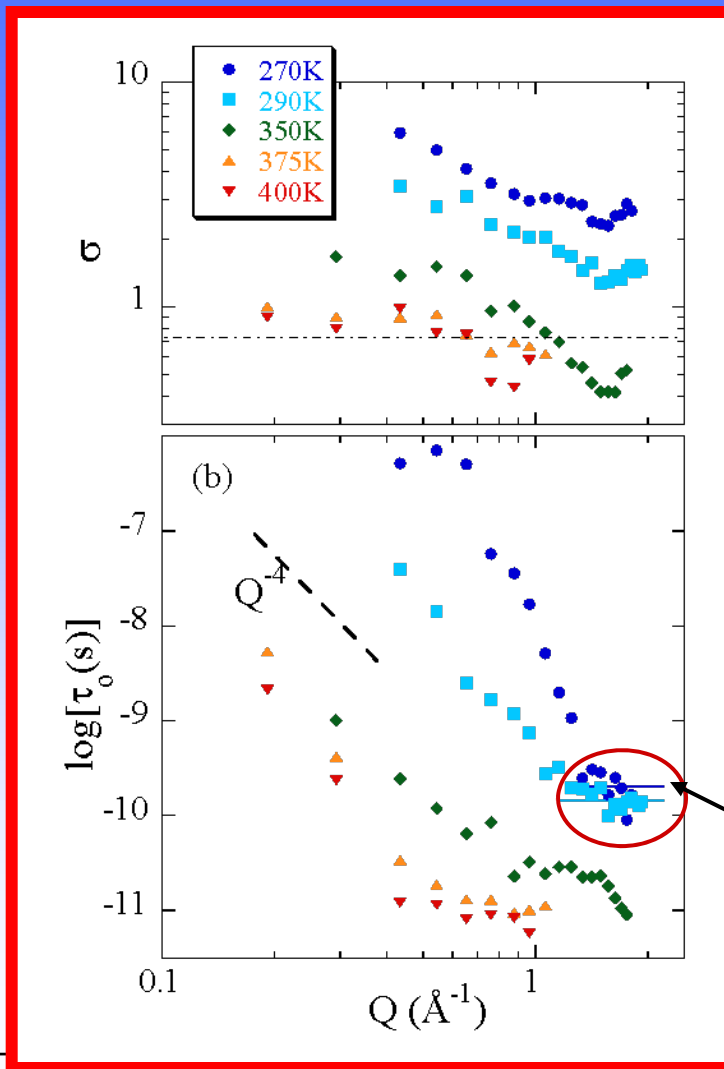
Lodge McLeish Model



Tyagi, *Macromolecules*, 2007

Backscattering Measurements: PEO in hPEO/dPVAc

