NSE mainstream & bizarroids

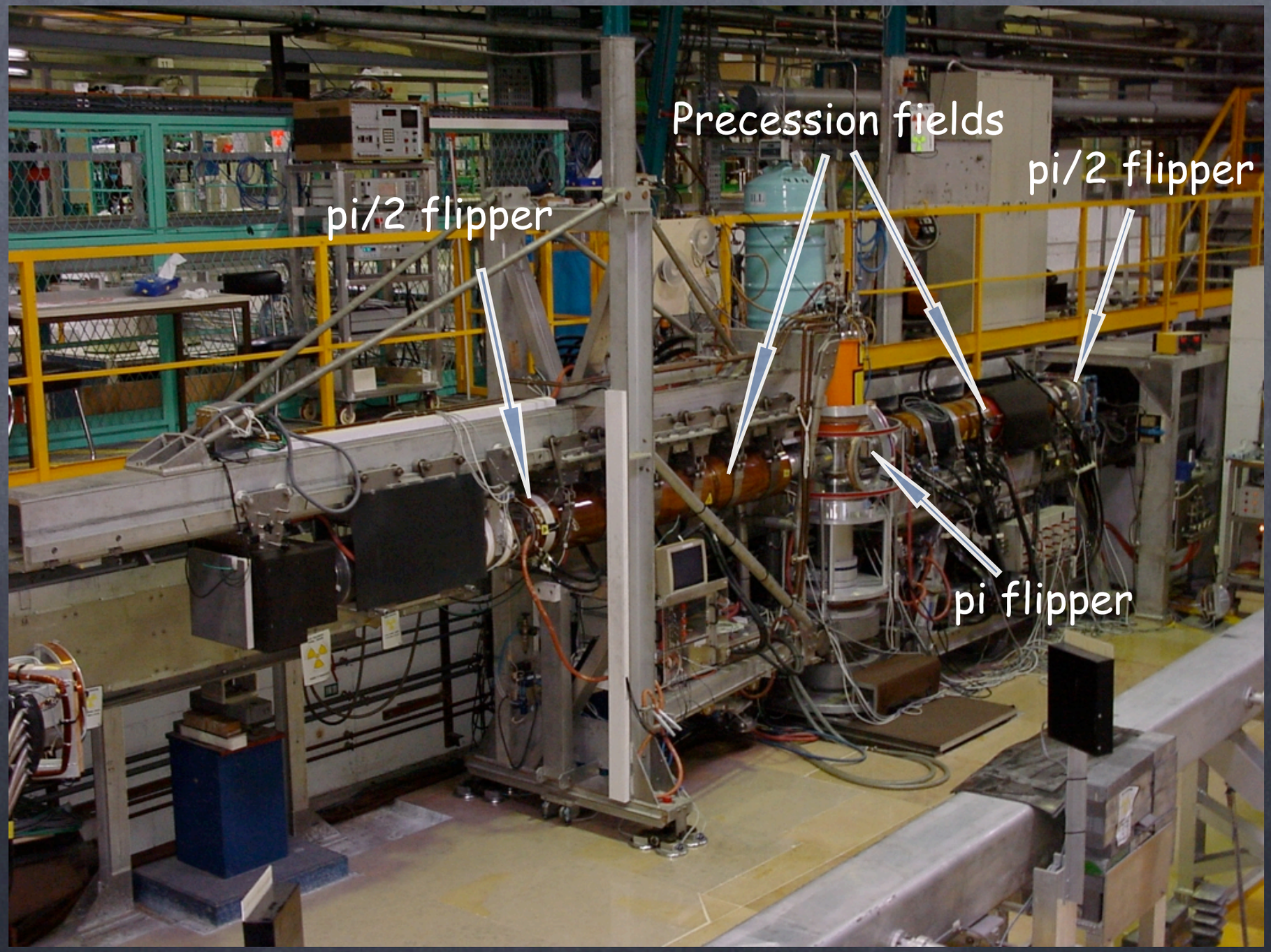
Outline (... I will run out of time)

- the instruments at the ILL
- polymers in solution and melt
- complicating the architecture...
- glassy system (a blend)
- microemulsions (a last wind up)
- free standing film
- zeolite
- Magnetism
- Bizarroids

NSE mainstream & bizarroids

Fourier time (in nsec):

4Å		6Å		8Å		10Å	
t min	t max	t min	t max	t min	t max	t min	t max
0.01	3.3	0.04	11.1	0.09	26.4	0.18	51.7



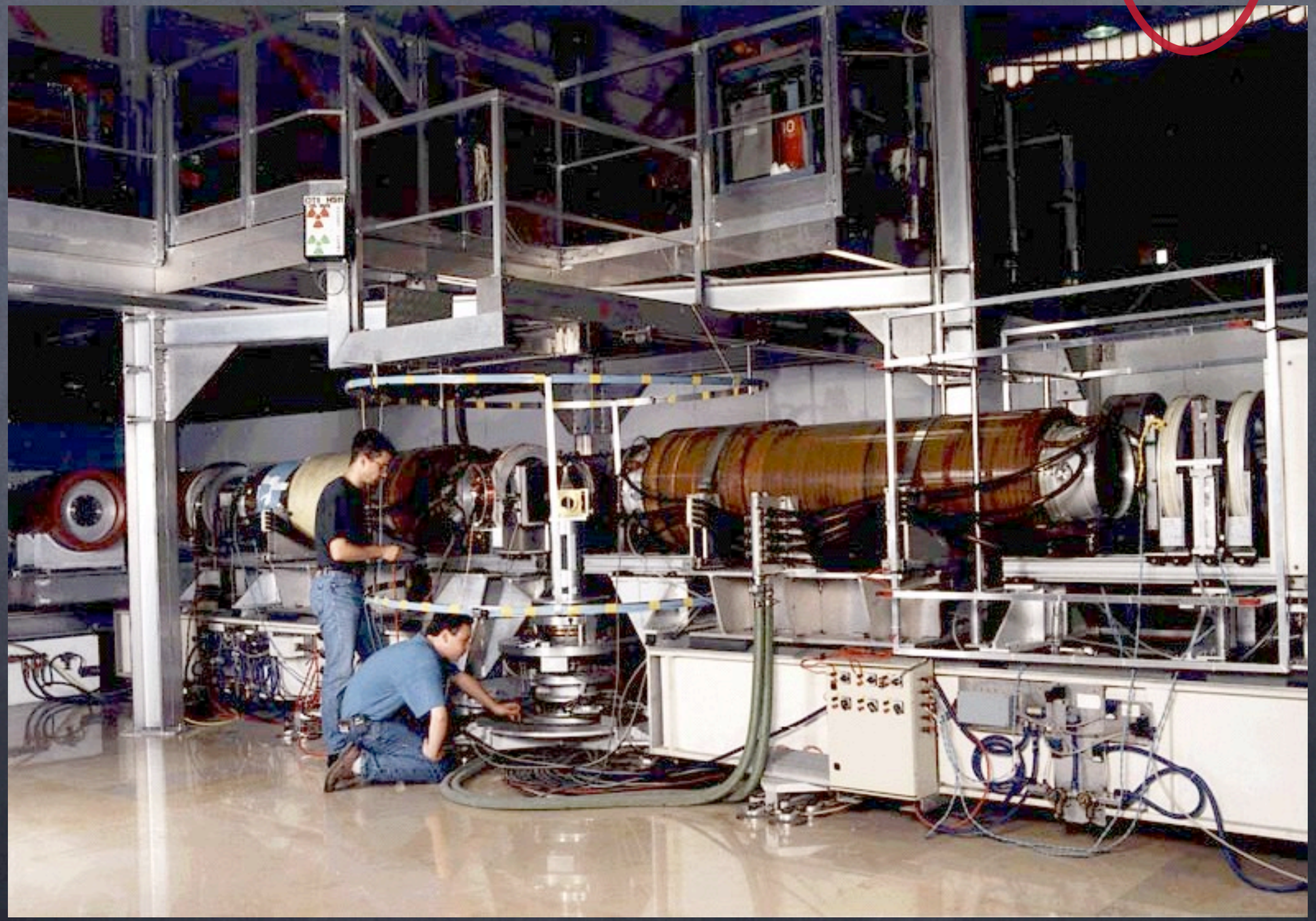
B. Farago

NSE mainstream & bizarroids

In15 the fat

Fourier time (in nsec):

8Å		10Å		16Å		22Å		27Å
t min	t max	t min	t max	t min	t max	t min	t max	t max
0.12	26.3	0.34	51.5	0.8	174	1.9	520	1µs

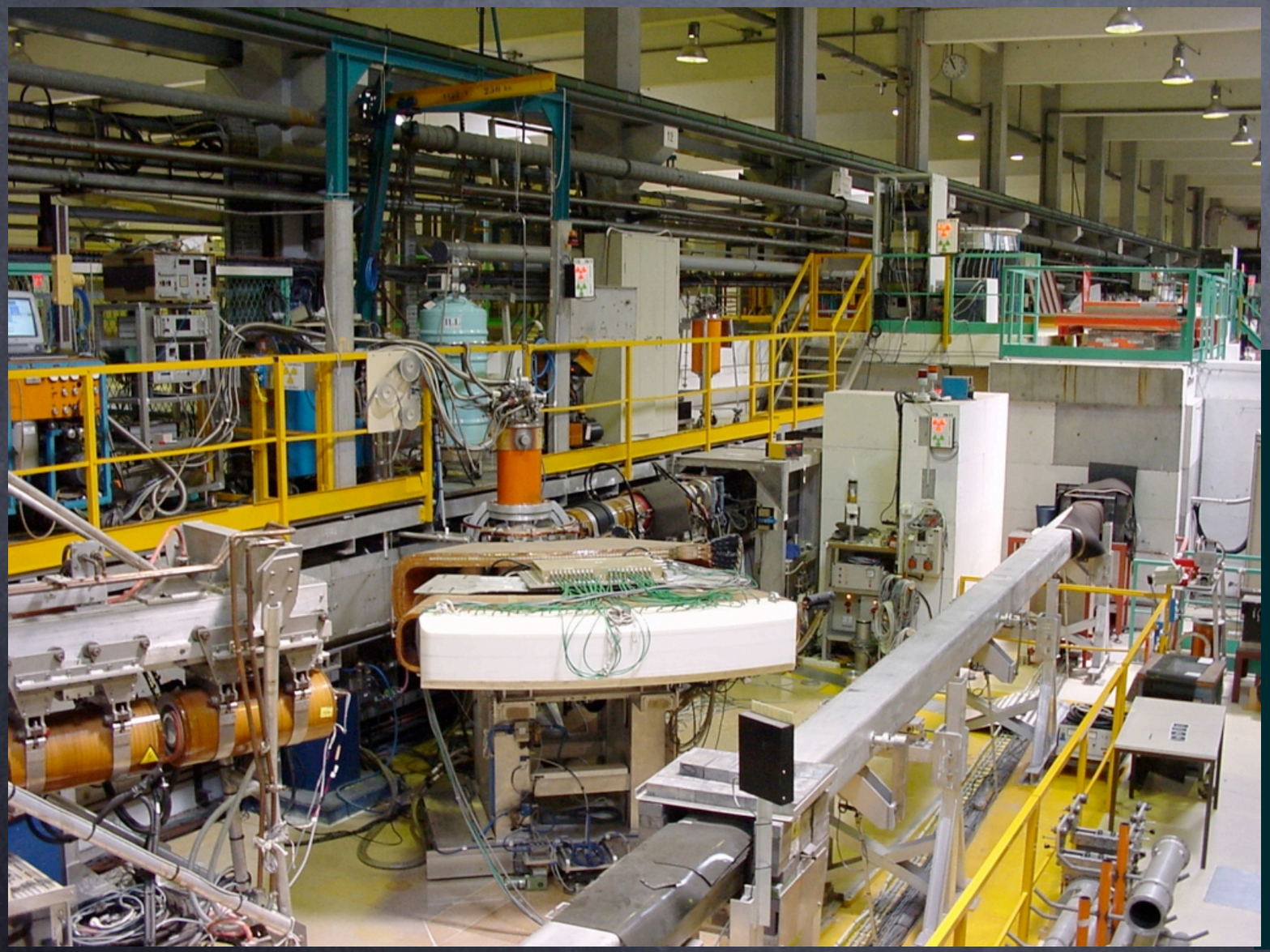


B. Farago

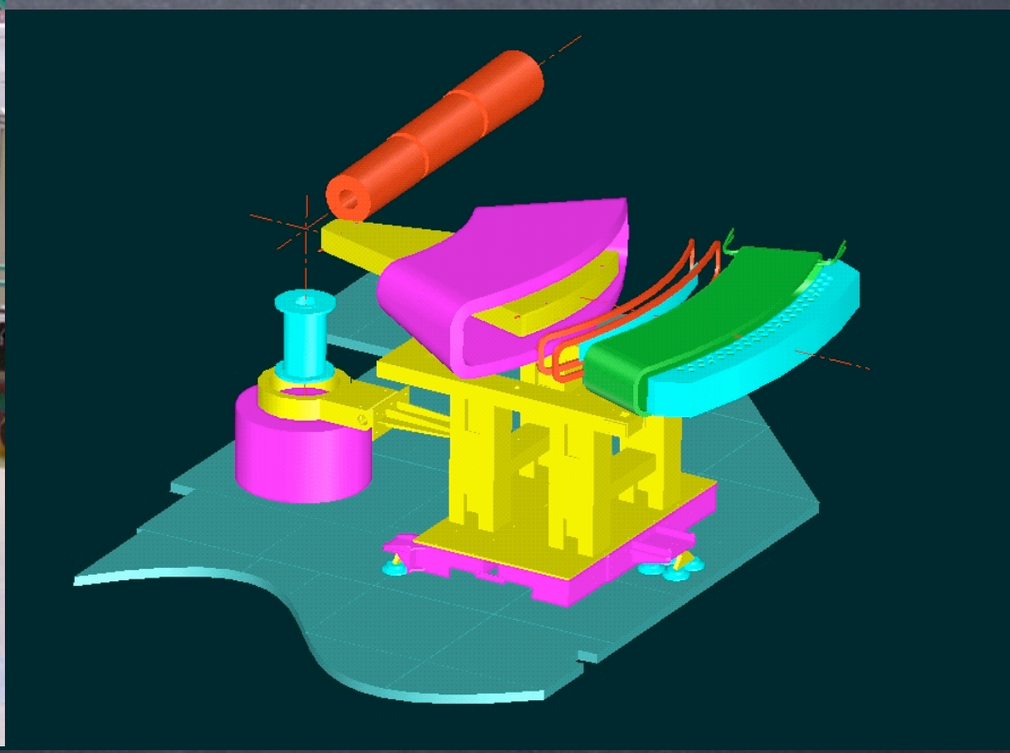
NSE mainstream & bizarroids

Fourier time (in nsec):

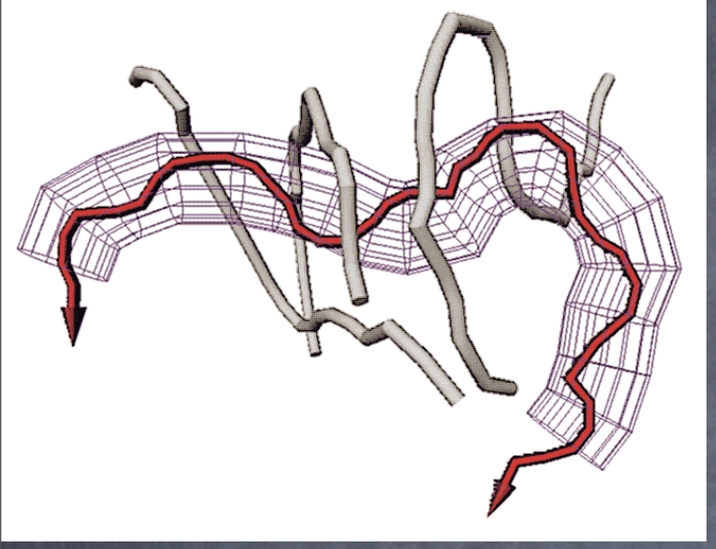
4Å		6Å		8Å		10Å	
t min	t max	t min	t max	t min	t max	t min	t max
0.01	0.5	0.04	1.83	0.09	3.1	0.18	4.2



1/4 time range of In11
20x the intensity



NSE mainstream & bizarroids

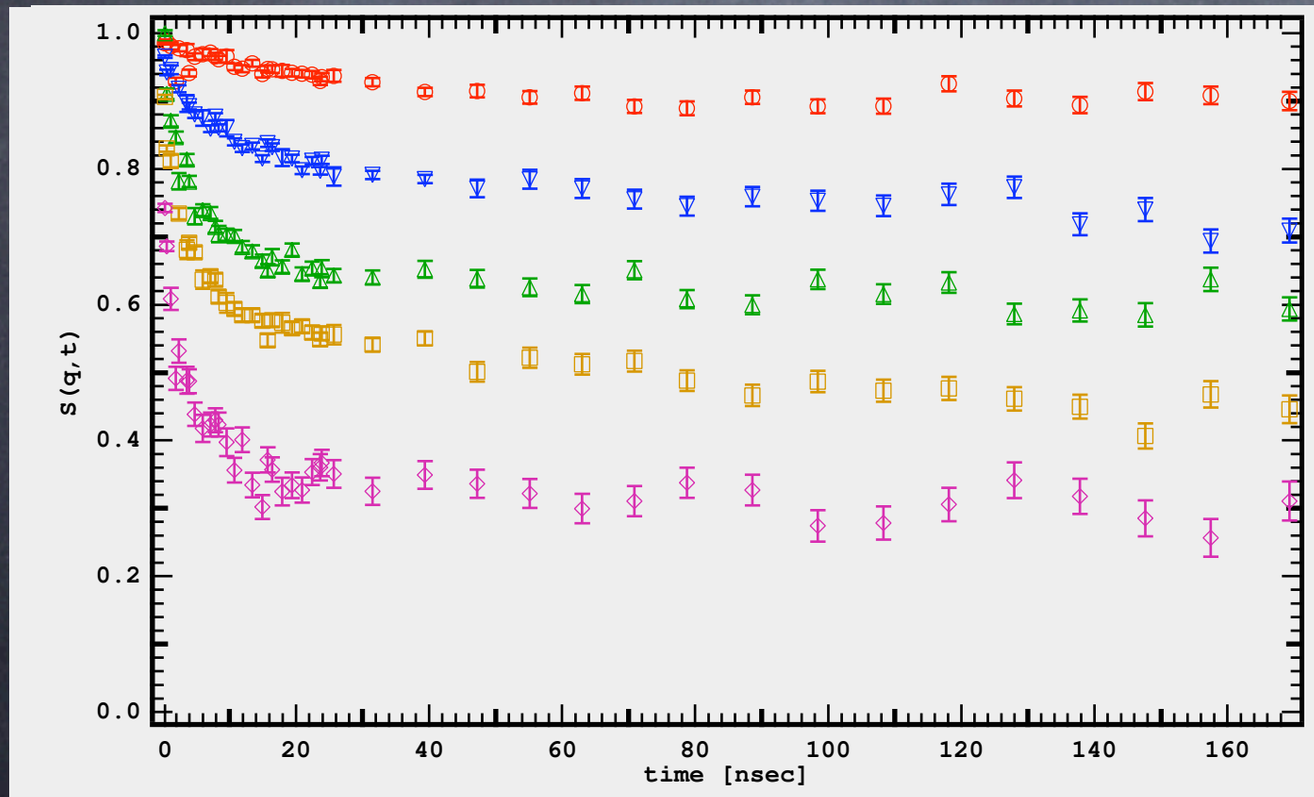


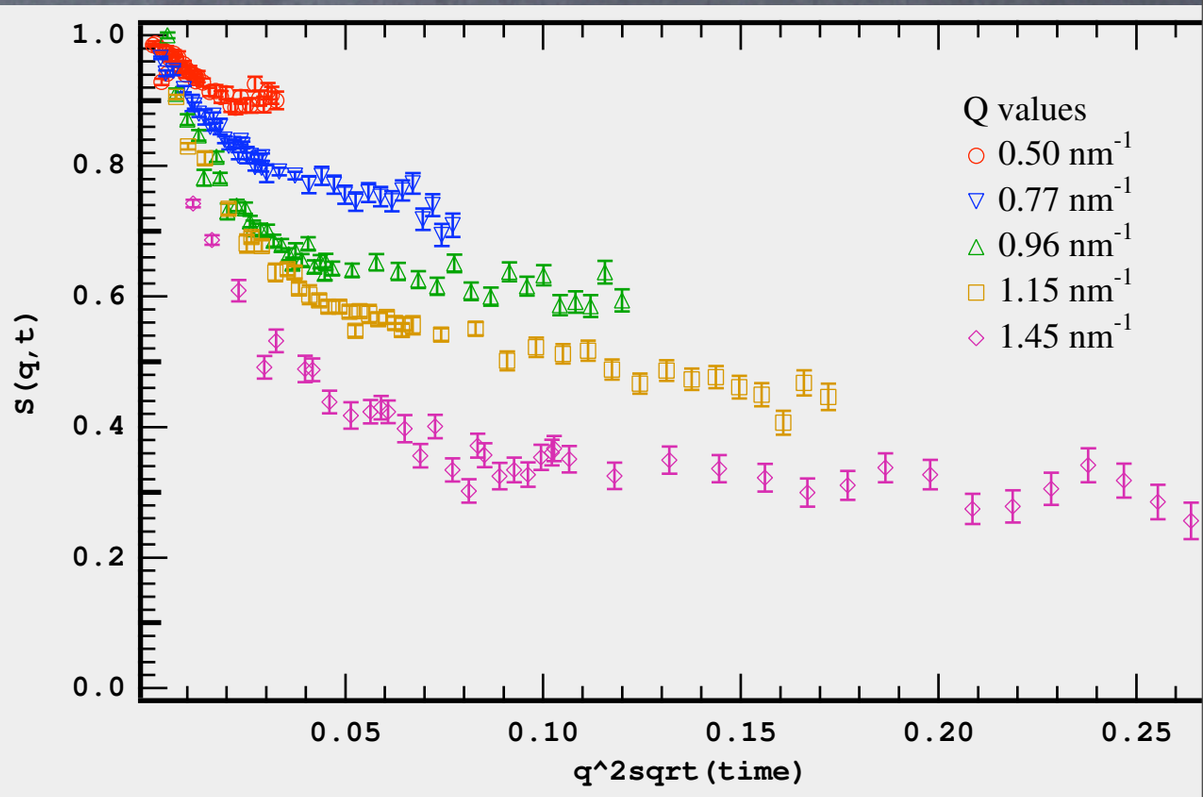
10% marked polymer chain(H) in deuterated matrix of the same polymer melt

at short time => Rouse dynamics $1/\tau \sim q^4$

at longer times starts to feel the "tube" formed by the other chains (deGennes)

