# Structural Role of Elements in Glasses from Classical Concept to a Reflexion over Broad Composition Range

Cargèse

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## Organic Glasses

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# Glassforming molecular liquids and polymers

I- phenomenology of the glass formation
key features of interest

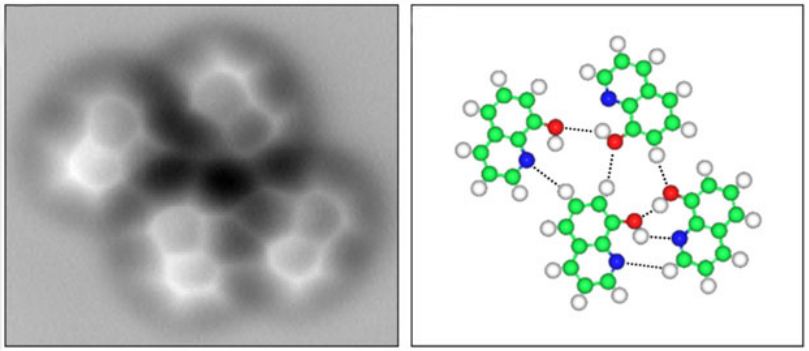
II- Notion of “Fragility”
role of control parameter temperature and density
effect of intermolecular interactions

III- local order and mesoscopic order ;
underlying length scales
high T activation energy
ultra stable glasses

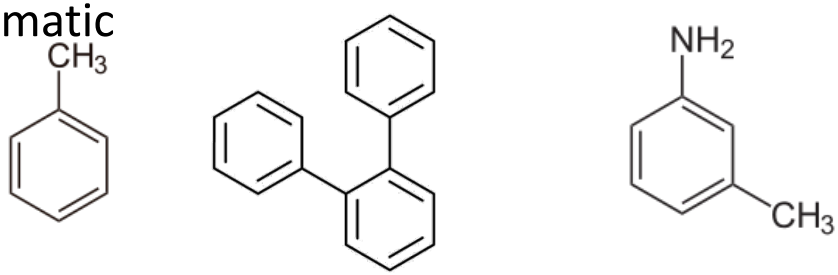
IV- molecular networks ?
**Reflexion over Broad Composition Range**
solutions and mixtures

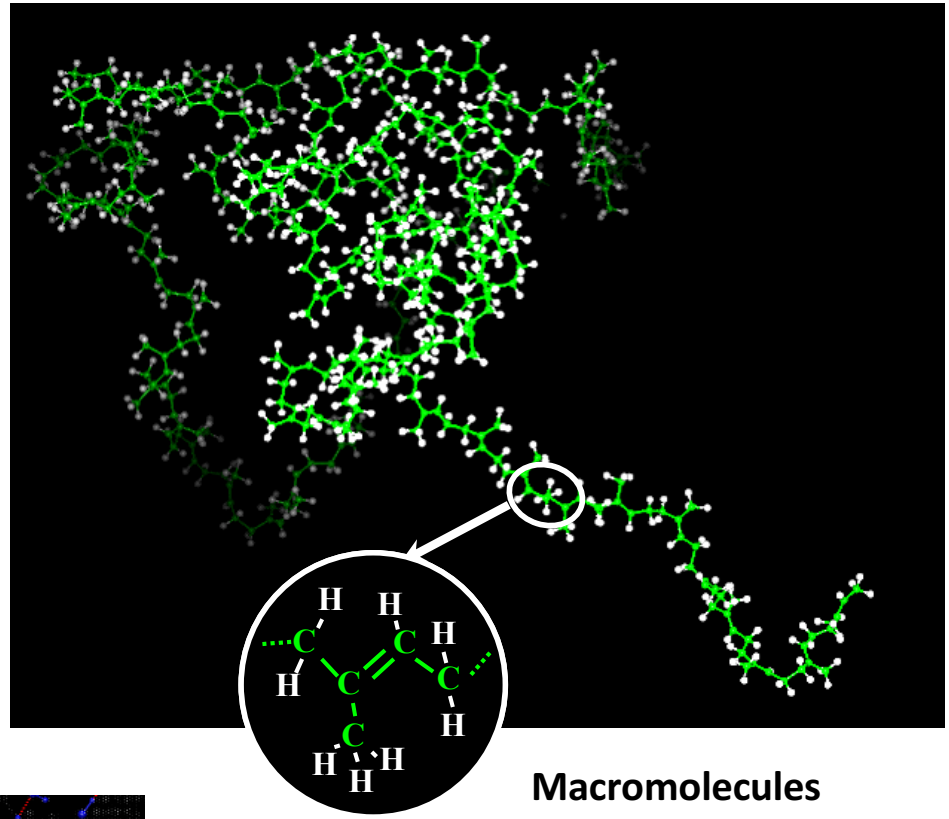
# Molecules and polymers

**AFM 2009 IBM**



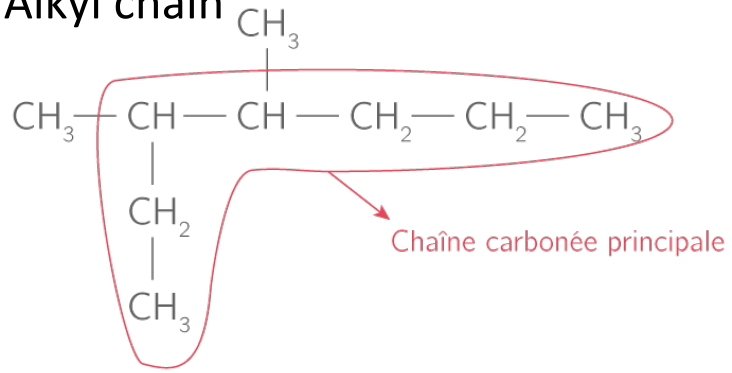
Aromatic



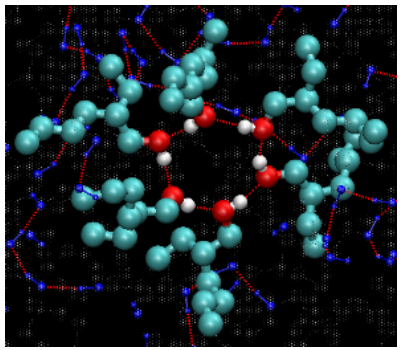




**Macromolecules**
**Repetition of**
**N Monomers**

Alkyl chain

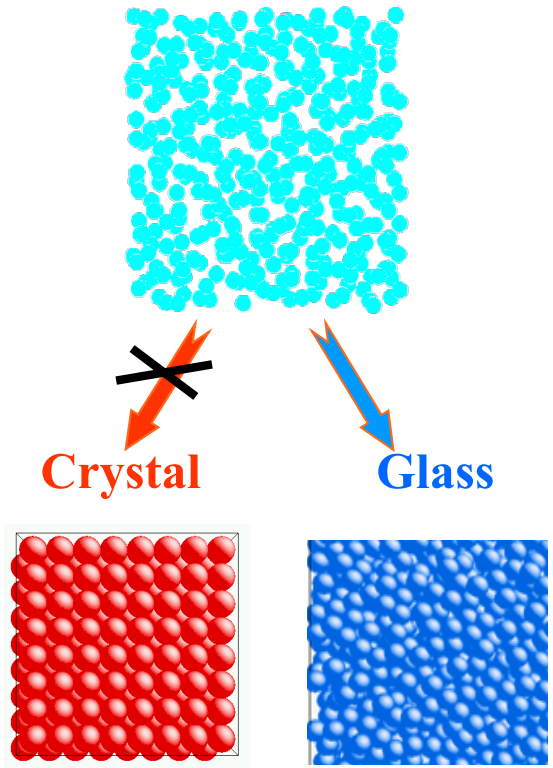



alcohol



**A minimal complexity is required** :
Argon does not form a glass , neither binary Lennard-Jones systems

avoiding the crystallisation
with locally preferred structures




- **Intramolecular** Covalent bonds
200-600 kJ/mole

- **Intermolecular** interactions :
  Hydrogen bond 1-40kJ/mole
  L-J ~10 kJ/mole
  coulombic

**No network**

**Molecules Low Tg = 56K- 350K**

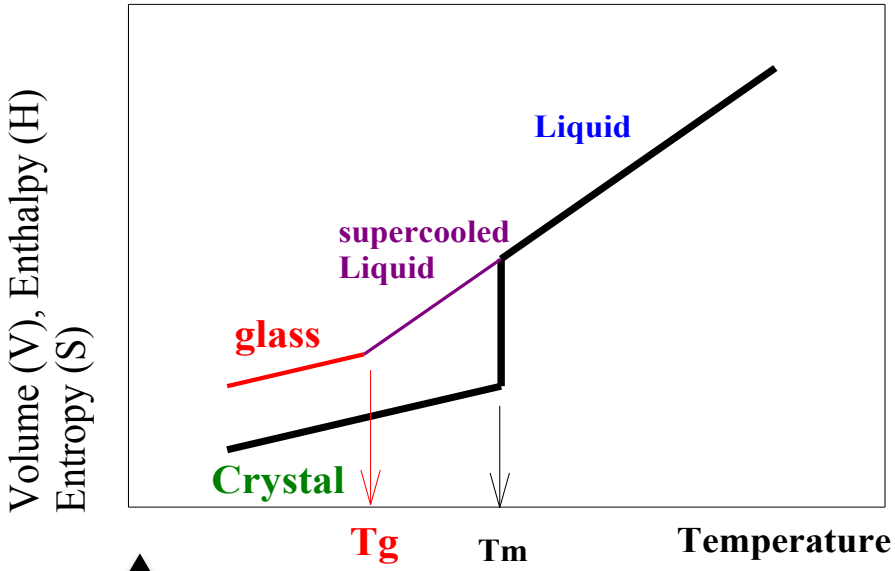
**Polymers Tg = 150K 470K**

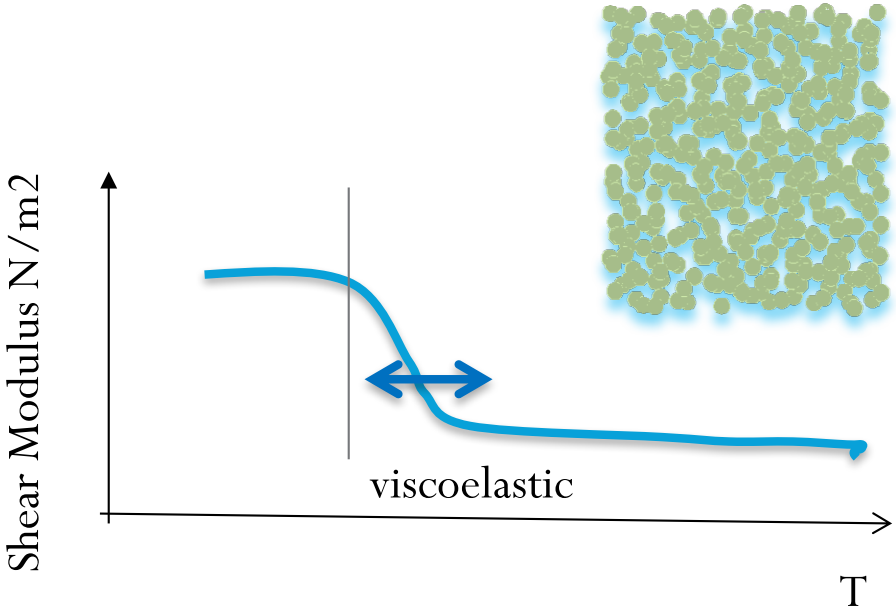
**Empirical rules** :
**Tb /Tg >2**
Tg/Tm ~2/3

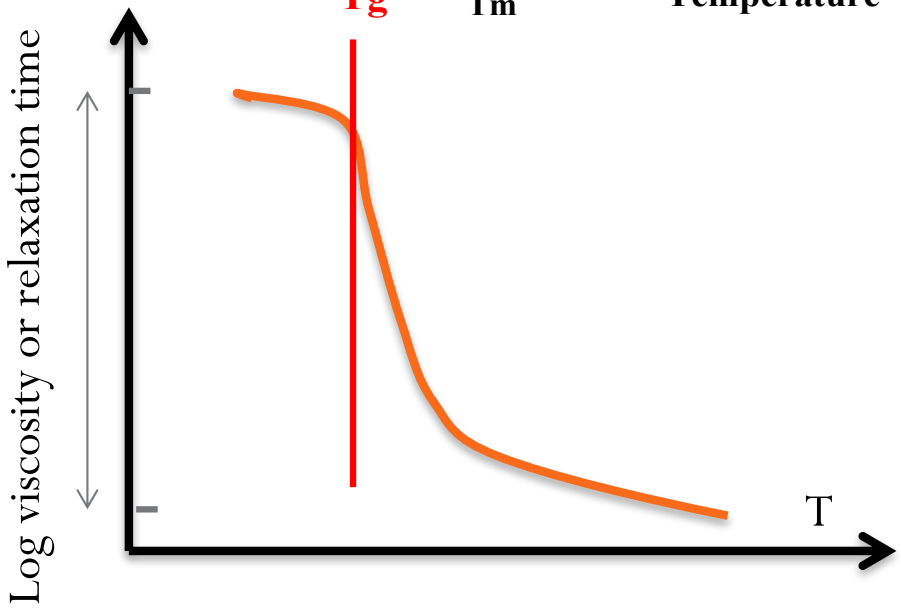
Glass formation = solidification without crystallization
Quench easy, sometimes in liq N2

at atmospheric pressure

Looking for an universal relationship between thermodynamics, structure and dynamics

