

Transition vitreuse et hétérogénéités dynamiques
dans les liquides moléculaires et les polymères
*Glass transition and dynamical heterogeneities in
molecular liquids and polymers*

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- ❖ Glass transition phenomenology
- ❖ Number of dynamically correlated molecules
- ❖ Signature of the liquid in the glass

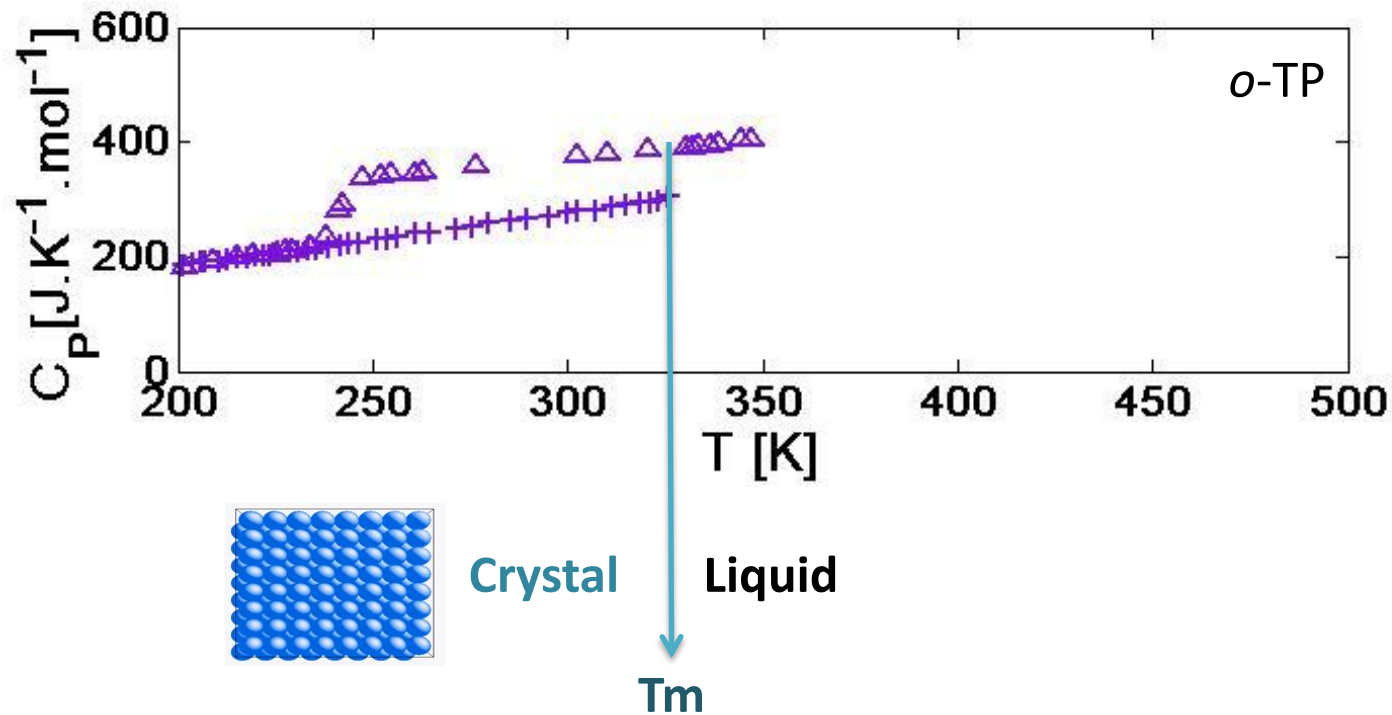
❖ Glass transition phenomenology

- Viscous slowing down
- Fragility
- Control parameters

❖ Number of dynamically correlated molecules

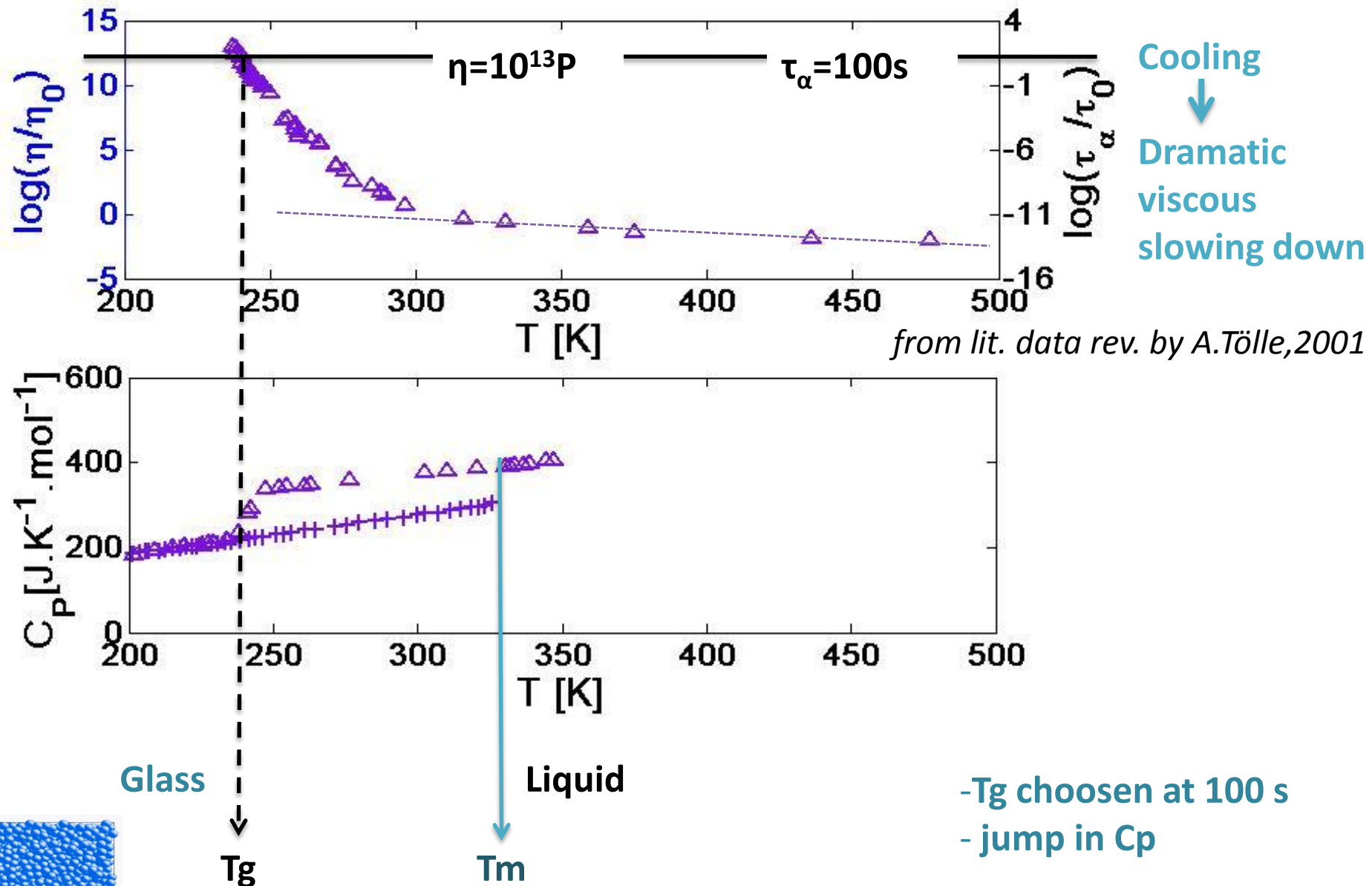
❖ Signature of the liquid in the glass

Glass transition



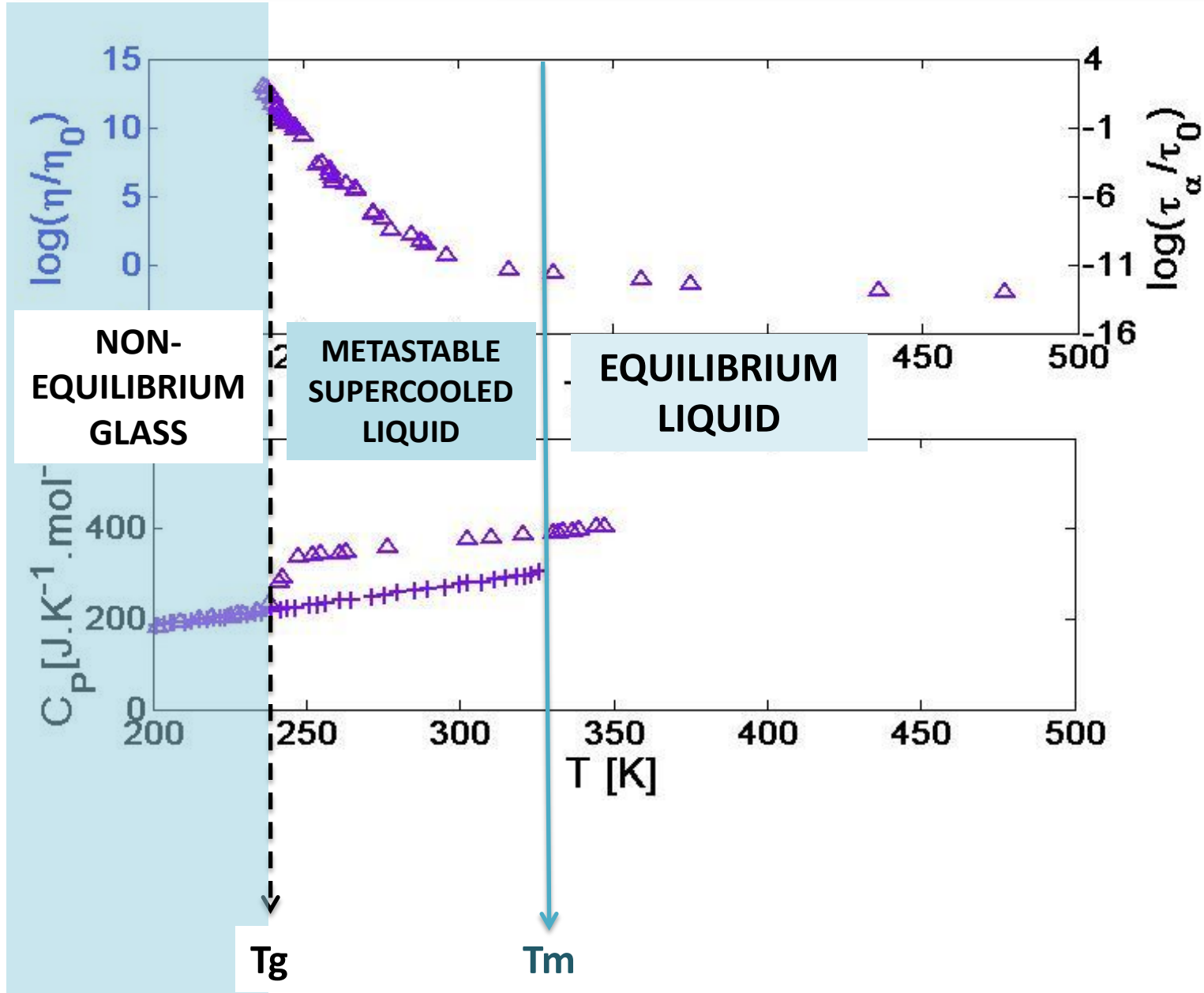
Data from Chang and Bestul, 1972

Glass transition



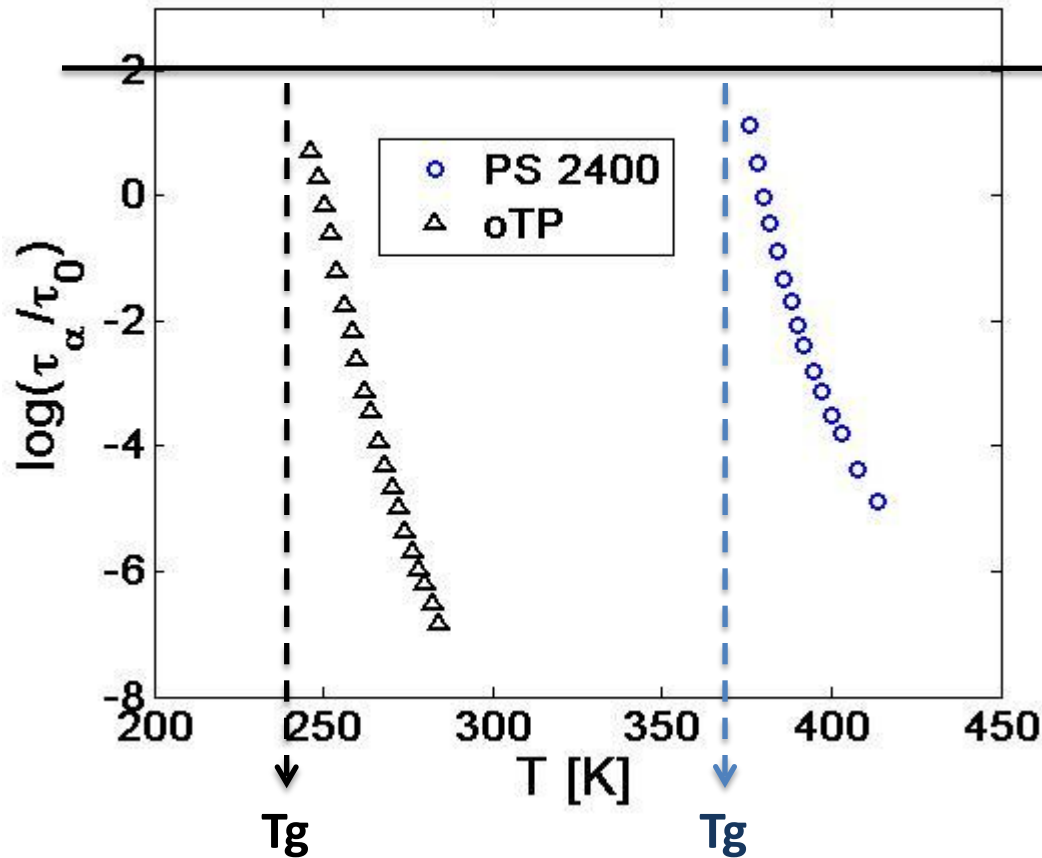
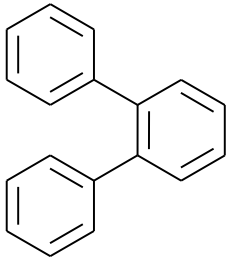
- T_g chosen at 100 s
- jump in C_p

Glass transition

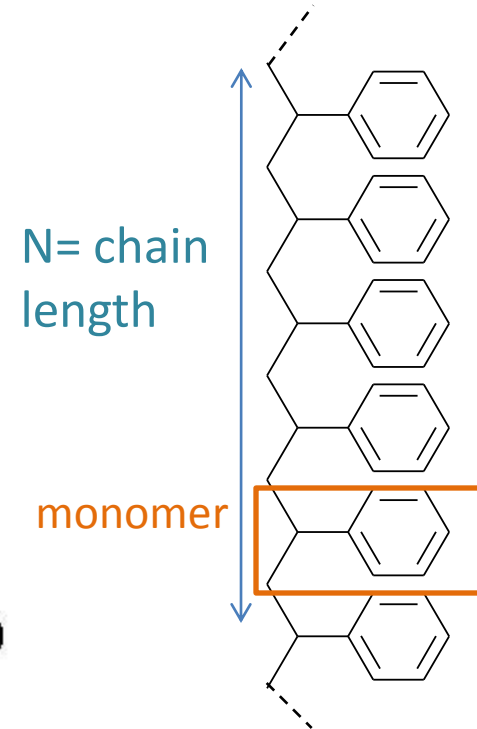


Dramatic viscous slowing down

o-terphenyl



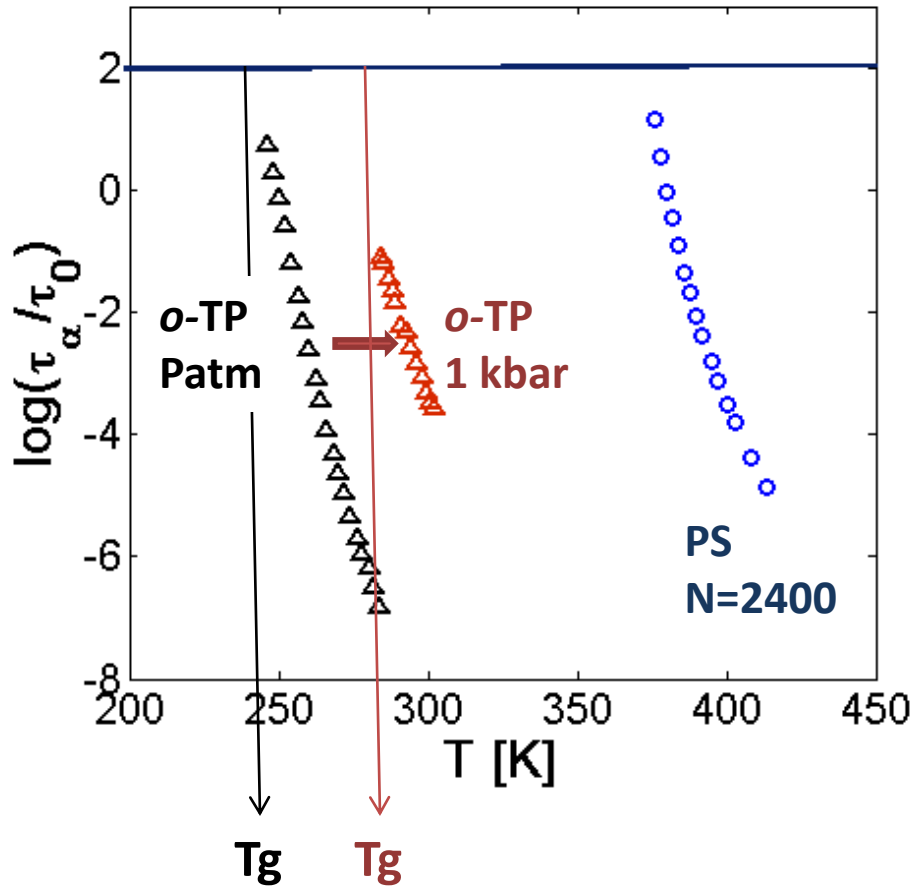
Polystyrene



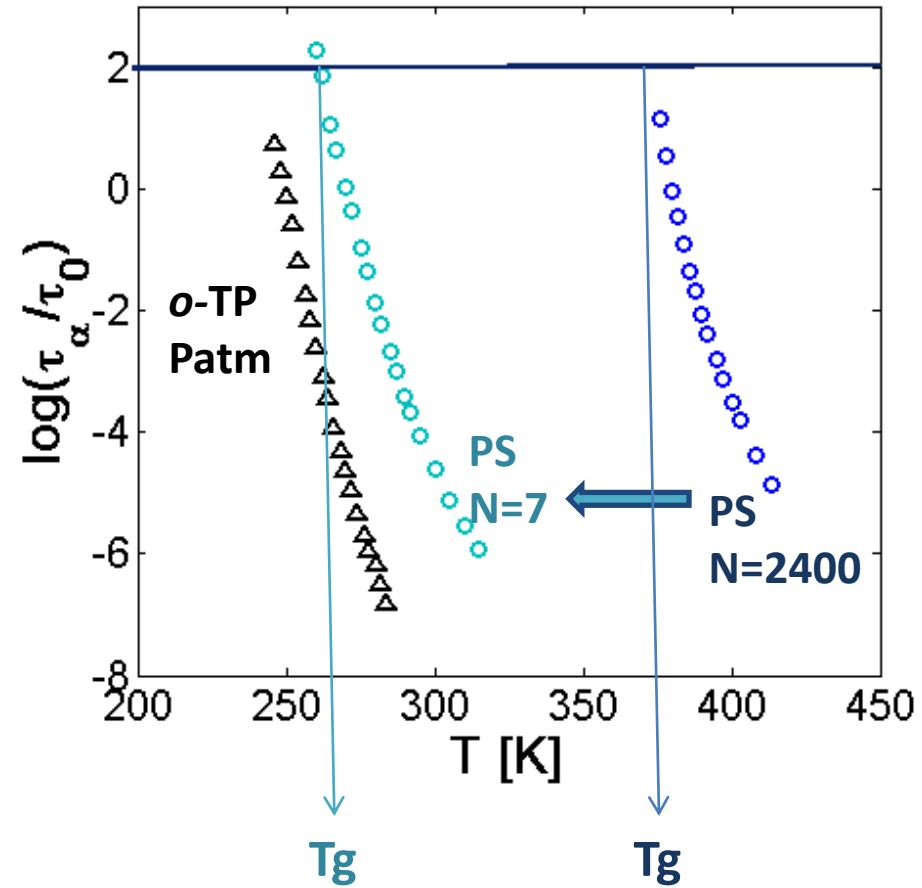
Dramatic viscous slowing down approaching the glass transition
How sensitive to external parameters?