Gaussian distribution of log



270K

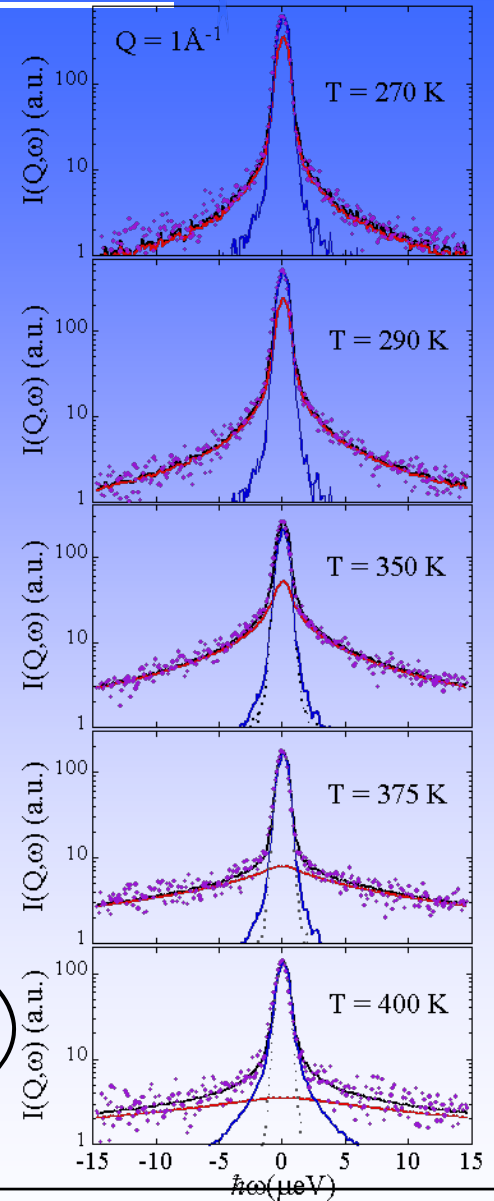
dynamic
confinement

350K

standard
scenario

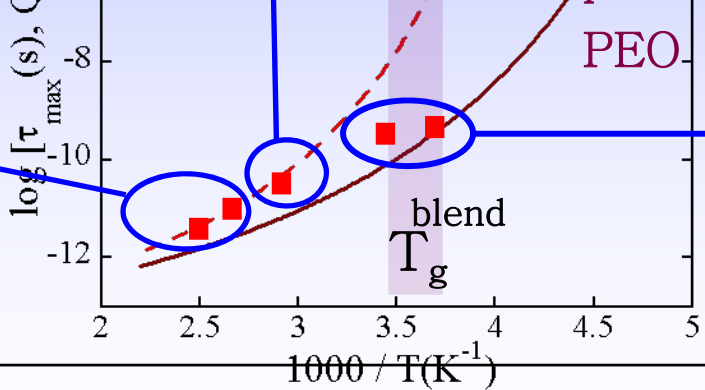