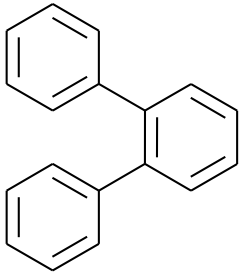


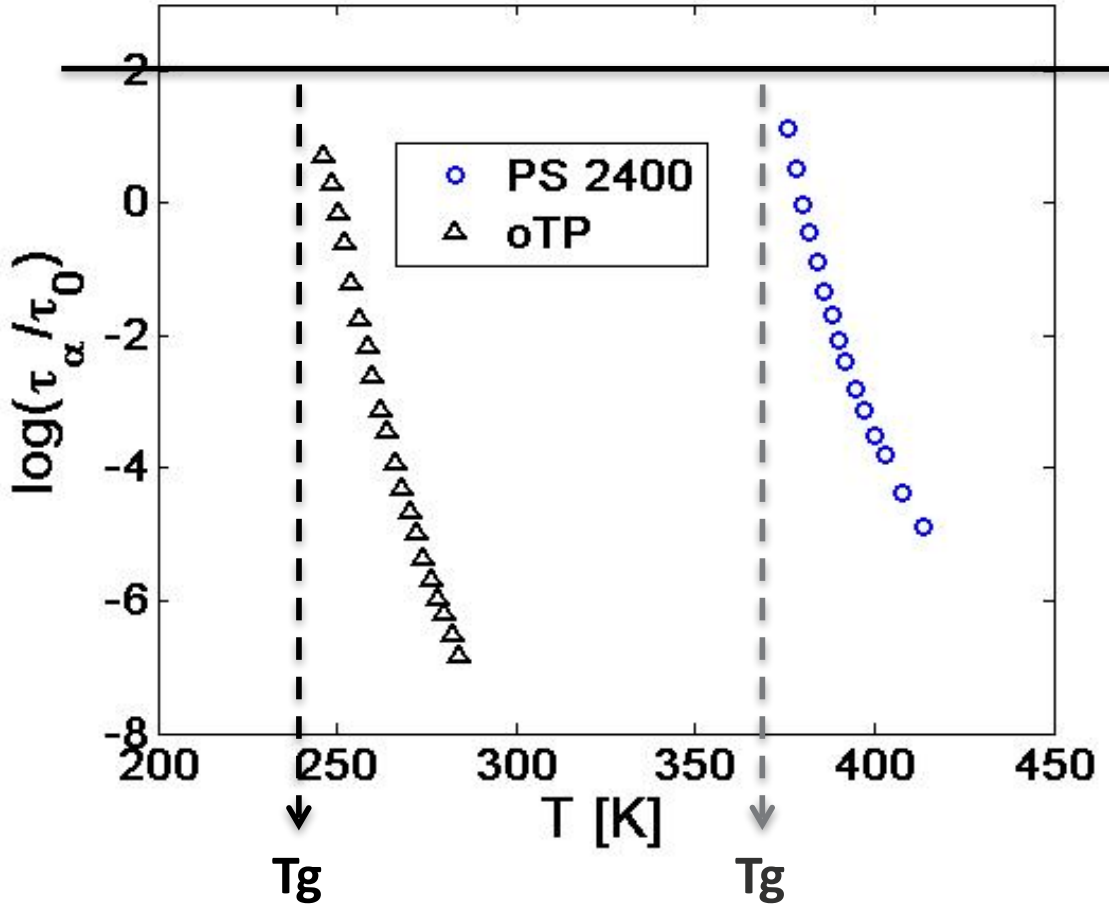




# Dramatic viscous slowing down

***o*-terphenyl**

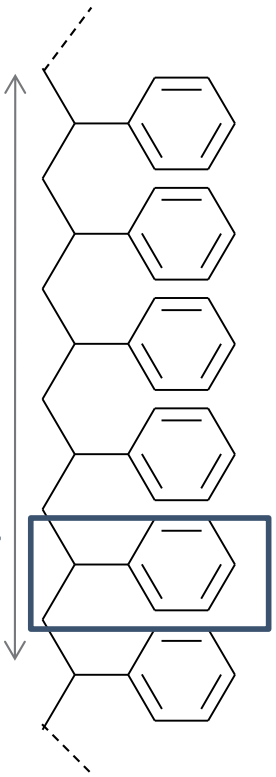





**Polystyrene**

N= chain length

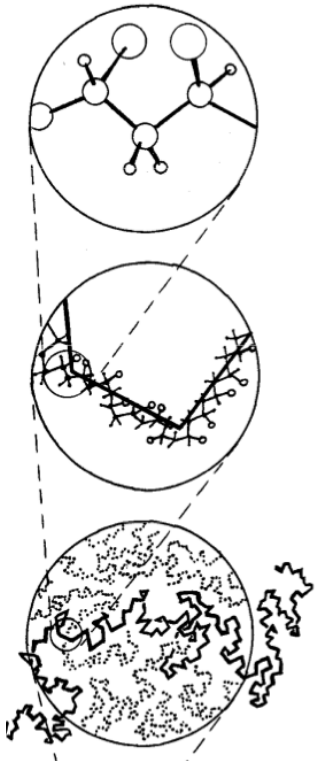
monomer



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

# Polymers : Molecular Weight effect on Tg

$$Tg = A + \frac{B}{Mw}$$ (Flory)



Monomère

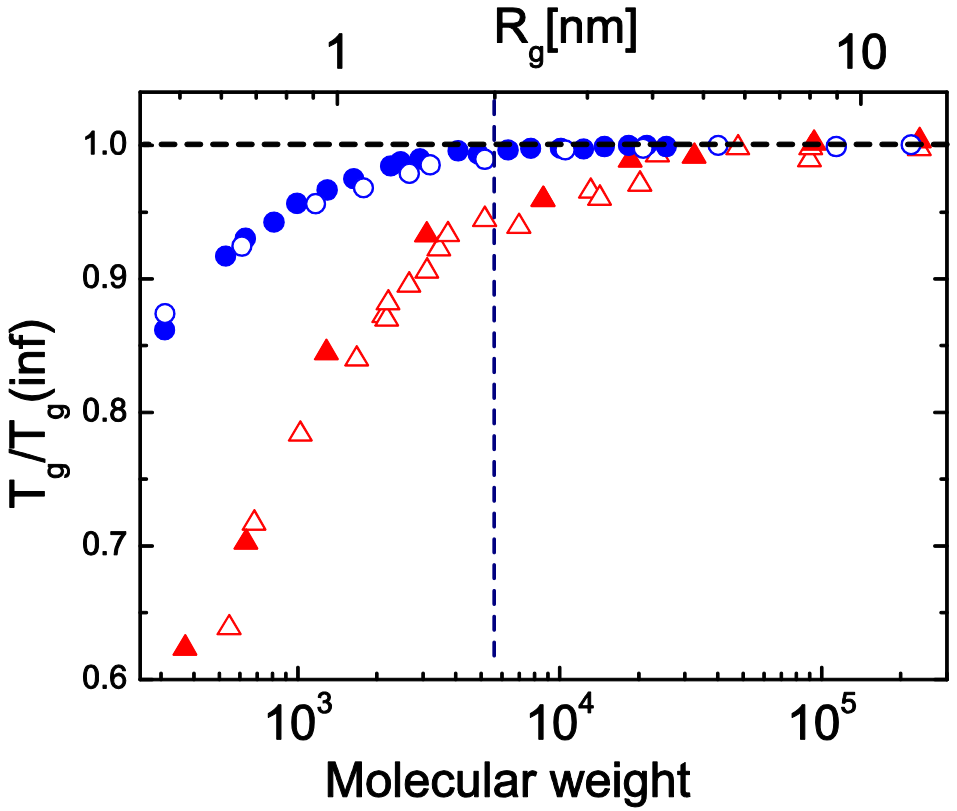
Bond lengths,
atomic radii
~ 0.1 nm

Longueur de persistance

Statistical (Kuhn)
segment length *b*
~ 1 nm

random Coil Rg

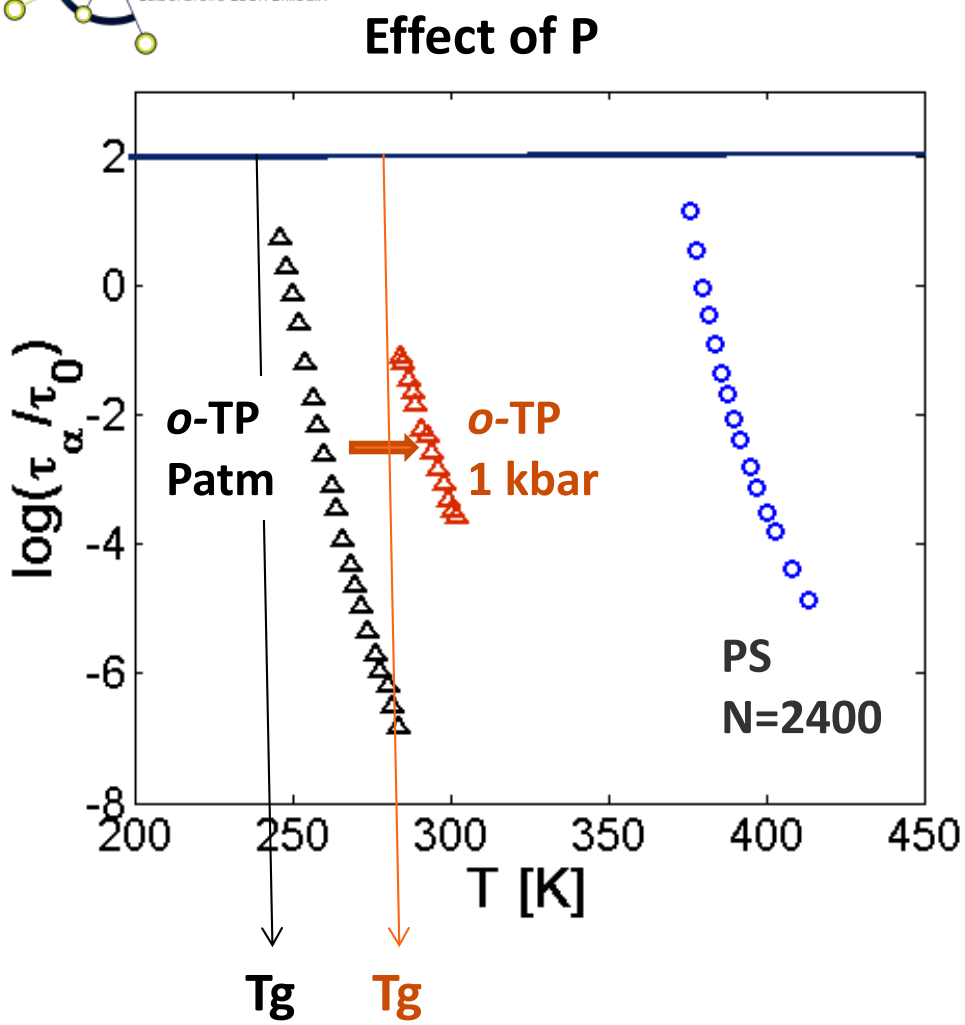
Chain radius of
gyration
~ 10 nm

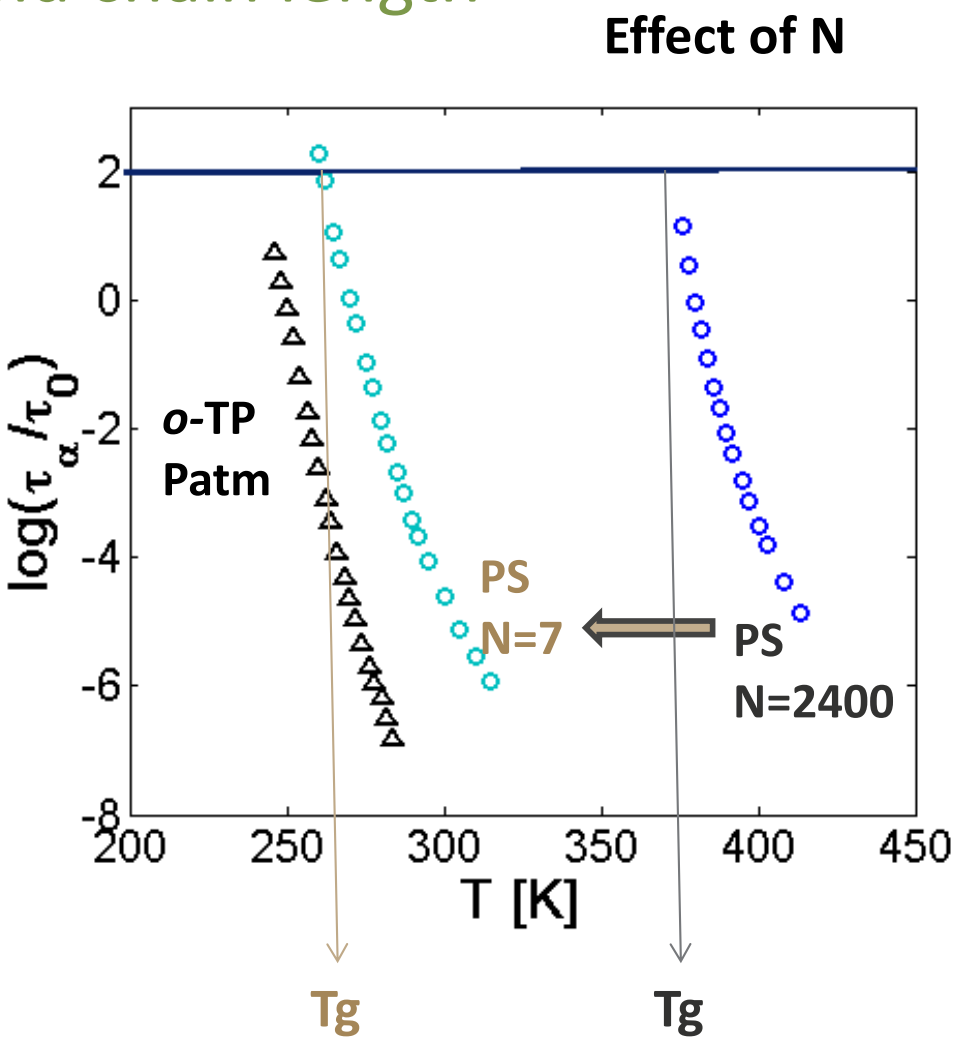



**Flexible Polymer PDMS** vs **rigid polymer PS**

*Rg versusMw*

# Other control parameters : pressure and chain length



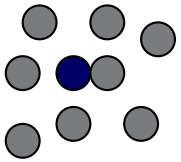

Tg changes with pressure P and chain length N

*Data from Naoki et al.,1987*

*Data from Hintermeyer et al.,2008*

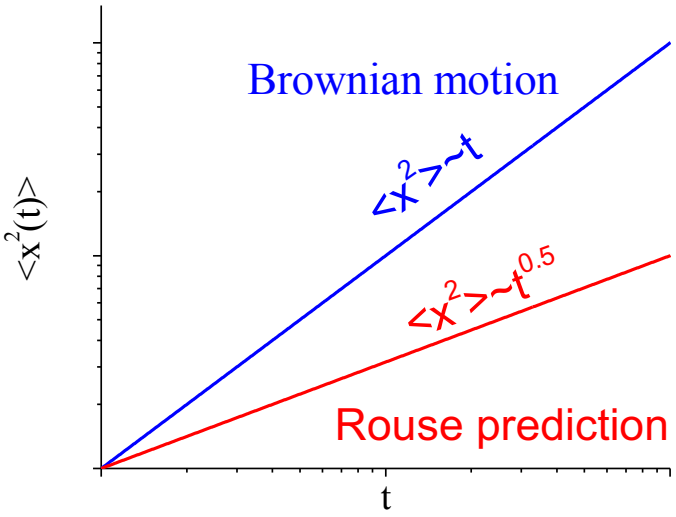
# Differences between molecules and polymers

Brownian motion $\xi \frac{dx(t)}{dt} = f(t)$ $\xi$ is a friction, f(t) is a random force.