Other control parameters : pressure and chain length

Effect of P

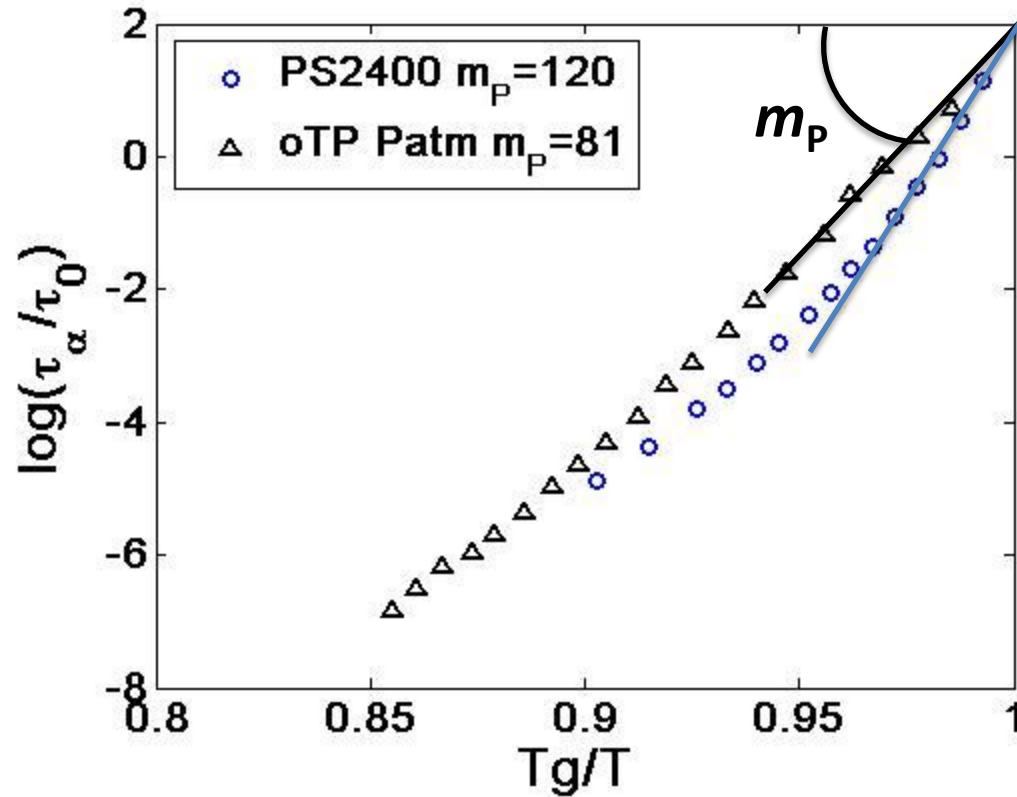


Effect of N



Tg changes with **pressure P** and **chain length N**

Viscous slowing down and fragility



Isobaric fragility :

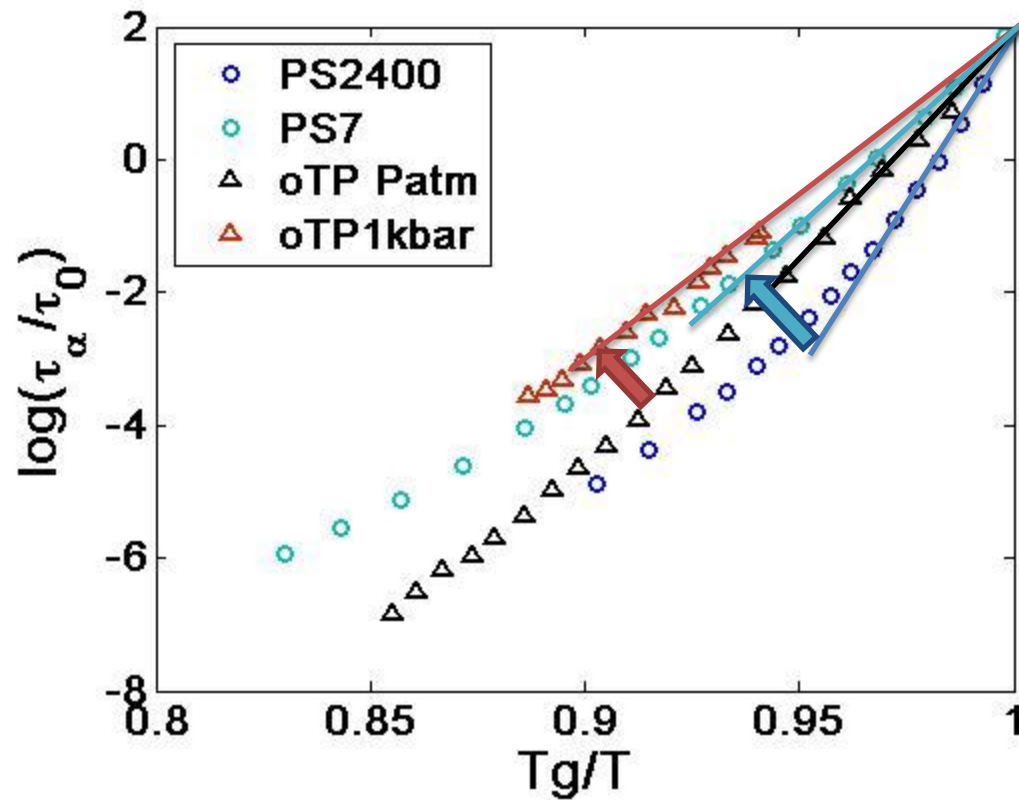
$$m_P = \left. \frac{\partial \log_{10}(\tau_\alpha)}{\partial T_g/T} \right|_P (T = T_g)$$

strong $20 \leq m_p \leq 200$ fragile

A. Angell, 1985

The viscous slowing down and the fragility are poorly understood nowadays.

Fragility – sensitivity to control parameters

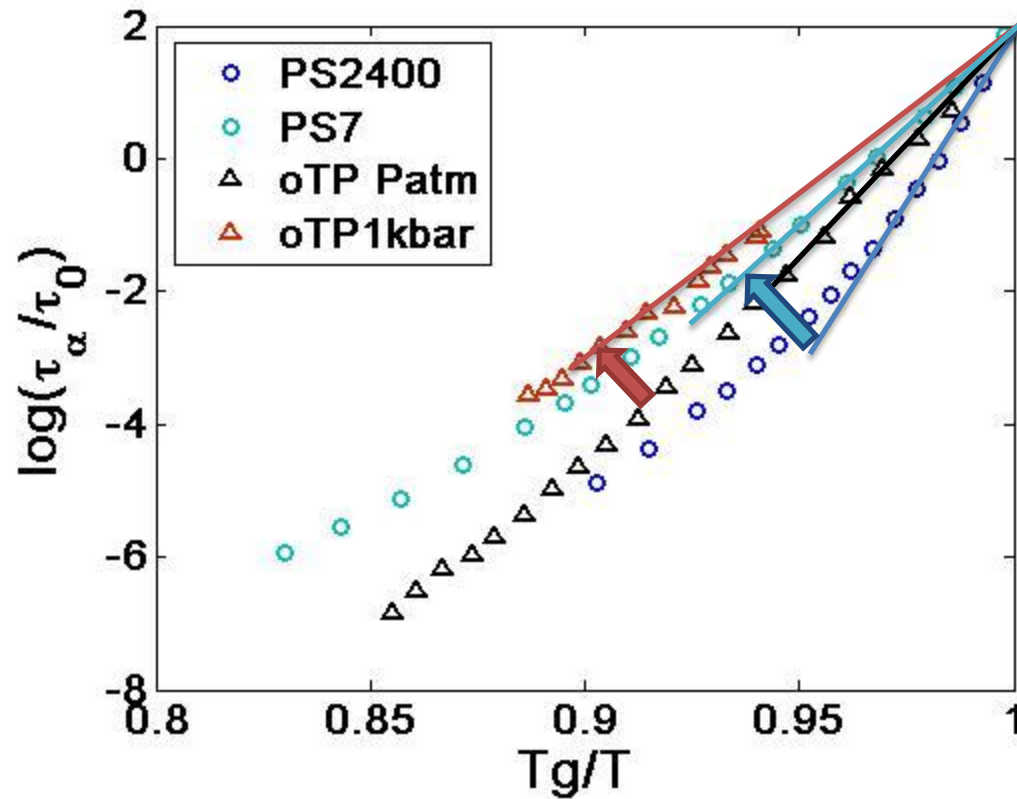


Isobaric fragility :

$$m_P = \left. \frac{\partial \log_{10}(\tau_\alpha)}{\partial T_g/T} \right|_P (T = T_g)$$

Fragility changes - with P
- with N

Fragility – sensitivity to control parameters



Isobaric fragility :

$$m_P = \left. \frac{\partial \log_{10}(\tau_\alpha)}{\partial T_g/T} \right|_P (T = T_g)$$

Fragility changes - with P
- with N

The divergence of a relaxation time in a system is always accompanied by the divergence of a characteristic length

❖ Glass transition phenomenology

❖ Number of dynamically correlated molecules

- Notion of cooperativity
- Getting a number of correlated molecules
- Results on various molecular liquids

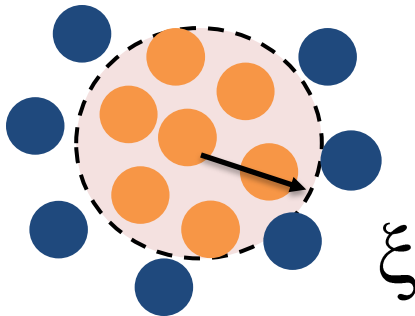
❖ Signature of the liquid in the glass

Cooperativity and correlation length

Cooperativity length

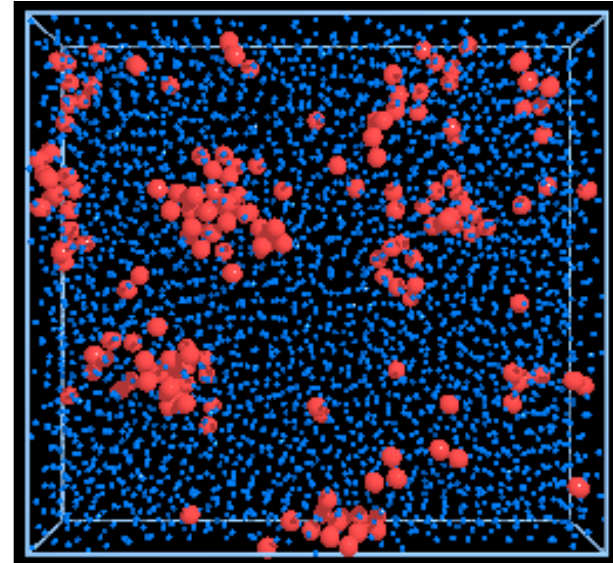
$$\tau(T) = \tau_0 \exp \left[N_{\text{coop}}(T) \frac{\Delta\mu}{k_B T} \right]$$

$N_{\text{coop}} \nearrow$ as $T \searrow$



Adam and Gibbs, 1965

Correlation length



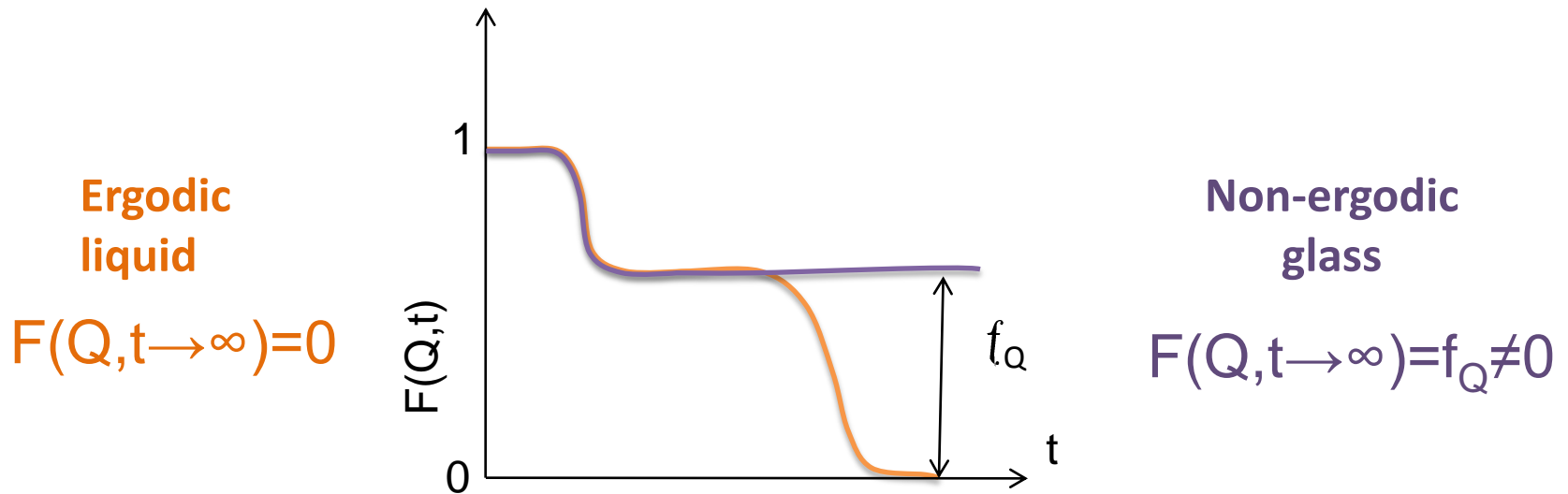
E. Weeks *et al.*, *Science* 287, 627 (2000)
www.physics.emory.edu/~weeks/lab/glass

$\Phi = 56\%$ supercooled fluid
5% fastest of the particles in red

Large clusters of cooperative fast particles :
spatially heterogeneous dynamics

Order parameter of the glass transition

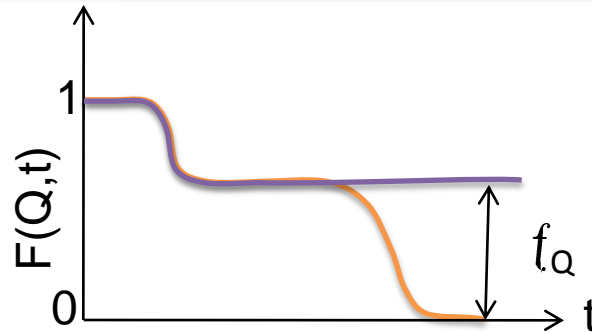
- Divergence of relaxation time associated to a diverging correlation length
- Ergodic to non-ergodic transition



- f_Q^c = non-ergodicity parameter at T_c = order parameter

Correlation length

Ergodic liquid
 $F(Q, t \rightarrow \infty) = 0$



Non-ergodic glass
 $F(Q, t \rightarrow \infty) = f_Q \neq 0$

Intermediate scattering function :
 averaged correlation function

$$F(Q, t) = \langle C(t) \rangle$$

Standard 2-time correlation function

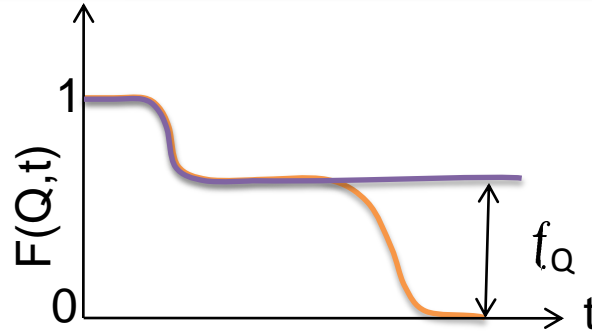
$$C(t) = \frac{1}{V} \int d^3 \vec{r} c(\vec{r}, t)$$

$$c(\vec{r}, t) = \delta\rho(\vec{r}, 0) \delta\rho(\vec{r}, t)$$

Density fluctuations in r at time t $\delta\rho(\vec{r}, t) = \rho(\vec{r}, t) - \langle \rho \rangle$