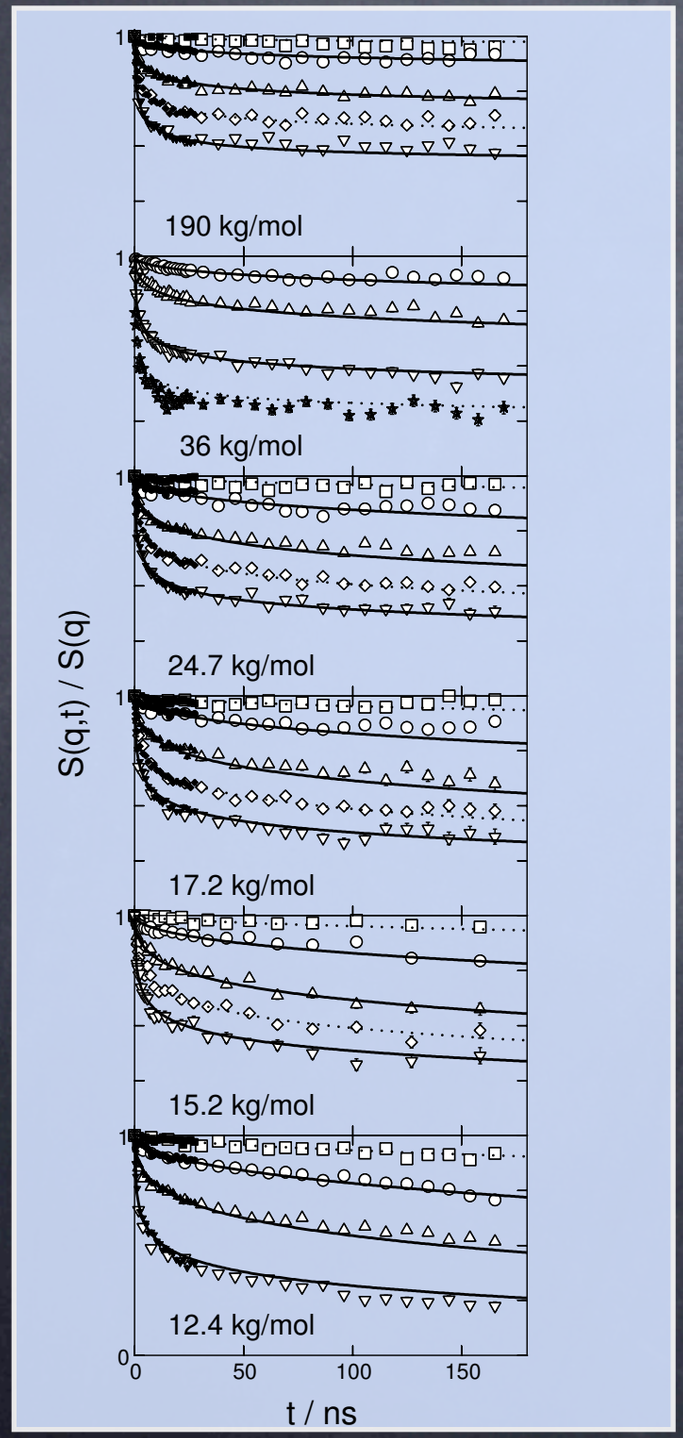
D. Richter, B. Ewen, B. Farago, et al., Physical Review Letters **62**, 2140 (1989).





P. Schleger, B. Farago, C. Lartigue, et al., Physical Review Letters **81**, 124 (1998).

NSE mainstream & bizarroids



A. Wischnewski, M. Monkenbusch, L. Willner, D. Richter, A. E. Likhtman, T. C. B. McLeish, and B. Farago. Physical Review Letters, 88(5):art. no. 058301, 2002.
M. Zamponi, M. Monkenbusch, L. Willner, A. Wischnewski, B. Farago, and D. Richter. Europhysics Letters, 72:1039–1044, 2005.
M. Zamponi, A. Wischnewski, M. Monkenbusch, L. Willner, D. Richter, A. E.Likhtman, G. Kali, and B. Farago. Physical Review Letters, 96(23):art. no. 238302, 2006.

S. Rathgeber, L. Willner, D. Richter, et al.,
Journal of Chemical Physics **110**, 10171 (1999).

MW dependence to see the gradual build up of constraints

A mixture of short ($1xN_e$) and long ($3xN_e$) chains

mode analysis with the help Pulsed Gradient NMR

10% long

87% long

NSE mainstream & bizarroids

PS semidilute solution ⇒ Zimm dynamics $S(q,t) \approx e^{-(t/\tau)^{\frac{2}{3}}}$ with $\tau^{-1} \propto \frac{q^3}{\eta}$

scale with: $q^3 t$

scale with: η

the monomers-solvent contact is preferred over monomer-monomer contact (benzene is a good solvent)

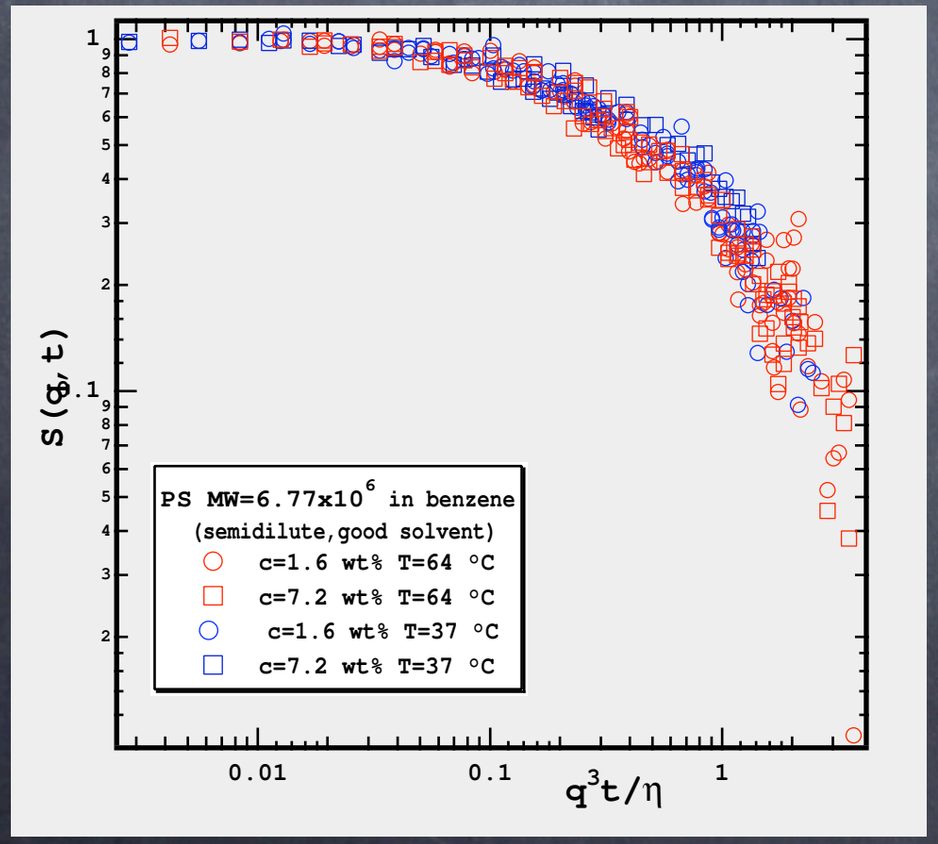
six q values two concentrations, two temperatures => one mastercurve

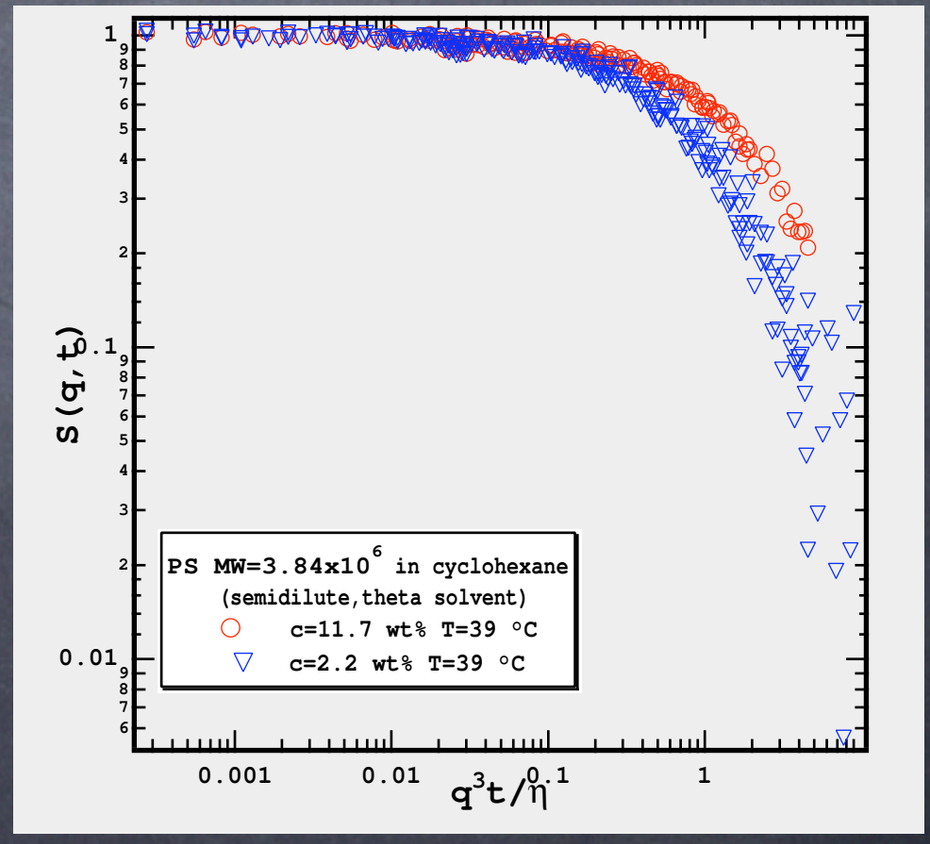
PS in Cyclohexane 39°C

THETA solvent

no preferred neighbour

scaling with q is OK, but concentration dependence!

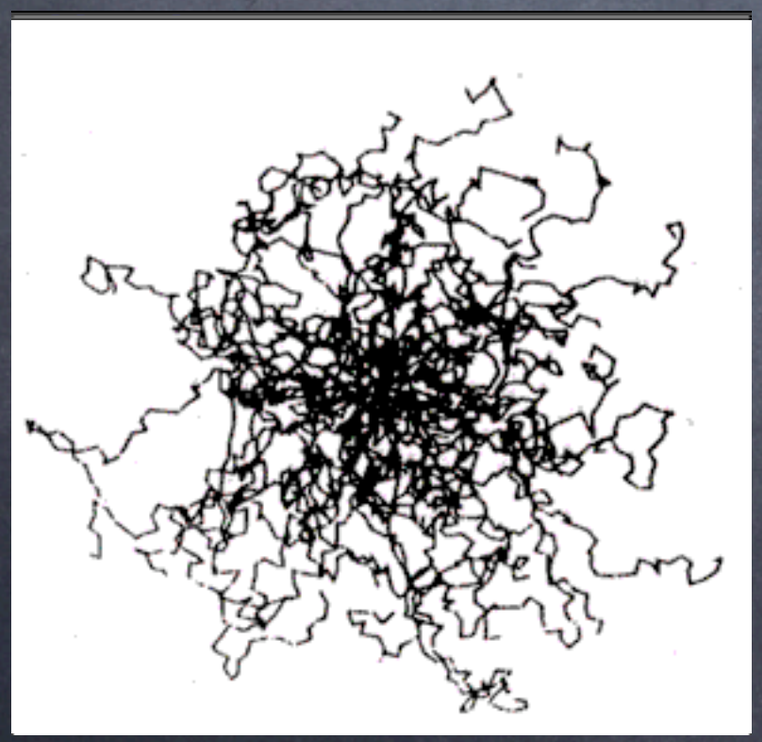


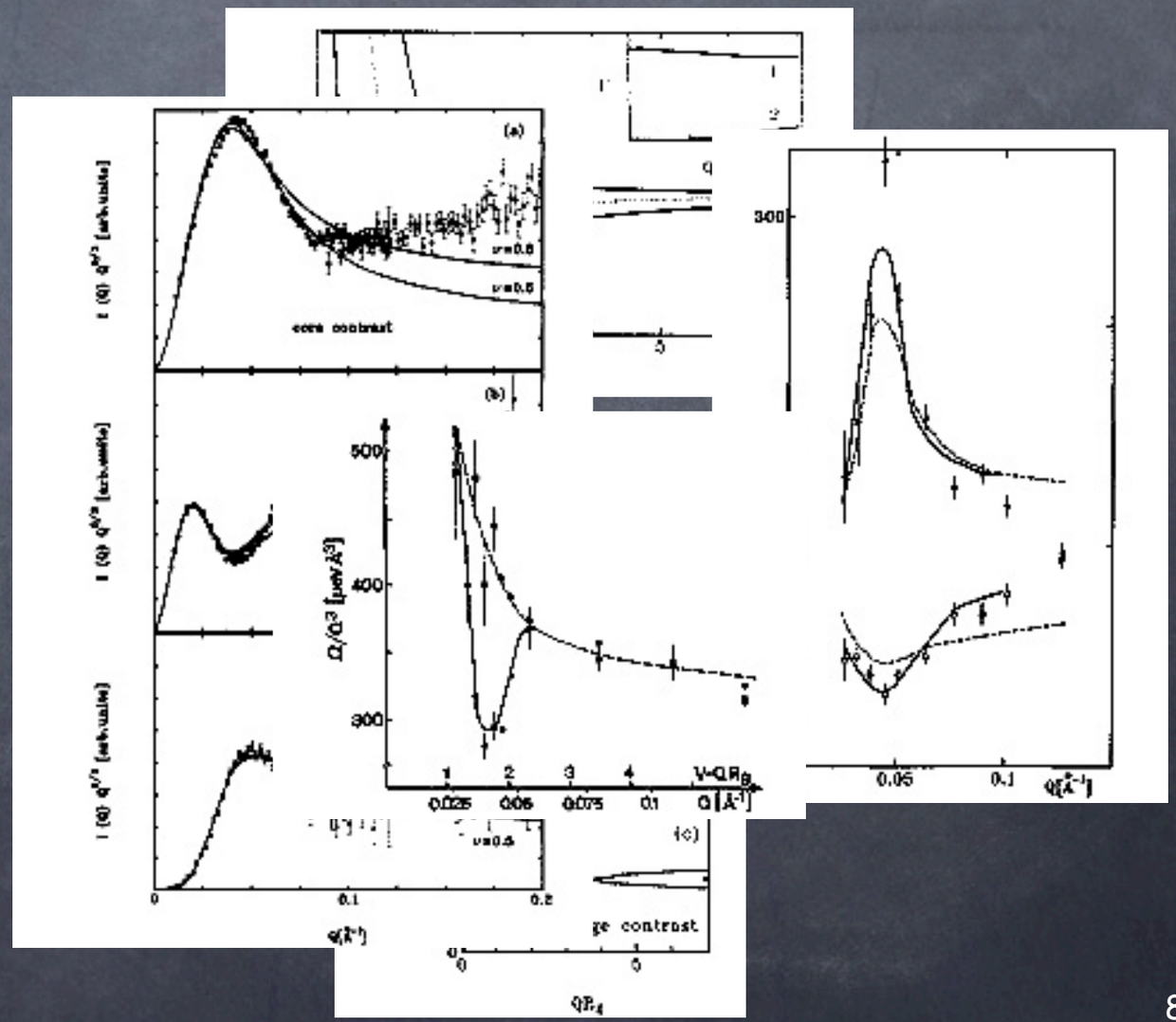


M. Adam, D. Lairez, E. Raspaud, et al., Physical Review Letters **77**, 3673 (1996).
M. Adam, B. Farago, P. Schleger, et al., Macromolecules **31**, 9213 (1998).