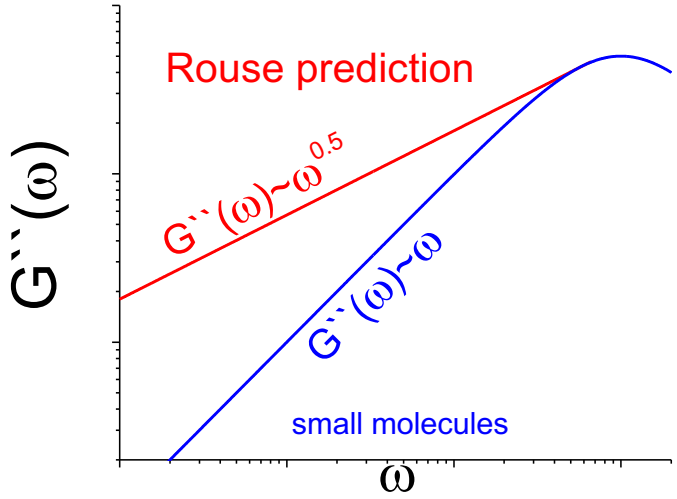


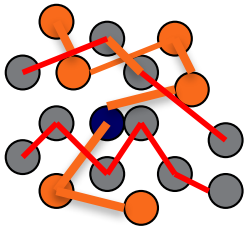
Molecular liquids

Diffusion




Loss modulus



Polymeric system

Additional force appears in a polymer due to chain connectivity.

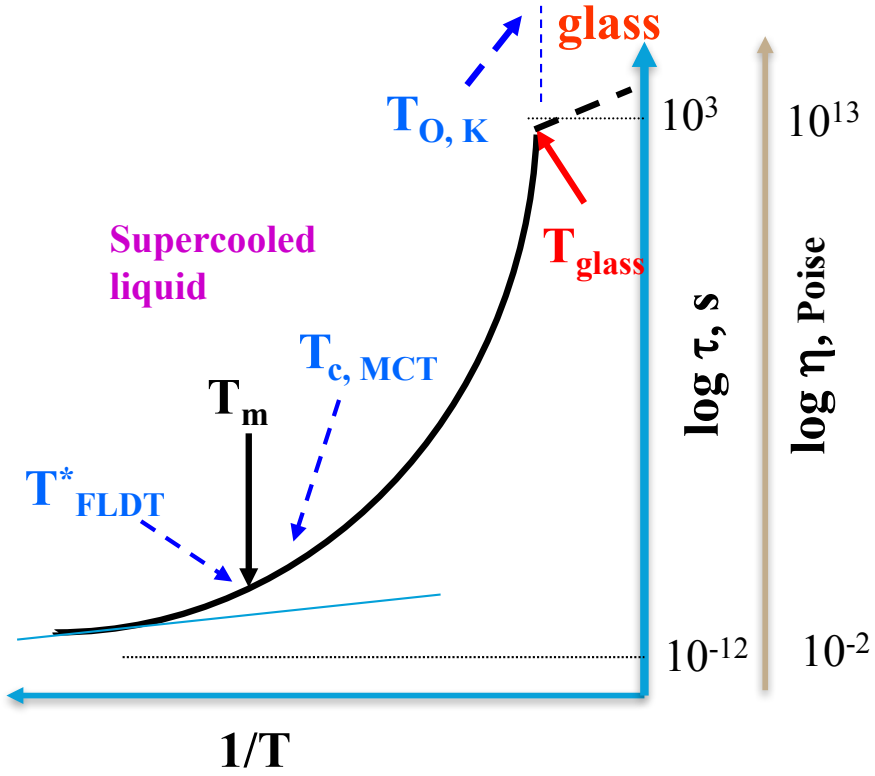
Rouse model assumes Gaussian statistics of the chain and:

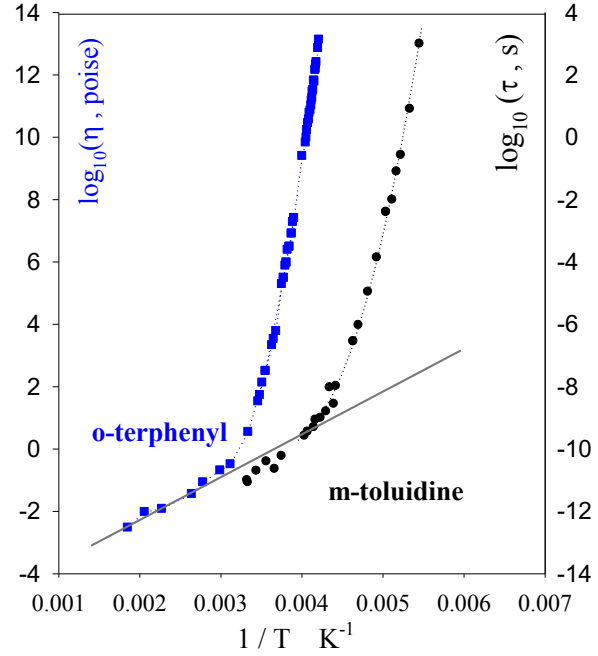
$$\xi \frac{dx(t,n)}{dt} = \frac{3T}{a^2} \frac{\partial^2 x(t,n)}{\partial^2 n} + f(t)$$

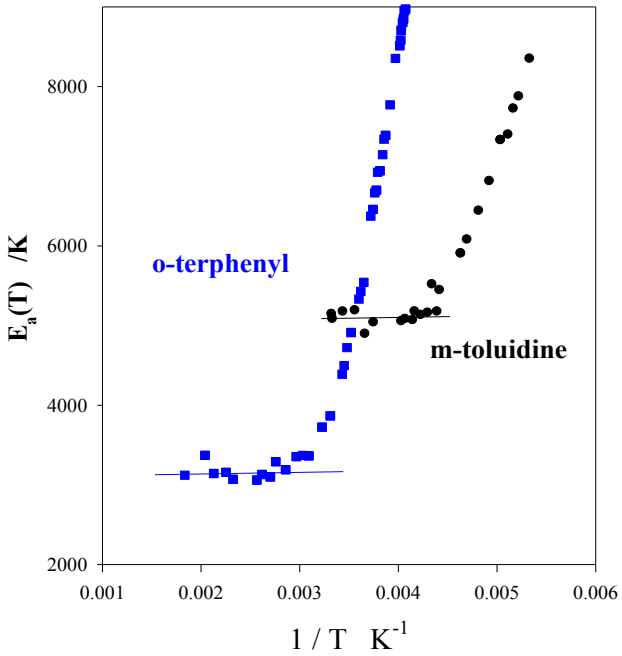
It predicts: $\langle x^2 \rangle \sim t^{0.5}$ and $G``(\omega) \sim \omega^{0.5}$

# Viscous slowing down and dynamical arrest
# thermally activated kinetics

$$\tau = \tau_\infty \exp [ E_a(T) / k_B T]$$




Increase of an effective activation energy

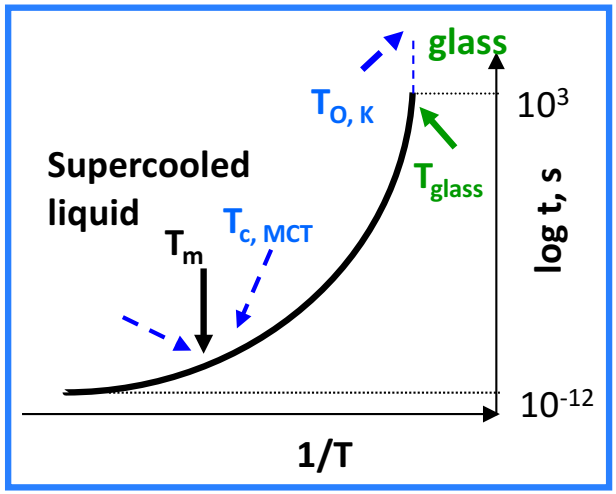
→ **collective behavior**

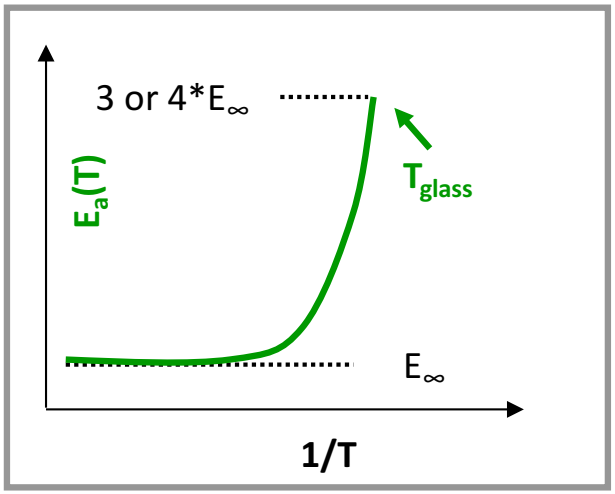
suggests an **heterogeneous dynamics**

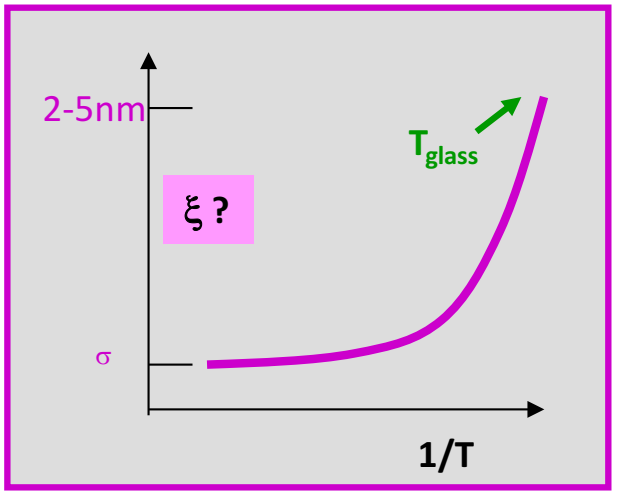
## Central question :

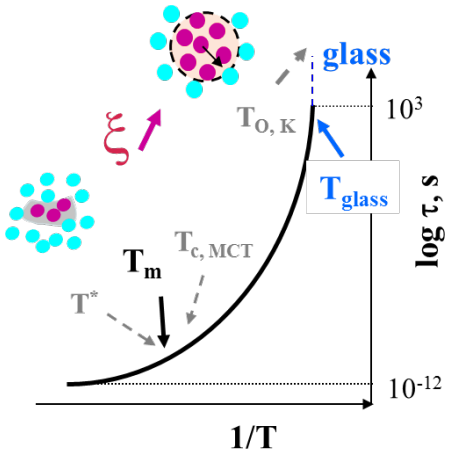
**Is the sharp increase of the viscosity related to the growth of a 'cooperative' length scale ?**

$\tau = \tau_\infty \exp [ E_a(T) / k_B T]$ and $E_a(T) \propto \xi(T)^?$




**Glass Science : a jungle of phenomenology**

**Summarized by a quest for characteristic lengthscale(s)**

**provided by dynamical properties**

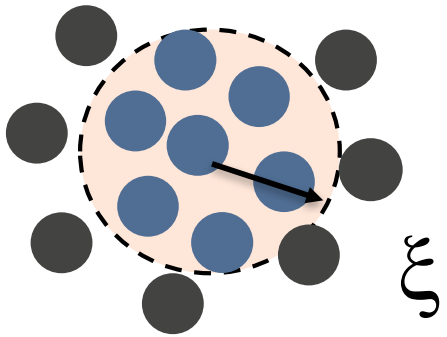
Space-time 4-point correlation function

# Cooperativity and correlation length

## Cooperativity length static

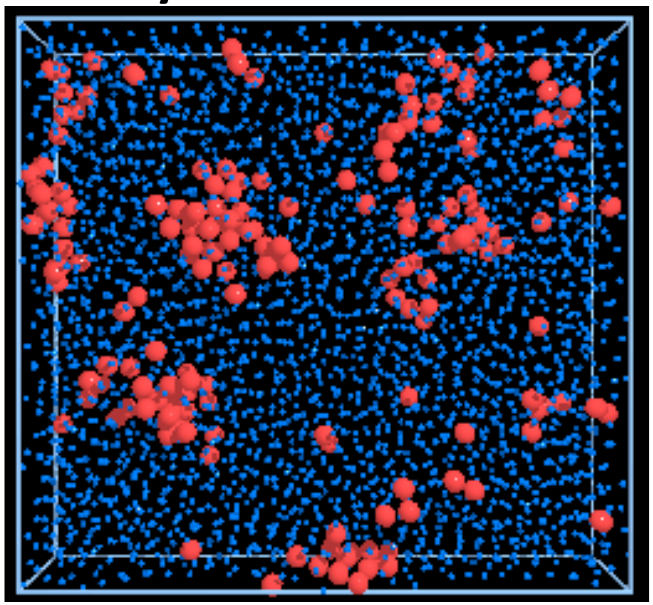
$$\tau(T) = \tau_0 \exp\left[N_{\text{coop}}(T)\frac{\Delta\mu}{k_B T}\right]$$

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




*Adam and Gibbs, 1965*

## Correlation length Dynicamical



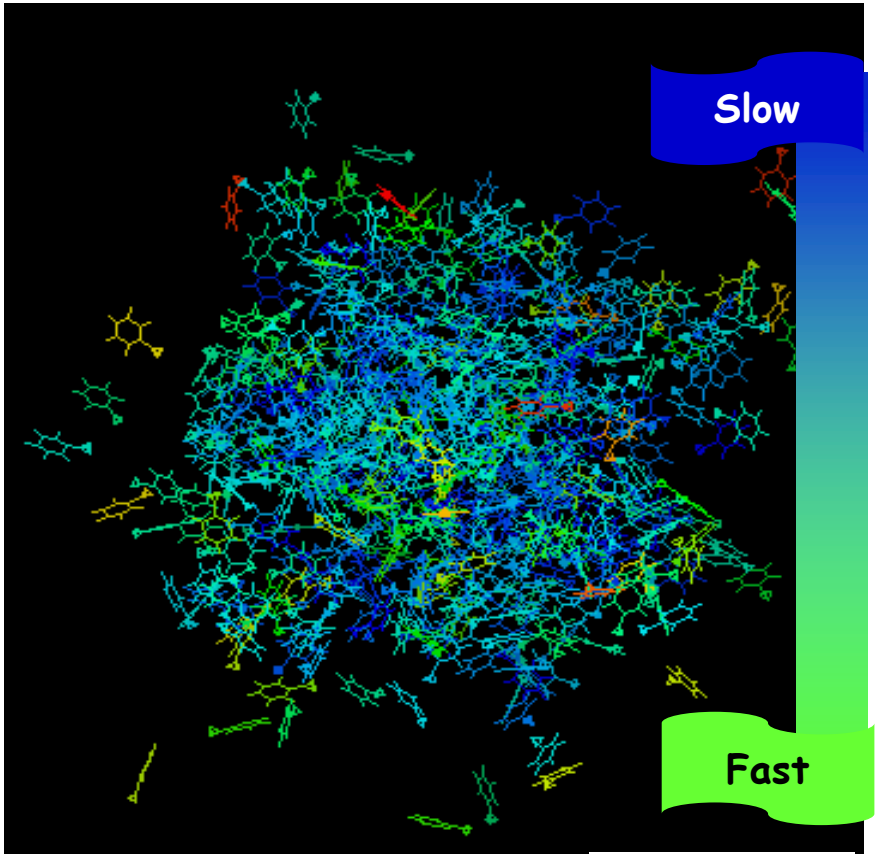
E. Weeks *et al*., Science 287, 627 (2000)
www.physics.emory.edu/~weeks/lab/glass