Correlation length

**Ergodic
liquid**
 $F(Q, t \rightarrow \infty) = 0$



**Non-ergodic
glass**
 $F(Q, t \rightarrow \infty) = f_Q \neq 0$

f_Q^c = non-ergodicity parameter at T_c

Space-time 4-point
susceptibility

$$\chi_4(t) = N \langle \delta C(\mathbf{0}, t)^2 \rangle$$

$$\chi_4(t) = \rho \int d^3r \langle \delta C(\mathbf{0}; 0, t) \delta C(\mathbf{r}; 0, t) \rangle$$

Fluctuations of $C(t)$ around its average value : $\delta C(\mathbf{0}, t) = C(\mathbf{0}, t) - F(t)$
 $C(\mathbf{0}, t) = \delta\rho(\mathbf{0})\delta\rho(t)$

Relaxation function and correlation length

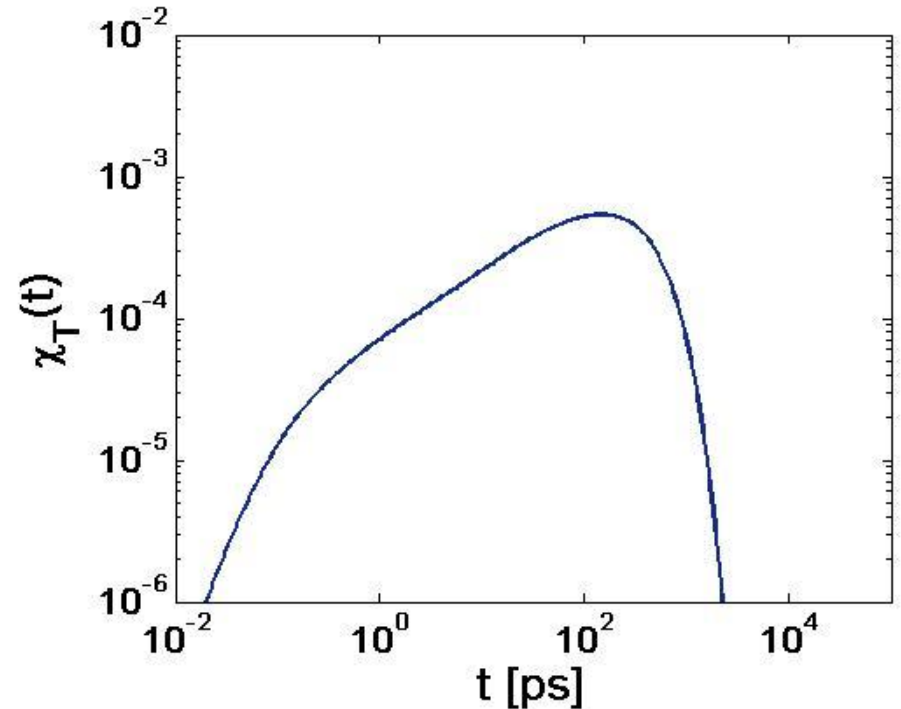
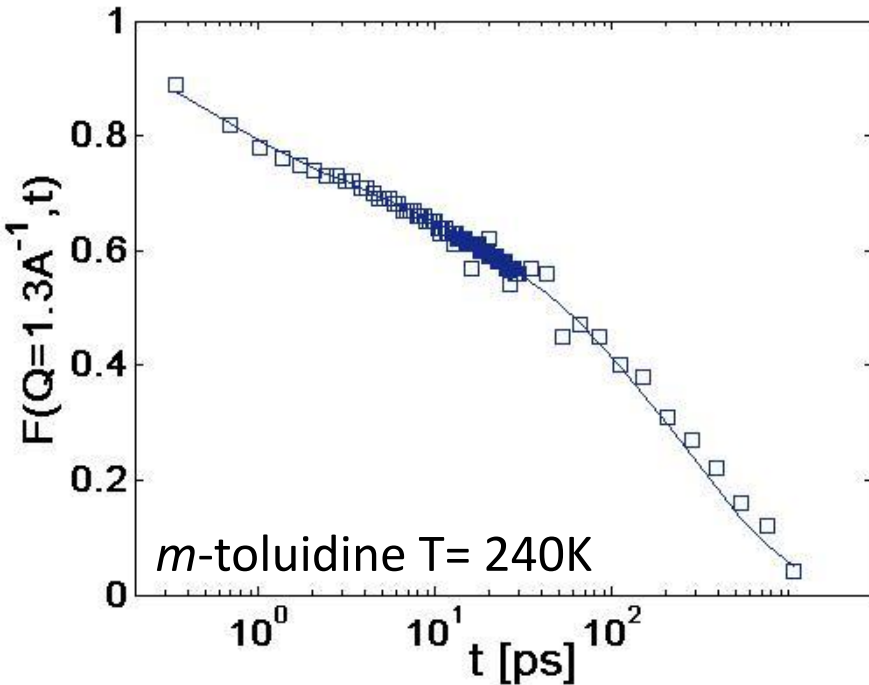
Number of dynamically correlated molecules :
Ncorr

$$\chi_4^{NPT}(t) = \frac{RT^2}{C_P} (\chi_T^{NPT}(t))^2 + \chi_4^{NPH}(t)$$

L. Berthier et al., science, 2005

F(t)

$$\chi_T^{NPT}(t) = \left(\frac{\partial F(t)}{\partial T} \right)_P$$



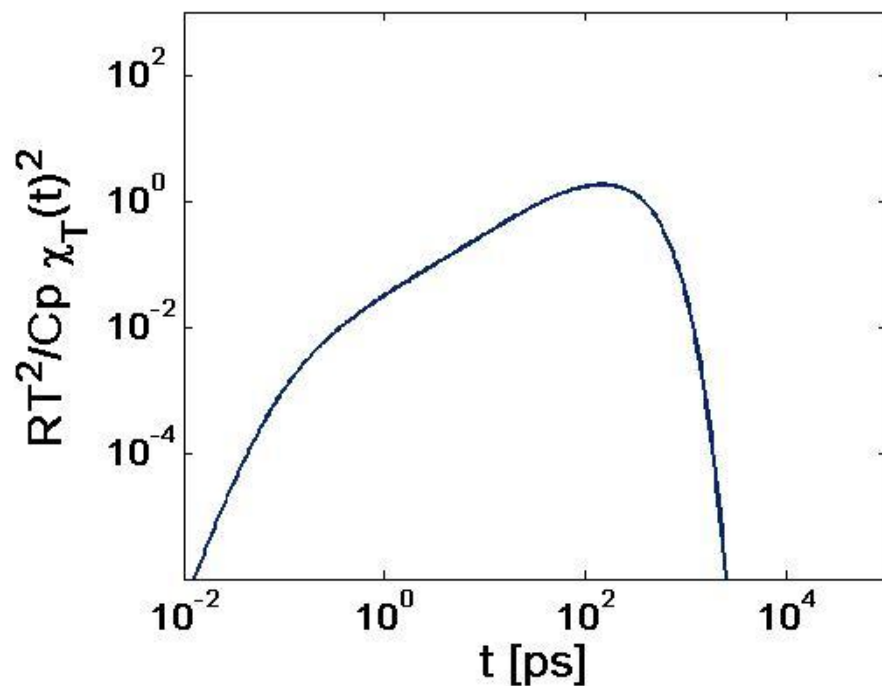
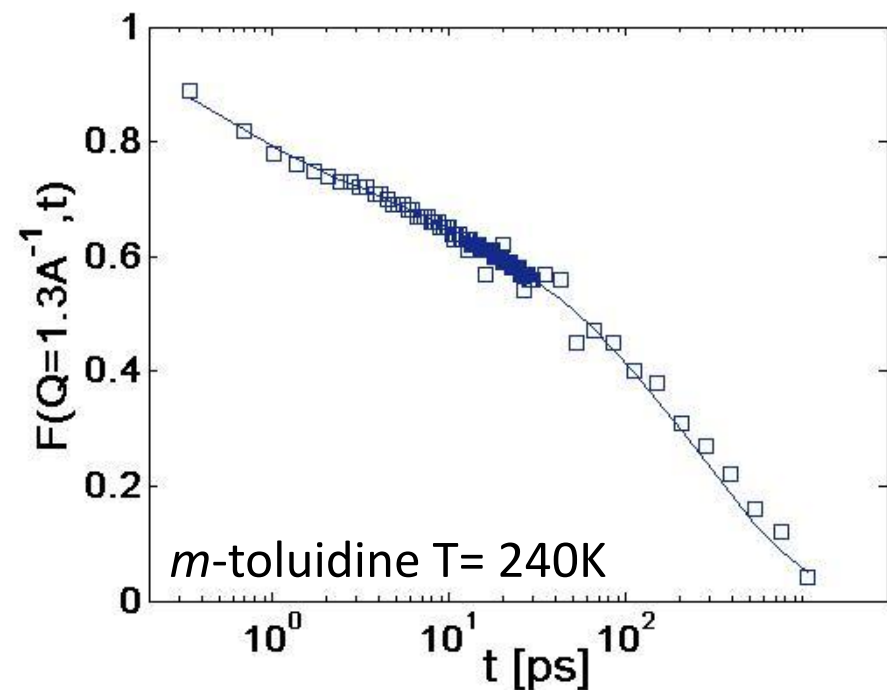
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F(t)

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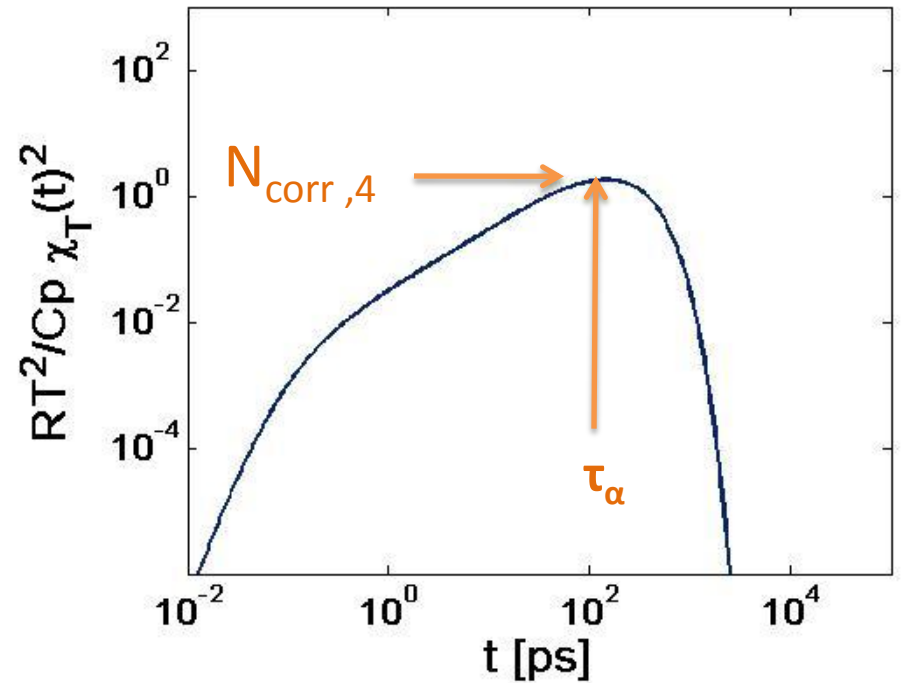
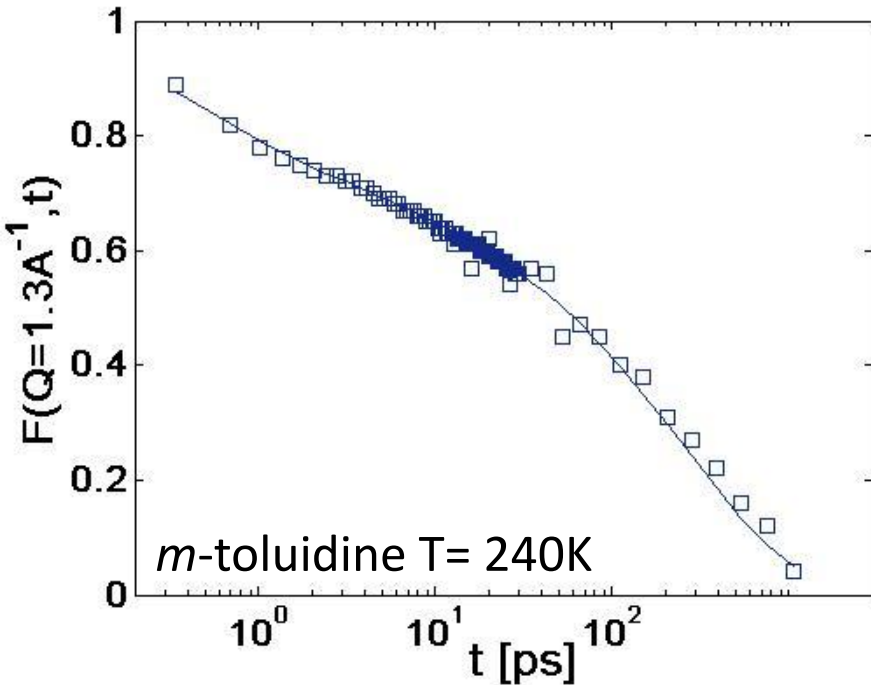
Relaxation function and correlation length

Number of dynamically correlated molecules :
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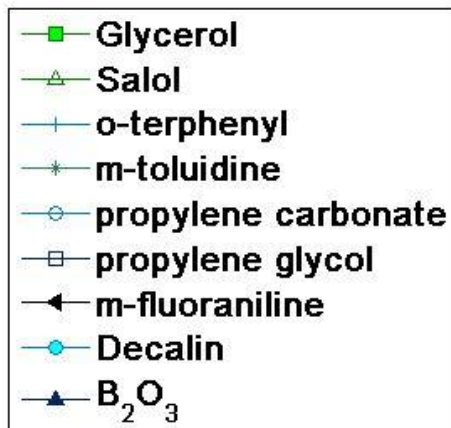
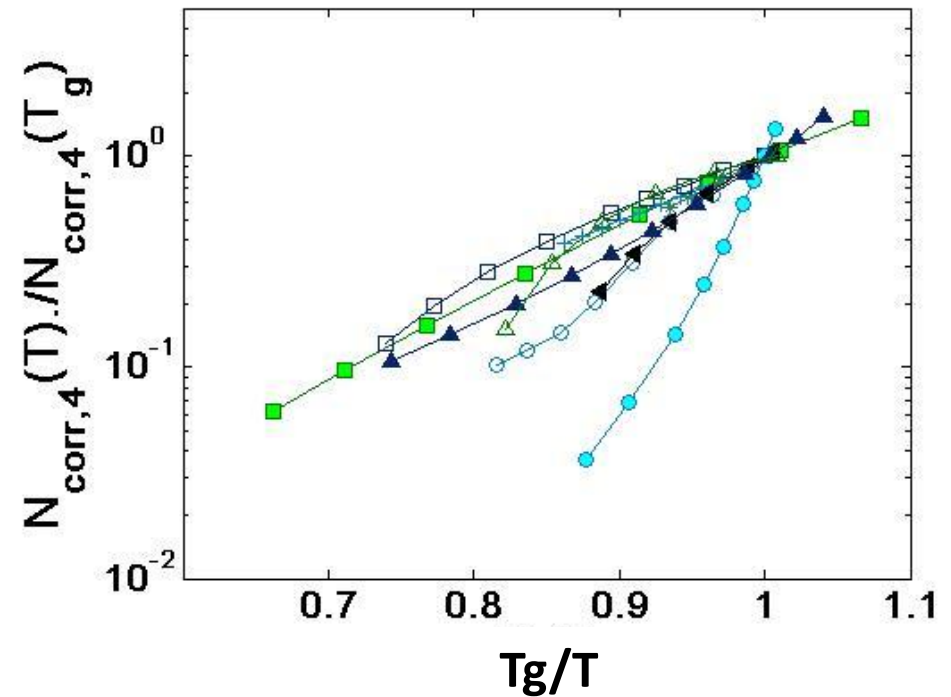
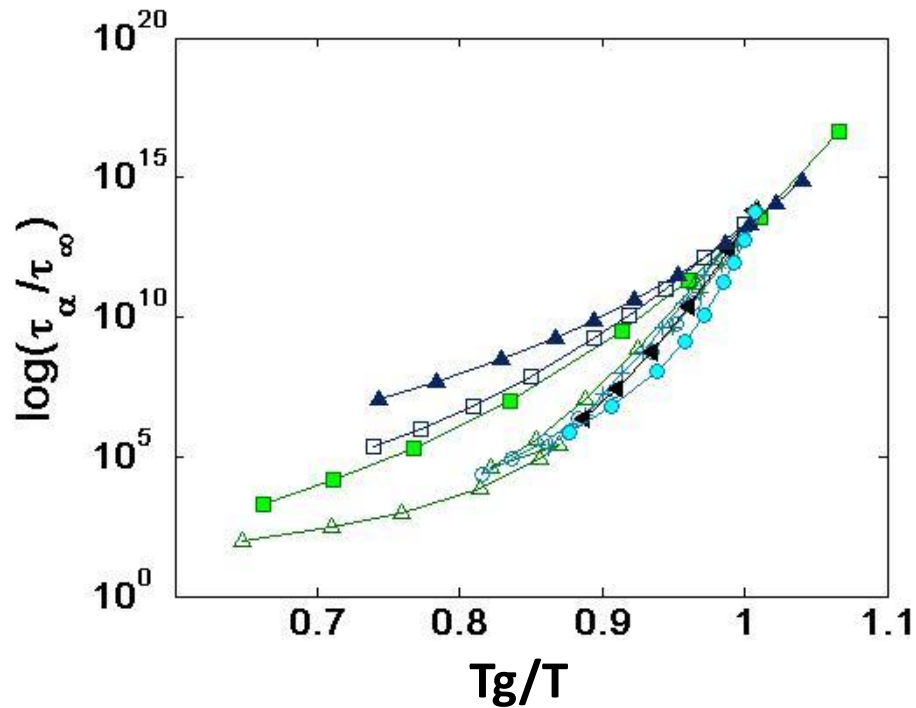
$F(t)$