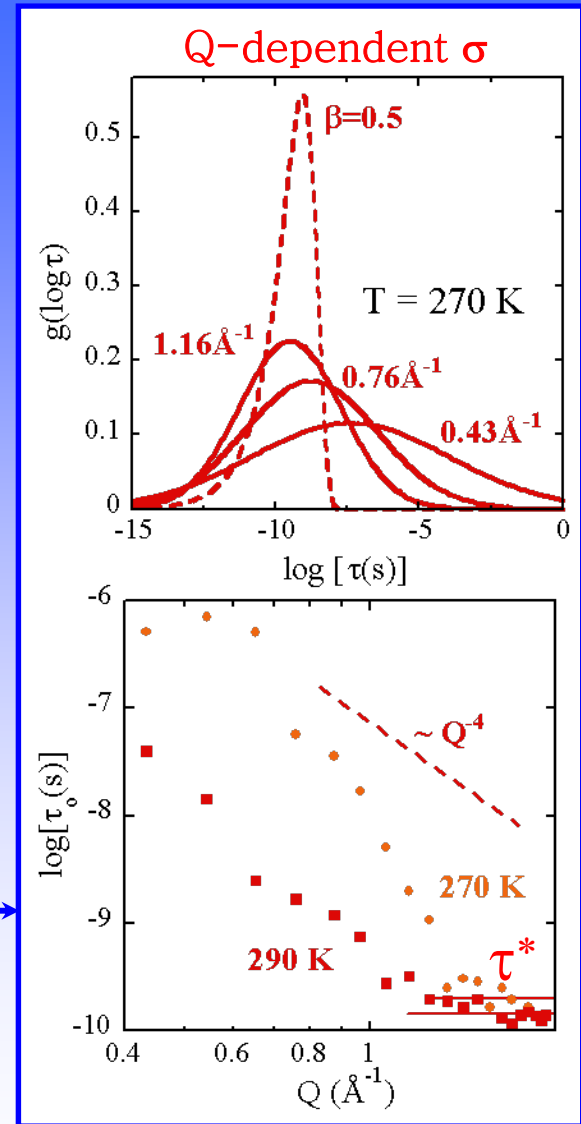
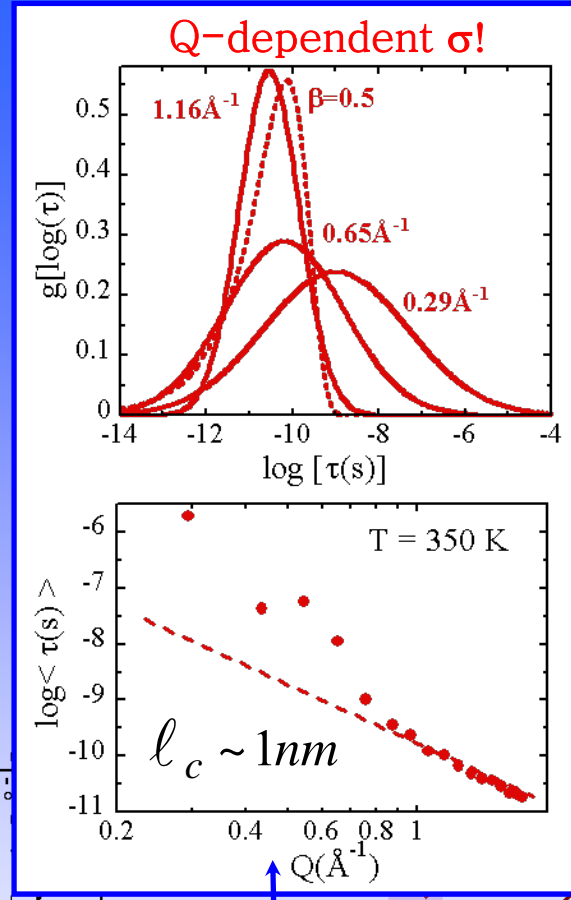
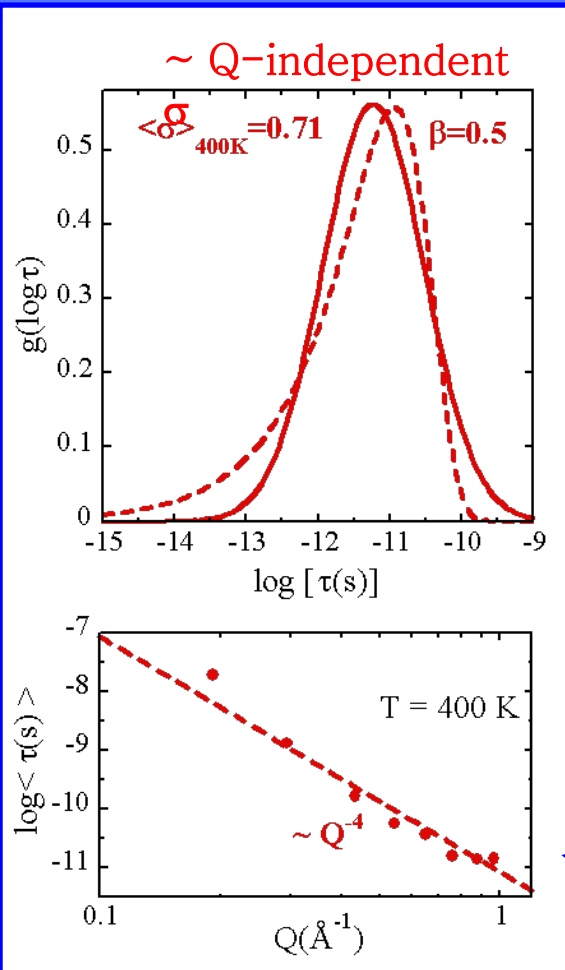
400K