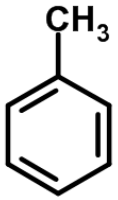
Φ = 56% supercooled fluid
5% fastest of the particles in red

Large clusters of cooperative fast particles :
spatially heterogeneous dynamics

# Relevant length : dynamic or static ?

Toluene




MD simulations V Teboul

"**Dynamic heterogeneities**": at low T, liquid made of regions with widely different mobilities

**Spatial correlations in the dynamics**

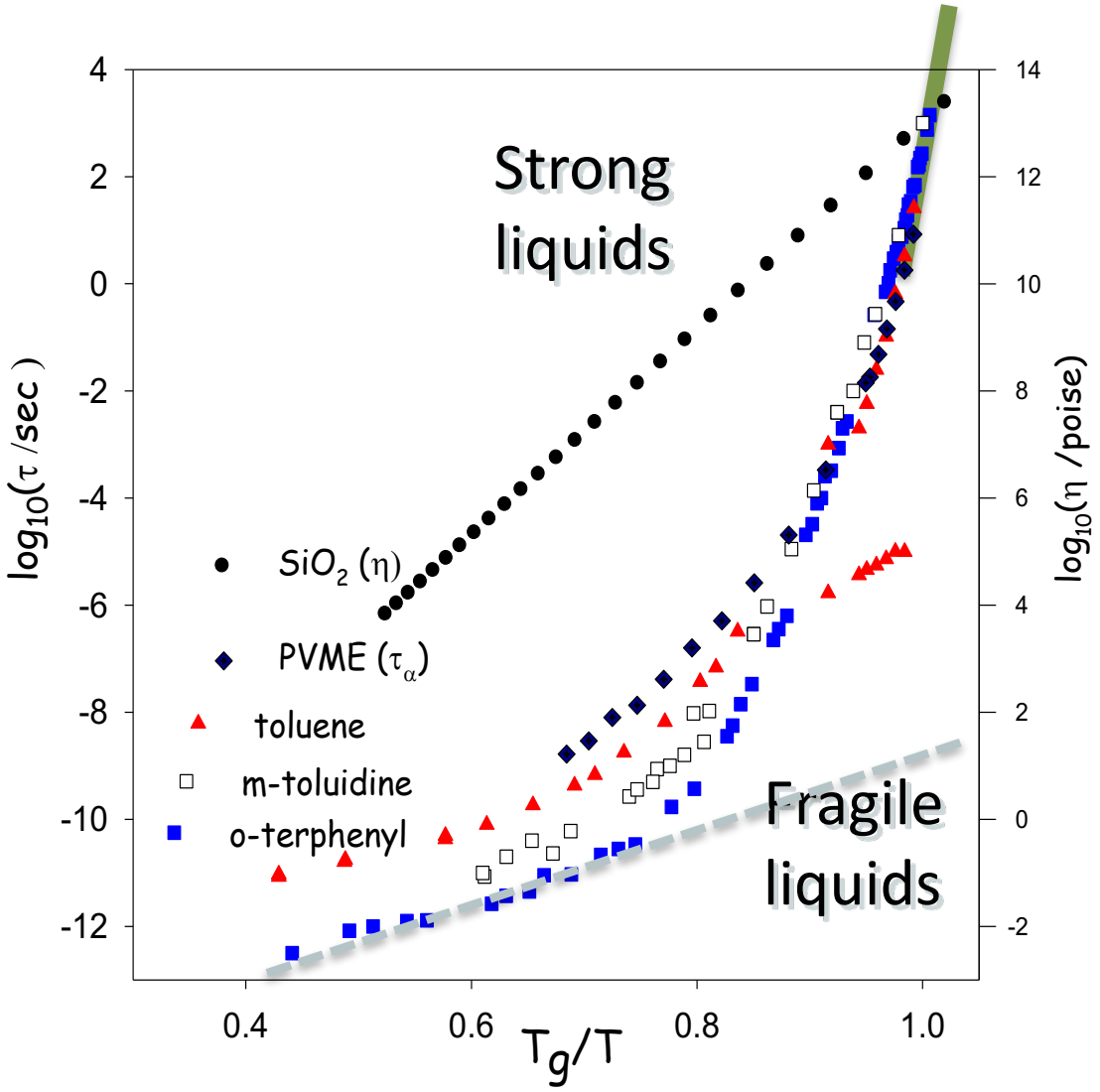
From Standard 2-time correlation function

to

Space-time 4-point correlation function

# Viscous slowing down and glass transition

## 1- Notion of fragility




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

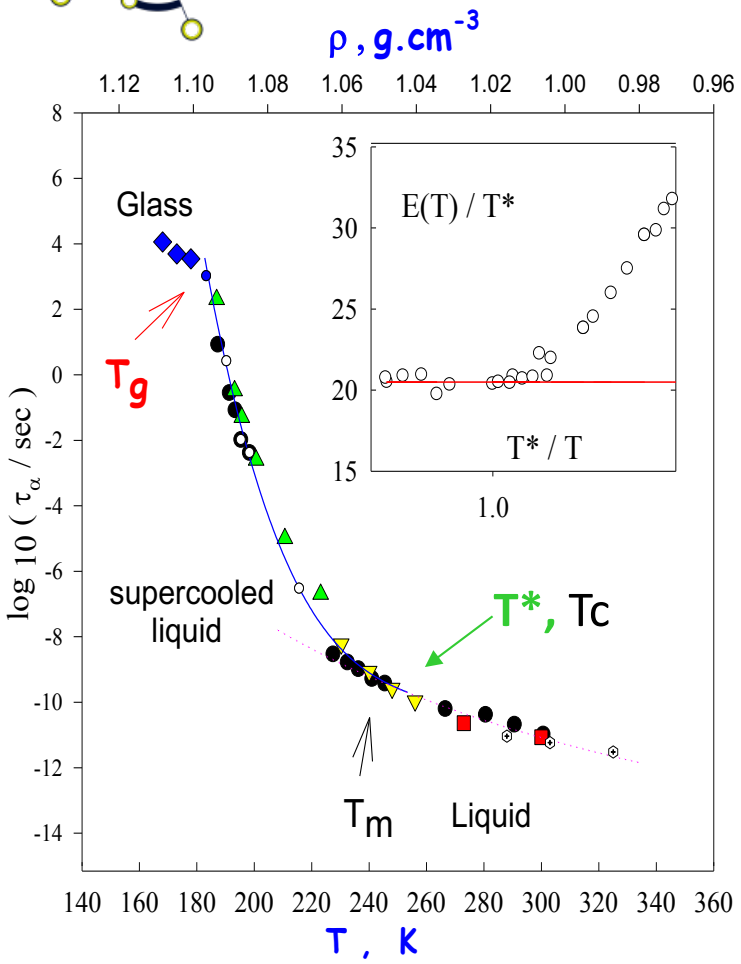
**Fragility** = the fact that the dynamical slowdown has stronger than Arrhenius temperature dependence

**Correlations of m with various properties in the corresponding glass or liquid**

Thermal expansivity 6-10 $*10^{-4}$ $K^{-1}$

Angell's classification (1985) :
comparing systems different T-dependence of $\tau_\alpha$ or $\eta$

# How to scale out the density at atmospheric pressure ?




m-toluidine

due to T  due to ρ

$$\left(\frac{\partial \ln\tau}{\partial T}\right)_P = \left(\frac{\partial \ln\tau}{\partial T}\right)_\rho + \left(\frac{\partial \ln\tau}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P$$

$$= -\left(\frac{\partial \ln\tau}{\partial \ln\rho}\right)_T \left(-\alpha_\tau + \alpha_P\right)$$

isobaric expansivity $\alpha_P = -\rho^{-1}\left(\partial\rho/\partial T\right)_P$

isochronic expansivity (cst τ or η) $\alpha_\tau = -\rho^{-1}\left(\partial\rho/\partial T\right)_\tau$

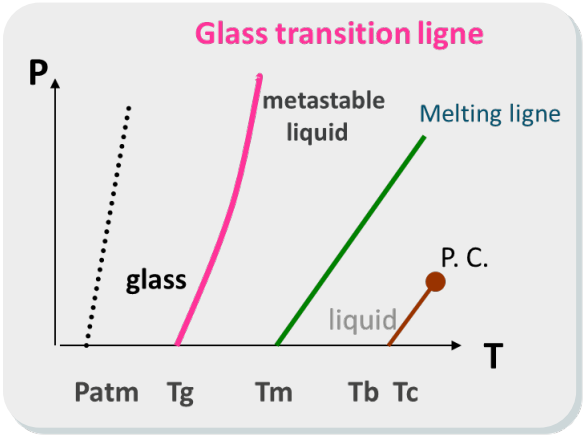
$$\frac{|\alpha_\tau|}{\alpha_P}$$ the relative importance of density and temperature

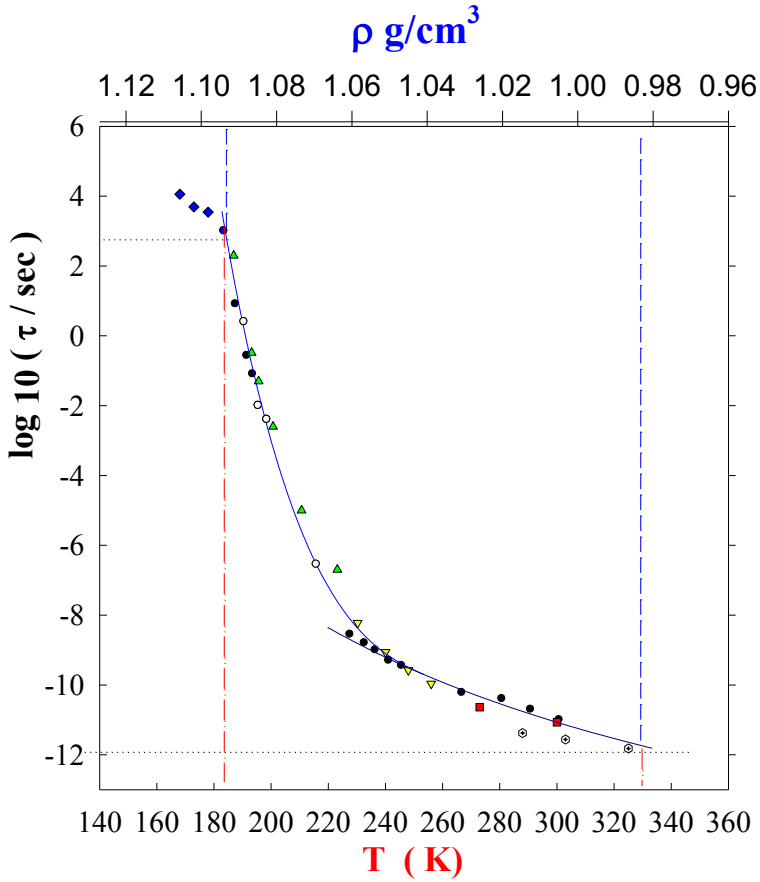
Suggesting high Pressure (or ρ) experiments

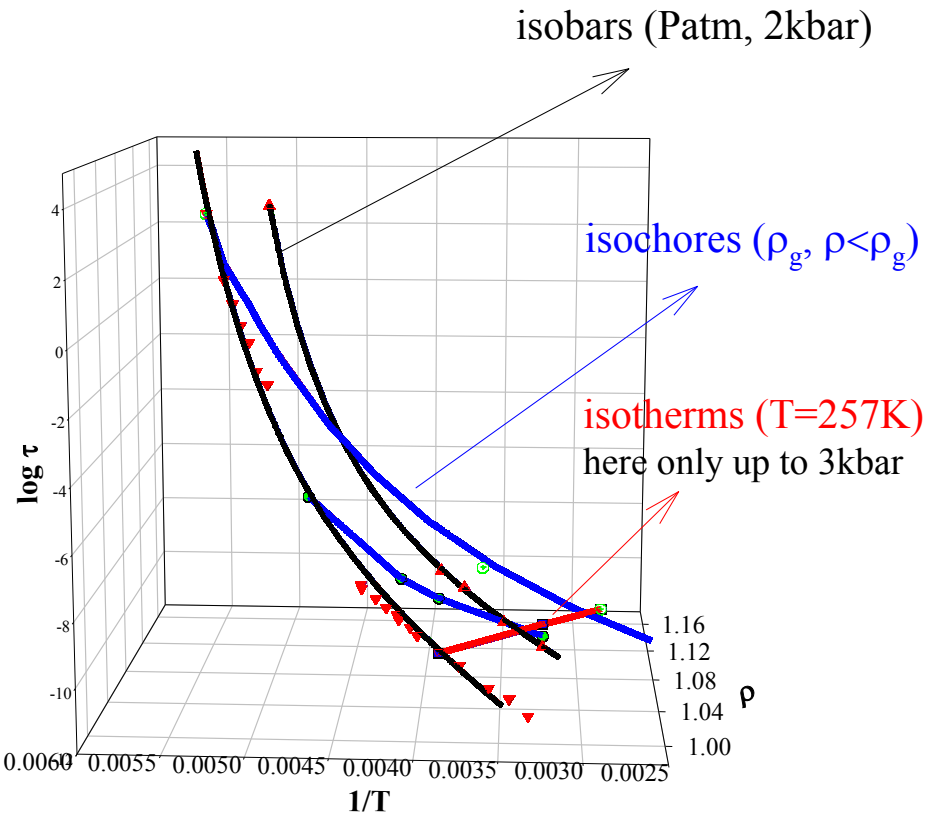
# Molecular liquid m Toluidine

## Patm

## high pressure



## why isochrones ? to disentangle ρ andT effects

**along an isobar**

$$\left(\frac{\partial \ln \tau}{\partial T}\right)_P = \left(\frac{\partial \ln \tau}{\partial T}\right)_\rho + \left(\frac{\partial \ln \tau}{\partial \rho}\right)_T \left(\frac{\partial \rho}{\partial T}\right)_P$$

$$\left(\frac{\partial \ln \tau}{\partial T}\right)_P = \left(\frac{\partial \ln \tau}{\partial \rho}\right)_T \left(-\alpha_\tau + \alpha_P\right)$$