Star polymers with different isotope labeling

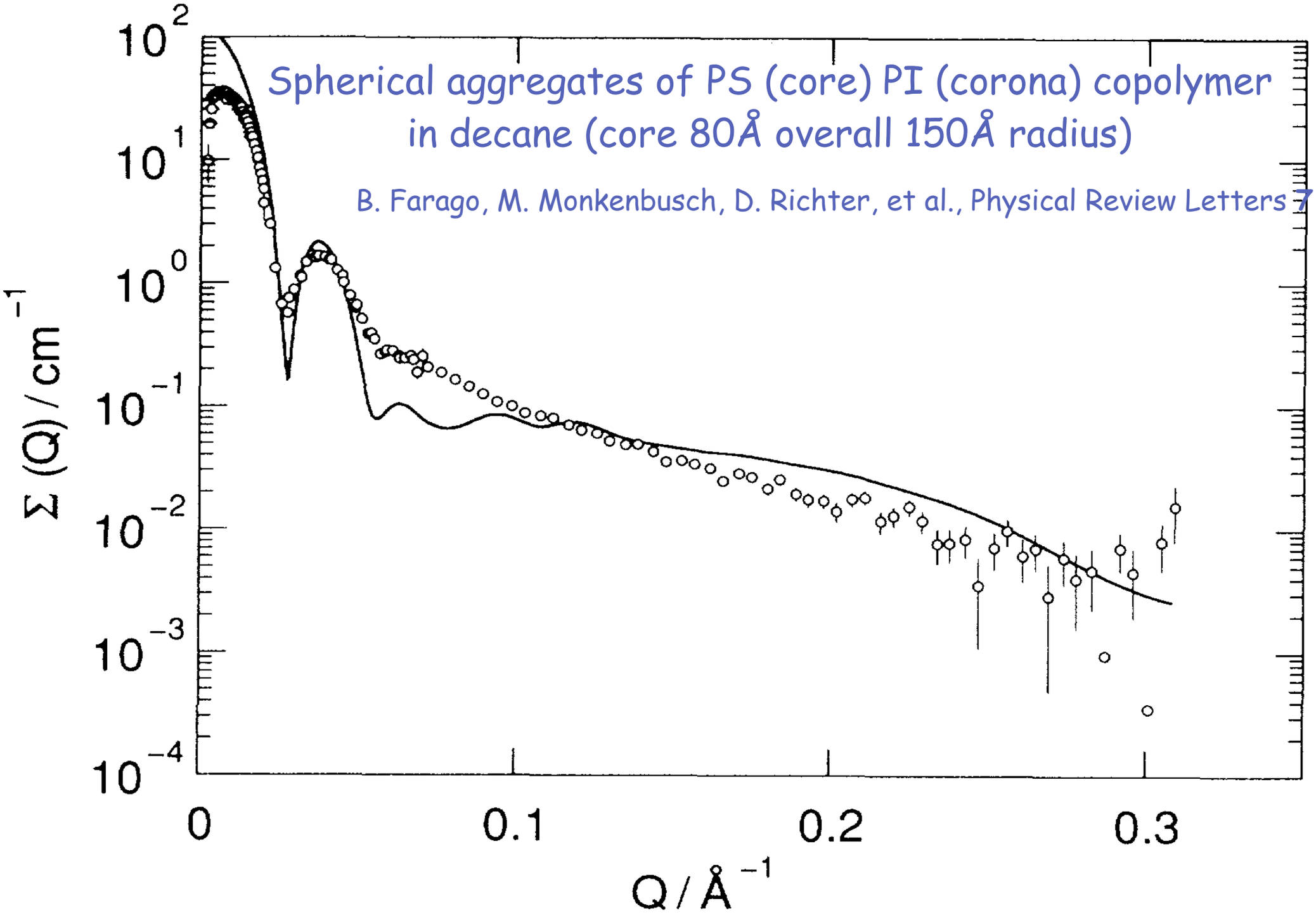
D. Richter, B. Farago, J. S. Huang, et al., Macromolecules **22**, 468 (1989).
D. Richter, B. Farago, L. J. Fetters, et al., Macromolecules **23**, 1845 (1990).





Spherical aggregates of PS (core) PI (corona) copolymer in decane (core 80Å overall 150Å radius)

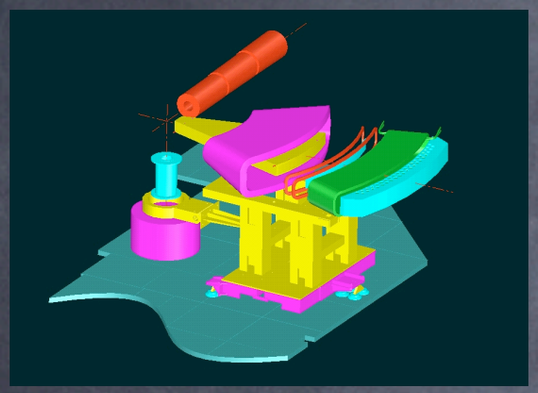
B. Farago, M. Monkenbusch, D. Richter, et al., Physical Review Letters **71**, 1015 (1993).



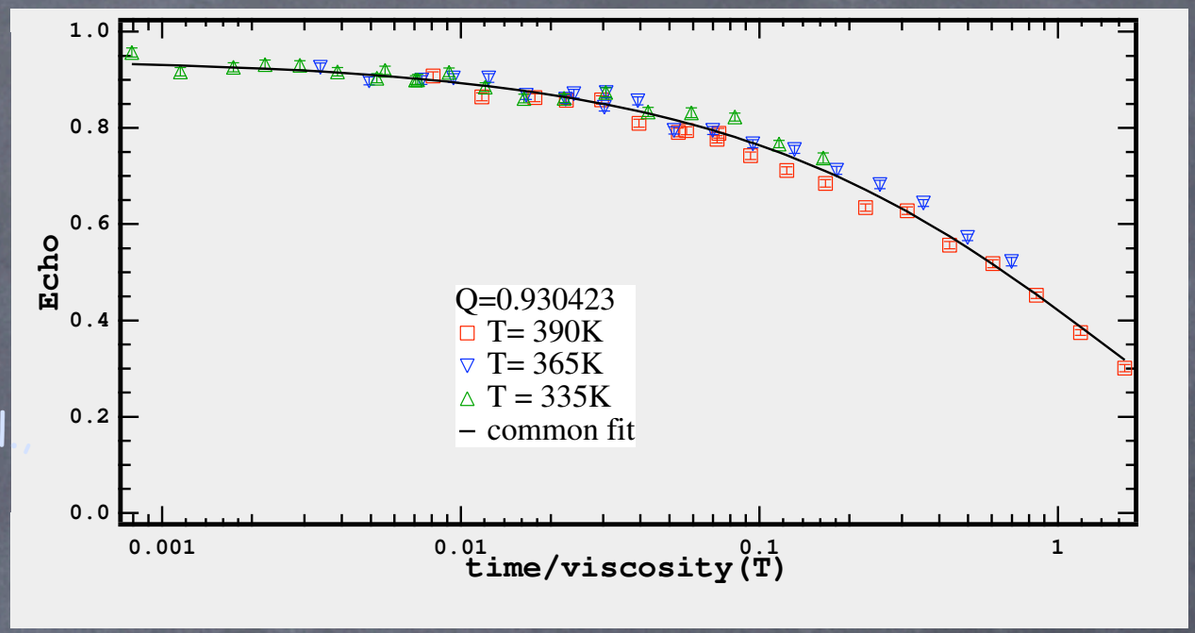
Glassy systems

-Time temperature superposition

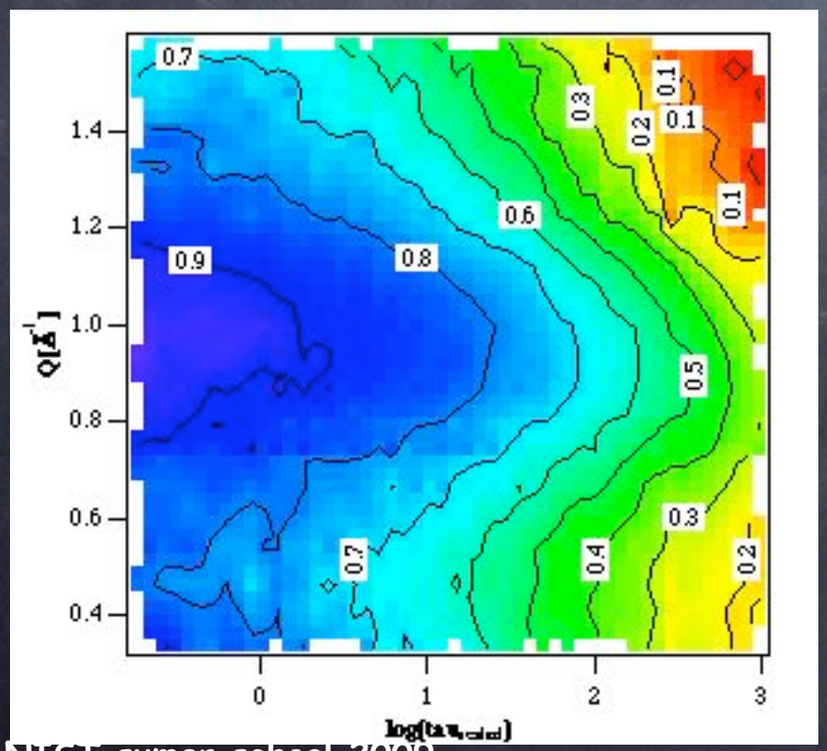
- two distinct relaxations



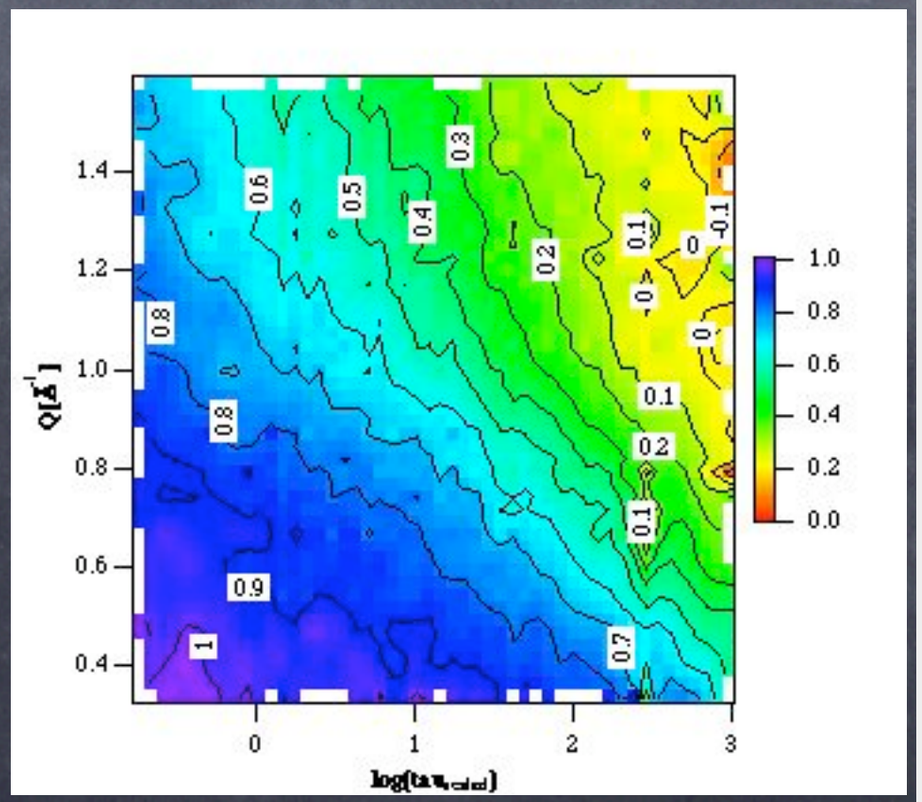
B. Farago, A. Arbe, J. Colmenero, et al., Physical Review E **65**, (2002).

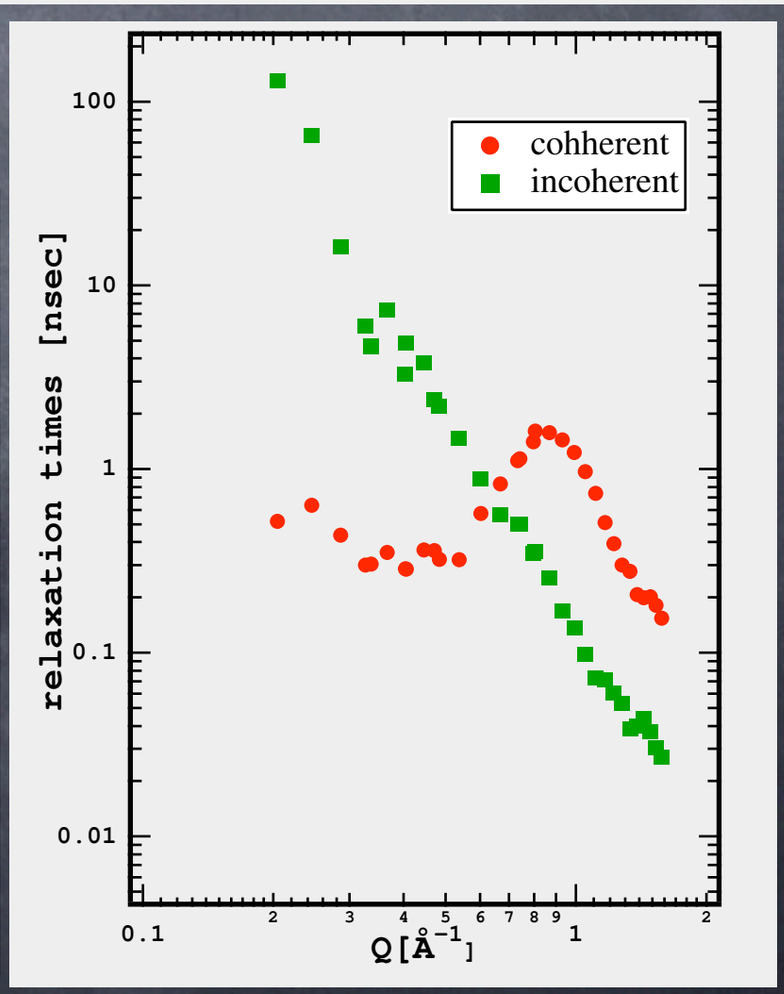


dPIB



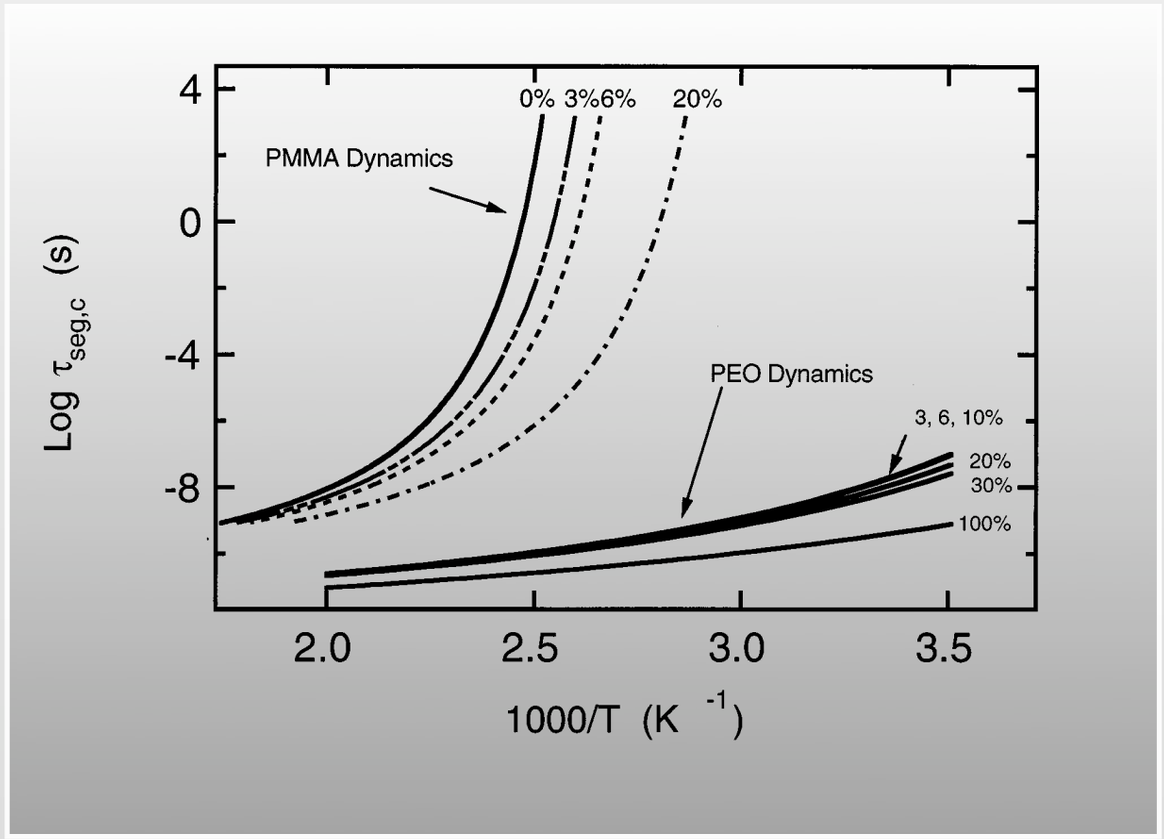
hPIB





PEO Tg=221K PMMA Tg=402K

- Polymer blend with very different Tg
- Colby at al finds tTs does not work
- Lutz et al dNMR finds 12 order of magnitude difference at Tg-blend and explains it with surviving local segmental dynamics



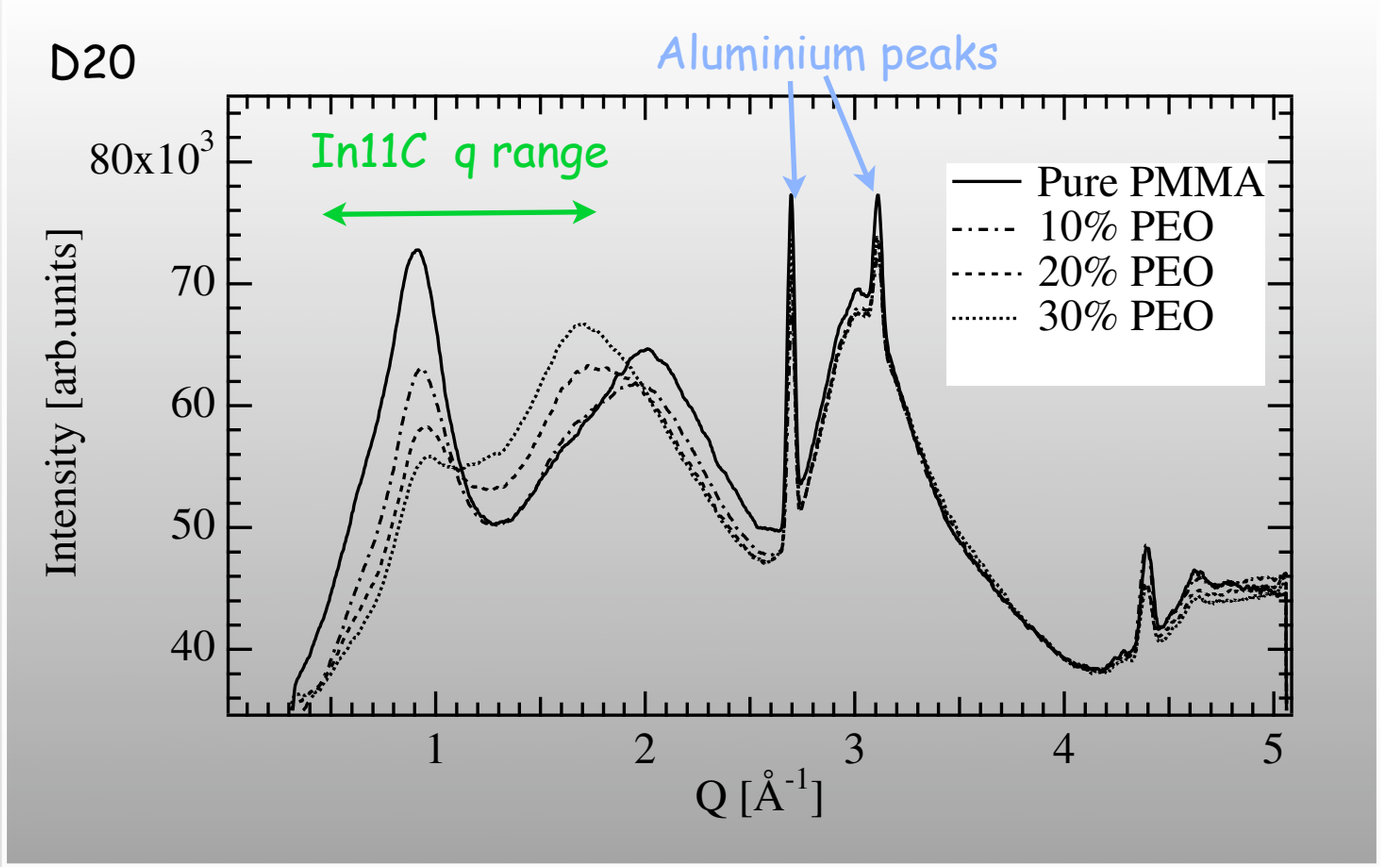
T. R. Lutz, Y. Y. He, M. D. Ediger, H. H. Cao, G. X. Lin, and A. A. Jones, Macromolecules 36, 1724 (2003).

NSE mainstream & bizarroids

10%, 20%, 30% dPEO in dPMMA (coherent scattering)

Tg = 365, 348, 326K, NSE done at 273K ≤ T ≤ 412K

Shell we see anything?