Q-independent time
scales at high Q



Overall Picture

Tyagi, *Macromolecules*, **39** (2006)

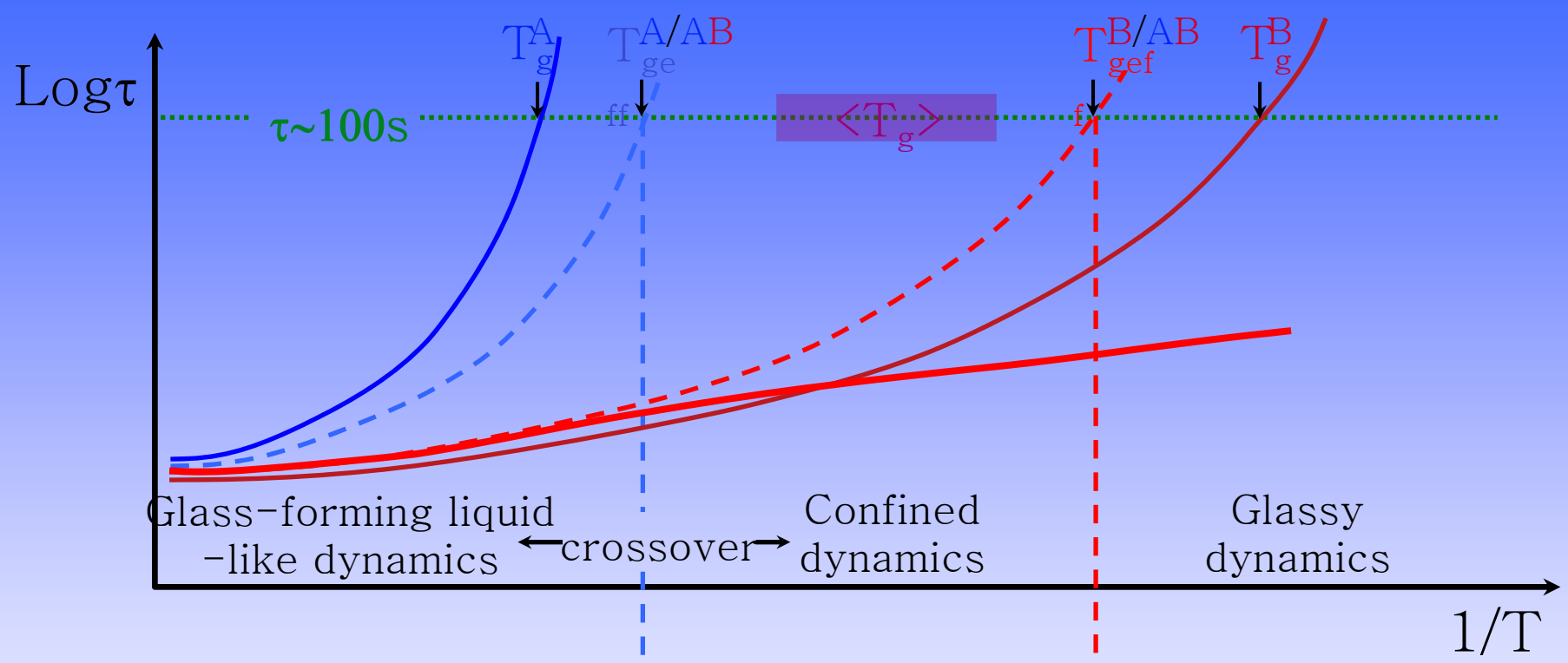


Glass-forming liquid-like dynamics

crossover

confined

Confinement Effects in Polymer Blends

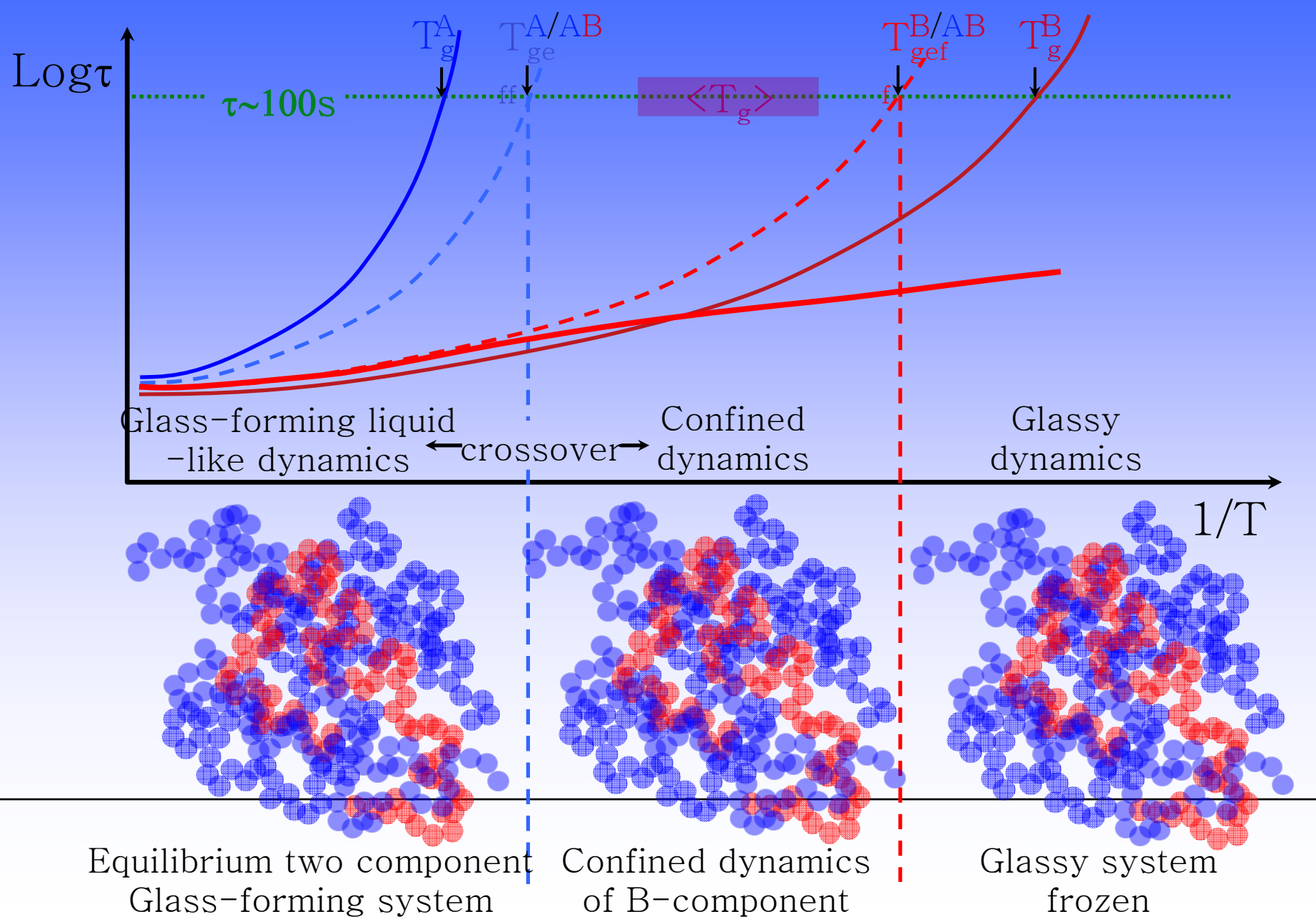


Equilibrium two component
Glass-forming system

Confined dynamics