$$\chi_T^{NPT}(t) = \left(\frac{\partial F(t)}{\partial T} \right)_P$$



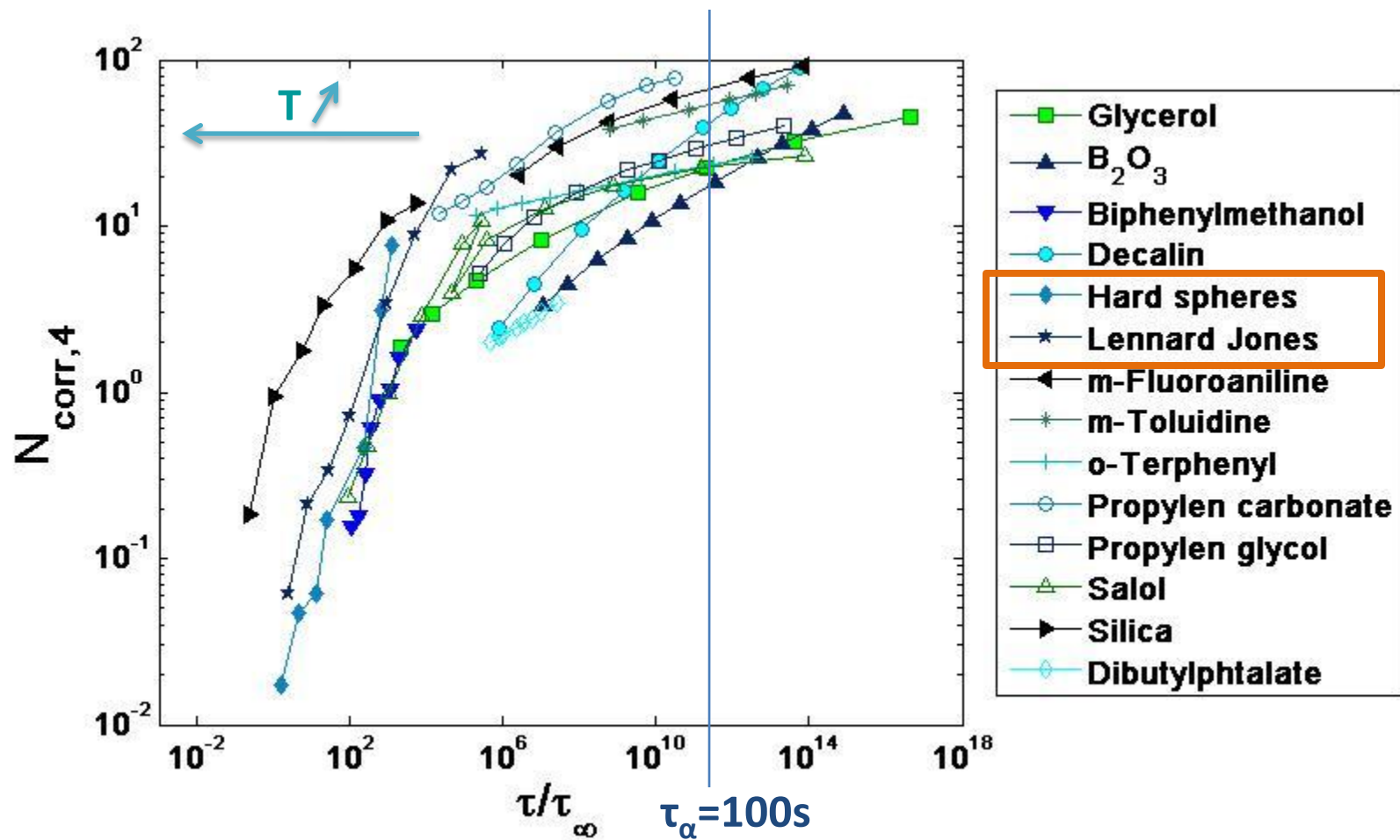
At a given T : $N_{\text{corr},4} \approx \max\{\chi_4(t)\}$

Growing number of dynamically correlated molecules

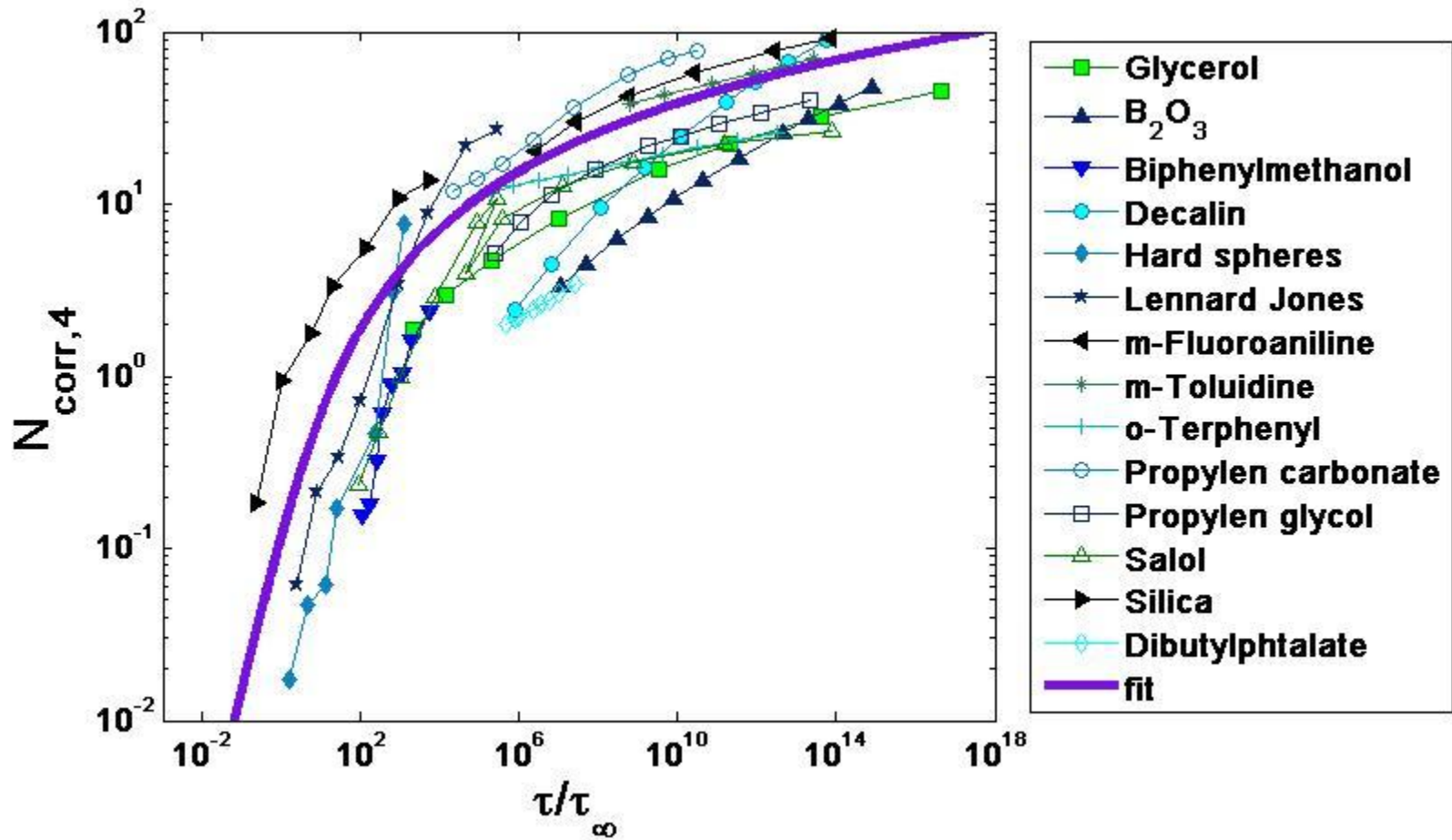


Growth of the number of dynamically correlated molecules for different molecular liquids

Generalization to other systems : N_{corr} vs τ_{α}



Generalization to other kinds of systems : N_{corr} vs τ_α



$$\tau_\alpha \simeq A \left(\frac{N_{corr,T}}{N_0} \right)^\gamma \exp \left[\left(\frac{N_{corr,T}}{N_0} \right)^\Psi \right]$$

MCT
Activated processes

❖ Number of dynamically correlated molecules

- N_{corr} growth over the whole T-range associated to the viscous slowing down

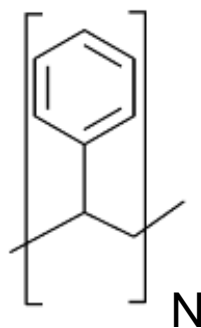
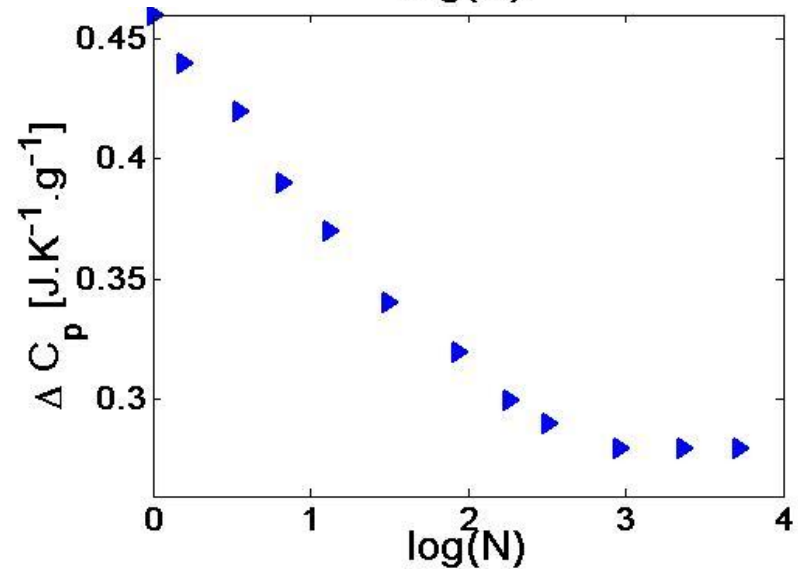
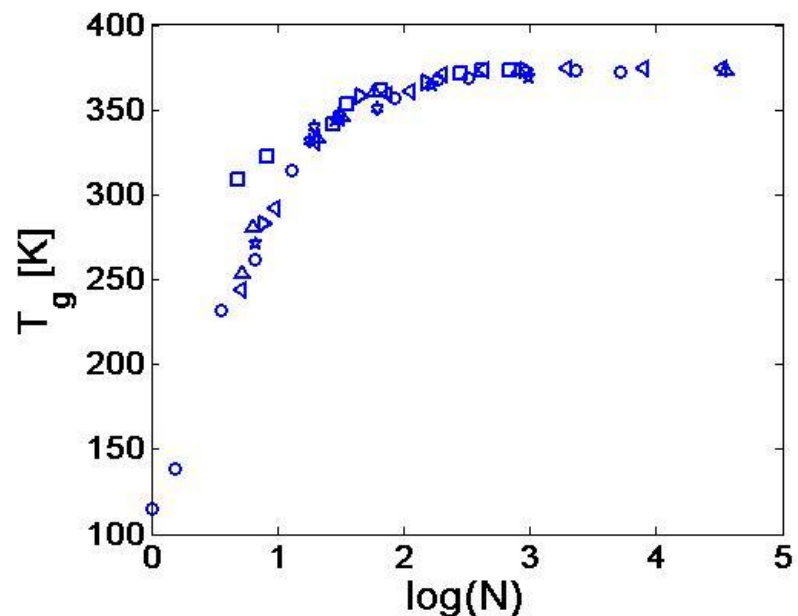
- T-dependence on many systems

Comparison of absolute values at T_g rather at different P or N

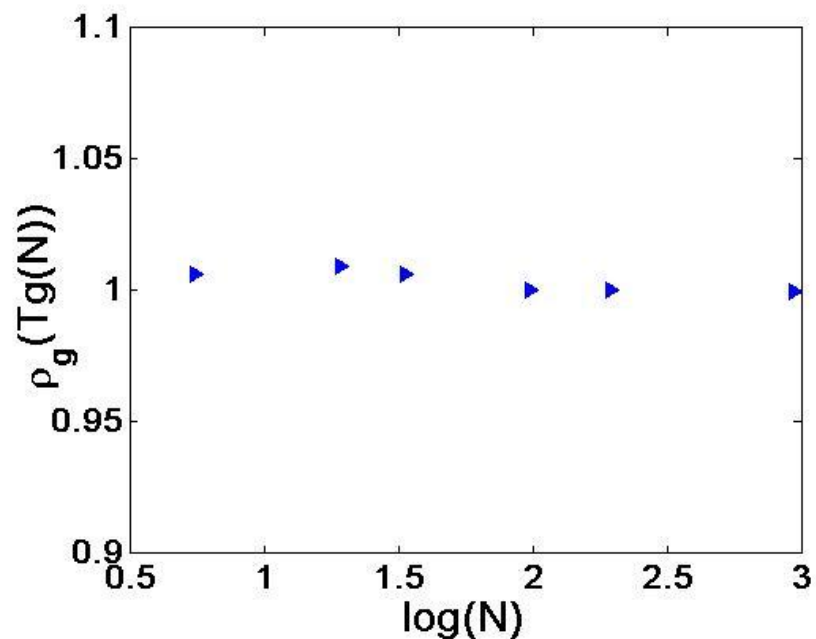
- New tool to understand glass transition