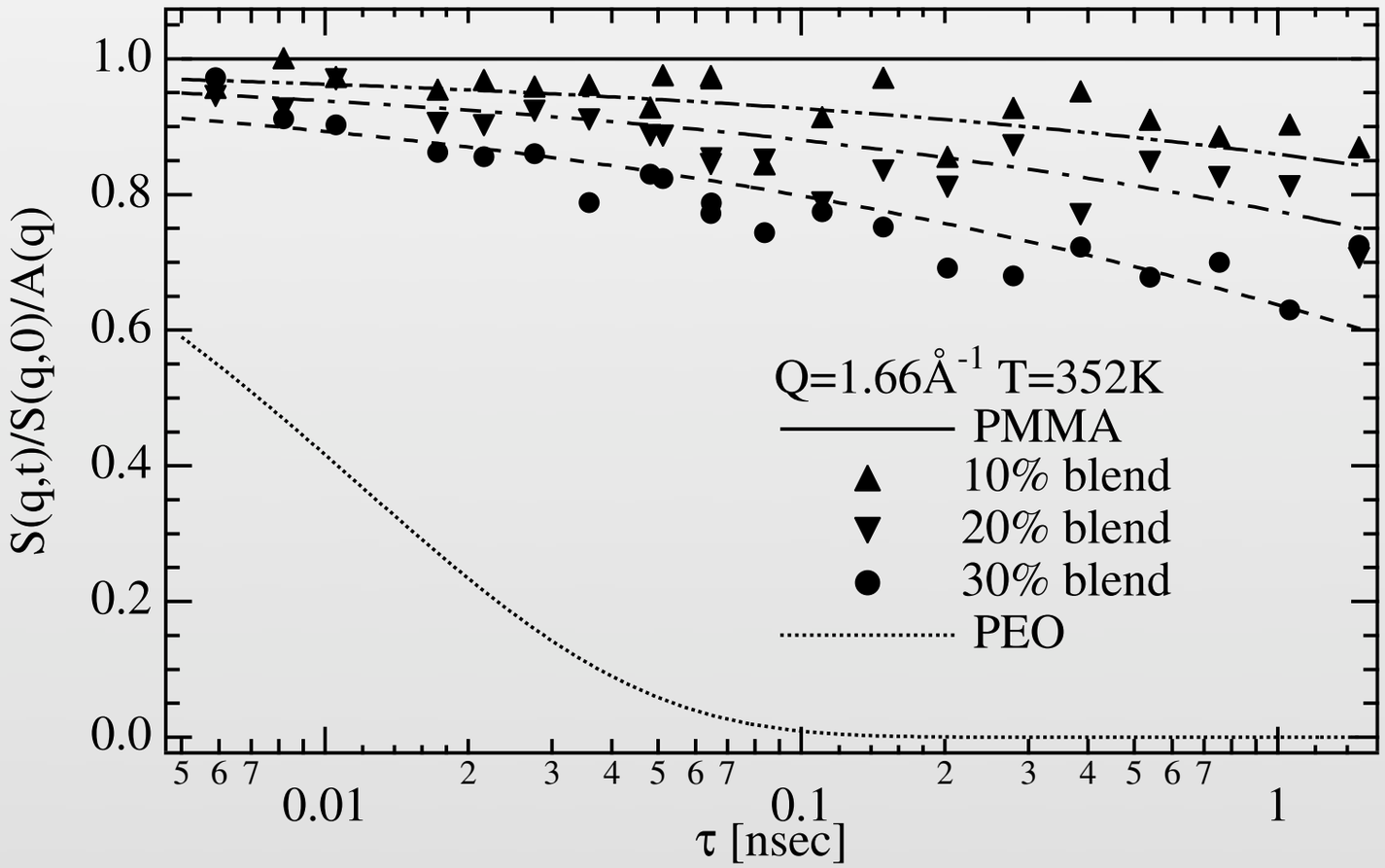
Break up I(q,t) into partial structure factors

$$I(q,t) = \sum_{\substack{i\in PMMA \\ j\in PMMA}} \left\langle b_i b_j \exp[i\vec{q}\cdot\vec{r}_{ij}(t)]\right\rangle + 2\sum_{\substack{i\in PEO \\ j\in PMMA}} \left\langle b_i b_j \exp[i\vec{q}\cdot\vec{r}_{ij}(t)]\right\rangle + \sum_{\substack{i\in PEO \\ j\in PEO}} \left\langle b_i b_j \exp[i\vec{q}\cdot\vec{r}_{ij}(t)]\right\rangle$$

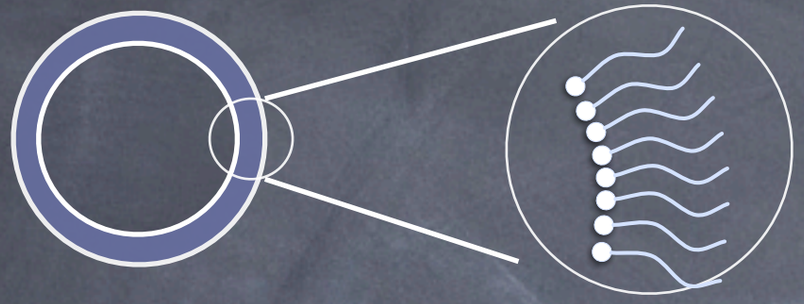
$$I(q,t) = I_{PMMA-PMMA}(q,t) + 2I_{PEO-PMMA}(q,t) + I_{PEO-PEO}(q,t)$$

If one component e.g. PMMA is immobile only the pure e.g. PEO factor shows dynamics!

Comparing pure components to the blends at a given temperature

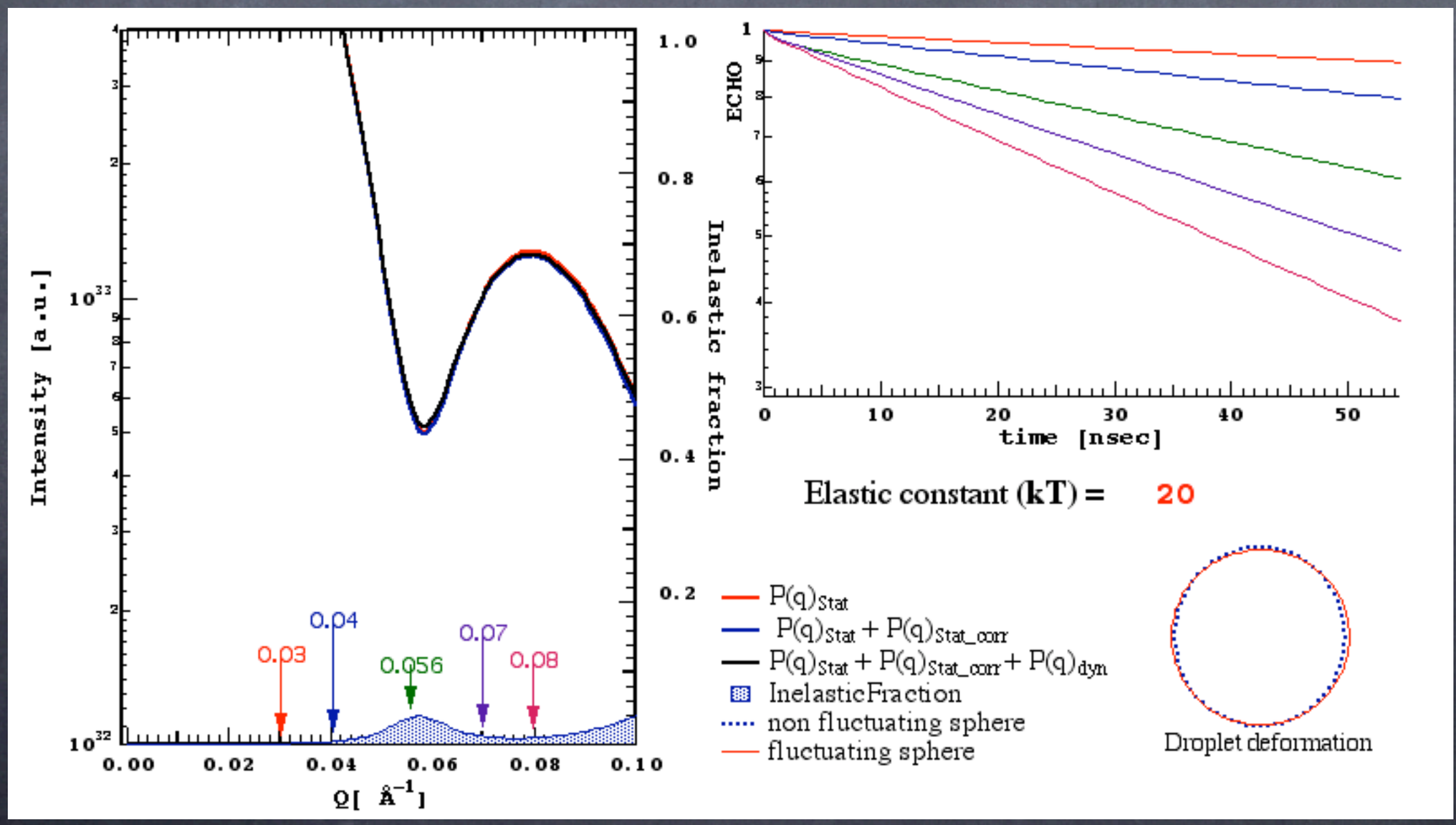


NSE mainstream & bizarroids



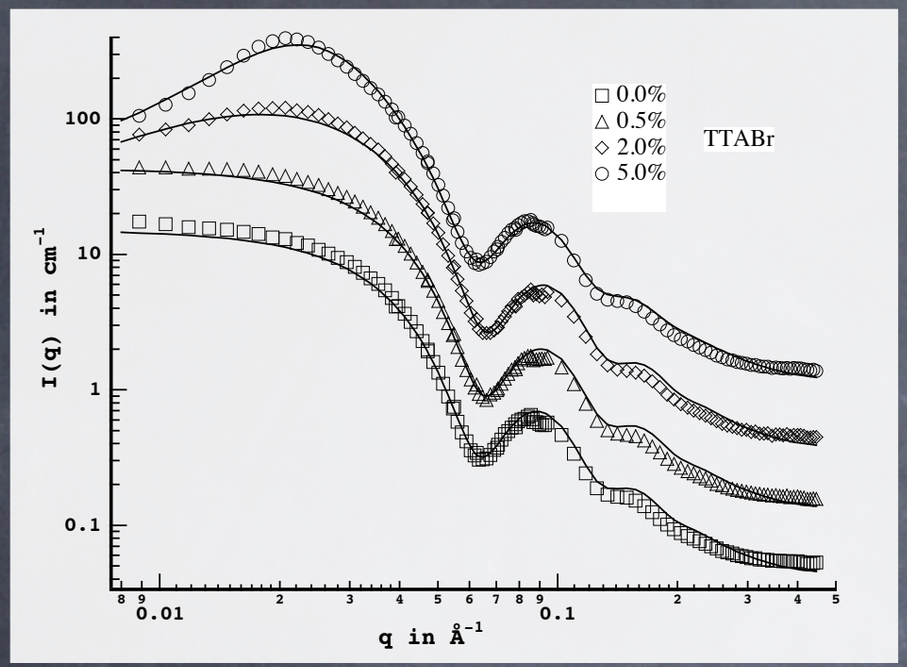
d-Water in d-oil microemulsion => soft layer

- low Q (<1/R) center of the mass diffusion: $\exp(-DQ^2t)$
- higher Q diffusion + shape fluctuations



J. S. Huang, S. T. Milner, B. Farago, et al., Physical Review Letters **59**, 2600 (1987).
B. Farago, D. Richter, J. S. Huang, et al., Physical Review Letters **65**, 3348 (1990).

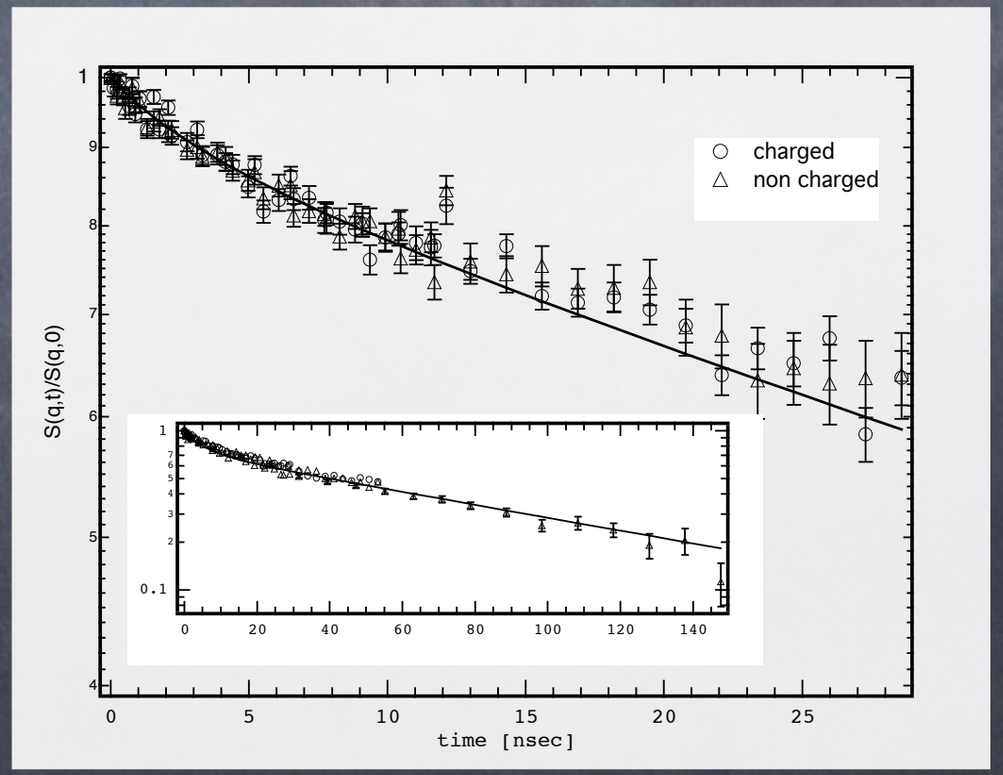
NSE mainstream & bizarroids



Mixing charged (TTABr) and non charged (TDMAO) surfactants hexanol, decane the surface charge can be varied (z= 0 -> 12.1)

B. Farago and M. Gradzielski, Journal of Chemical Physics **114**, 10105 (2001).

No influence on the bending elasticity!