of B-component

Glassy system
frozen

Confinement Effects in Polymer Blends



Geometrical Confinement: T dependence of microscopic dynamics

Assuming Gaussian distribution of elastically scattered intensities:

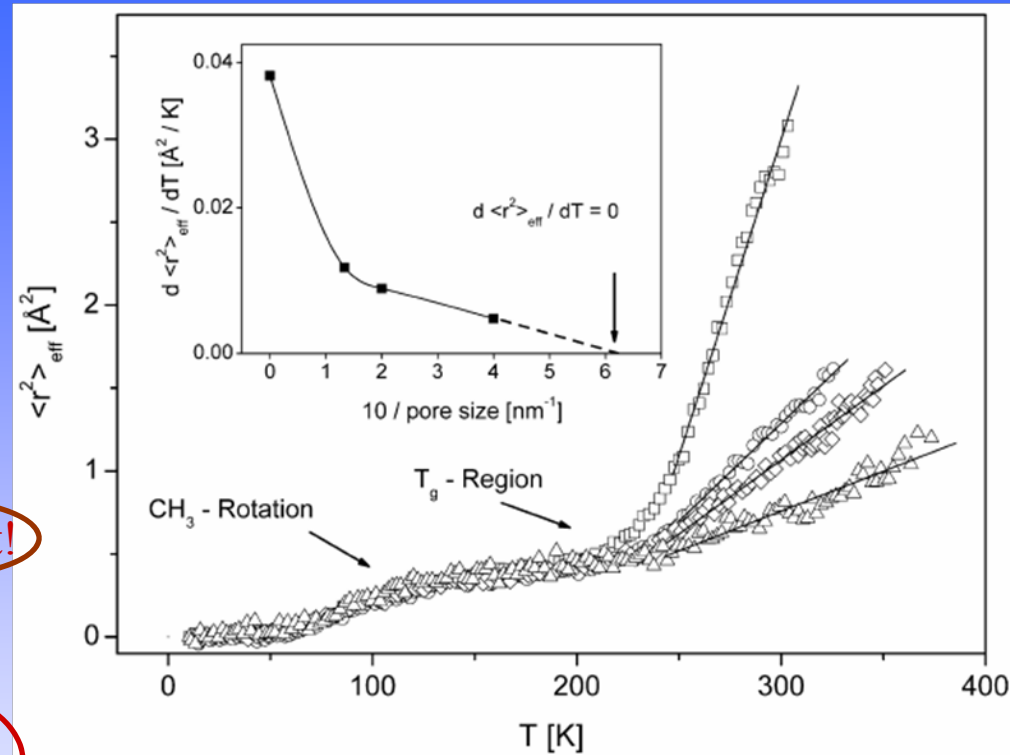
$$I_{el} / I_0 = \exp \left[- \frac{Q^2 \langle r^2 \rangle_{eff}}{3} \right]$$