May be compared to other properties related to glass transition

Chain length dependence of glass transition : N effect



N = chain length

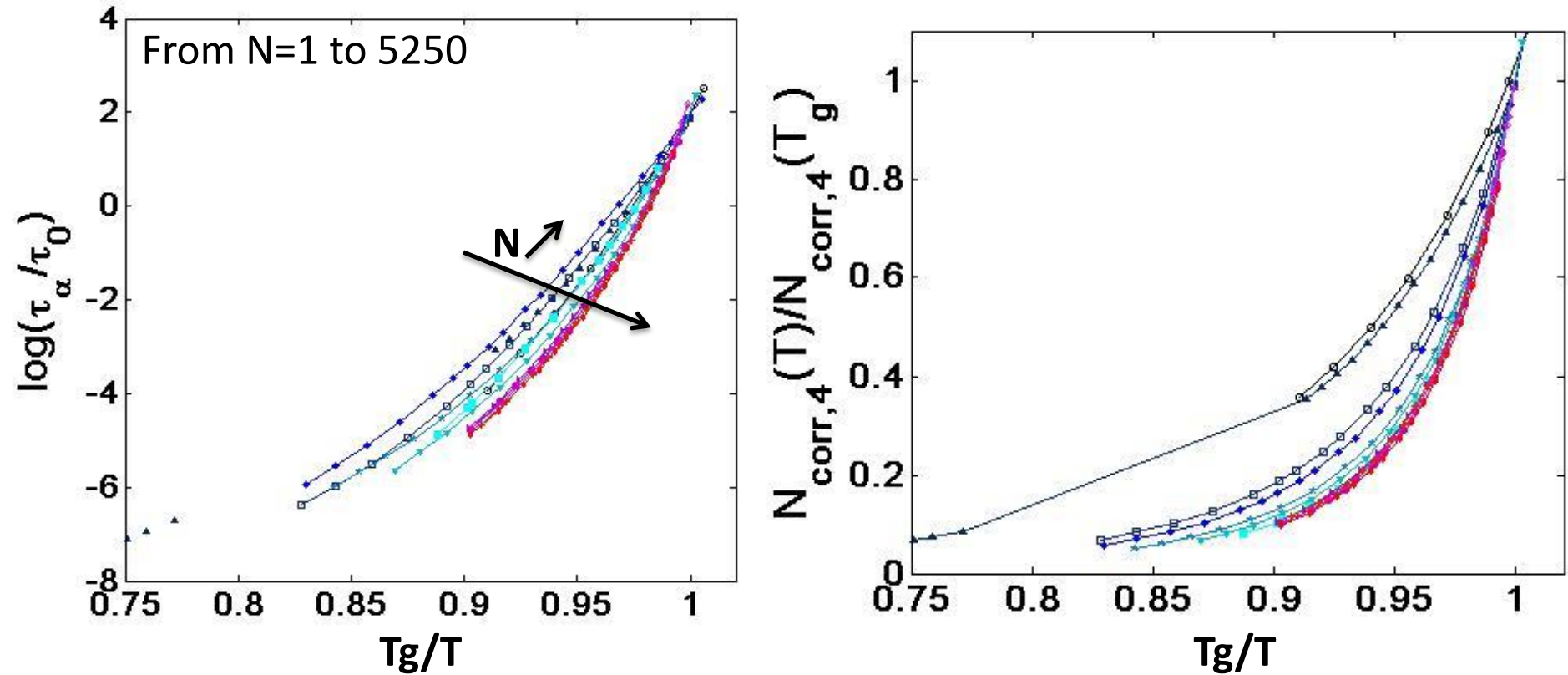


Thermodynamical properties versus N

Santangelo 98, An 97

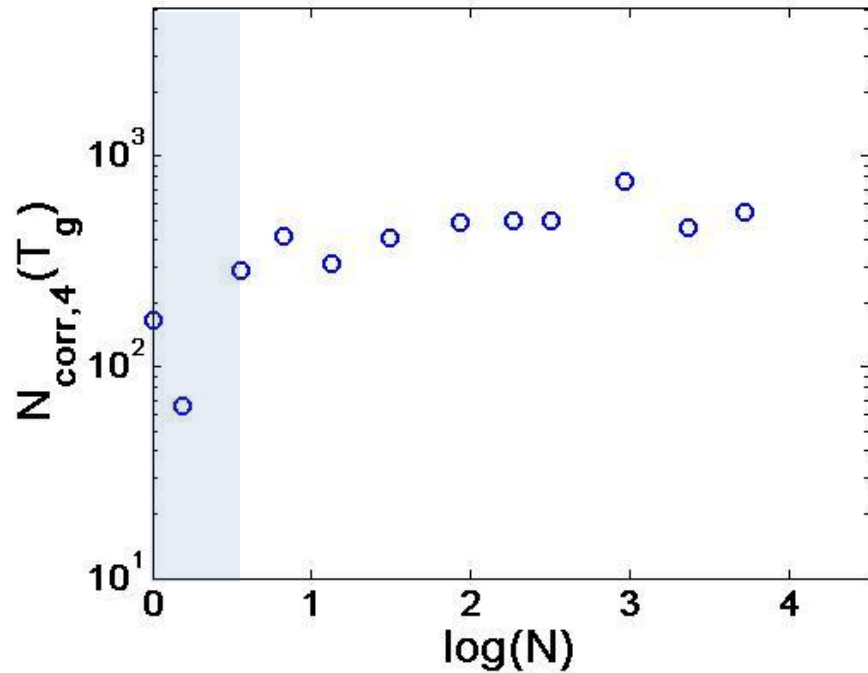
Tg data from lit. and from this work

Polymeric systems : PS of different chain lengths

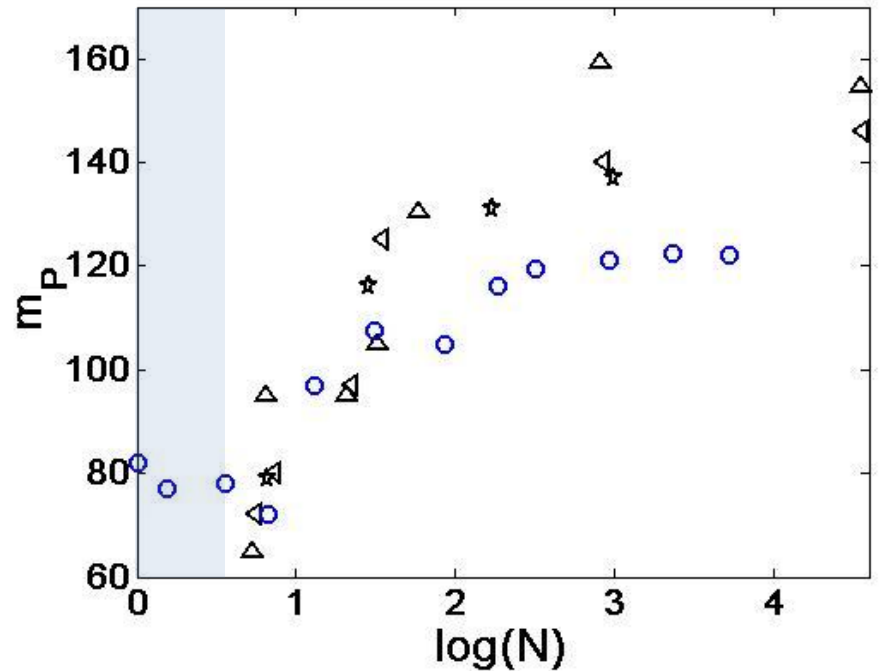


$N_{\text{corr}}(T)$ very similar to $\tau_\alpha(T)$

At the glass transition temperature T_g



Small chain length dependence in N_{corr}



/ compared to the effect on fragility

○ *Hintermeyer et al., 2008*

△ *other lit.data including ours*

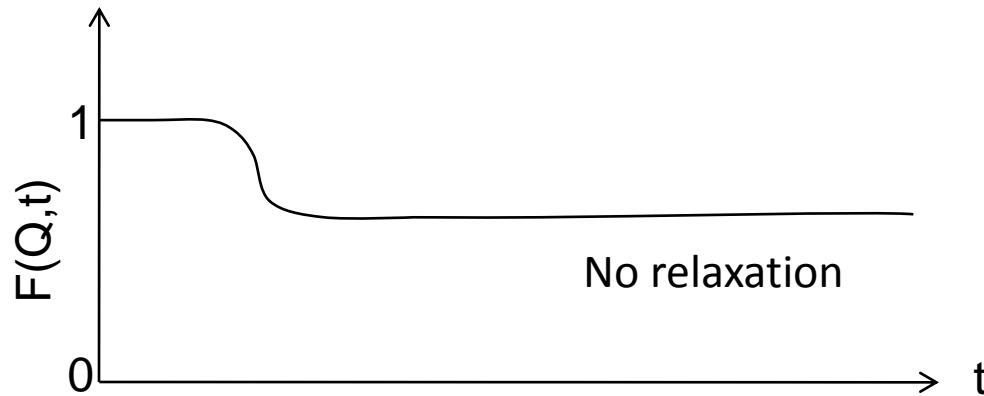
❖ Glass transition phenomenology

❖ Number of dynamically correlated molecules

❖ Signature of the liquid in the glass

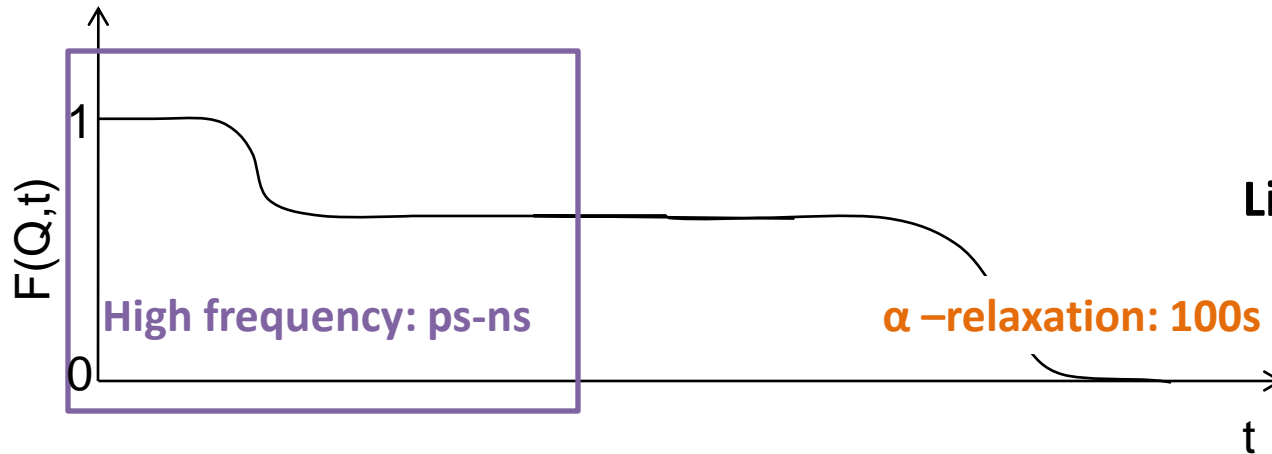
- Mean-square displacement
- Non-ergodicity factor
- Boson peak

Glass at T_g = frozen liquid



Glass $T < T_g$

Glass = instantaneous picture of the liquid frozen at T_g

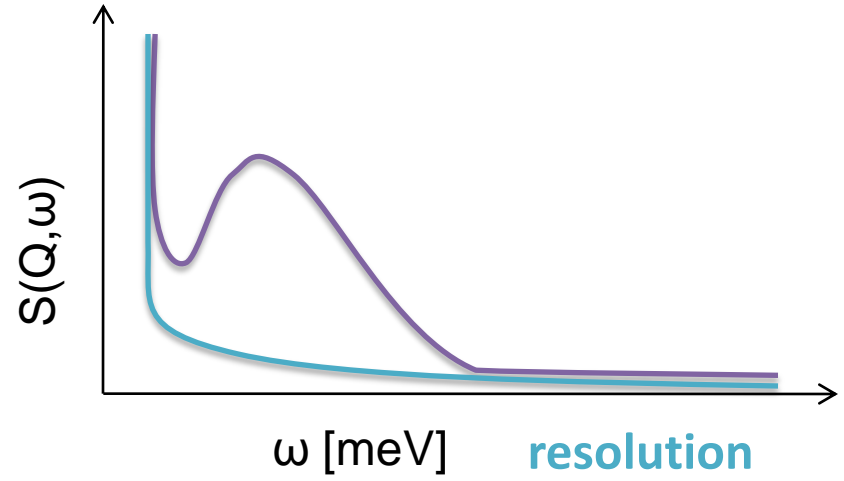
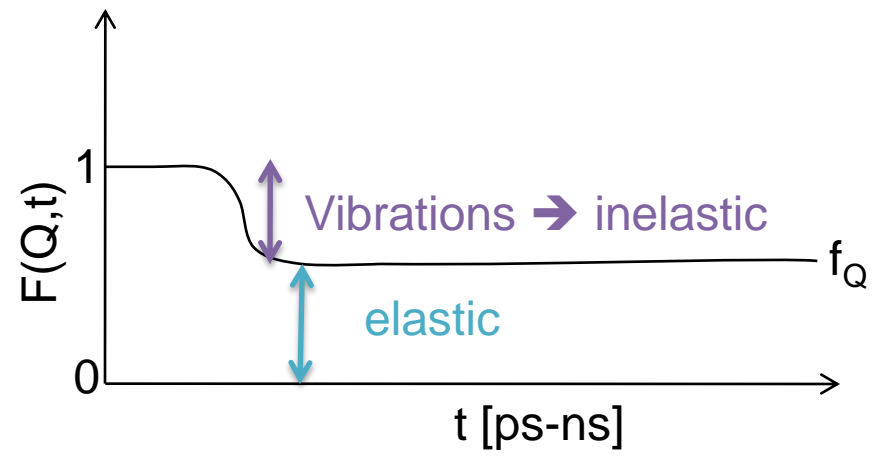


Liquid at T_g

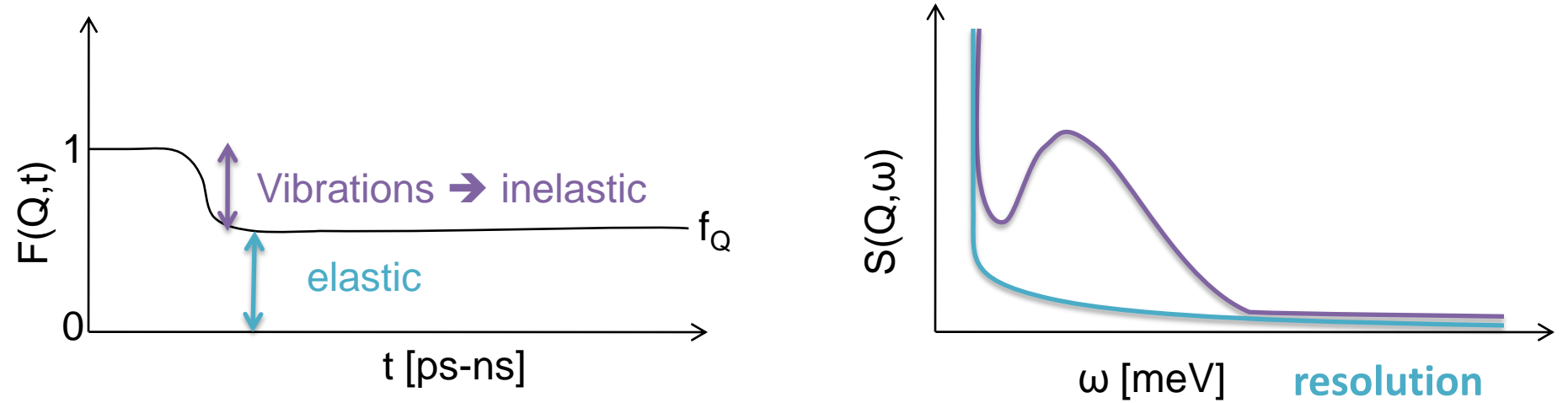
Short time processes as precursors of long time processes such as α relaxation ?

Correlation between fast and slow dynamics

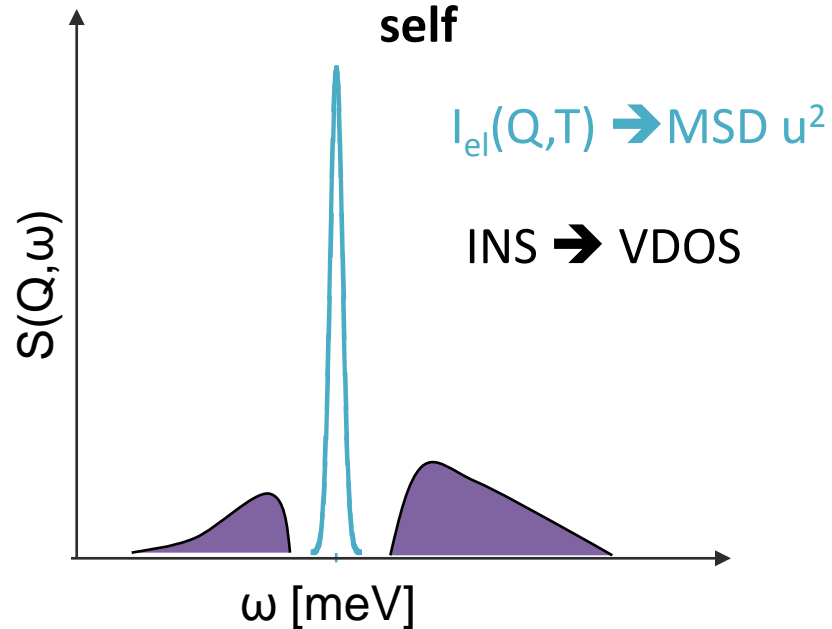
Fast and slow dynamics correlation



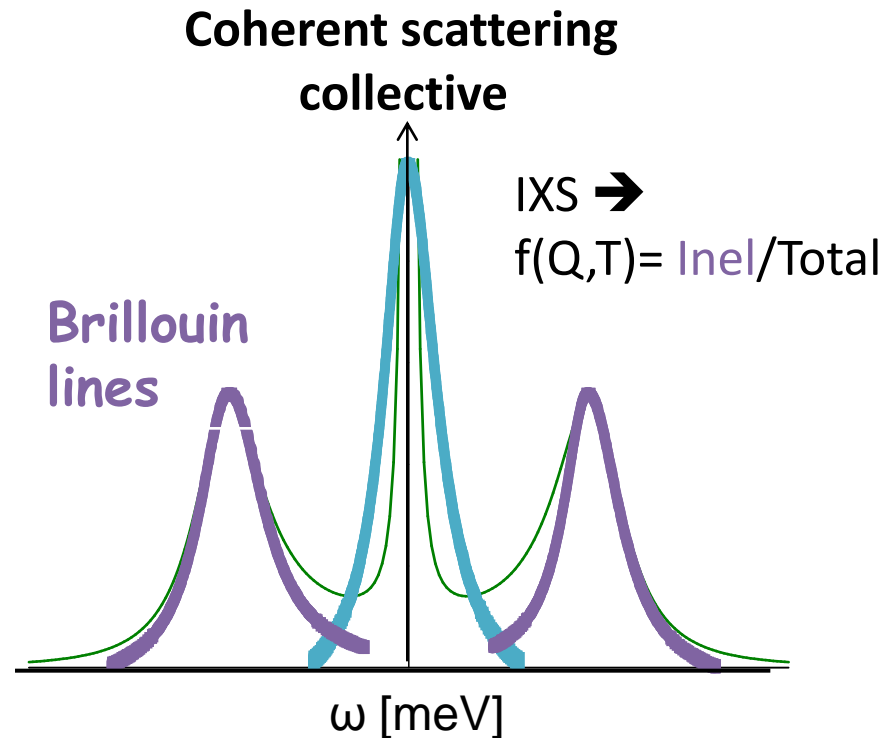
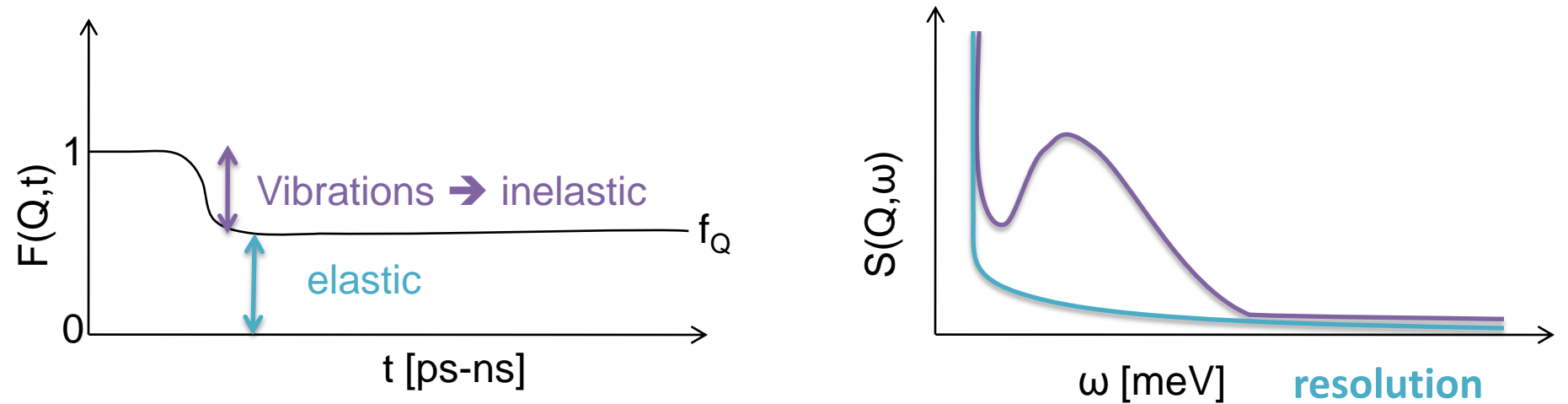
Incoherent scattering



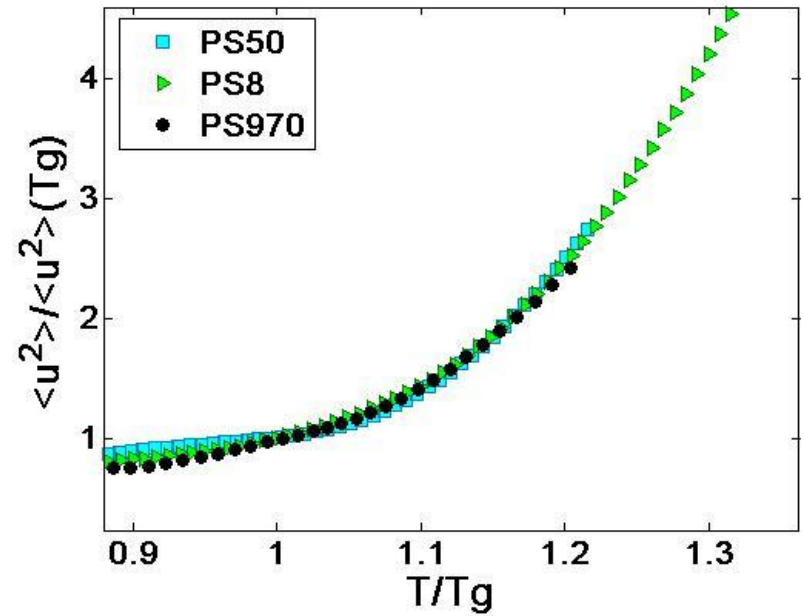
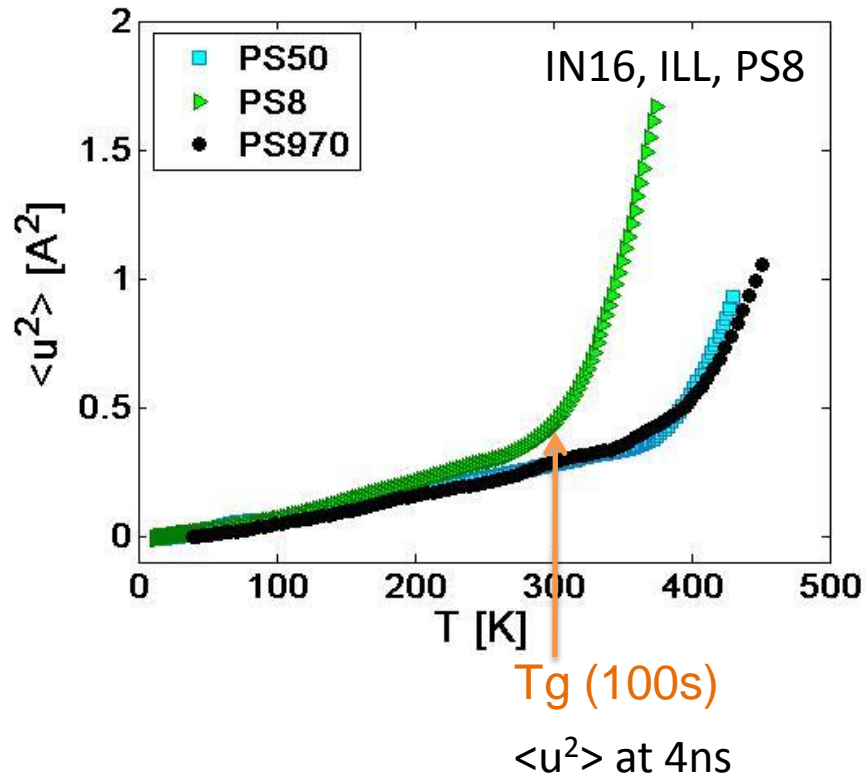
Incoherent scattering self