**isobaric thermal expansivity coefficient** $\alpha_P = -\rho^{-1}\left(\partial\rho/\partial T\right)_P$

**isochronic expansivity coefficient** ( at η or τ constant) $\alpha_\tau = -\rho^{-1}\left(\partial\rho/\partial T\right)_\tau$

**ratio** $|\alpha_\tau|/\alpha_P$ = quantitative estimation of the relative contributions of the temperature and the density to the change of the relaxation time along a given isobar

| | isochrone | $\alpha_P$ $10^4 K^{-1}$ | $-\alpha_\tau$ $10^4 K^{-1}$ | $\lvert\alpha_\tau\rvert/\alpha_P$ |
|---|---|---|---|---|
| **polybutadiene** | **$\tau=10^{-9}$sec** | 6.5 | 10.6 | 1.6 |
| **glycerol** | **$\tau=10^{-9}$sec** | 4.2 | 25 | 6.2 |
| **m-toluidine** | **$\tau=10^{-9}$sec** | 7.3 | 11.5 | 1.6 |

$$|\alpha_\tau|/\alpha_P > 1$$

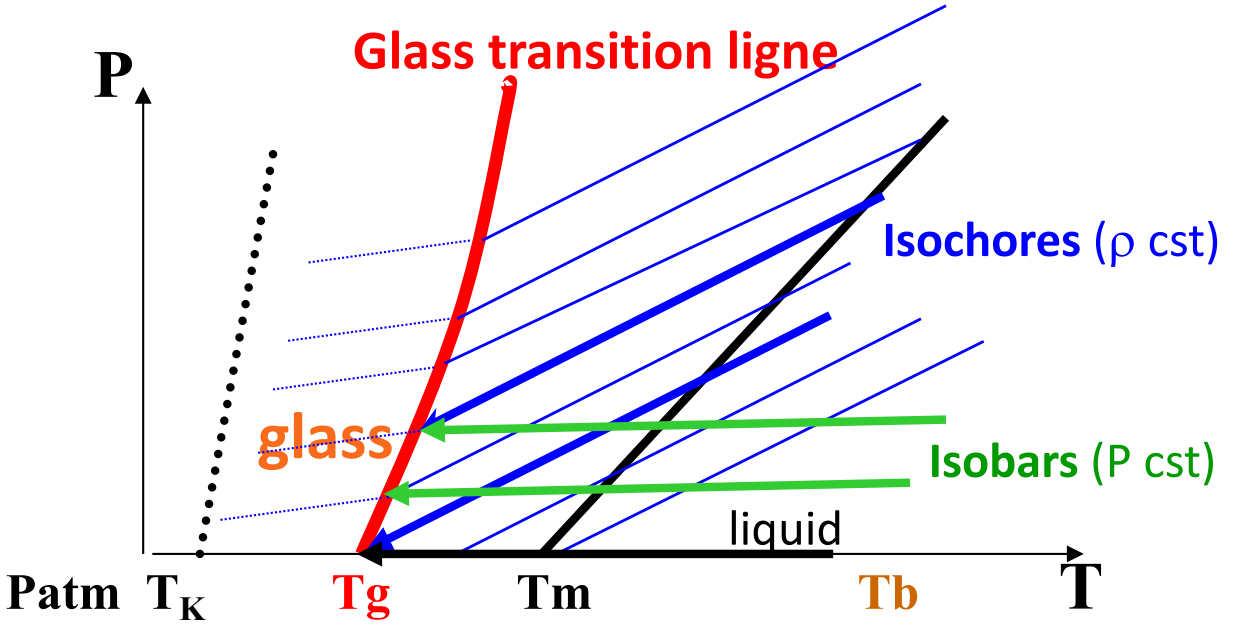
**T is the driving parameter of the viscous slowing down!**

**Test correlation to fragility by changing**

a) -the thermodynamic state or path

b) -the relaxation time

A property is then considered as "**intrinsic**" when it does not depend on a) and b)




$$m_\rho = \left.\frac{\partial \log_{10}(\tau_\alpha)}{\partial T_g(\rho)/T}\right|_{Tg(\rho)}$$

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

Isochoric and isobaric fragilities $m_{\rho,\tau}$ and $m_{P,\tau}$ related trough

$$m_{P,\tau}(P) = m_{\rho,\tau}(1 + \alpha_P/|\alpha_\tau|) \Longrightarrow m_{\rho,\tau} \leq m_{P,\tau}$$

$$\alpha_\tau = -\rho^{-1}(\partial\rho/\partial T)_\tau$$

$$\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_P$$

Ex : o-TP $m_{P,g}$=82, while $m_{\rho,g}$=45

# model-free assessment of the respective contributions of ρ and T in the viscous slowing down at P cst

$$\tau_\alpha(T, \rho) = \tau_\infty \exp\left[ E_a(T, \rho) / k_B T \right]$$

two extremes physical pictures

dynamic congestion due increase of density and drainage of free volume

activated dynamics (Ea > kT)
thermally activated processes
in cst density energy landscape

$$\log\left(\tau_\alpha(\rho, T)\right) = F\left[\frac{E_\infty(\rho)}{T}\right]$$

**ρ and T dependences of the α-relaxation time described by a single scaling variable $X=E_\infty(\rho)/T$**

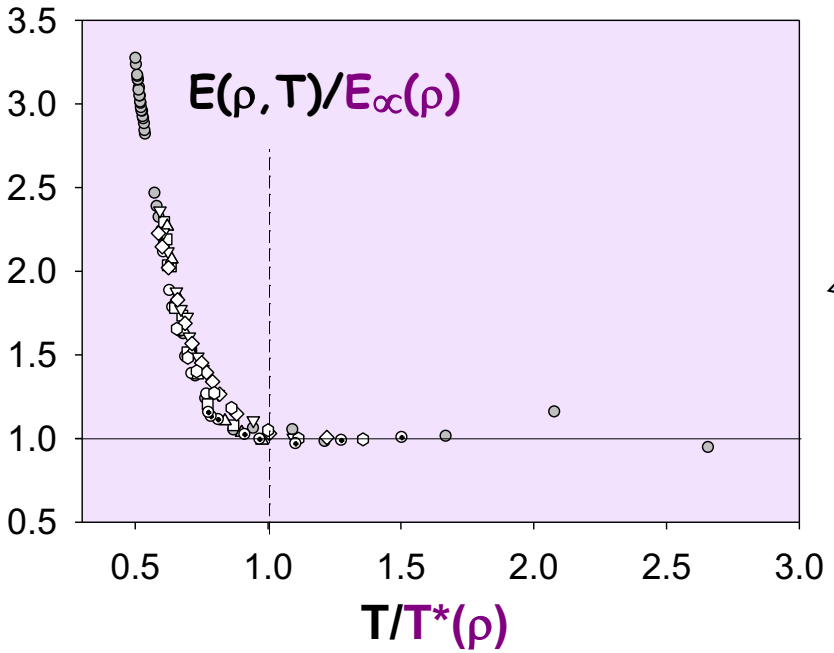
**$E_\infty(\rho)$** = effective activation energy
characteristic of high-T Arrhenius regime

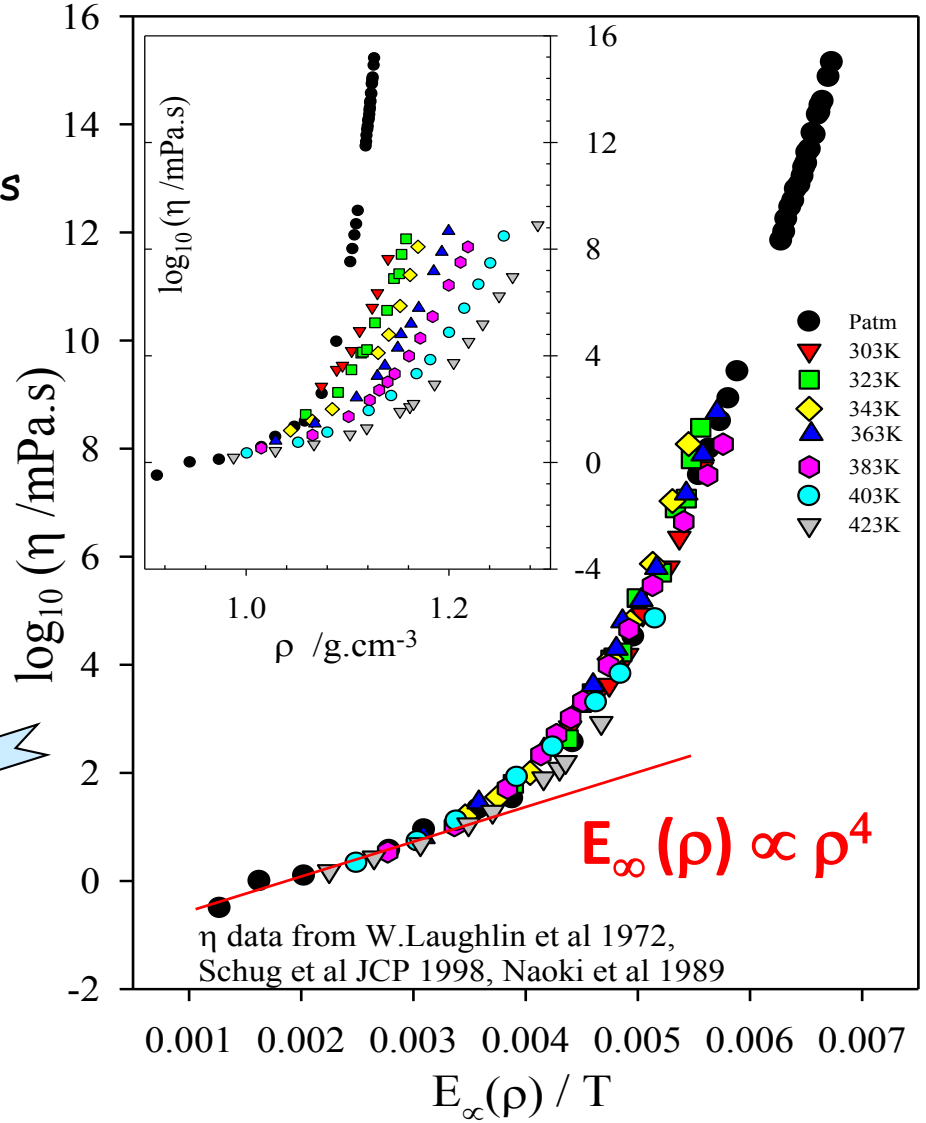
**One single energy scale !**

# How does the scaling work ? How well established ? on the E(ρ,T) or on log(τ)

reminiscent of soft spheres
scaling for dynamic and thermodynamic properties

$$\Gamma \rightarrow \Gamma^{-1}$$
$$\rho T^{-1/4} \rightarrow \rho^4/T$$




A crossover temperature T*(ρ) ∝ E∞(ρ)



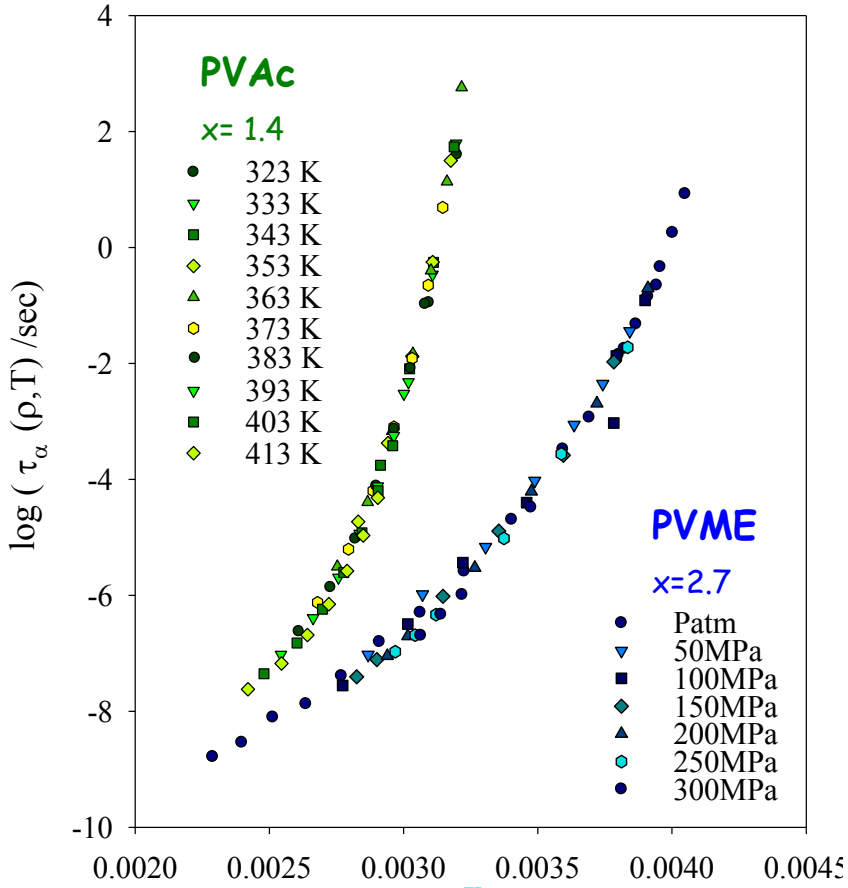
JCP 2004

# How well established ?

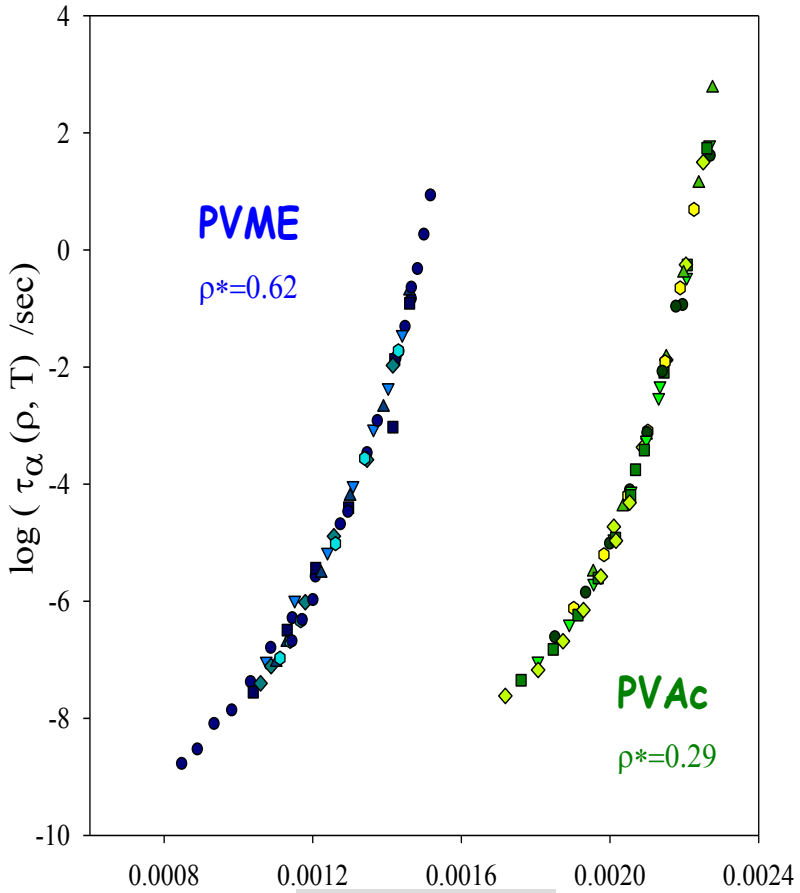
**When no high-T data are available ,**

**extension to polymers with e(ρ) ∝ E∞(ρ)**

$$\log(\tau_\alpha(\rho,T)) = F\left(\frac{e(\rho)}{T}\right) \quad where\ e(\rho)=\rho^{x}\ or\ e(\rho)=\rho-\rho^{*}$$