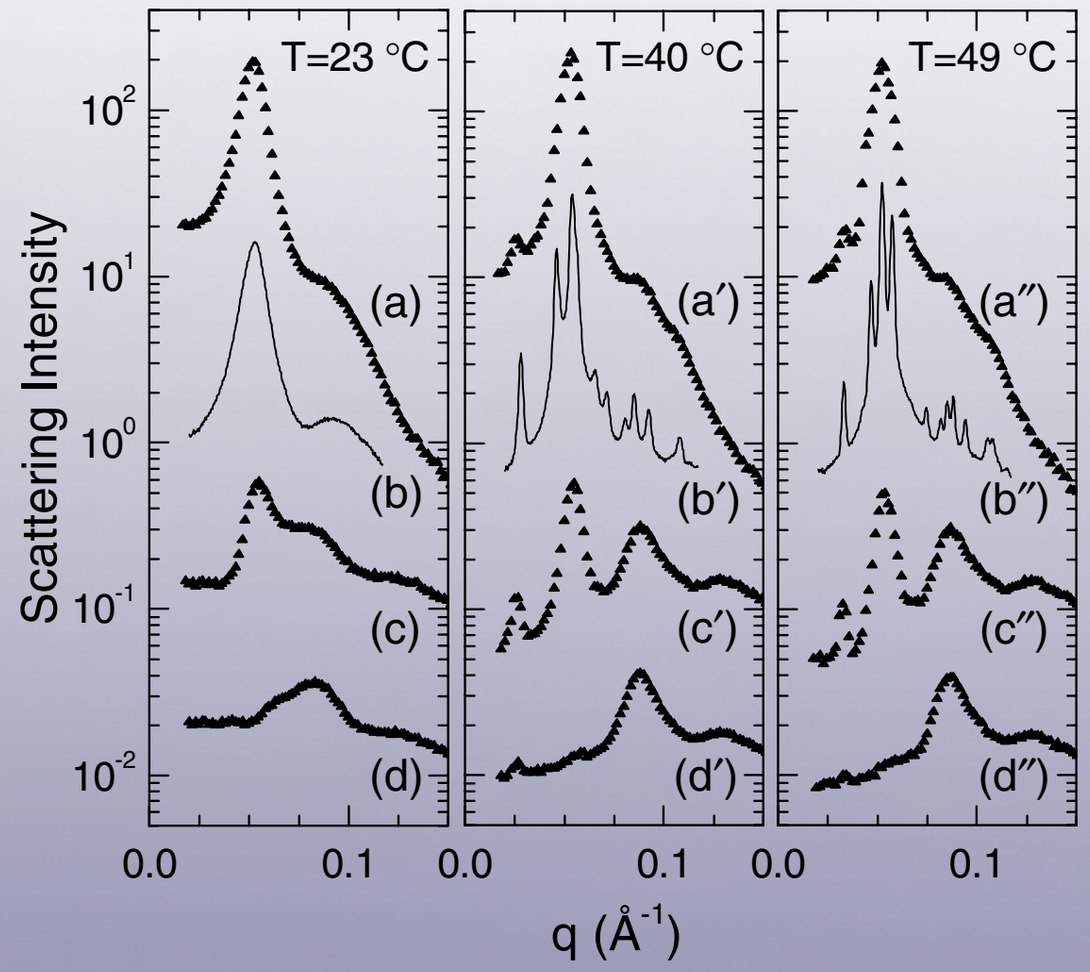
SDS/buthanol/brine/toulene

at 62% vf cubic (Fd3m) phase

polyhedral oil droplets d~150Å

separated by ~28Å water layer

phase: liquid Fd3m Pm3n

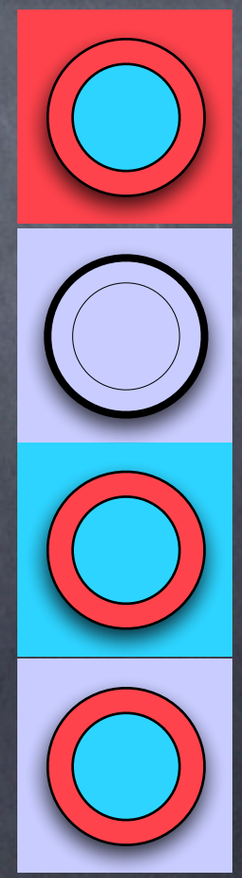


Core contrast

Xray diffraction

Shell contrast

Match contrast



NSE mainstream & bizarroids

J. Phys. Chem. B 2000, 104, 6610-6617

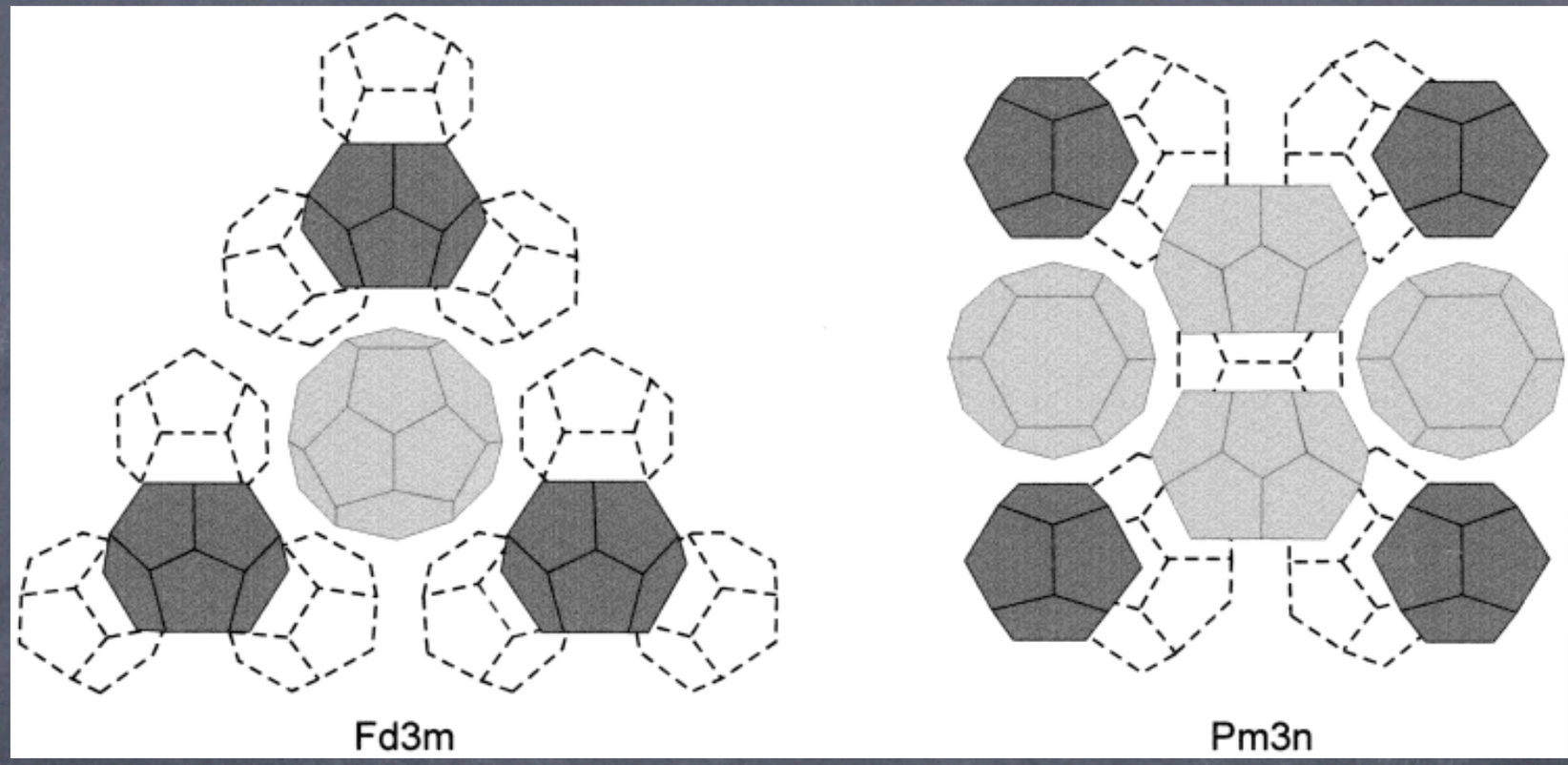
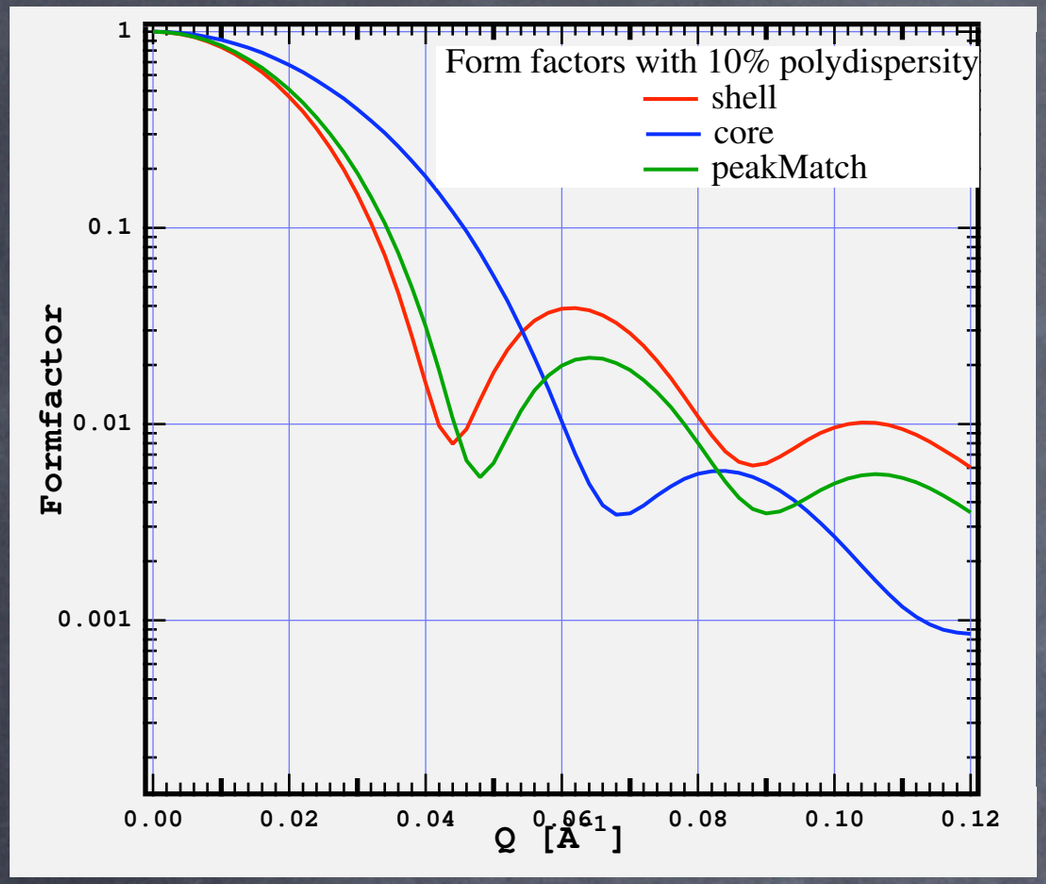
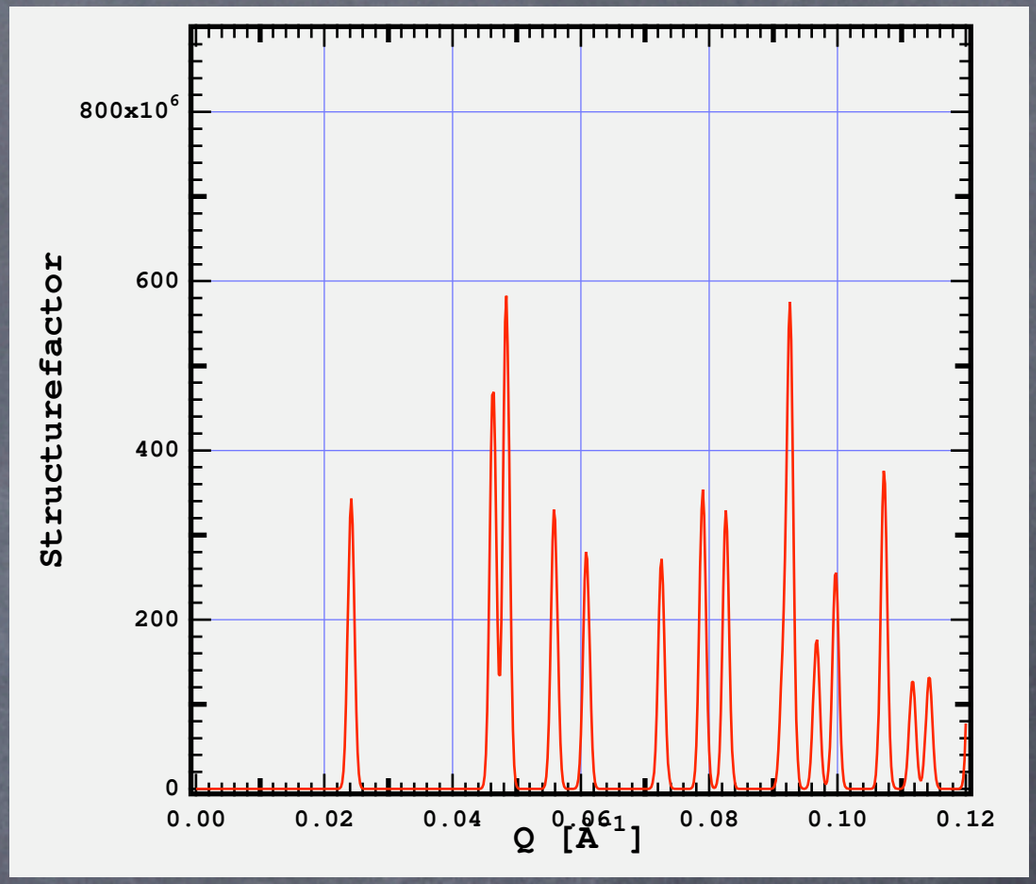


Figure 4. Schematic drawing of the A15 (*Pm*3*n*) and C15 (*Fd*3*m*) tetrahedrally close-packed structures proposed for the two cubic phases of the SDS/butanol/toluene/brine system. For both structures, an aqueous bilayer compartmentalizes the oil nanophase into tetrahedral networks that are combinations of pentagonal dodecahedra (dark gray) with 14-face polyhedra (light gray) in *Pm*3*n* and with 16-face polyhedra (light gray) in *Fd*3*m*. Only part of the *Fd*3*m* unit cell is represented.

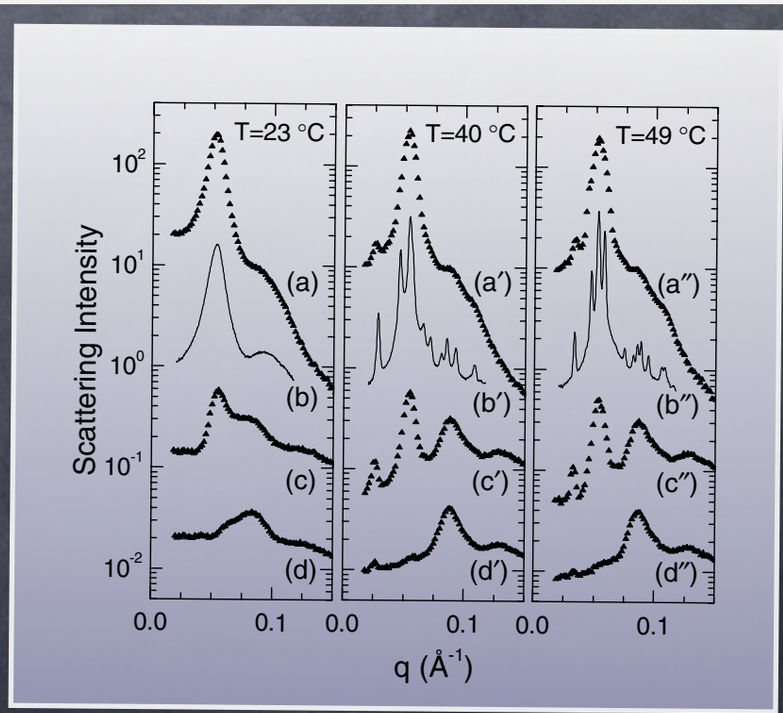
NSE mainstream & bizarroids



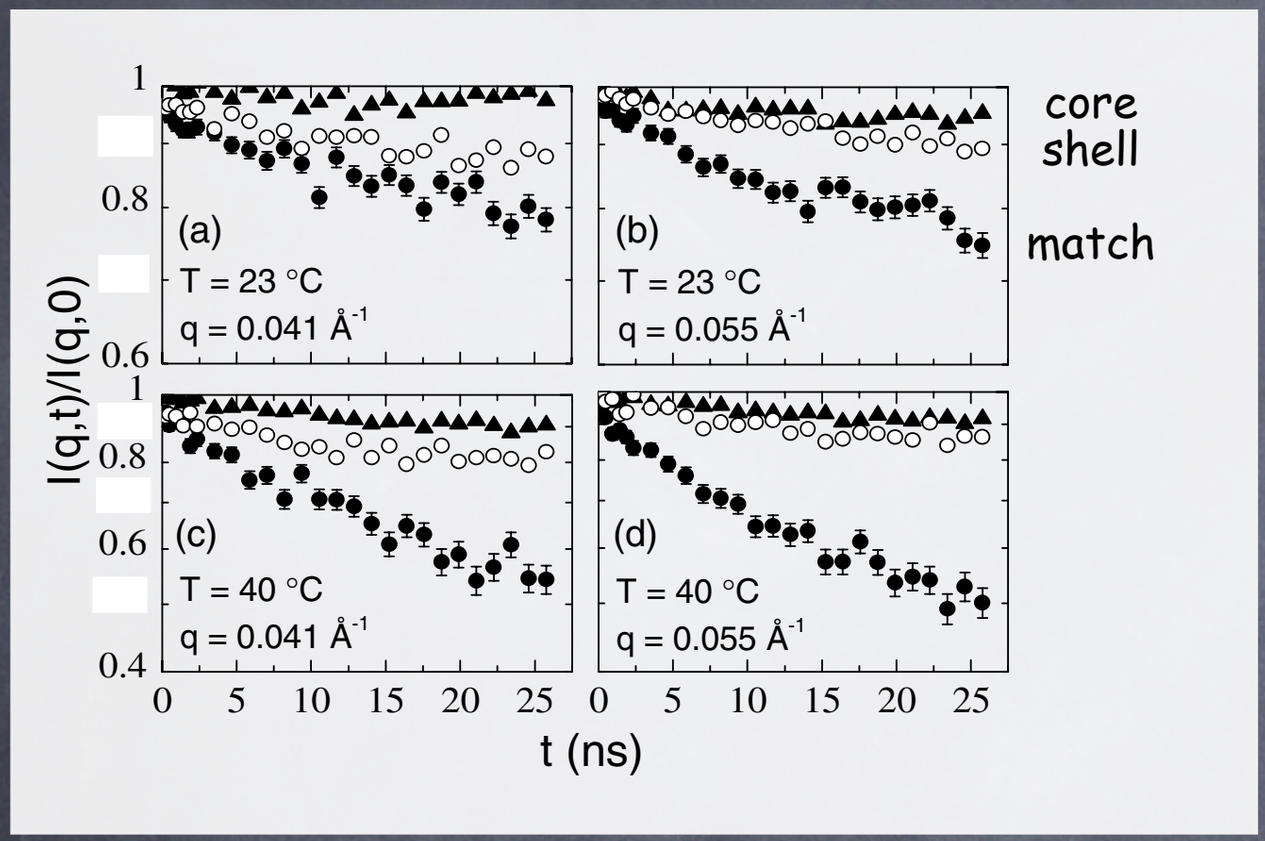


The shell formfactor minimum nearly coincides with a Bragg peak!

Peak matching contrast moves it to the correct position



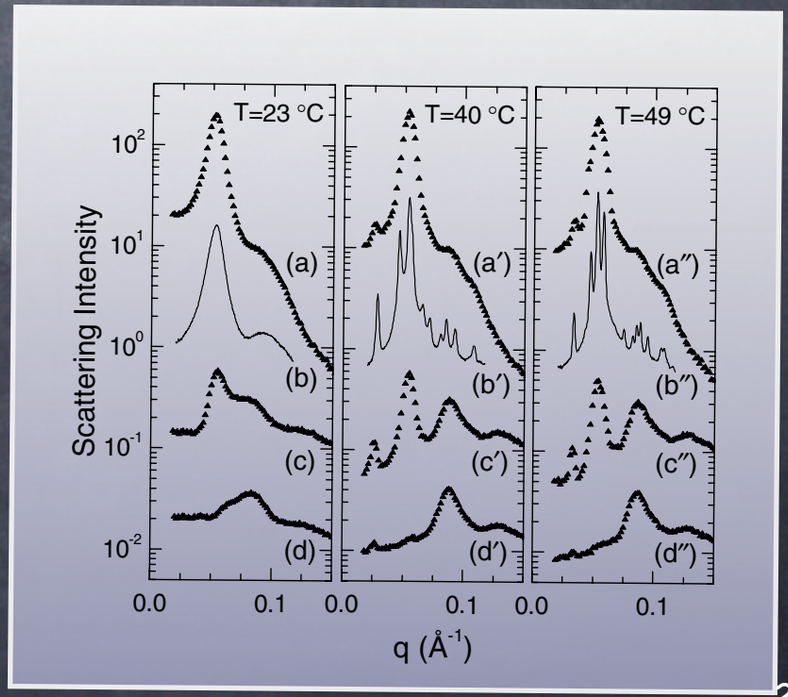
NSE mainstream & bizarroids



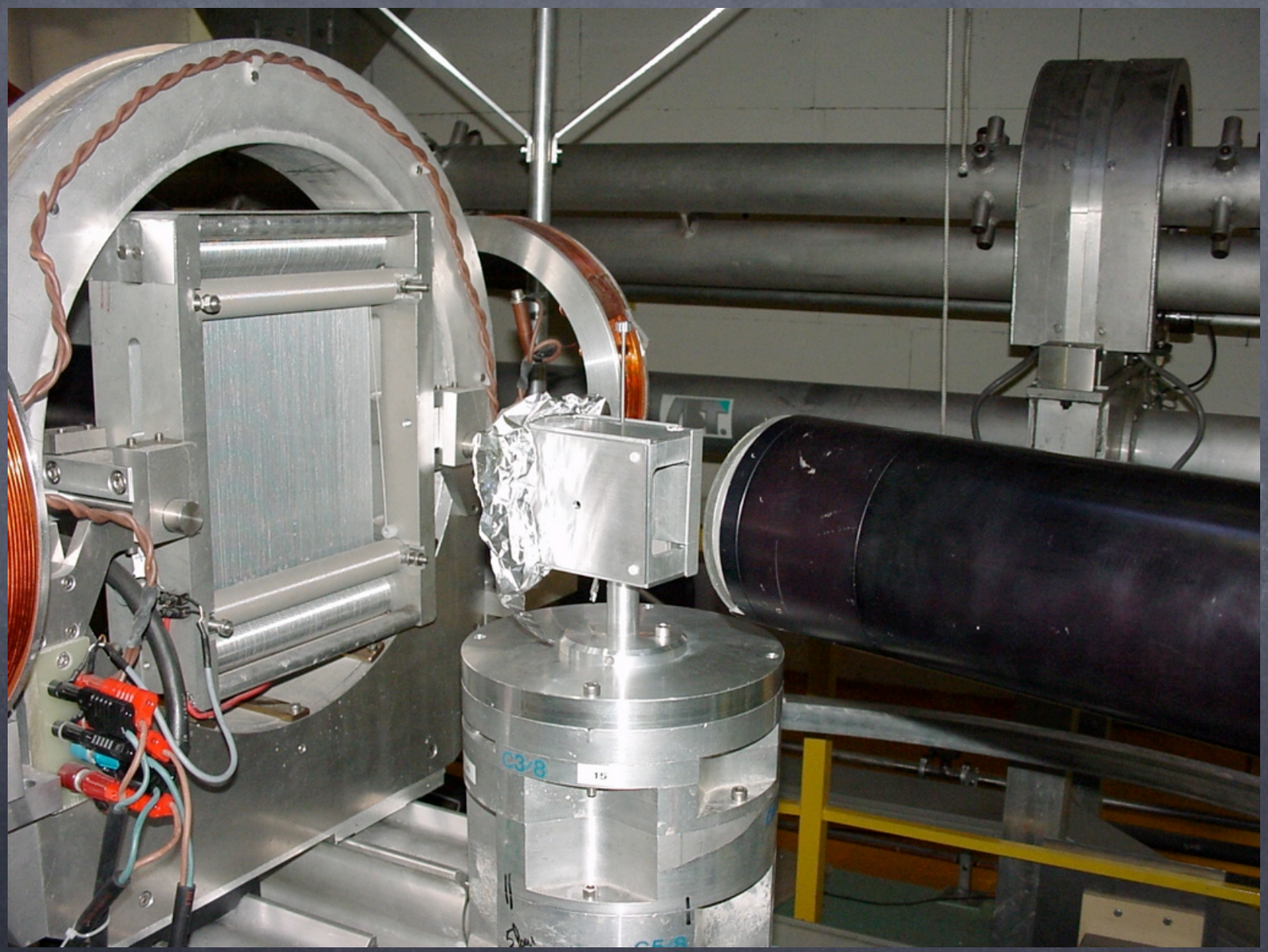
The core contrast is within limit elastic at the peak

The shell contrast shows a weak decay

The 'match' contrast has a well pronounced decay



NSE mainstream & bizarroids



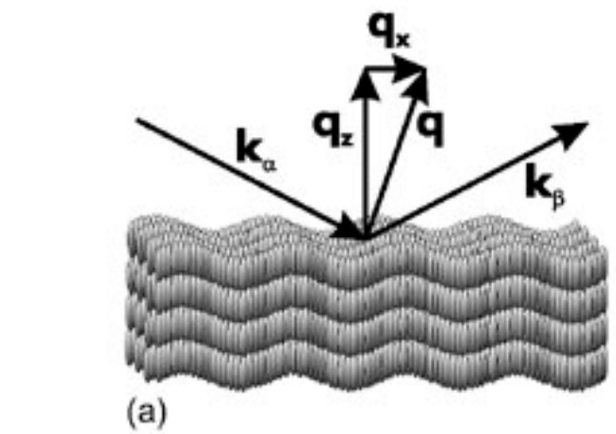
Sample thickness changes from 0.5 to several μm