Coherent scattering

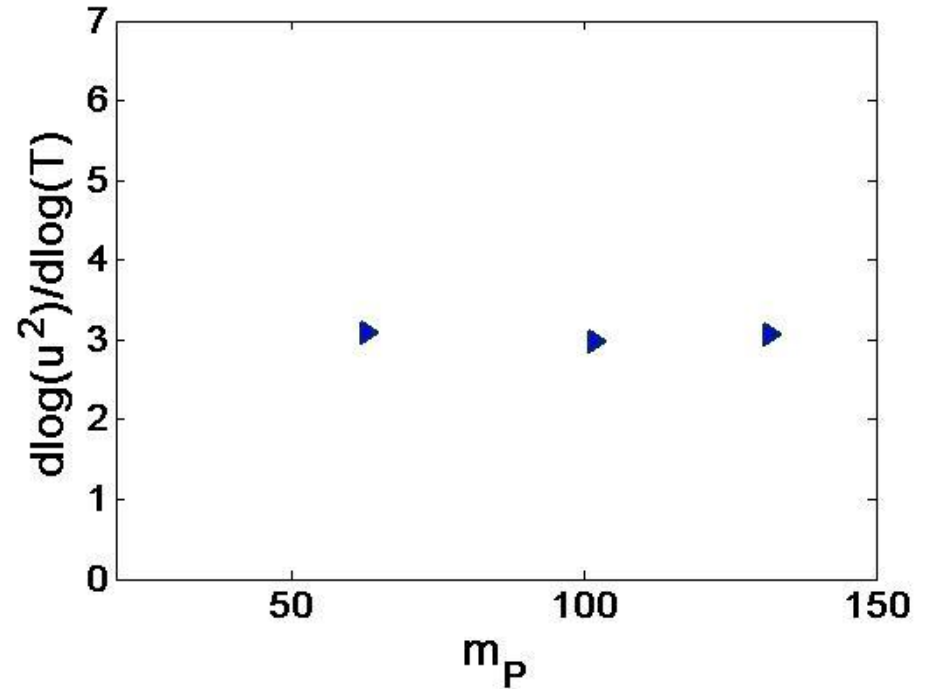
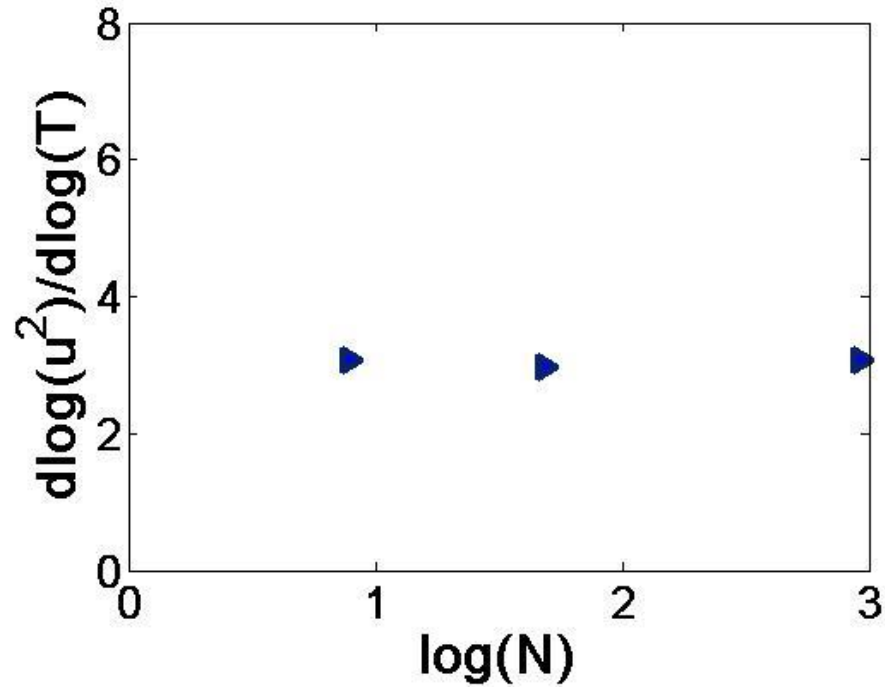


T-dependence of the mean-square displacement $\langle u^2 \rangle$



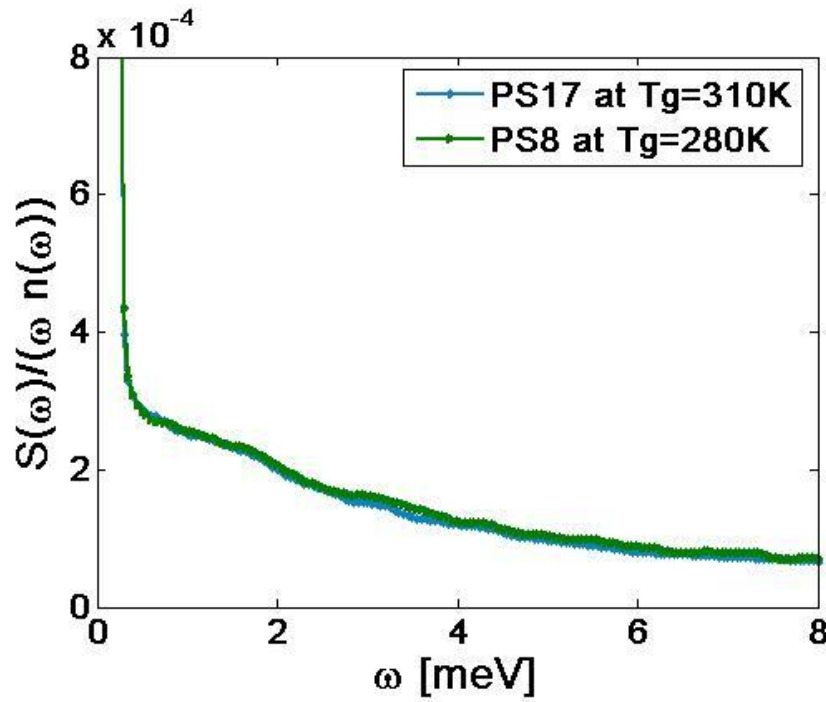
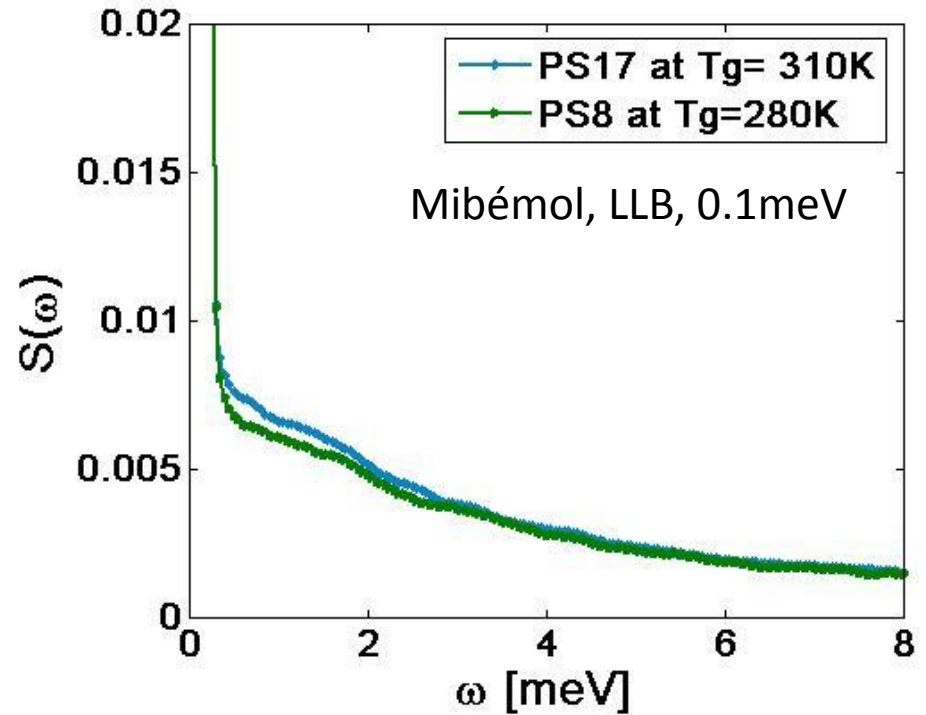
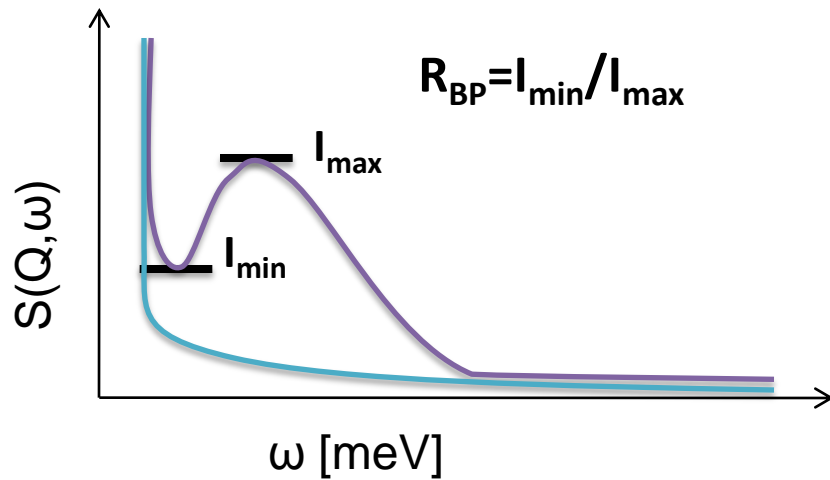
T-dependence of u^2 related to T-dependence of τ_α

T-dependence of the MSD



The slope of the MSD around T_g is independent of N
While m_p changes with N

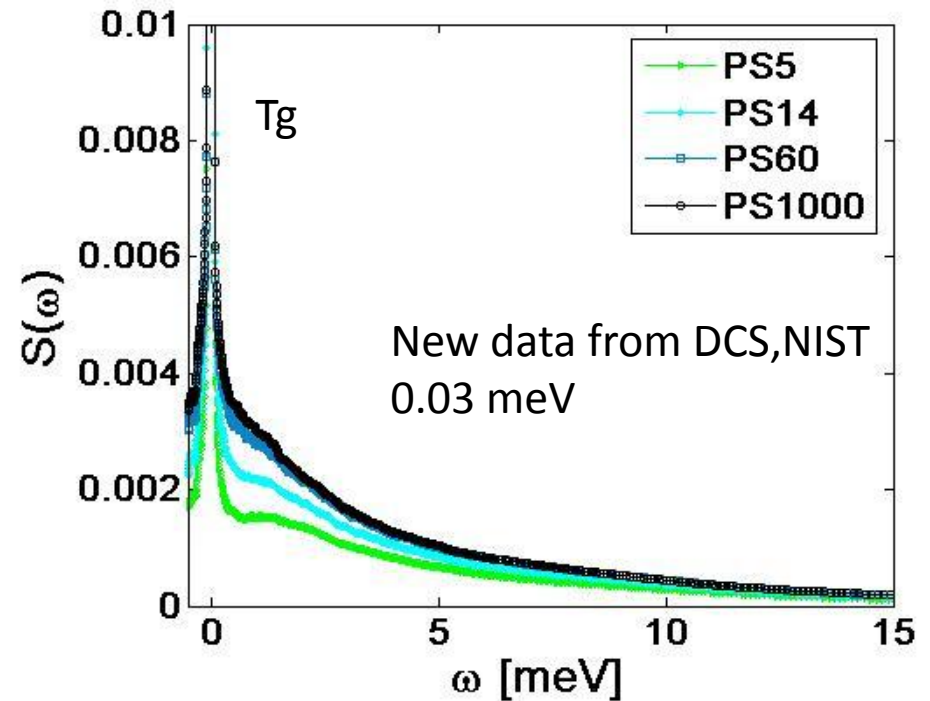
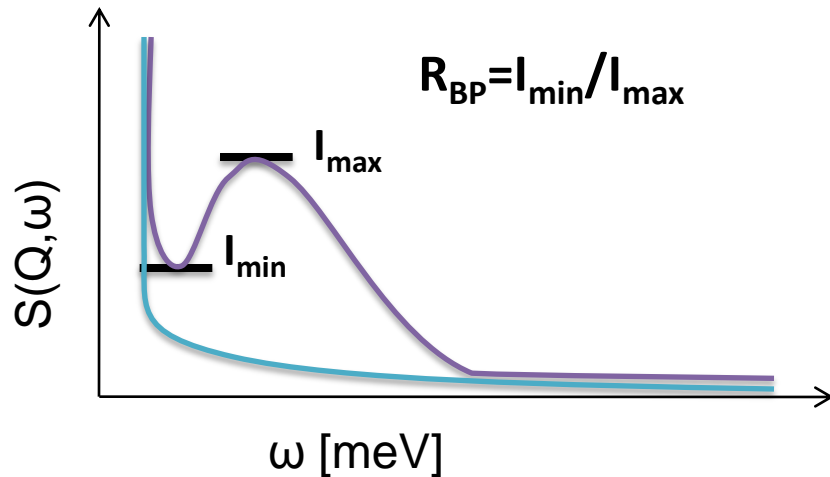
INS at the glass transition temperature



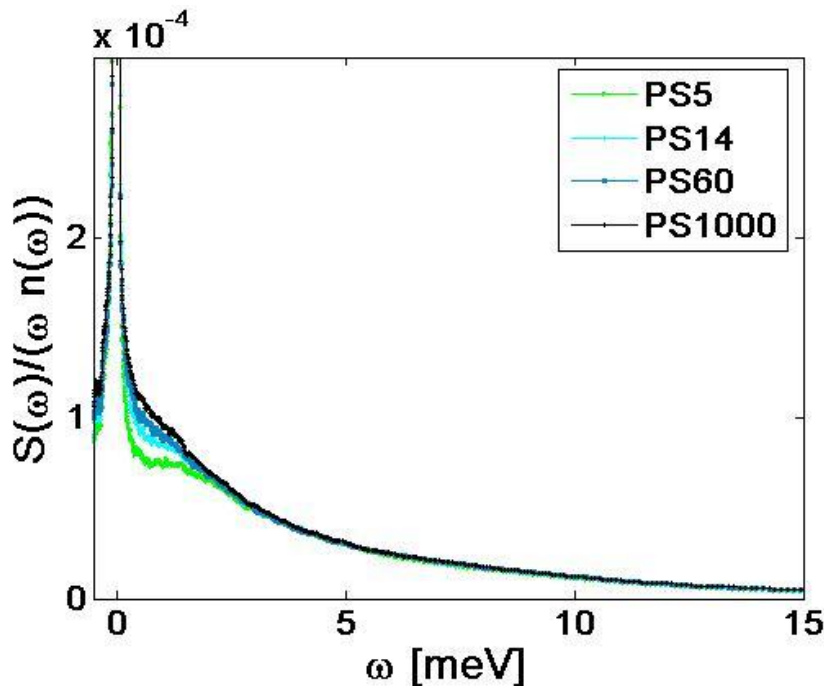
Small changes in the spectra at T_g with N

Related to T-effect: disappears by bose scaling

Incoherent INS at the glass transition temperature



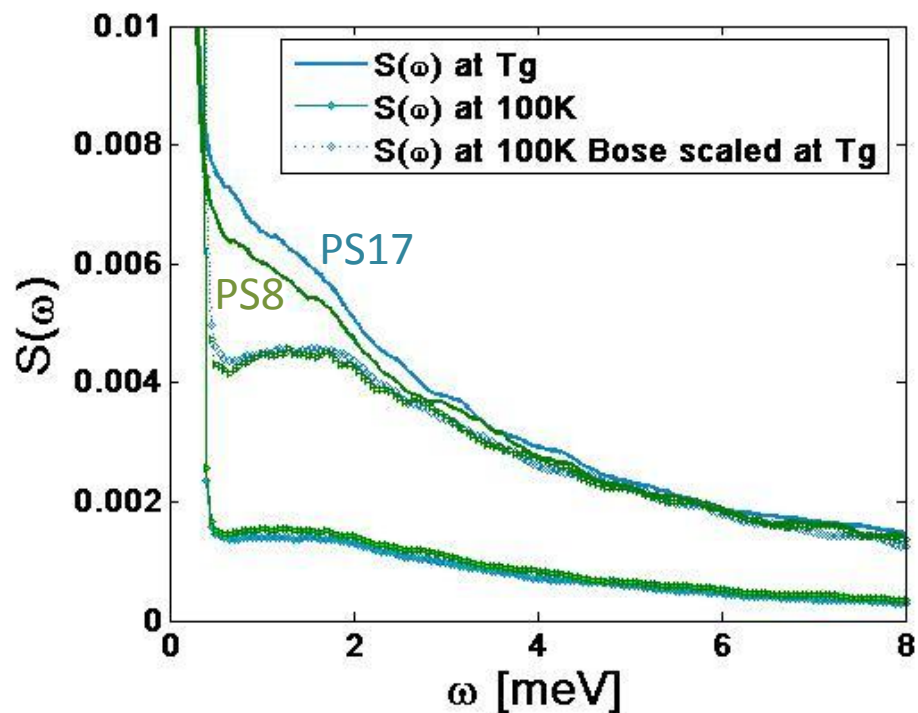
A. Sokolov, 1993



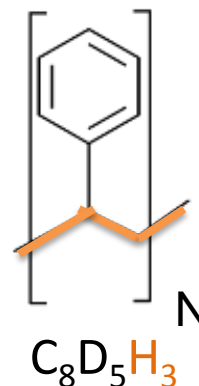
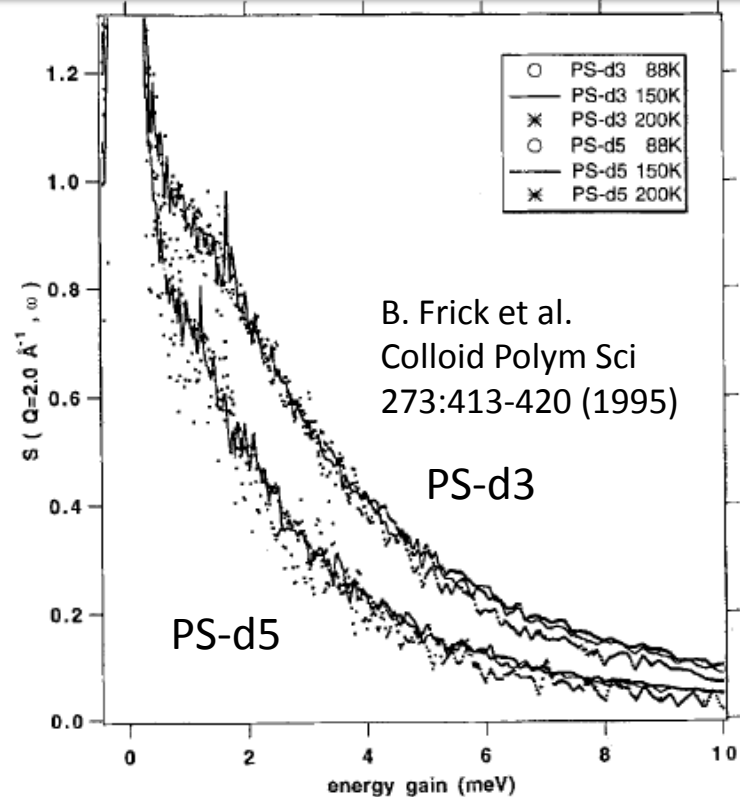
Small changes in the spectra at Tg with N that disappears by bose scaling except in QES region (**resolution effect**)