$\rho^{x}/T$




$\rho-\rho^{*}/T$

# How usefull?

## SCALING plot at the G.T. temperature (100sec),

## a modified Angell plot

**at cst P ( Patm),**
**log($\tau_\alpha$) vs Tg/T**

↓

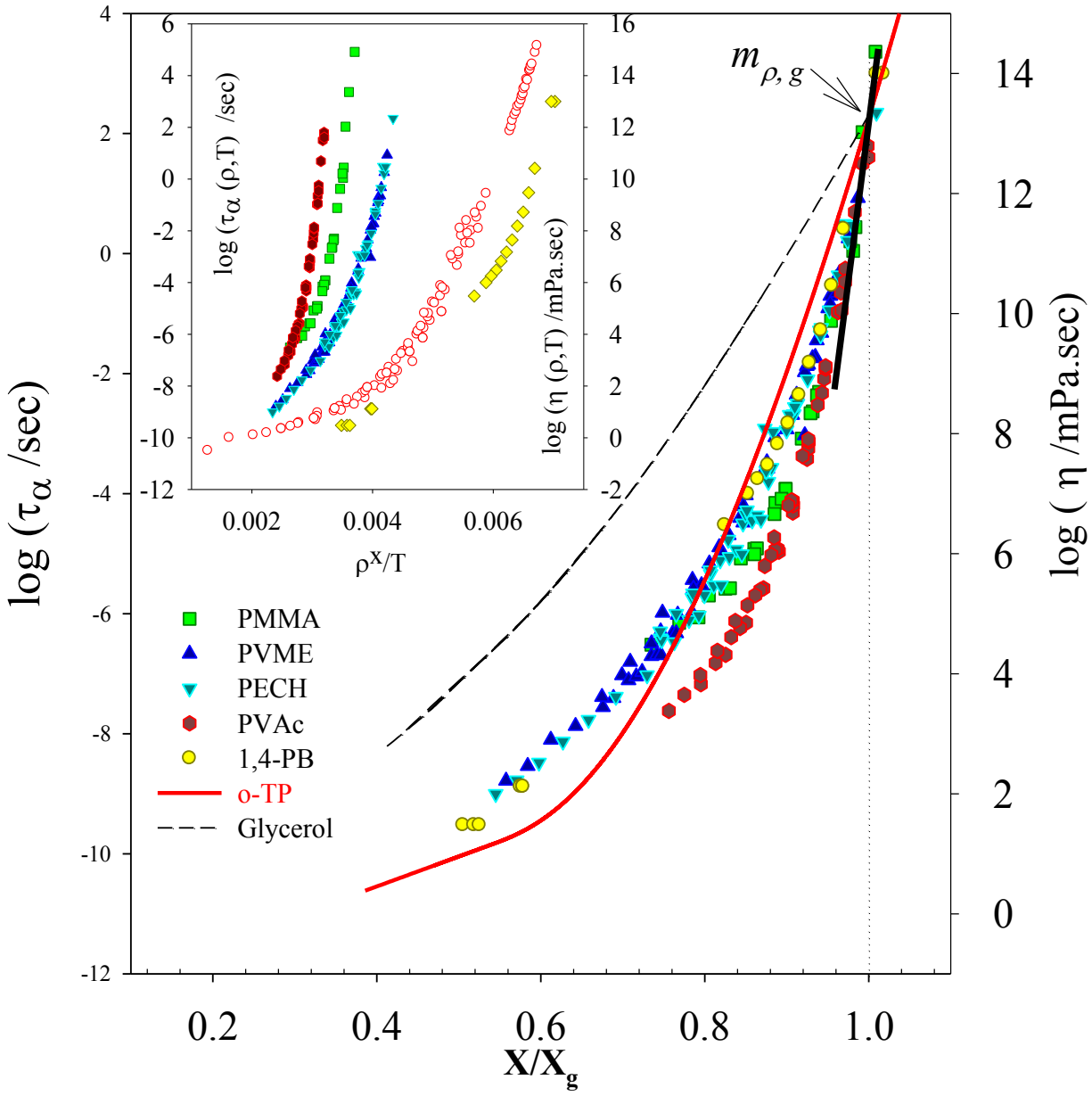
in a wide P-T range
**log($\tau_\alpha$)** vs **X/Xg**

**with X= e(ρ)/T**
**new scaling variable**
**Xg for τ=100sec**

Fragility index ?

$m = [d\log(\tau)/d(T/T_g)]_{T=Tg}$

$$m_\rho = \frac{\partial \ln[\tau\alpha(\rho,T)]}{\partial[Tg(\rho)/T]}\Big|_{Tg(\rho)}$$



**III - local order and mesoscopic order**
**underlying length scales**
**high T activation energy**
**ultra stable glasses**

**Looking for a simple* molecular system** :

- large number of partial contributions to S(Q) simplifying the shape?

- still able to form a (laboratory) glass and keep some disorder. (resisting to the crystallization).

- low high Temperature activation energy and high fragility?

$C_{10}H_{18}$ Decalin

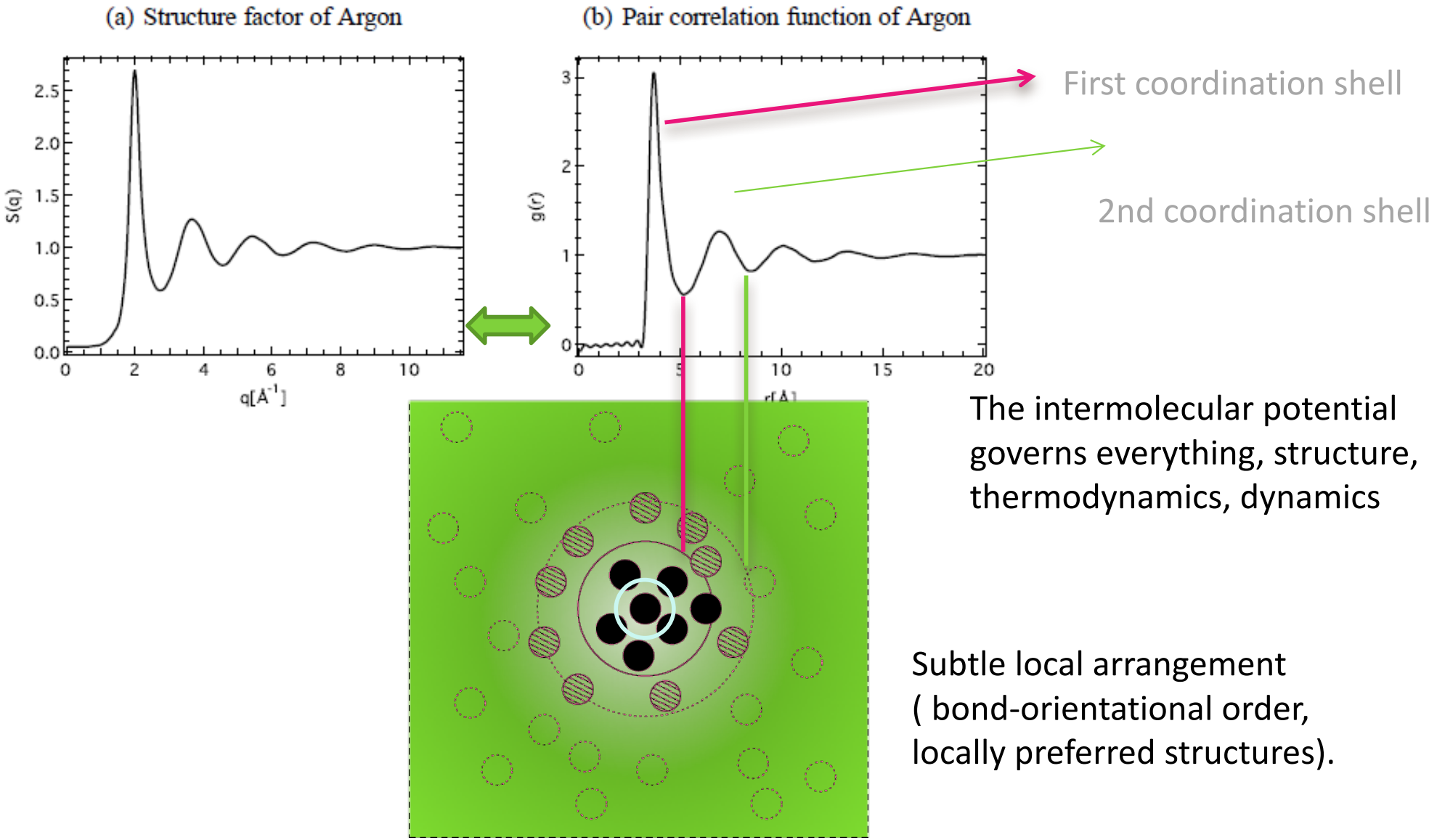

*** Simple = pseudo atomic ?**

## Structure of simple atomic liquids

(here assimilated to a sphere, no additional degrees of freedom)

neutron measurement in the Q space (F.T.)⇨the radial pair correlation function in real space g(r)

$$S_M(Q) = f_1(Q) + \frac{4\pi}{Q}\rho_M \int (g_L(r) - 1) r \sin(Qr) dr$$



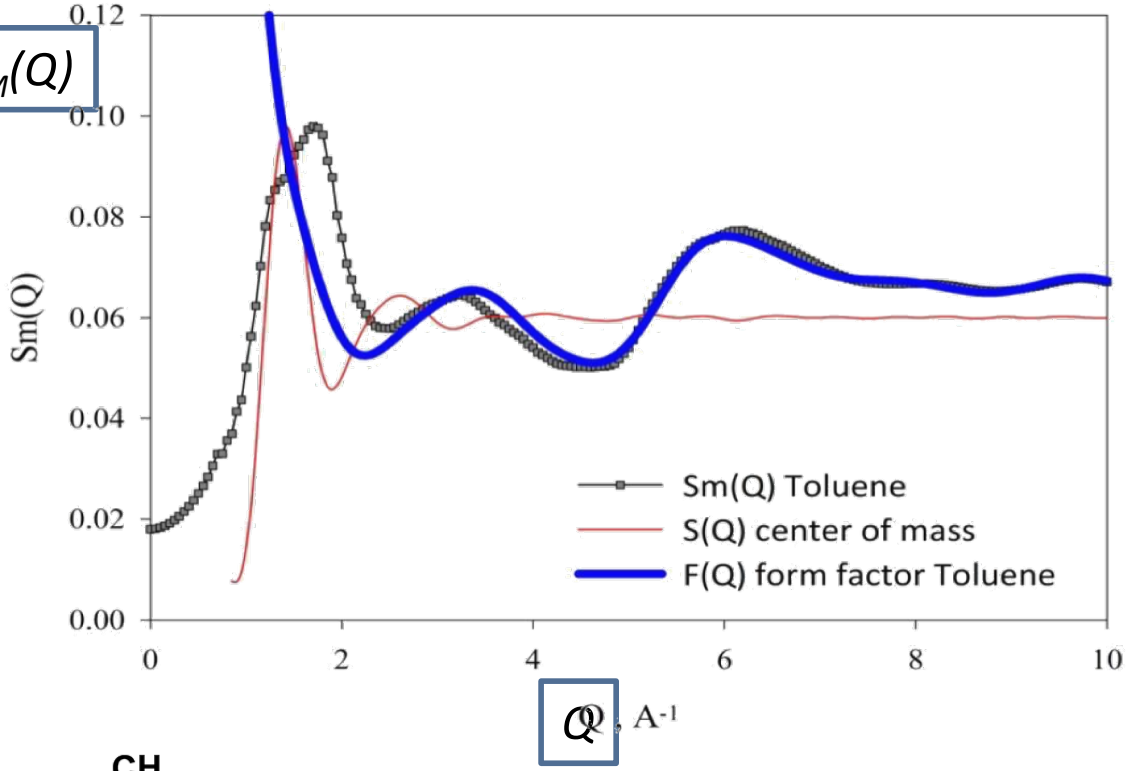

The intermolecular potential governs everything, structure, thermodynamics, dynamics

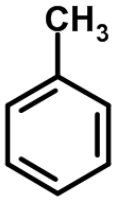
Subtle local arrangement
( bond-orientational order, locally preferred structures).