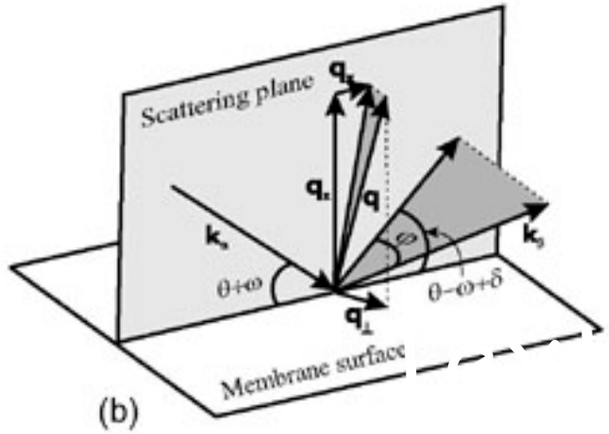
NSE mainstream & bizarroids

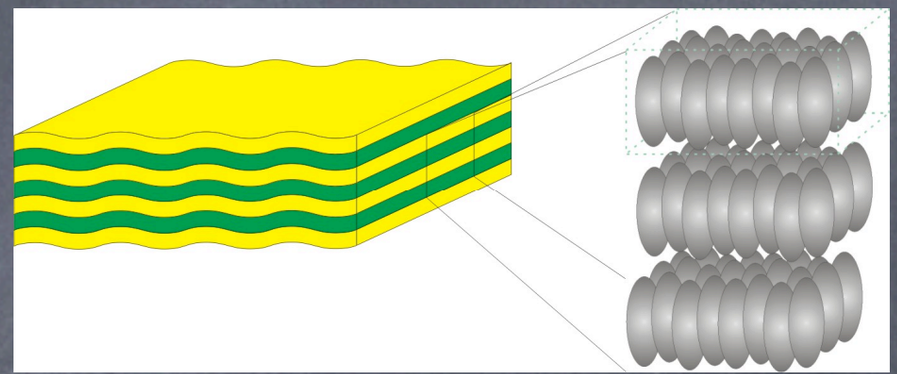
Free standing film

smectic-*A* membranes of the compound 4-octyl-40-cyanobiphenyl (8CB)

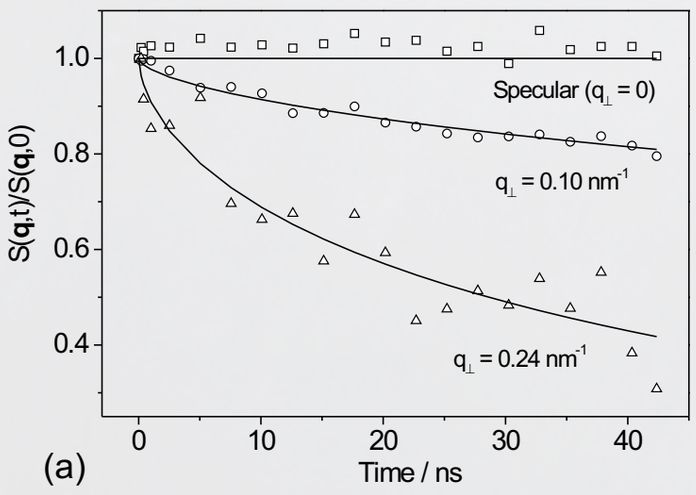
I. Sikharulidze, B. Farago, I. P. Dolbnya, A. Madsen, Wim H. de Jeu,Phys. Rev. Lett. 16 2003



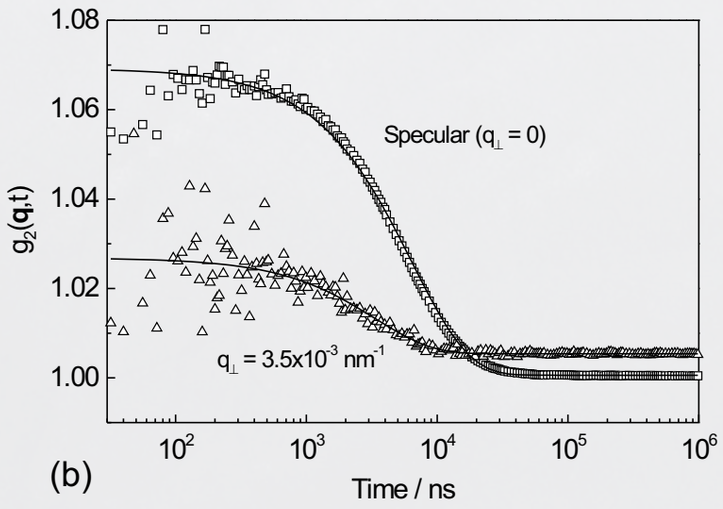


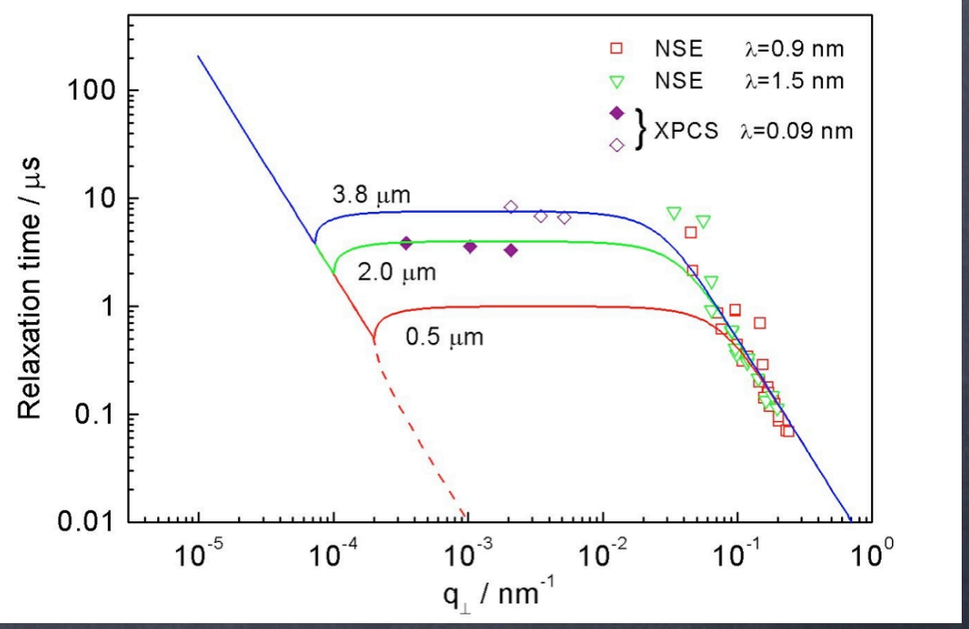


NSE



Xray Photon correlation





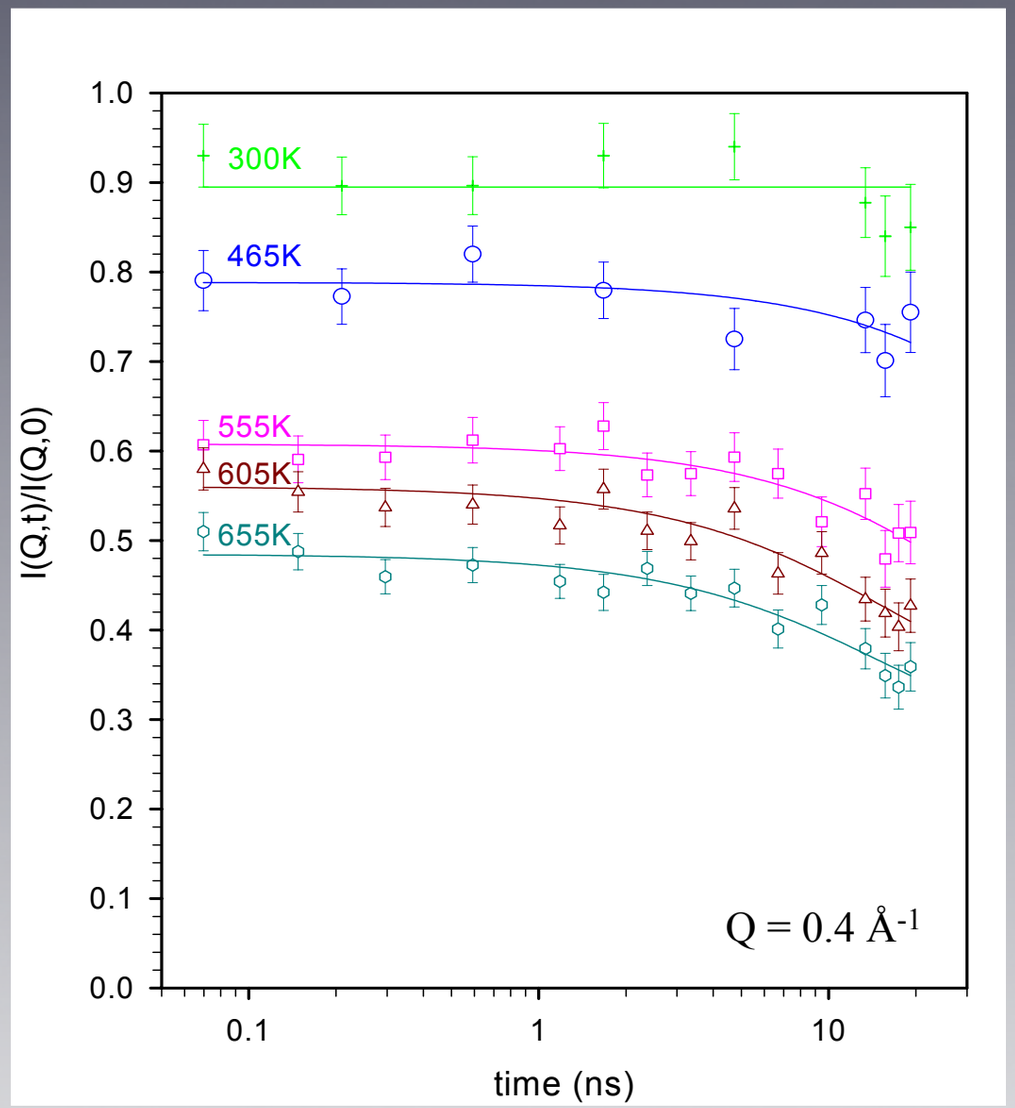
Zeolites are an extremely important class of material in particular for alkane chains (separation, catalysis...)

The diffusion is the key for functionality

- Has been extensively studied by incoherent scattering
- Also deuterated molecules were used to investigate the structure
- D-transport,D-self, D-cooperative are very close at low Q....
- Models and thermodynamics link them together

NSE mainstream & bizarroids

first trial



C_6D_6 / ZSM-5

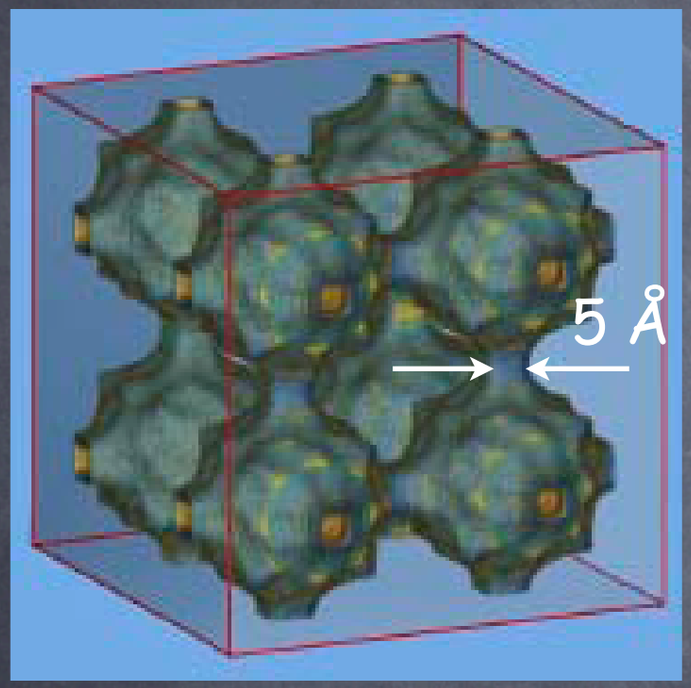
(3 molecules/u.c.)

IN11

Better resolution is needed

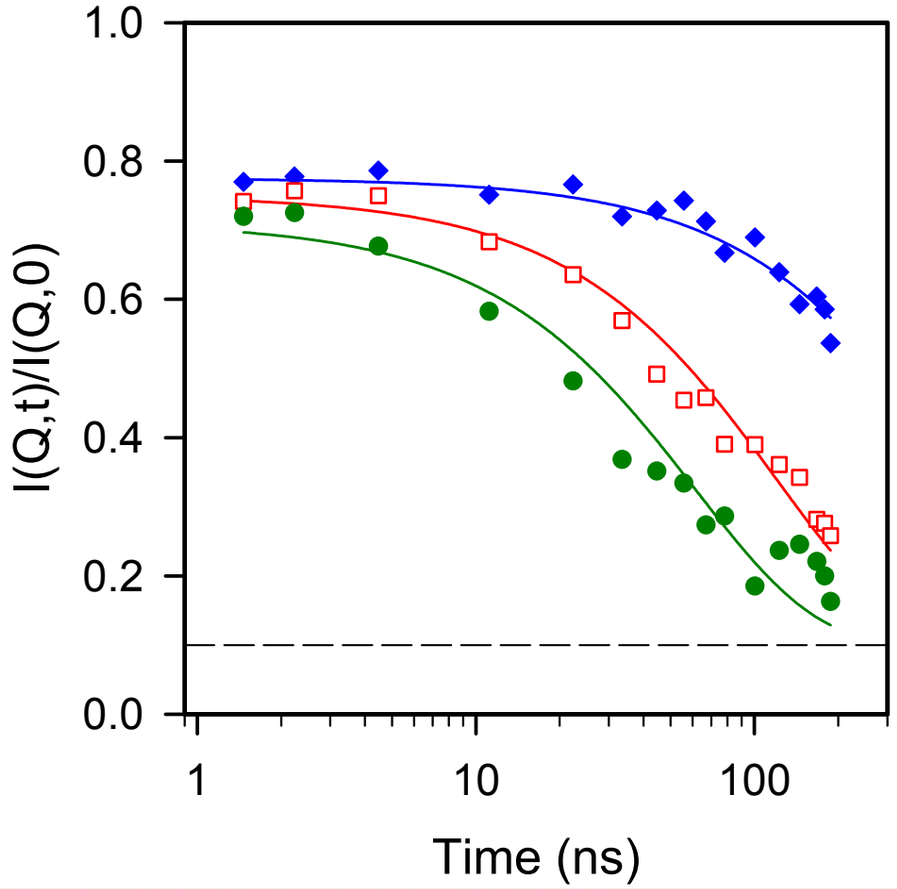
$$\sum_{\ell=1}^{\infty}(2\ell+1)\sum_{m,m'=1}^{n}\left\{b_{coh}^{m}\,b_{coh}^{m'}+b_{inc}^{m\;2}\,\delta_{mm'}\right\}j_\ell(Q\,r_m)\;j_\ell(Q\,r_{m'})\;P_\ell(\cos\Theta_{m\,m'})\,\Lambda_\ell{}^{rot}(\omega)$$

5A zeolite



n-alkanes in NaCaA (5A)

(T = 475 K, Q = 0.2 Å^{-1})



octane

decane

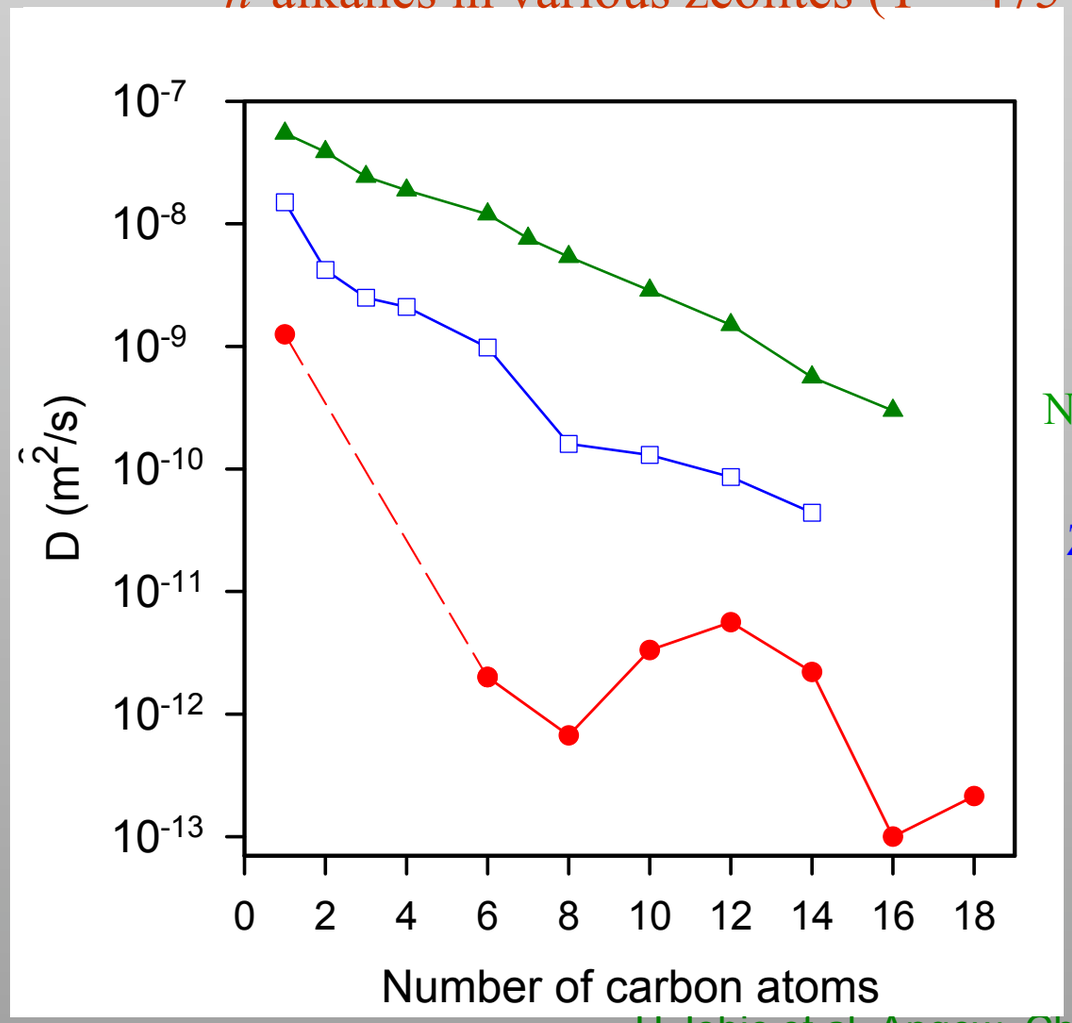
dodecane

IN15

NSE mainstream & bizarroids

‘Window effect’

n-alkanes in various zeolites (T = 475 K)



NaX (PFG NMR)

ZSM-5 (QENS)

5A (NSE)

H.Jobic et al. Angew. Chem. 43 (2004) 364

Examples on magnetic scattering

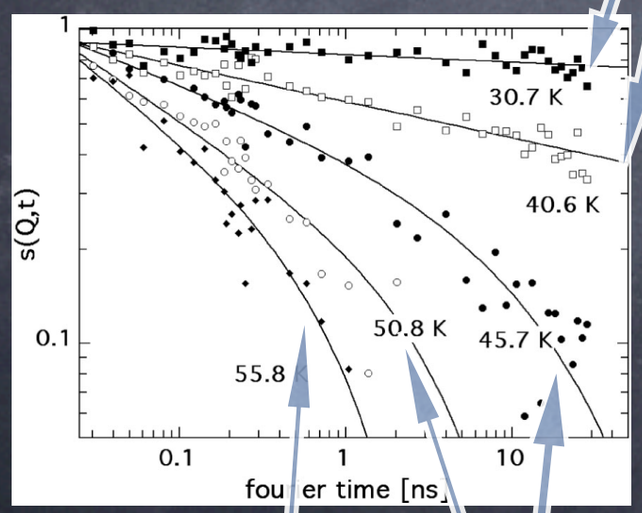
- Spin Glass
- Spin Ice
- Fe nanoparticles in Al