Extra process in QES

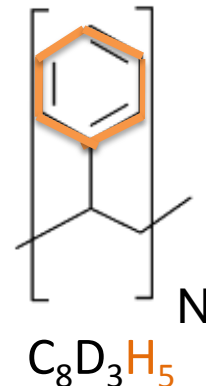
Extra relaxation process in QES



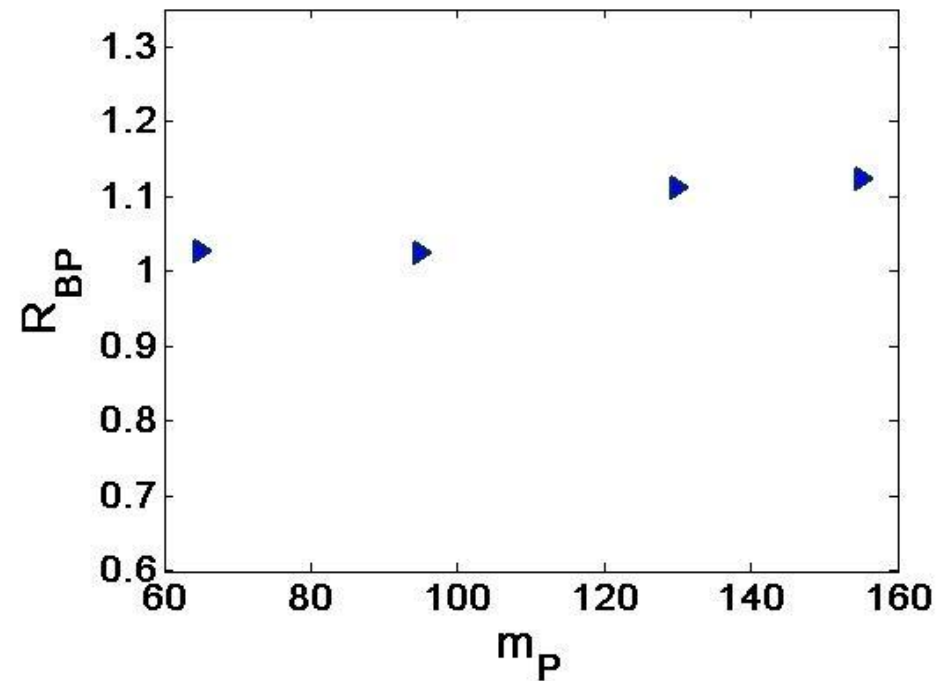
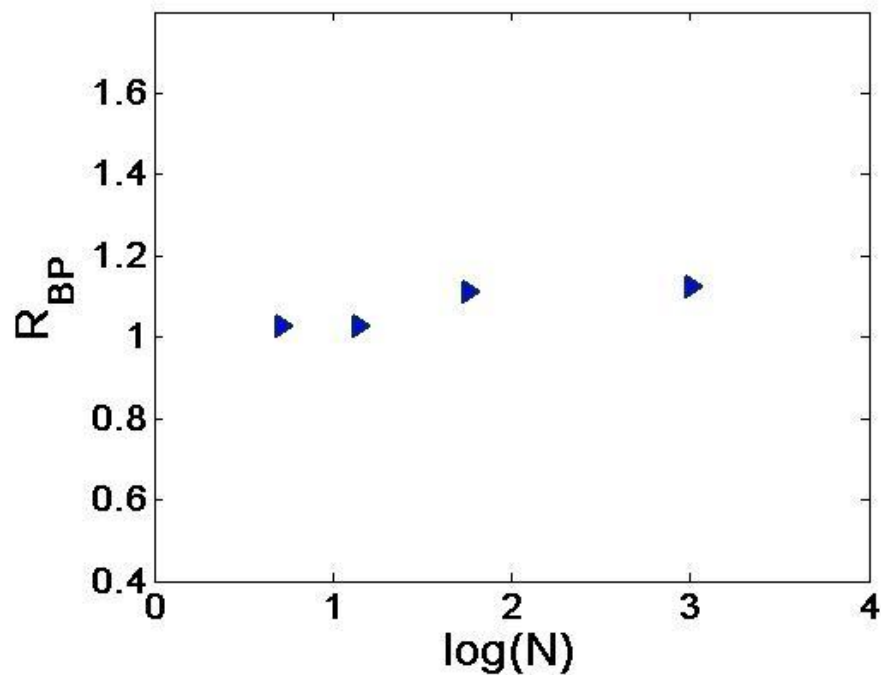
Extra relaxation process in QES at all N



Partial deuteration: related to the phenyl



Extra relaxation process in QES

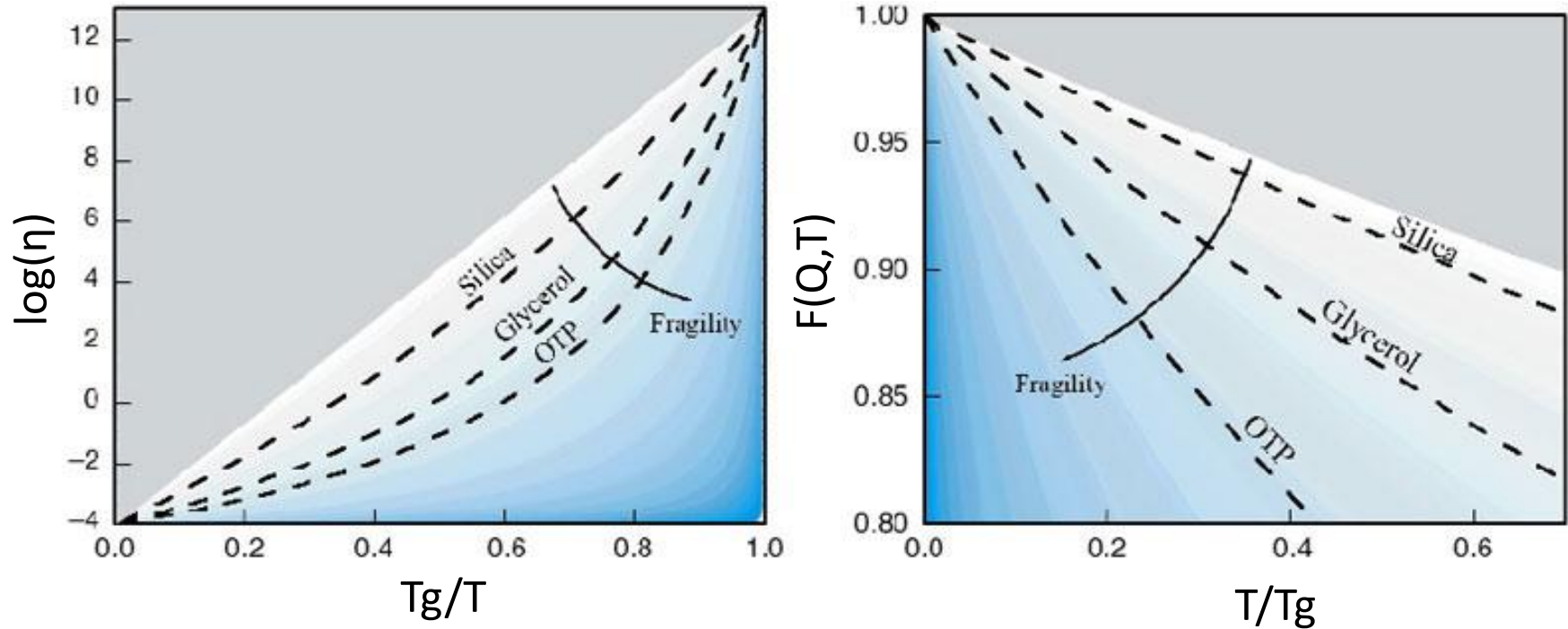


- R_{BP} independent of N while m_P changes a lot
- Problem of the physical meaning of R_{BP} (QES and Boson Peak)

“Is the fragility of a liquid embedded in the properties of the glass?”

Scopigno et al., Science, 2003

Correlation between m_p and nonergodicity factor

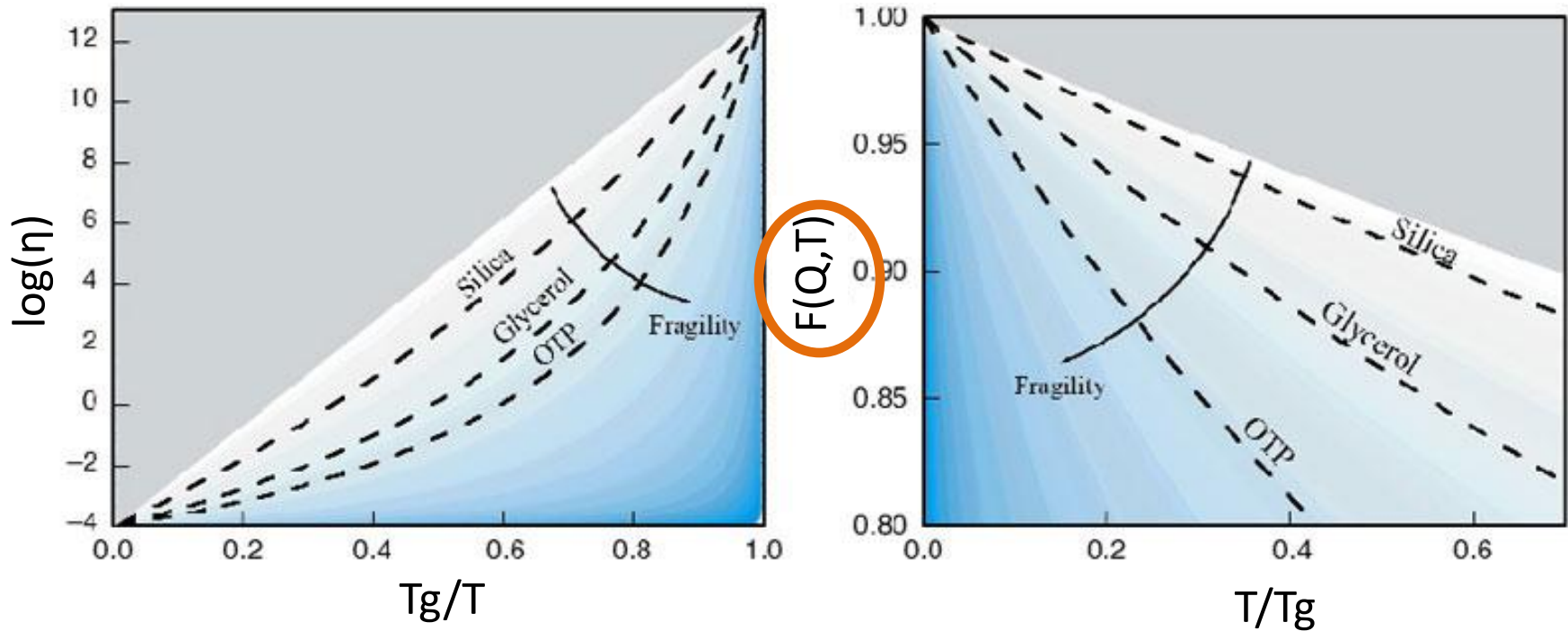


From ESRF website

Fragility of liquids or *fragility* of glasses?

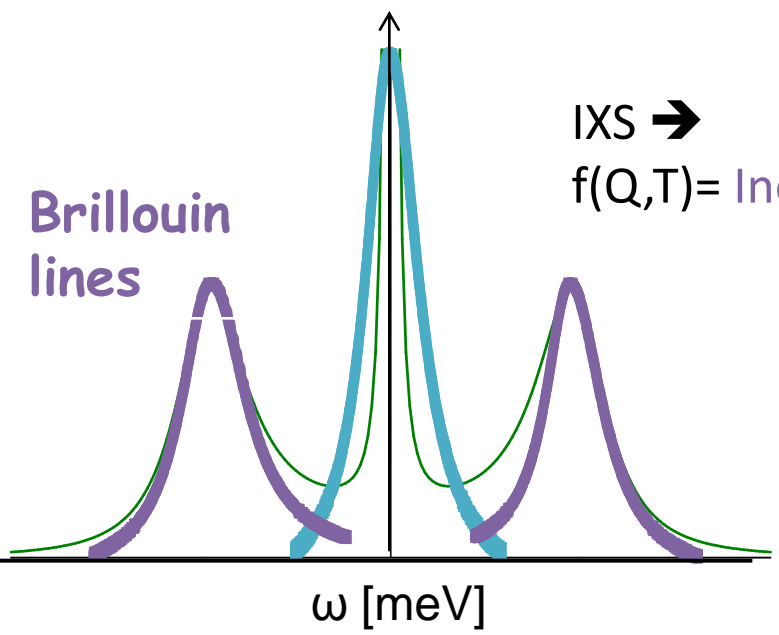
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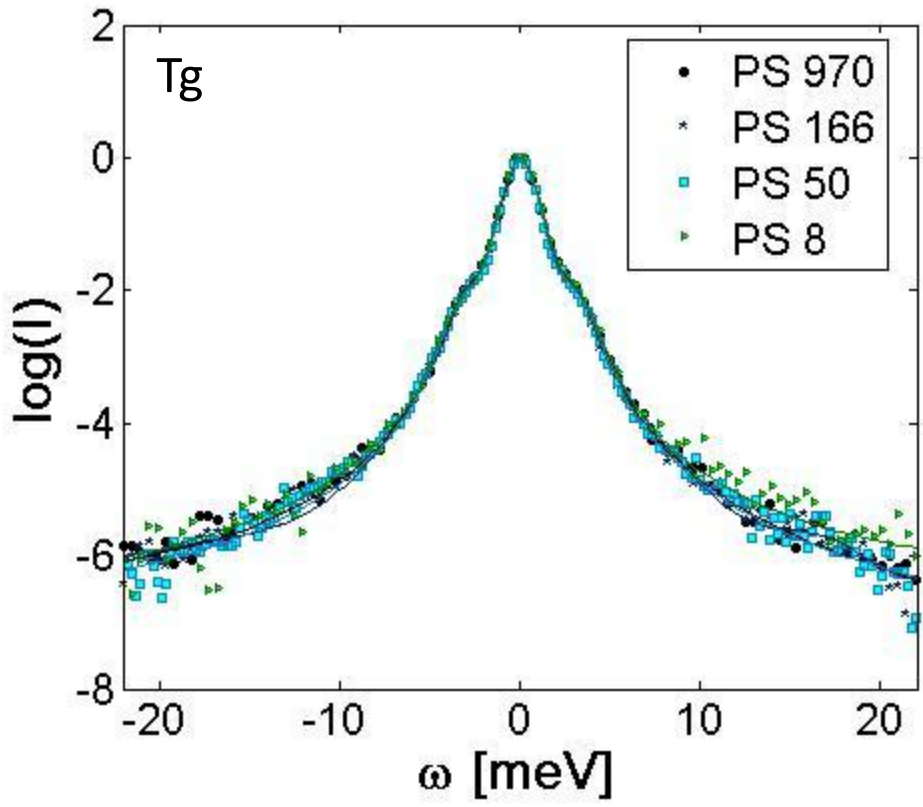