Sharp step in MSD around 100K –
Methyl group rotations

no effect!

Changes in MSD around 225K –
glass transition

strong effects!



Poly(methyl phenyl siloxane) $T_g=222K$

Both bulk and confined polymers show diffusive-like behavior above T_g !

Diffusive-like behavior would disappear around 1.6nm!

Minimal length scale for segmental relaxation

Schonhals et al., Colloid Poly Sci 282, 882 (2004)

Glass transition of thin polymer blend films

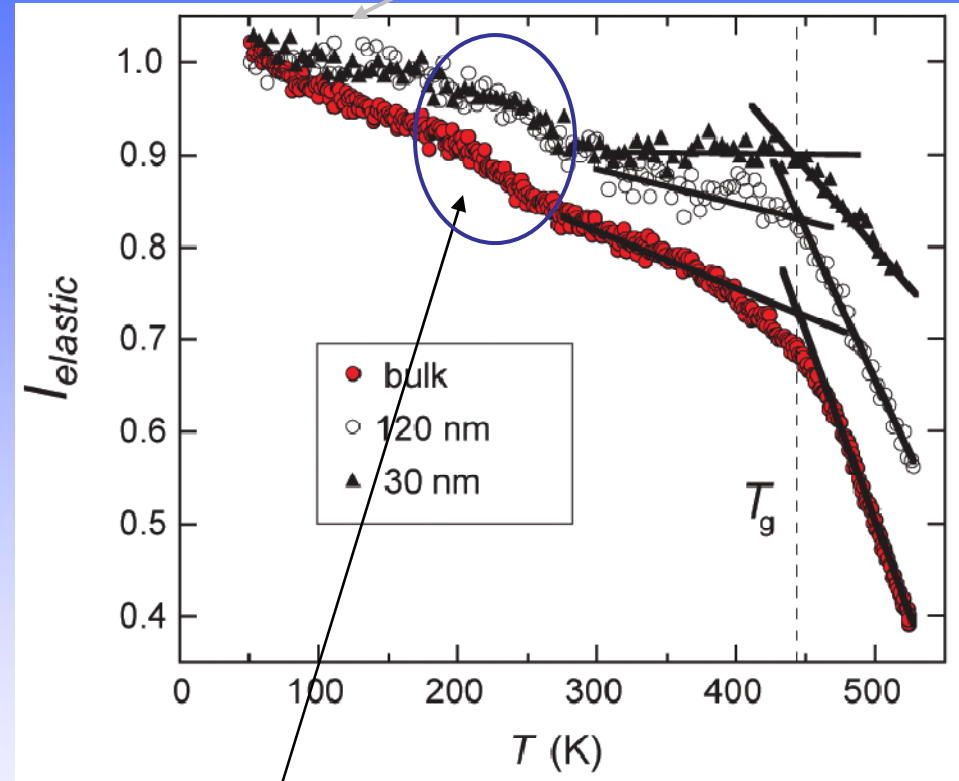
$$I(Q) = \exp(-Q^2 u^2 / 3)$$

Glass transition of thin films in polymer is influenced by two parameters

- i) Effect of confinements
- ii) Interfacial interactions

tetramethyl bisphenol-A Polycarbonate (TMPC);
 $T_g = 493\text{K}$

deuterated polystyrene; $T_g = 383\text{K}$



Influence of methyl group dynamics!