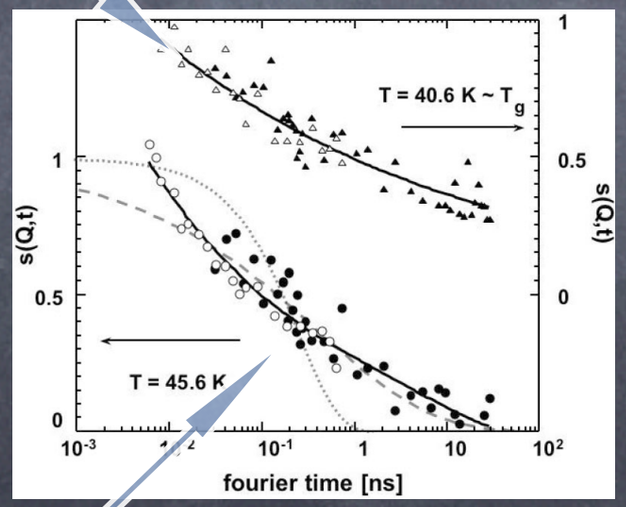
$Au_{0.86}Fe_{0.14}$ metallic Heisenberg spin glass

Just below the 0.15 concentration where becomes FM

=> strong Fm correlations => strong signal

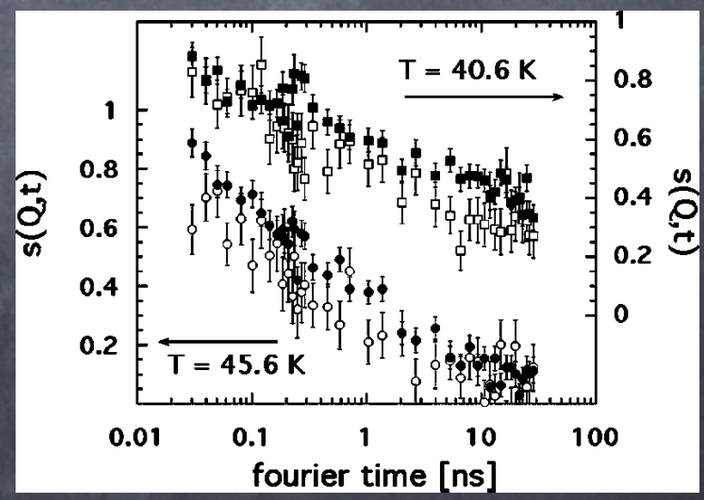
Power law decay for T<Tg





Q independent dynamics

open symb 0.4Å^{-1} closed symb 0.8Å^{-1}



Ogileski function (power law•KWW)

T>Tg

C. Pappas , Mezei ,F, Ehlers ,G, Manuel ,P, Campbell ,I A, Physical Review B 68, 054431 (2003).

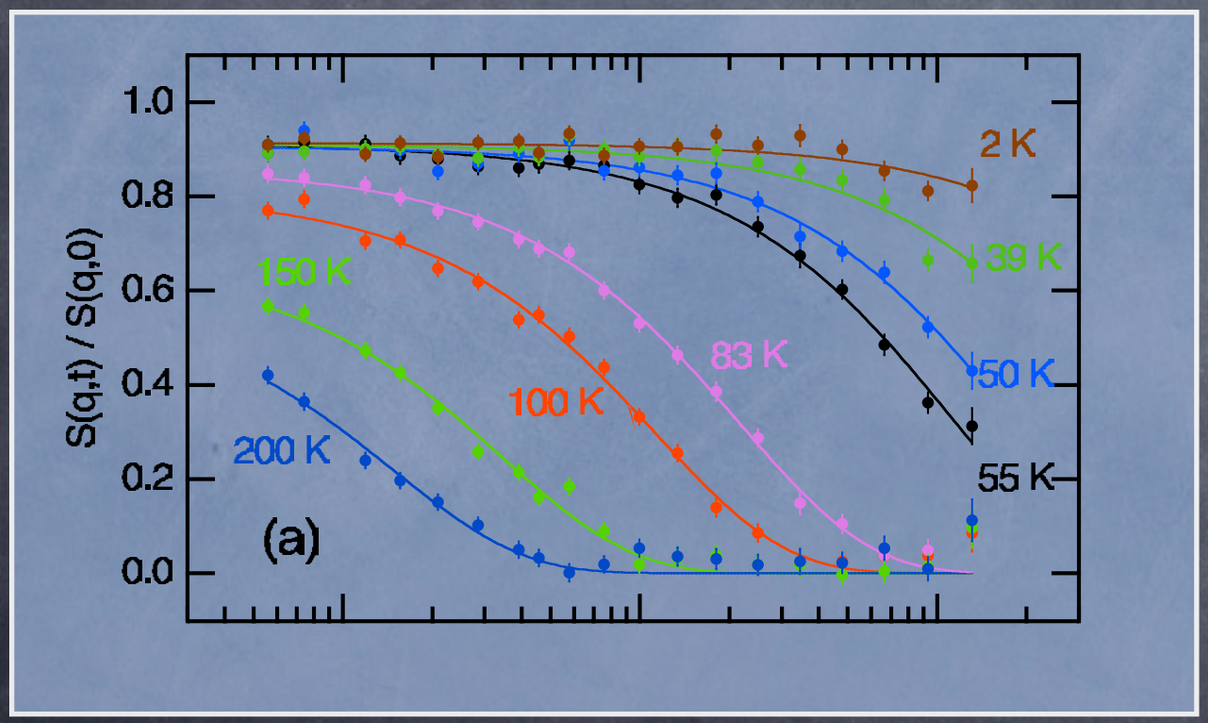
NSE mainstream & bizarroids

'spin ice' materials $Ho_2Ti_2O_2$, $Dy_2Ti_2O_7$ and $Ho_2Sn_2O_7$

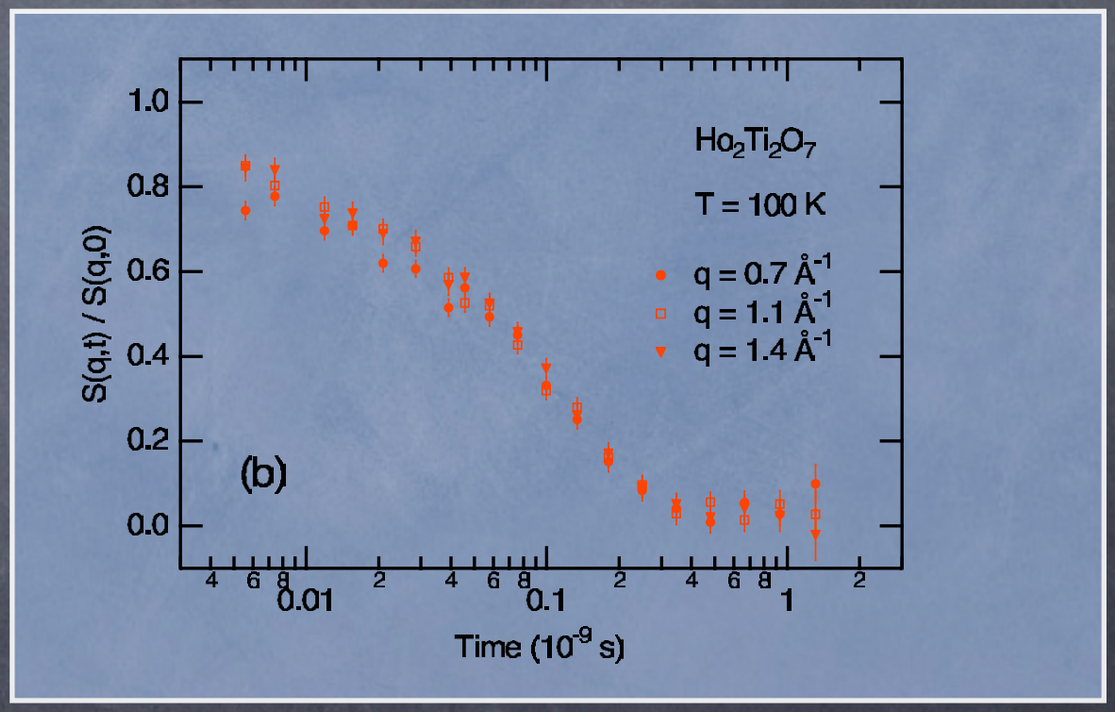
the spin is equivalent to the H displacement vector in water ice

all three has a peak in susceptibility at 1K but
missing 15K susceptibility peak in the Ho componds...

Single exponential thermally activated

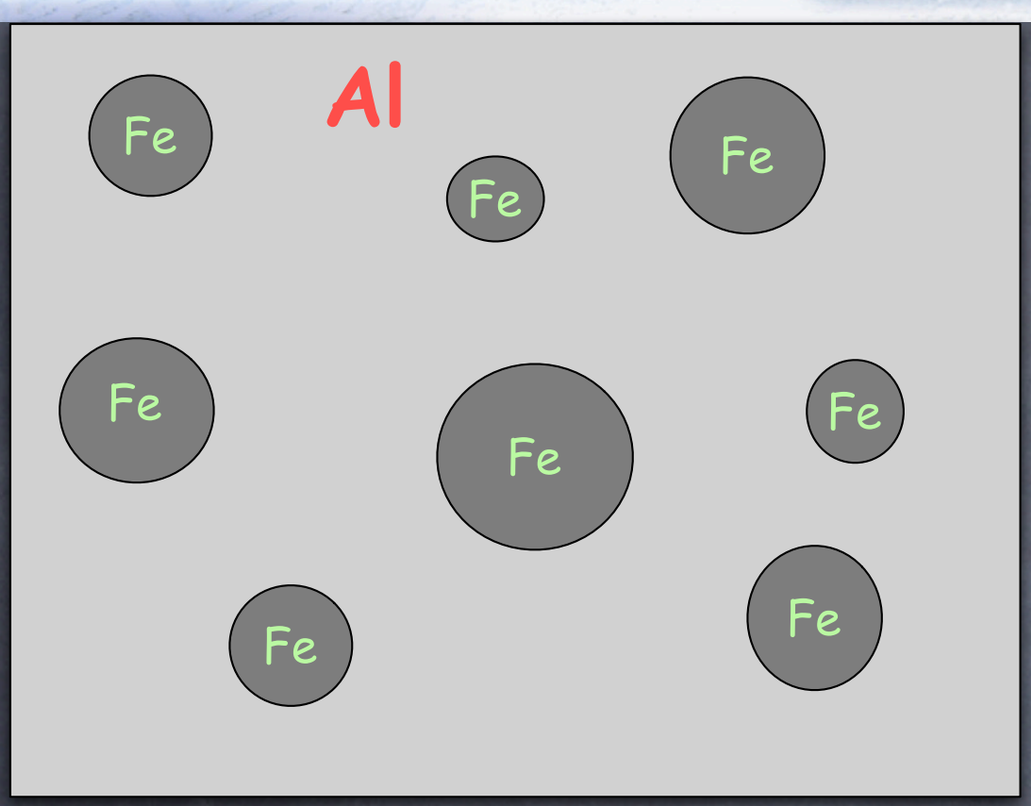


Q independent relaxation



Whichever of the two processes is faster relaxes completely the whole spin system

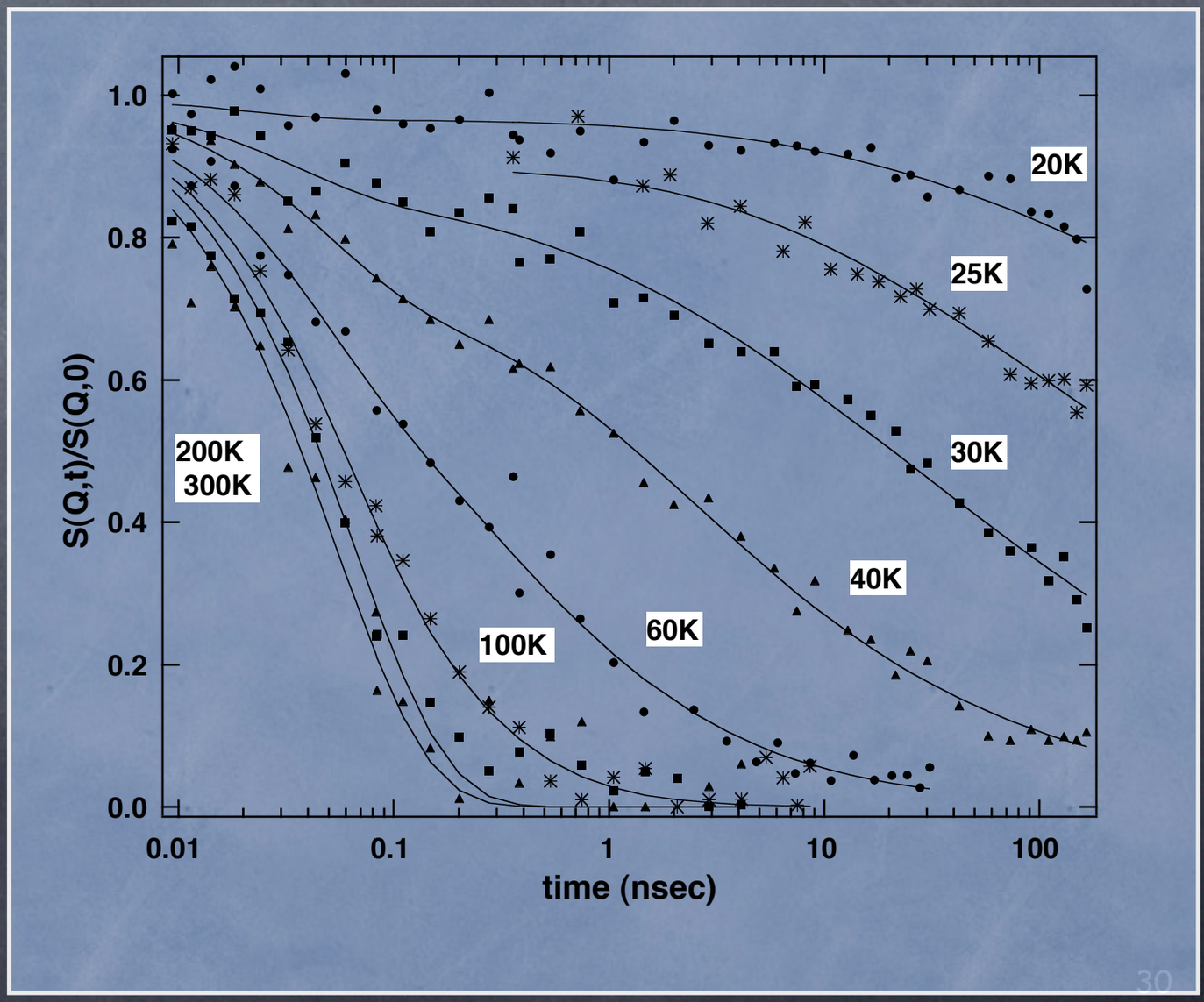
G. Ehlers , Cornelius ,A L, Orendac ,M, Kajnakova ,M, Fennell ,T, Bramwell ,S T, Gardner , Journal of Physics Condensed Matter 15, L9 (2003).



Needs integration over
particle size distribution
Switch over from single particle
relaxation to interparticle correlations
with lowering temperature

H. Casalta , Schleger ,P, Bellouard ,C, Hennion ,M, Mirebeau ,I, Ehlers ,G, Farago ,B, Dormann ,J L, Kelsch ,M, Linde ,M, Phillipp ,F, Physical Review Letters 82, 1301 (1999).

Monodomain iron particles in Al matrix superparamagnetic system

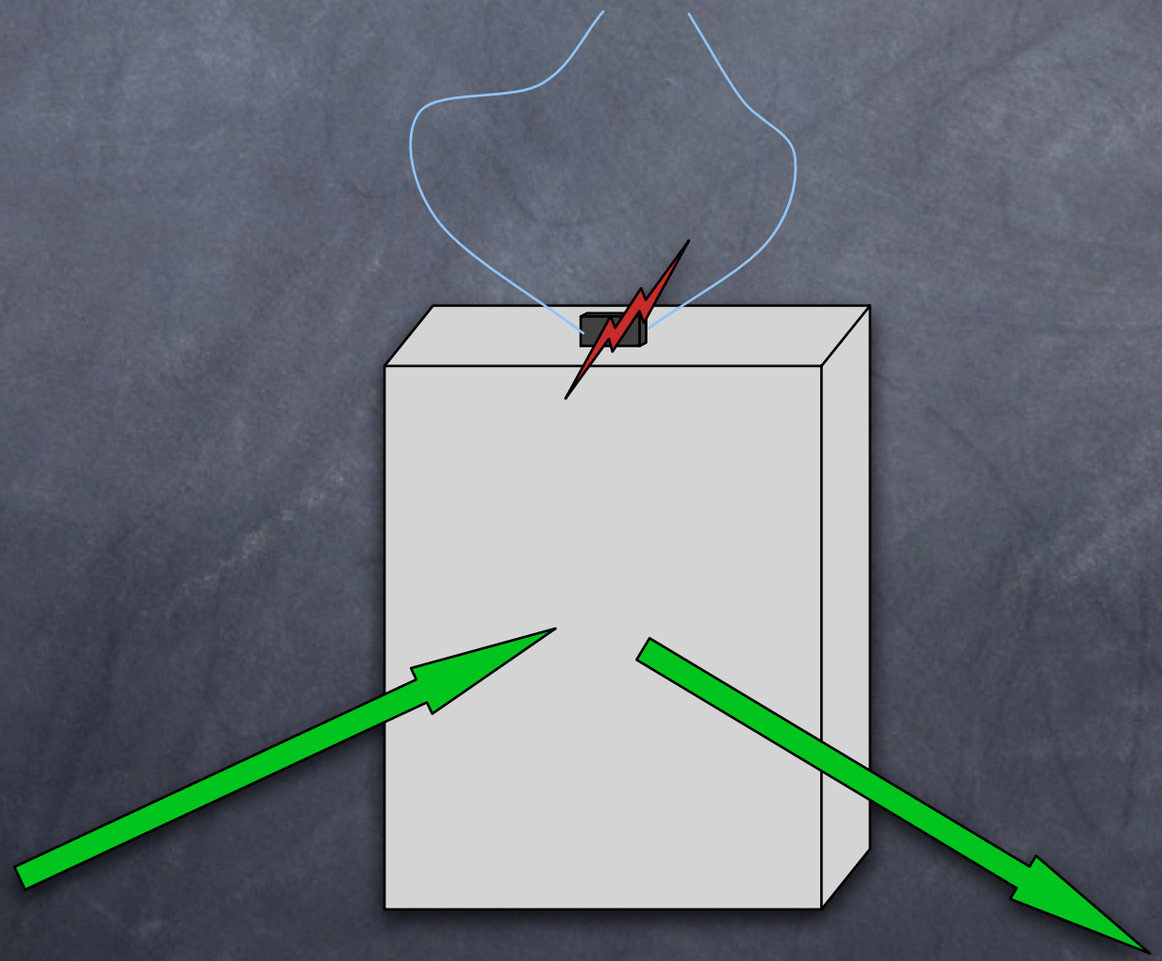


Bizarroids

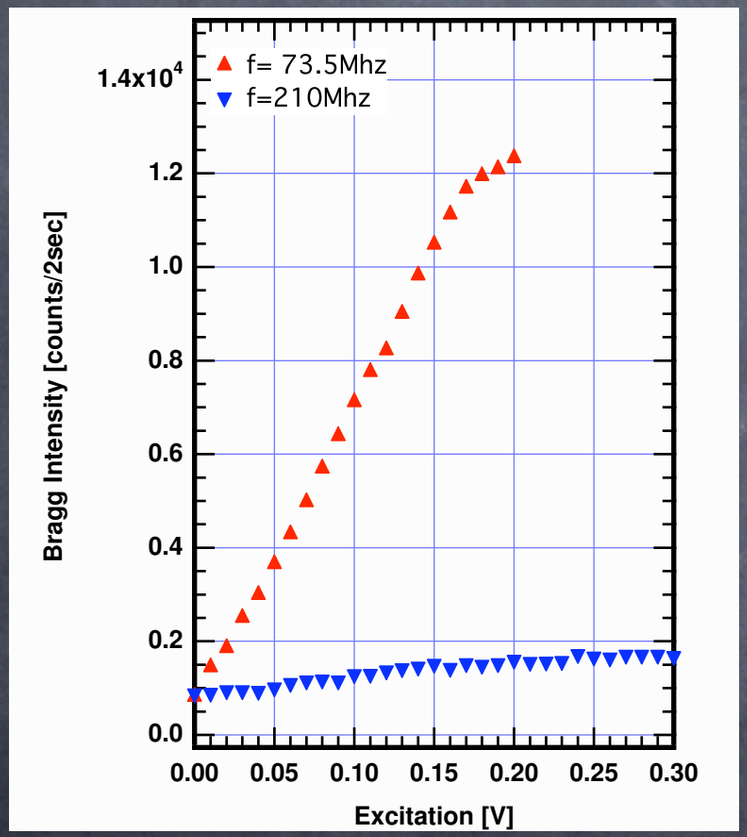
- Single Xtals & ultrasound
- Flux line lattice
- Cross section