IXS spectra and non-ergodicity factor

Scopigno et al., 2003

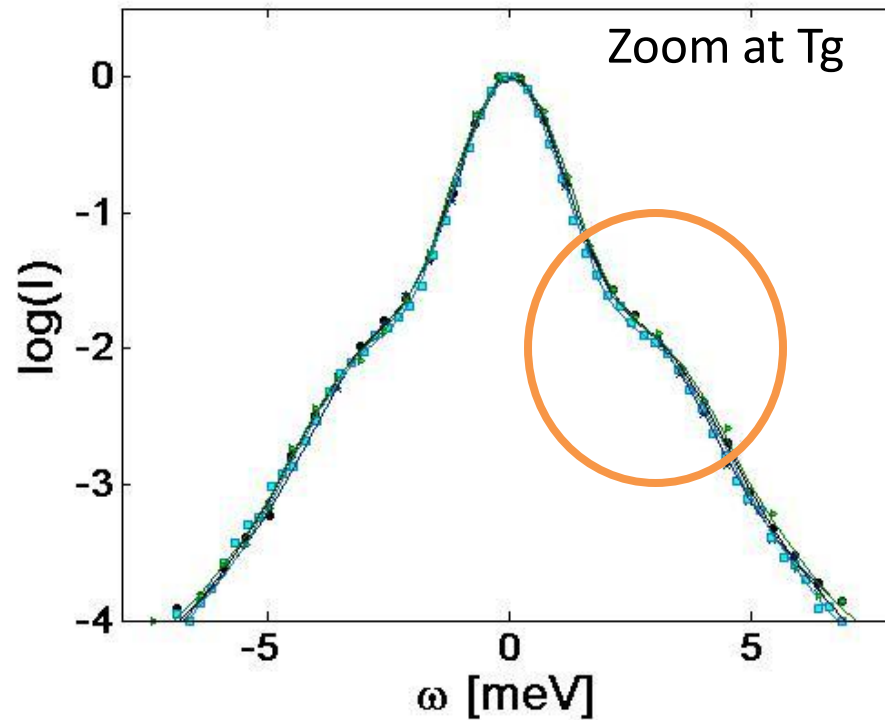


PS : No change in the spectra at T_g with N



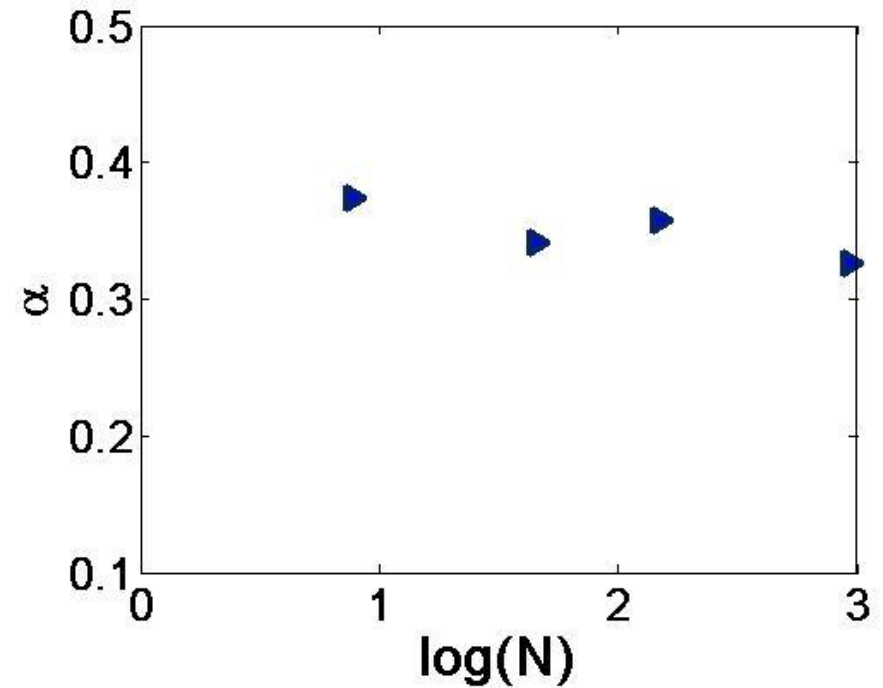
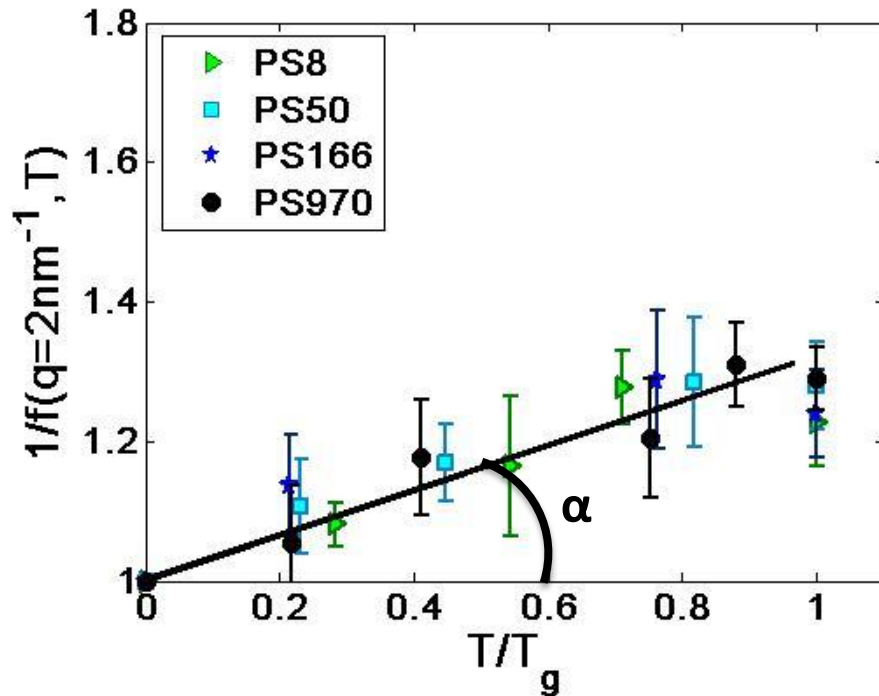
N dependence of IXS spectra at T_g and low T

Correlation between m_p and nonergodicity factor



- No change in the spectra at T_g with N
- Small change with N at low T

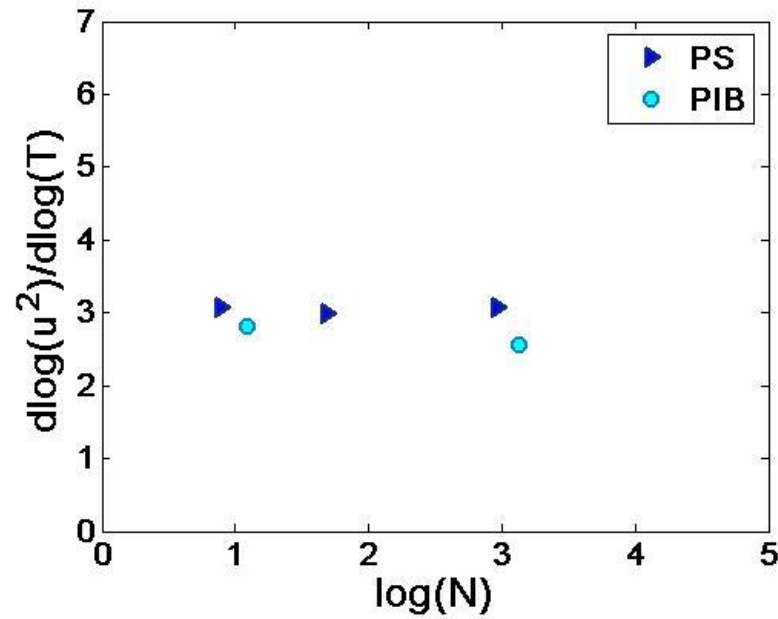
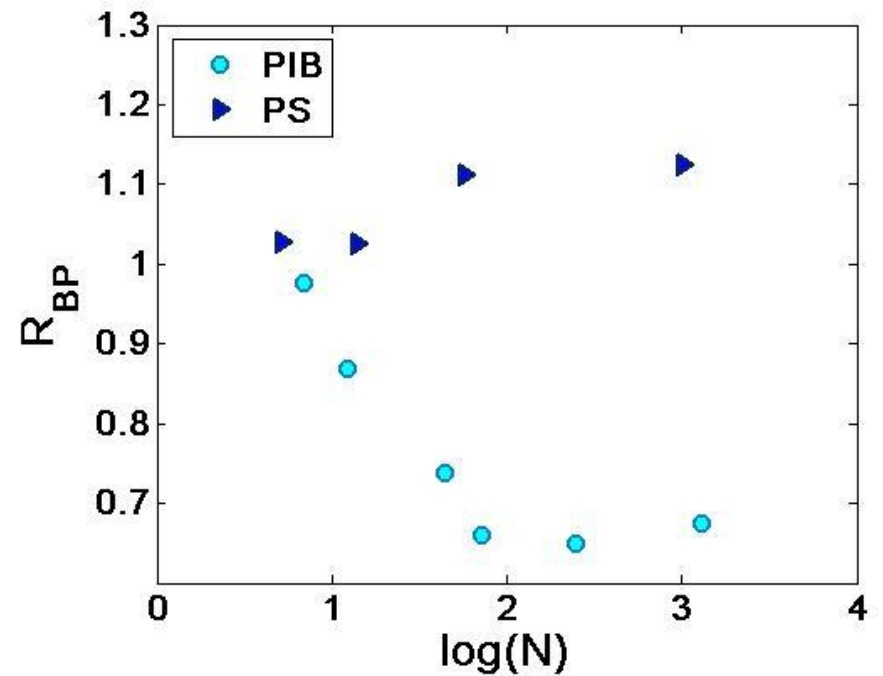
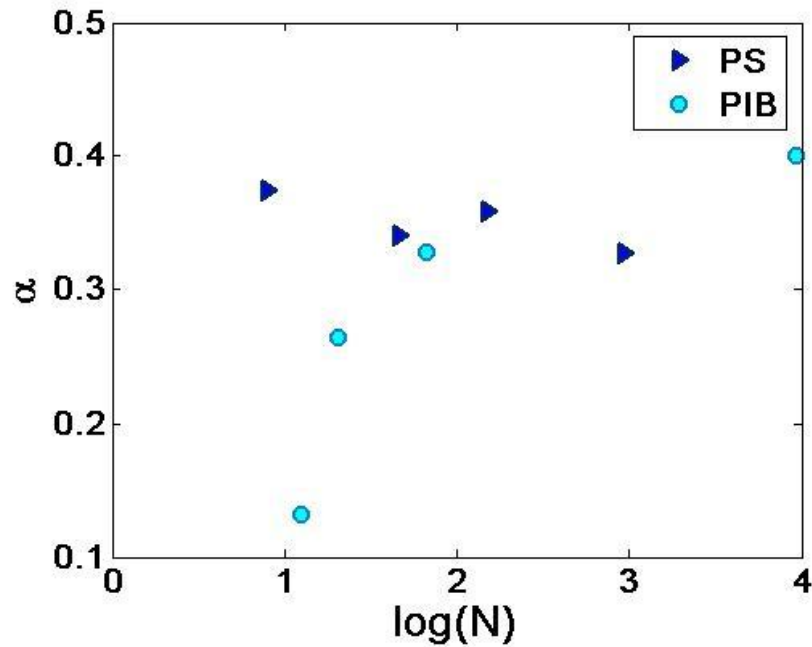
Non ergodicity factor versus T



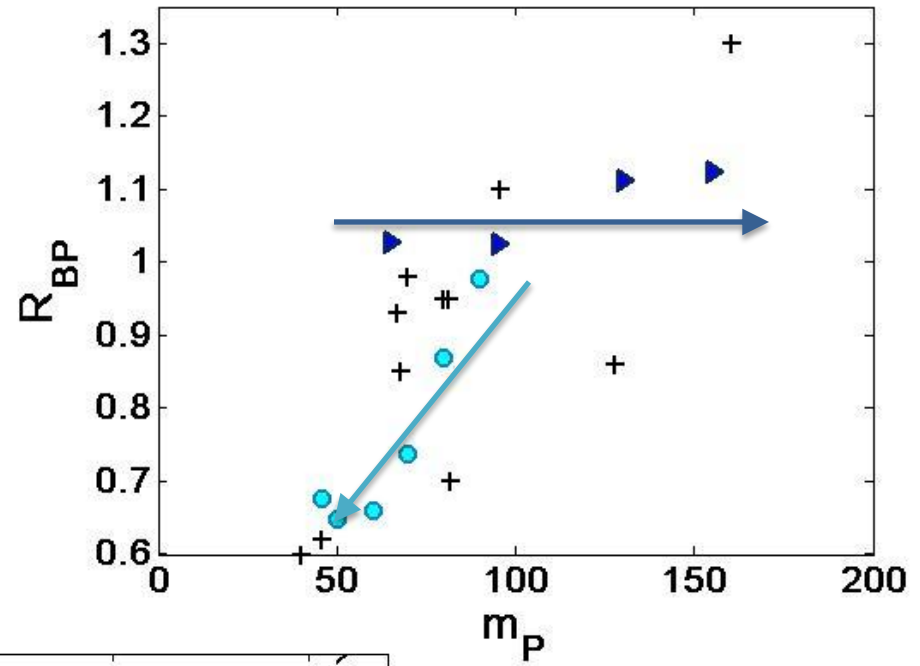
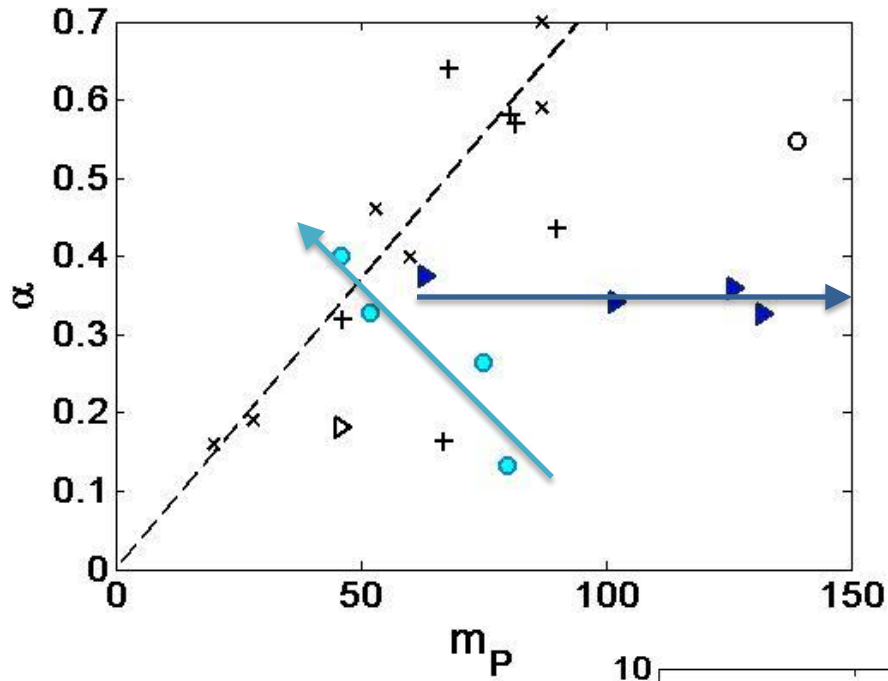
No change in the spectra at T_g with N

➔ Similar T-dependence for all N

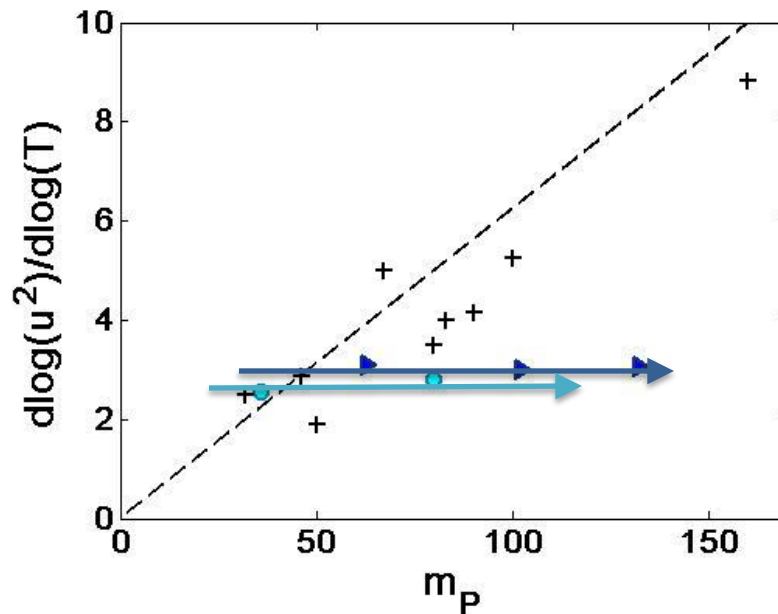
Summary of chain length dependences



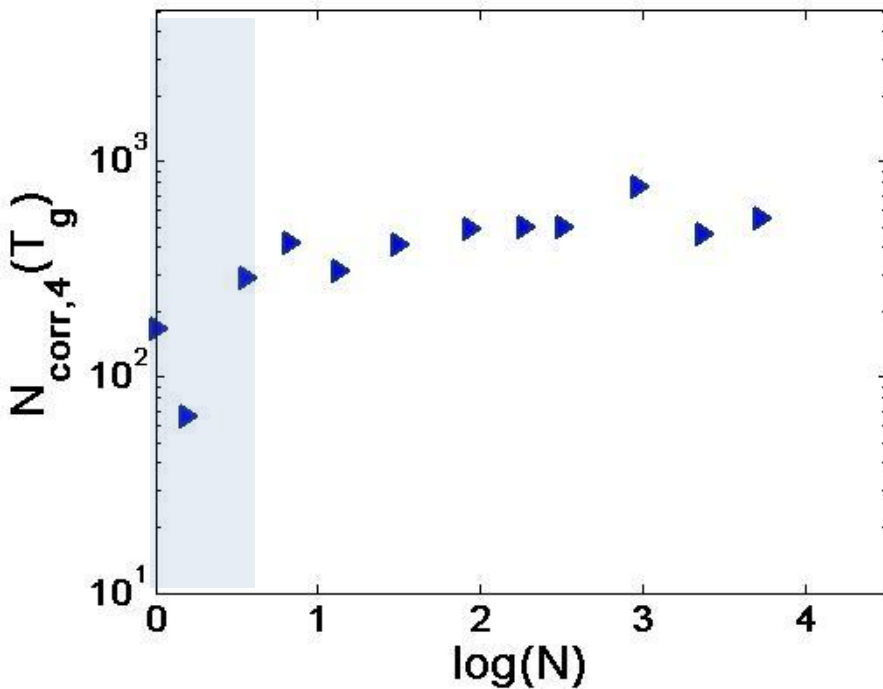
Conclusion part 3: Correlation between m_p and other properties



- + Lit. data including ours
- ▶ PS
- PIB



Conclusion part 3: Ncorr used as a new tool



- Same α and $f_Q(T_g)$ for all N
- Same R_{BP} for all N
- Same $d\log(u_2)/d\log(T)$ for all N
- Same β stretching parameter for all N
- Same ρ_g density at T_g for all N

BUT different m_p : from 60 to 160

Could the N-independent $N_{\text{corr},4}(T_g)$ be related to the N-independent high frequency properties measured in the glass?

rather than m_p

Summary of the context

Working on glass transition consists in working:

- on many different systems (universal phenomena)
- on a large t-range (from ps to 1000s): different spectroscopies
- by combining solid and liquid physics and equilibrium/non-equilibrium approaches

It necessitates to:

- choose good observables
- compare to theories

Key points were:

- the choice of the systems
- the extra external parameters

Conclusions

In this context, I chose to present :

- Ncorr on a large choice of systems including molecular liquids, colloids, simulations and polymers
- Fast dynamics versus chain length through various glass properties
- Specific case of polymers