$T_g = 445\text{K}$ for bulk blend and other thicknesses

Besancon et al. PRL 2006

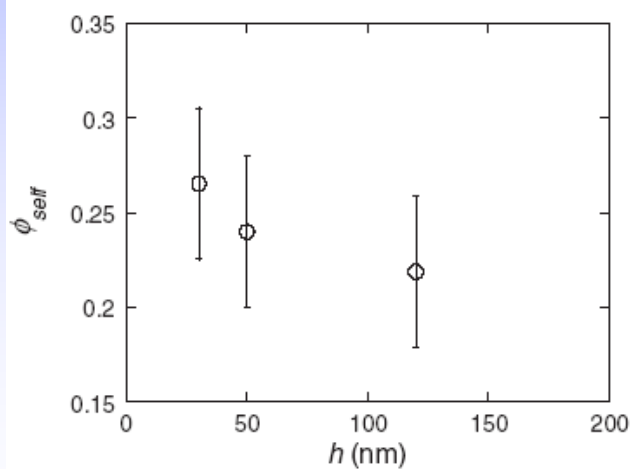
Glass transition of thin polymer blend films

Ellipsometry and DSC average T_g are same while the incoherent elastic neutron scattering measurements indicate a higher T_g for TMPC component!

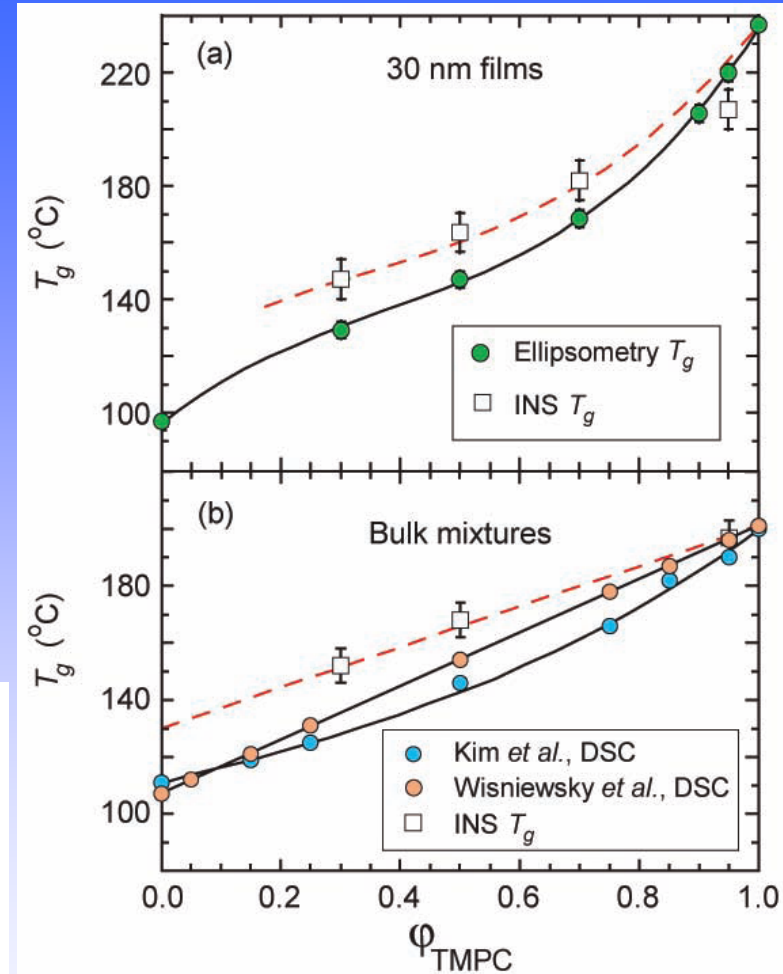
First evidence of two effective T_g s in a miscible blend!!

Lodge McLeish model works!

Signs of slight change in self concentration of the component.



Besancon et al. PRL 2006



$$\varphi_{eff} = \varphi_s + (1 - \varphi_s)\varphi$$

Acknowledgments

Craig Brown, Tim Jenkins, John Copley,
Dan Neumann and Yamali Hernandez