# Decomposition fo the structure factor (case of toluene C7D8)

Dm(Q) **f1(Q)**

$S_M(Q)$




$S(Q) = Dm(Q) + f1(Q)$

$$S_M(Q) = f_i(Q) + \frac{4\pi}{Q}\rho_M \int (g_L(r) - 1) r \sin(Qr) dr$$

$$S(q) = \frac{1}{\bar{b}^2}\left[\frac{1}{N}\left\langle\left|\sum_i b_i e^{i\mathbf{q}\cdot\mathbf{r_i}}\right|^2\right\rangle_t - \left(\bar{b}^2 - \bar{b}^2\right)\right]$$

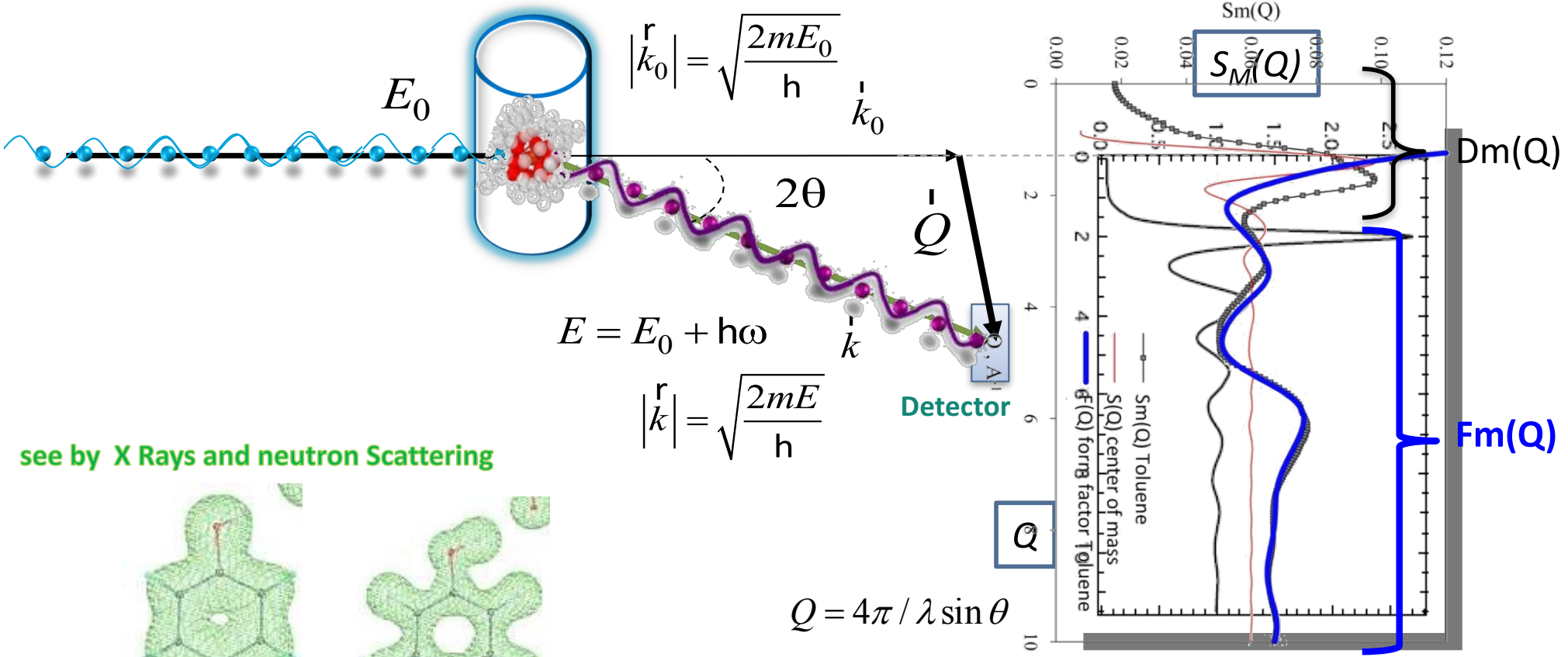
$$\bar{b}^2 = \left|\sum_\alpha c_\alpha b_\alpha\right|^2$$

$$\bar{b}^2 = \sum_\alpha c_\alpha b_\alpha^2$$

N =number of atoms in a molecule
*bi*: scattering length of atom I,
*ri* position vector,
$\alpha$, $c_\alpha$ atom type and its concentration

# Schematic of a diffraction experiment

$$S_M(Q) = f_1(Q) + \frac{4\pi}{Q}\rho_M \int (g_L(r) - 1) r \sin(Qr) dr$$




see by X Rays and neutron Scattering



X-ray (H)

Neutron(D)

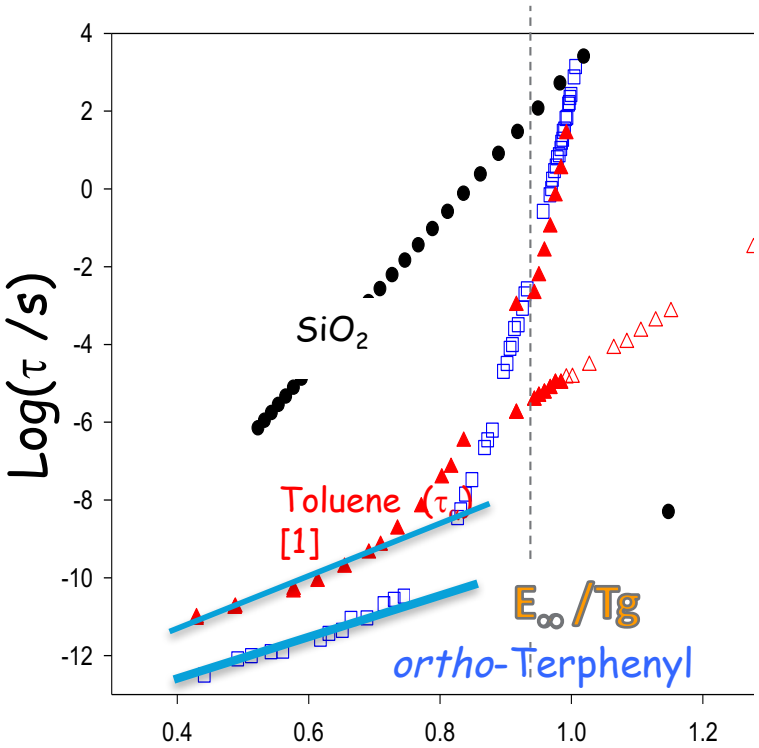
S(Q)= Dm(Q) + fm(Q)

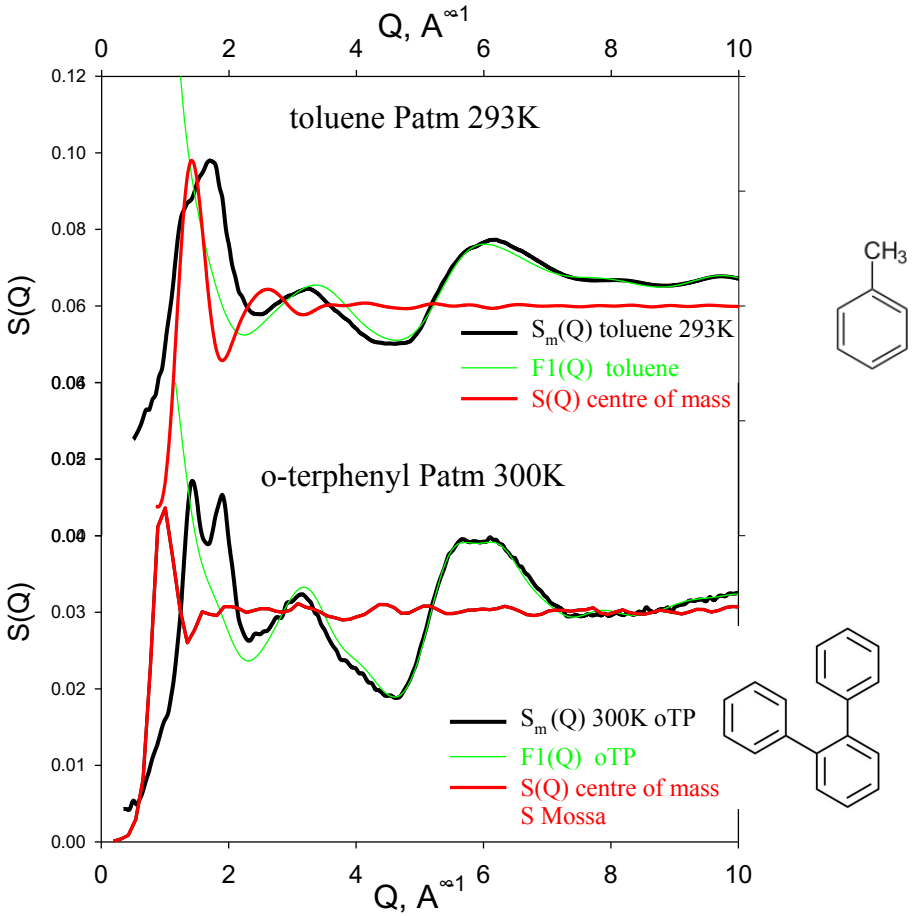
# Aromatic systems : same intermolecular interaction

## Importance of the High Temperature Activation Energy

Similar fragility index mp close to Tg (mp~80-100)

Tol :Rössler et al



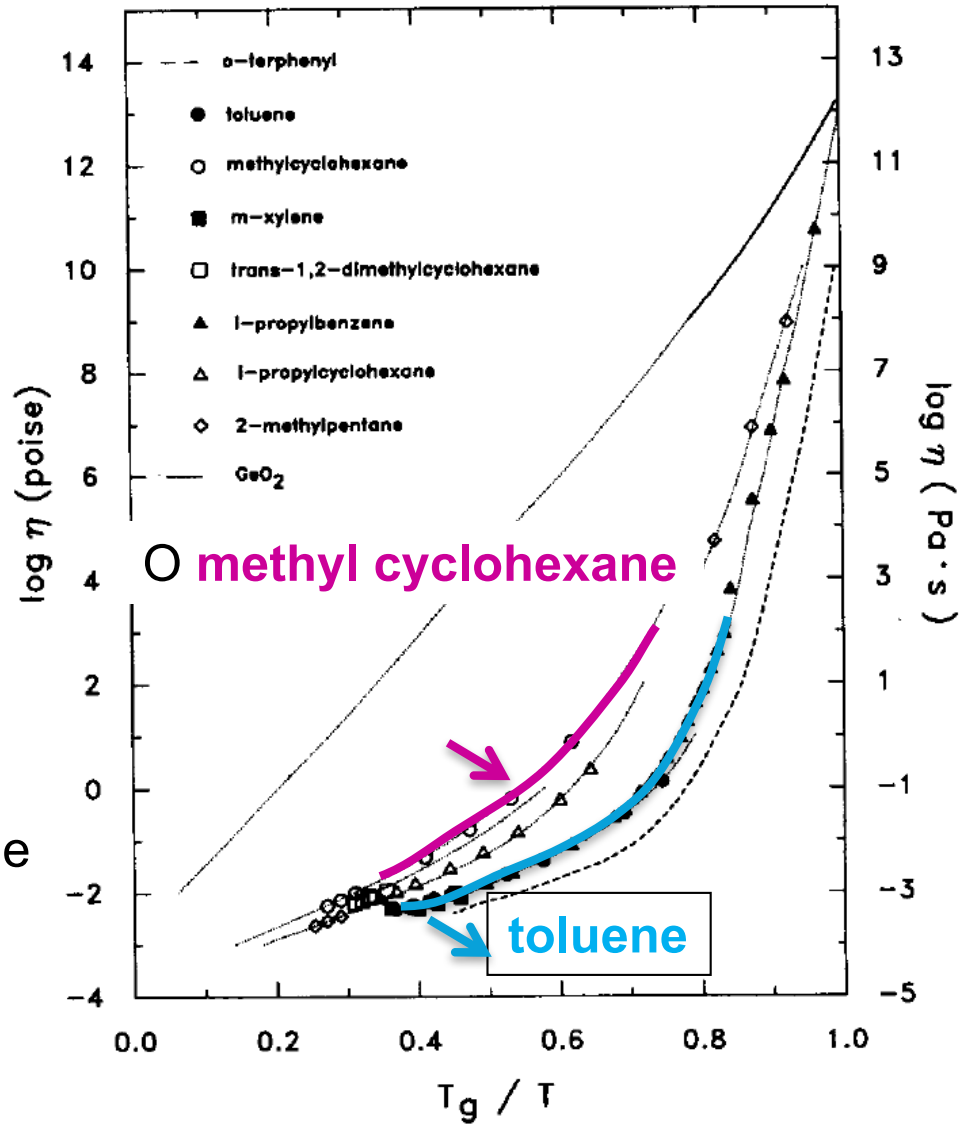




→ Toluene $E_\infty$= 1436~6.8 $k_B T_m T_g/T$

→ O-TP $E_\infty$= 2431~7.4 $k_B T_m$

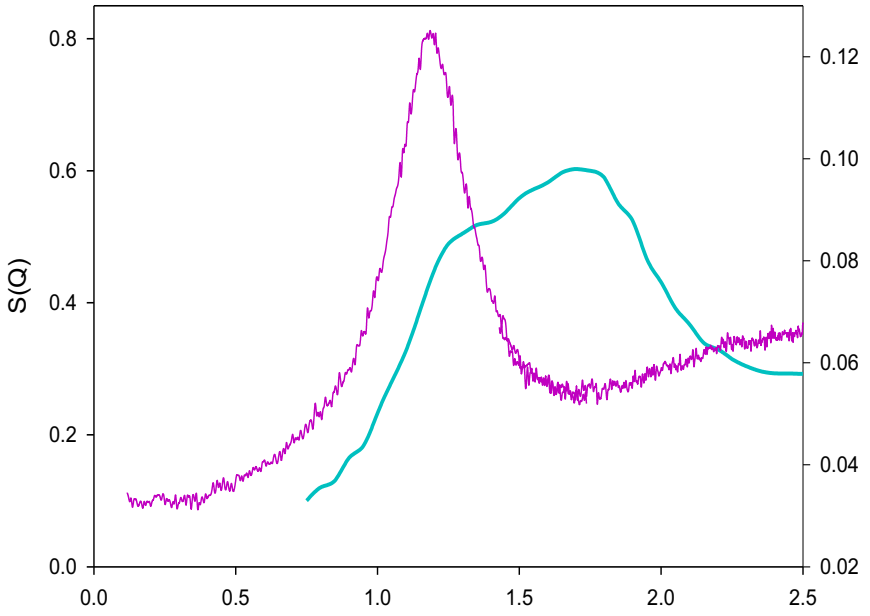
**$E_\infty$ changes from one molecule to another : combined effect of the strength of the intermolecular interactions, the shape of the molecule, and the short range correlations.**

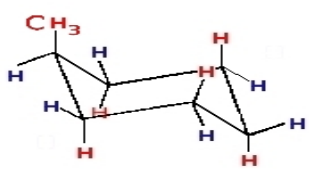
# Effect of the shape : unsaturated and saturated analogues