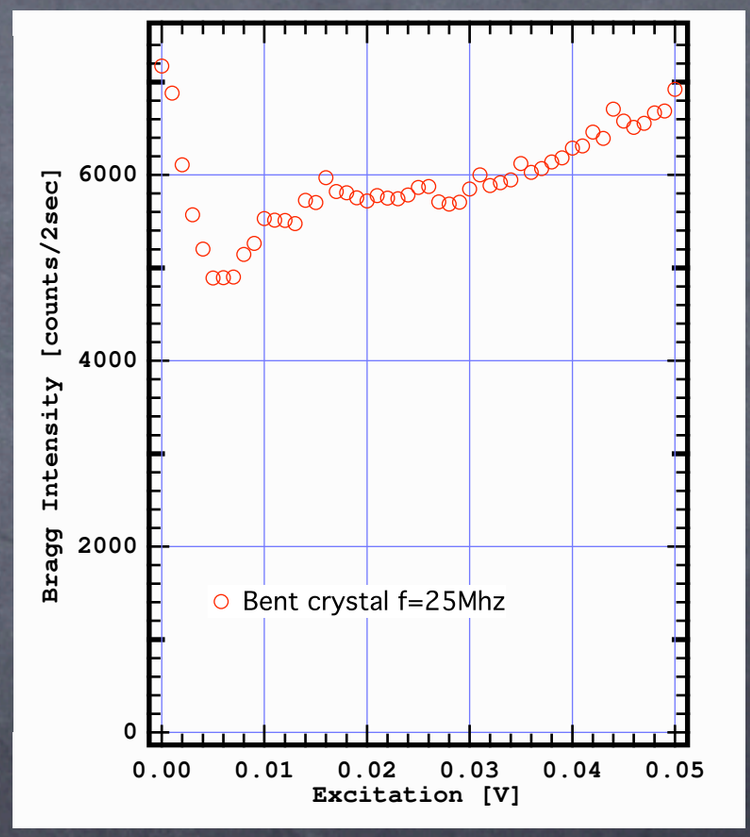
work with E Iolin and E Raitmann

Si single crystal excited with ultrasound in Bragg condition



Bragg intensity

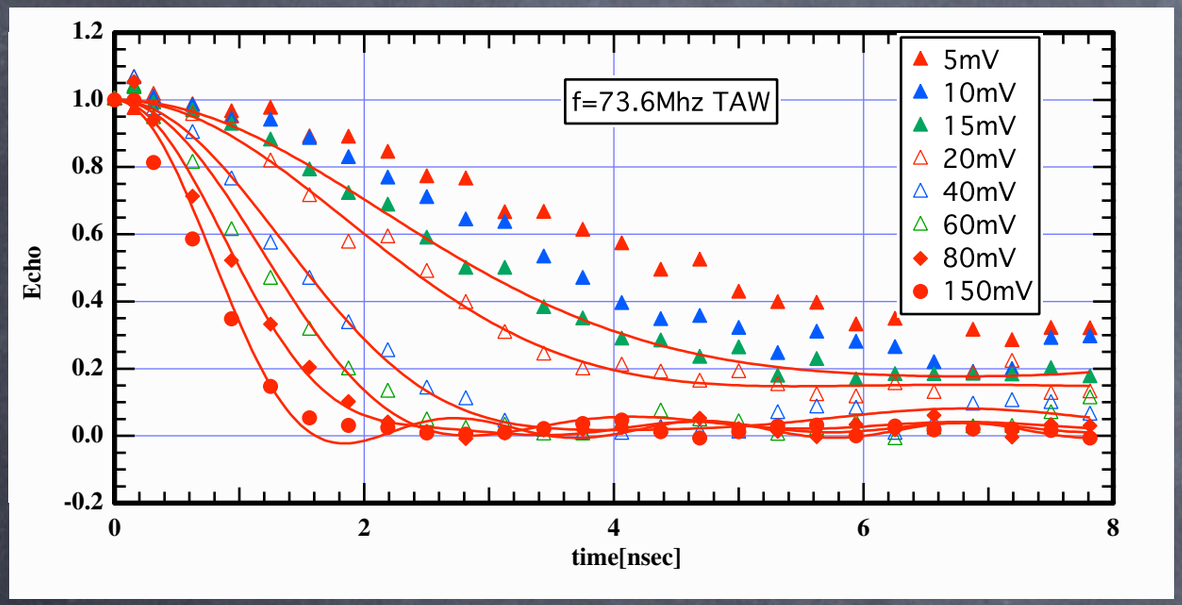




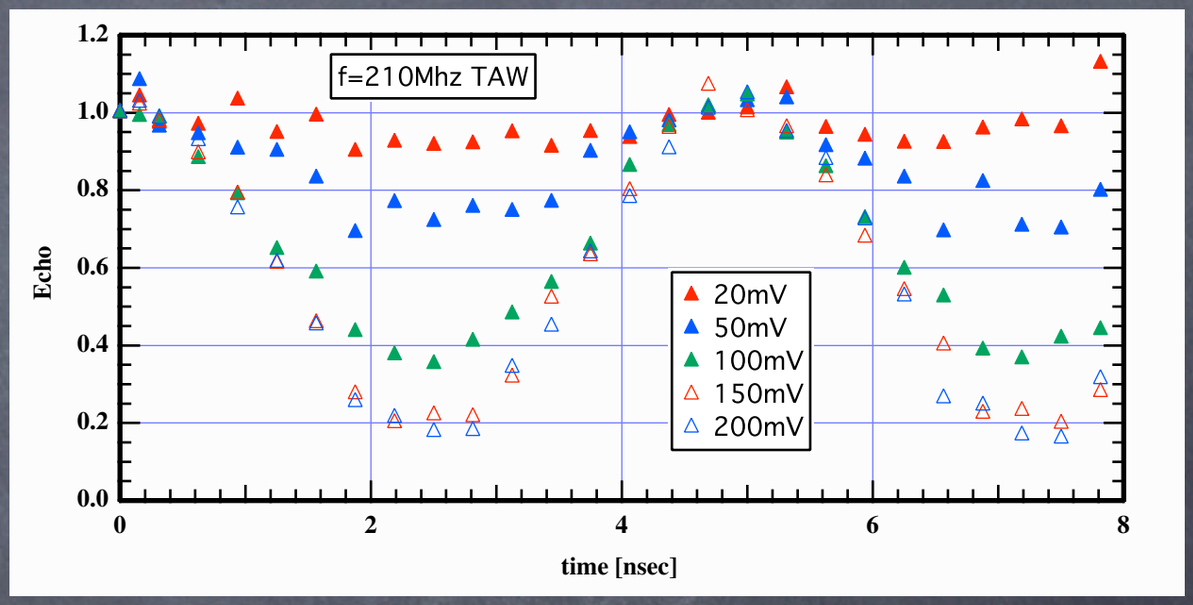
dynamics?

NSE mainstream & bizarroids

73.6 Mhz

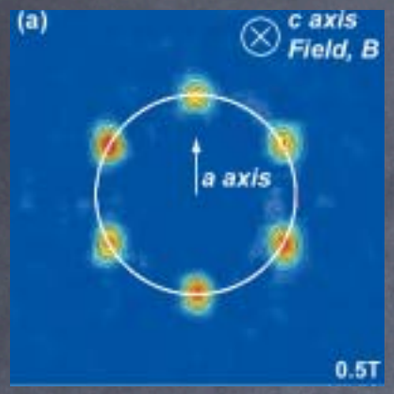


210 Mhz

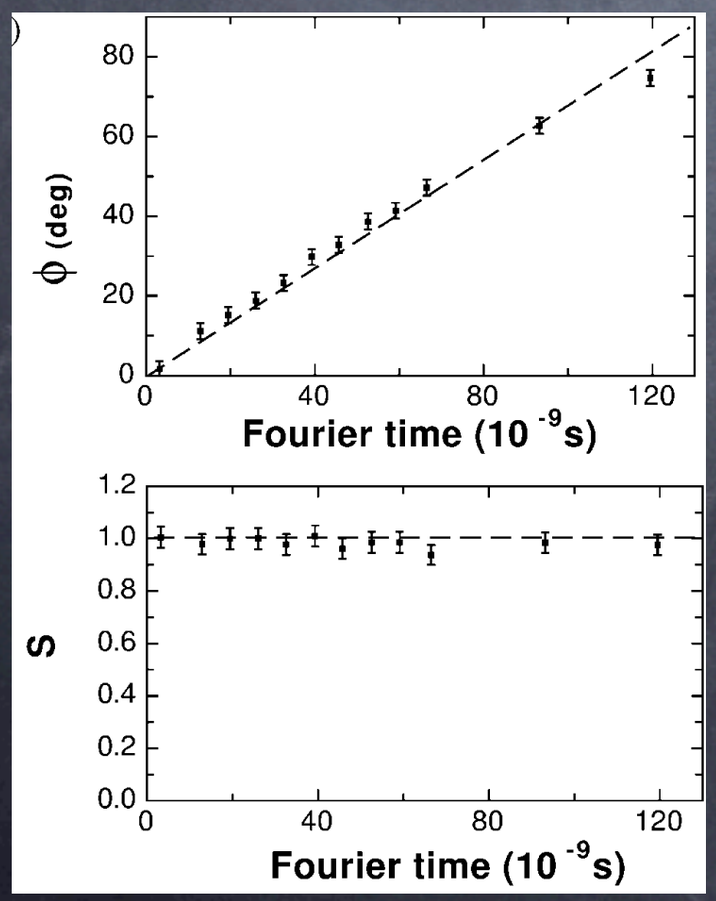


Brakes all known Murphy's laws

NSE mainstream & bizarroids



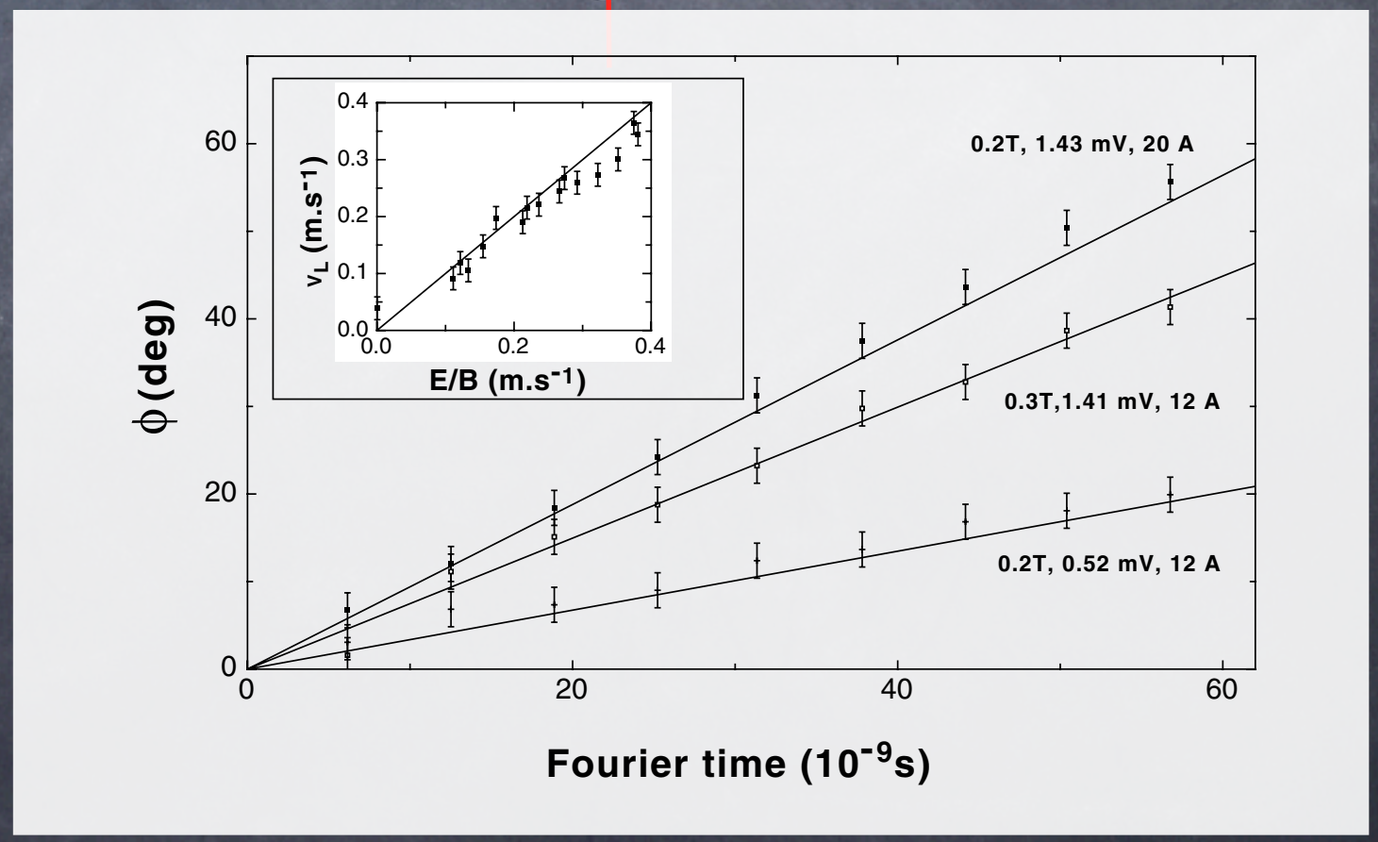
0.3T 2.2K 12A



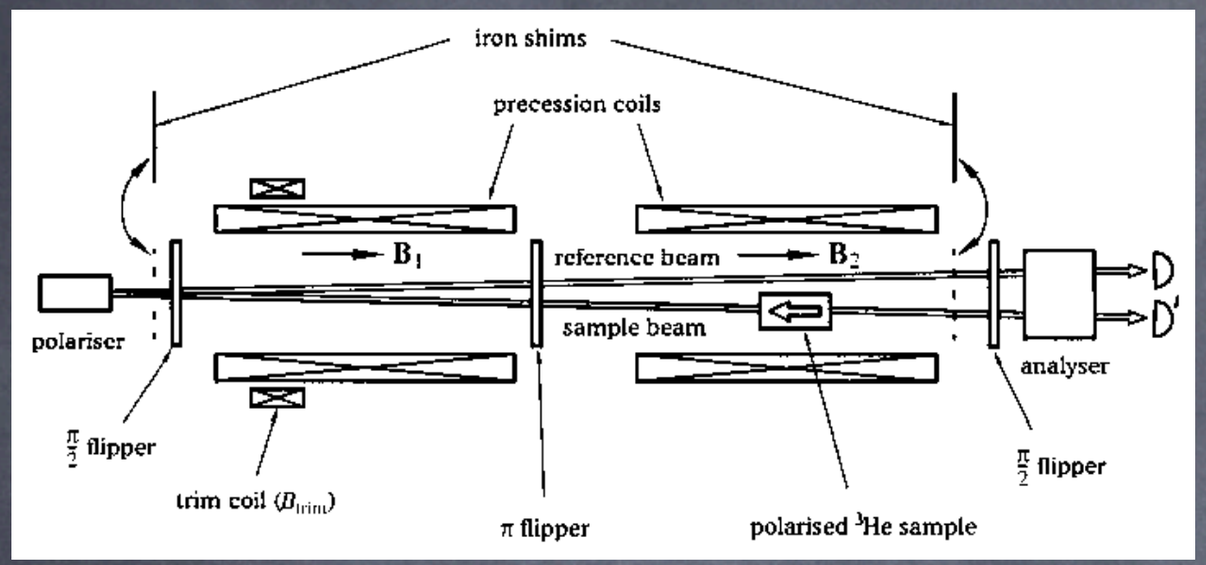
E (voltage)

B

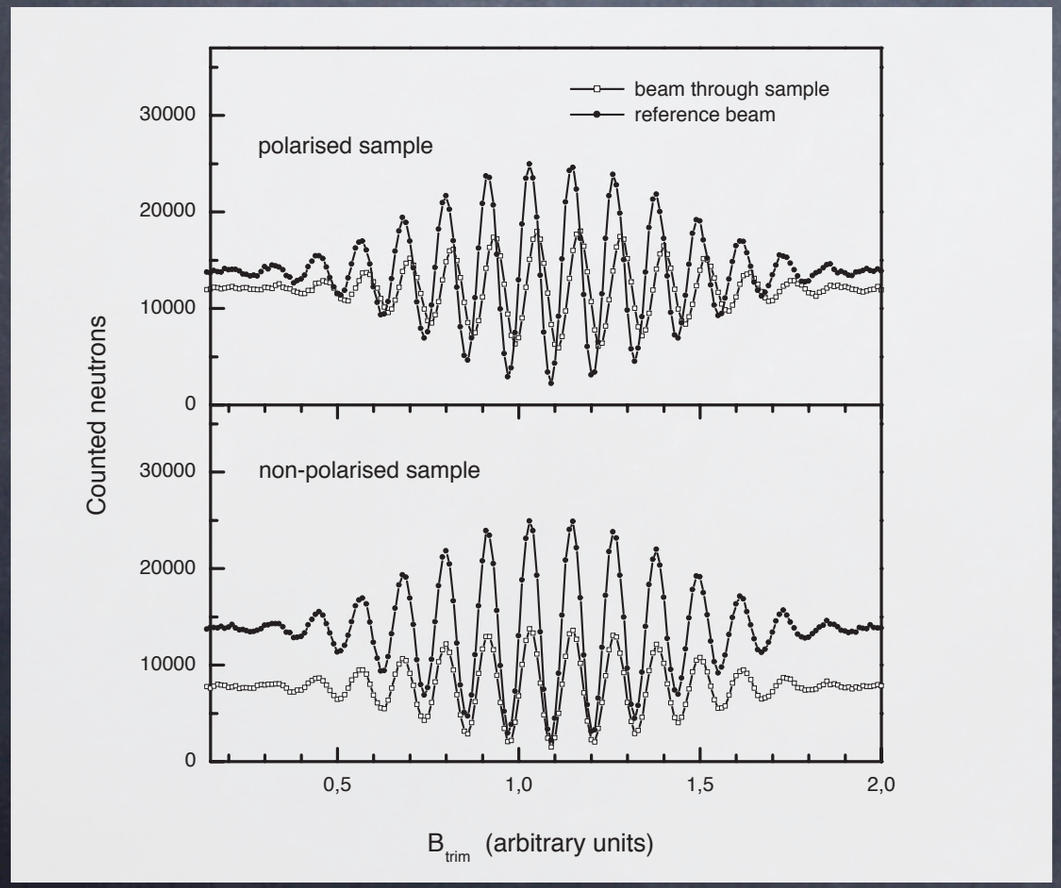
Displacement



NSE mainstream & bizarroids



Similar geometry for scattering length measurements (Sacha Frank)



He3

Spin dependent absorption

Different cross section for spin up and down

30 time improved measure of the spin dependent incoherent scattering length

Conclusions:

- NSE is well suited for many soft matter problems
- .. and to many more things

- still has some potential for evolution

Special thanks to all mentioned (and not mentioned) collaborators, users and colleagues....