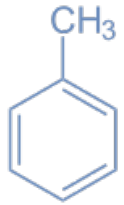



xane

Toluene (Tm= 178K) and methylcyclohexane (Tm= 146.8K)
Patm, ~295K



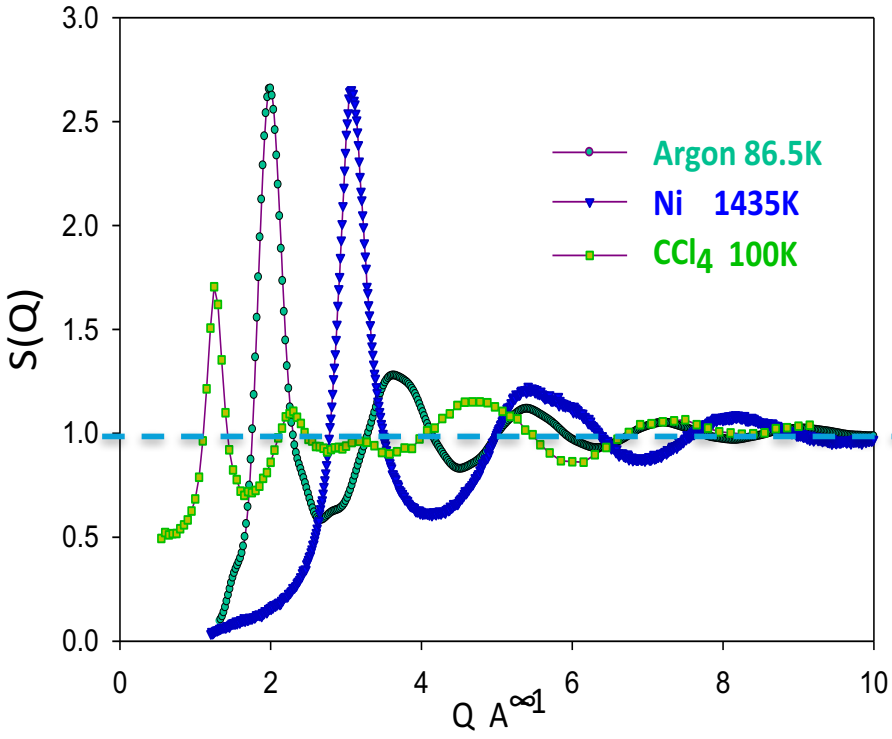



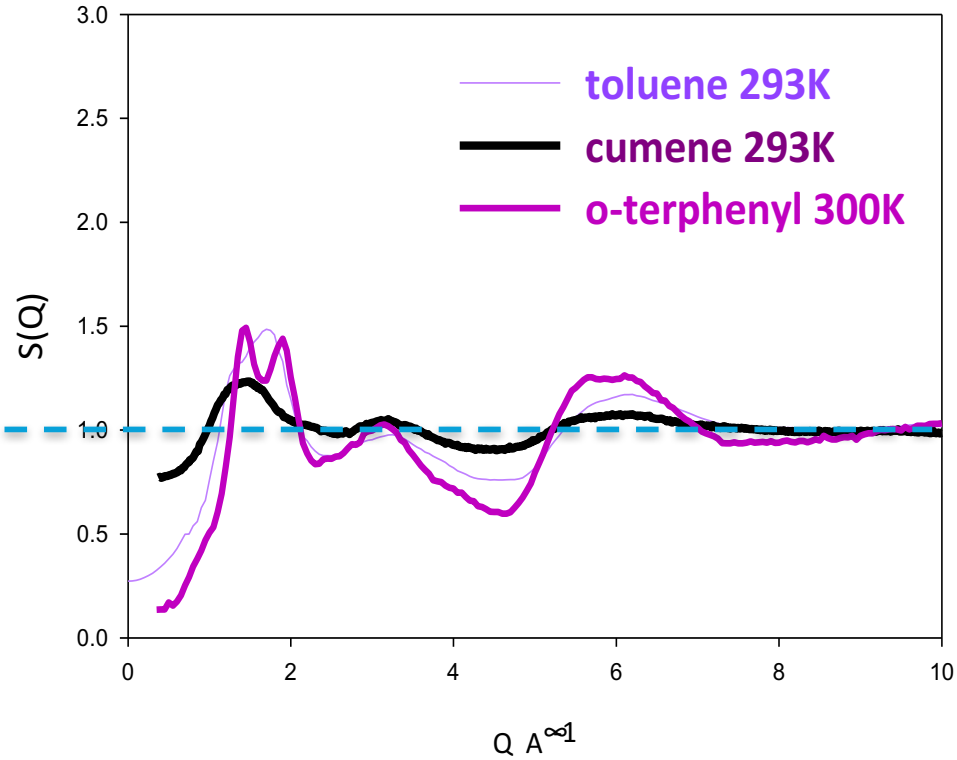

Molecular shape matters, not just size

**Consequence of the molecular shape, ability to form a glass**
**Introducing the comparison to metallic glasses**

**Atomic or spherical molecular liquids do not experience glass formation**

**Molecular Fragile Glassformers**
**Liquid, glass**



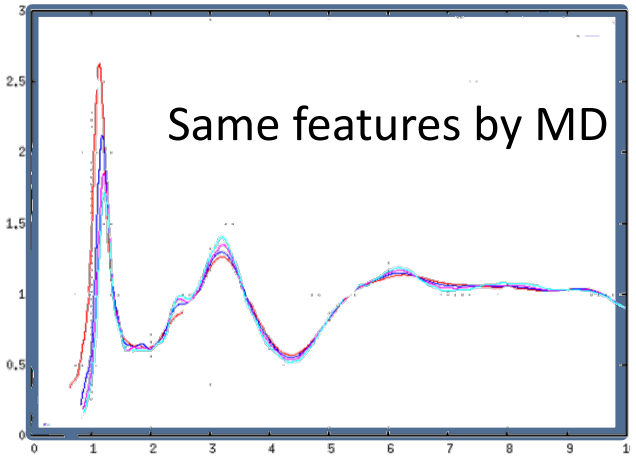




Ar : Yarnell 1973
Ni Holland-Moritz 2008
$CCL_4$ Pusztai 2009

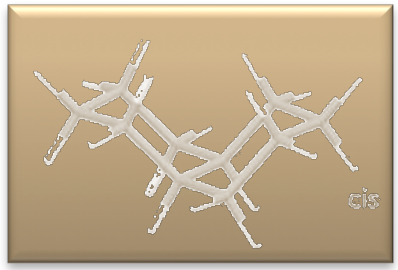
**Very Simple Liquids**
**(spherical shape)**
**Only Crystal formation**
***+ water, benzene***

## Analysis of the non-trivial behavior of the structure

**Huge decrease in intensity is related to the compaction of the system, better than simple spheres; whereas the S center-of-mass slightly increases as expected.**

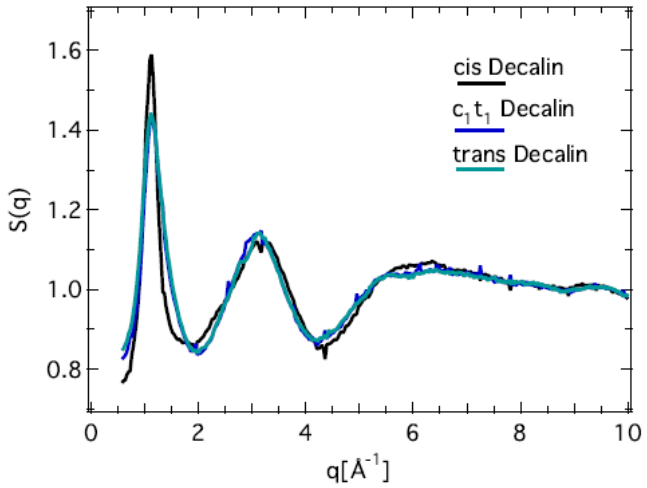


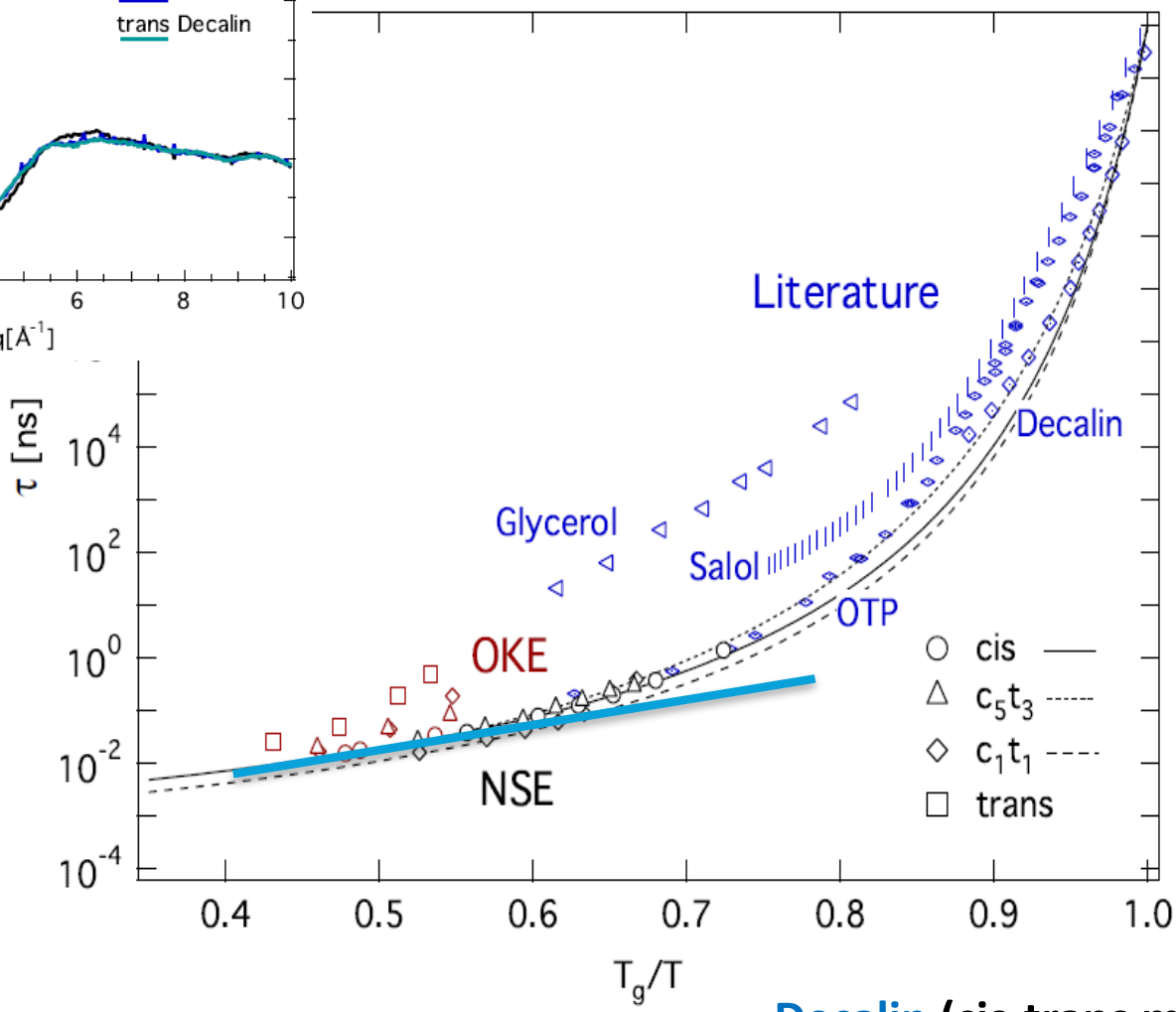

$\kappa_T$




Changes at ~2.4-2.5 $Å^{-1}$ and decrease in intensity of main peak are due to strong changes observed in S(Q) C-H partial, while growing of peak at ~3.2 $Å^{-1}$ is mainly due to the H-H partial. C-C partial does not seem to change much as the center of mass.

# Moreover this liquid might be the most simple et fragile one $m_p$ ~149

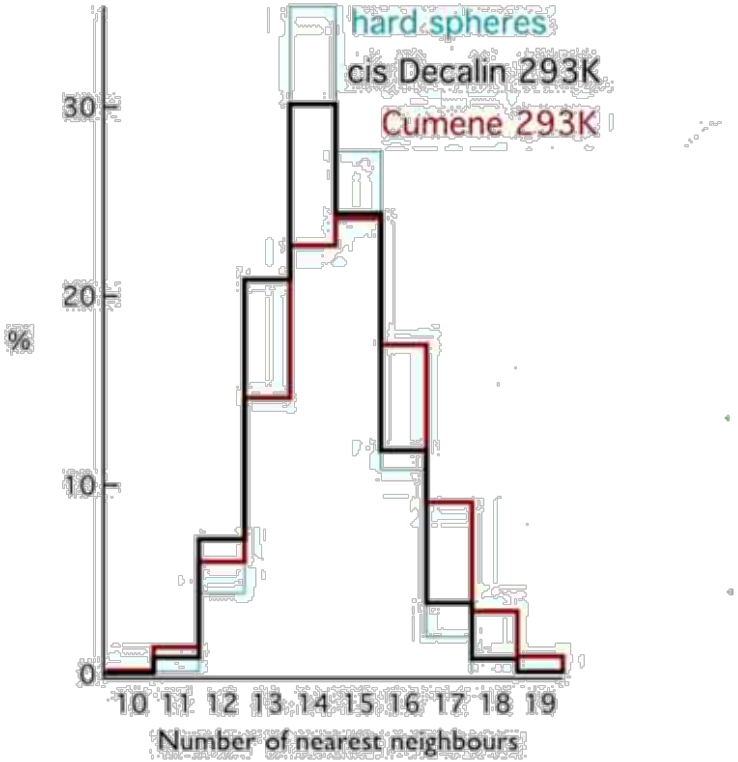


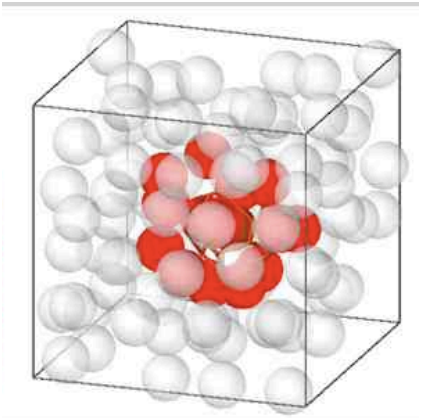




**Decalin (cis-trans mixture), mp = 147**
**From Duvvuri- Richert, JCP 2002**

Comparison with **Hard spheres** and **a good molecular glassformer**.

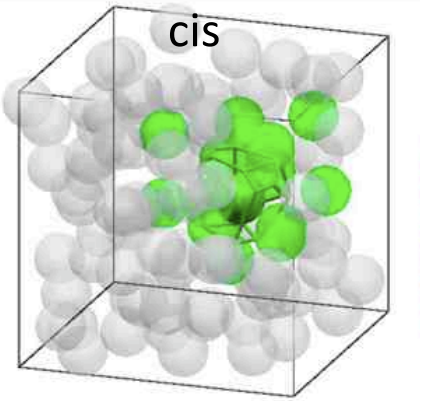
The size and the shape of the local arrangement is different



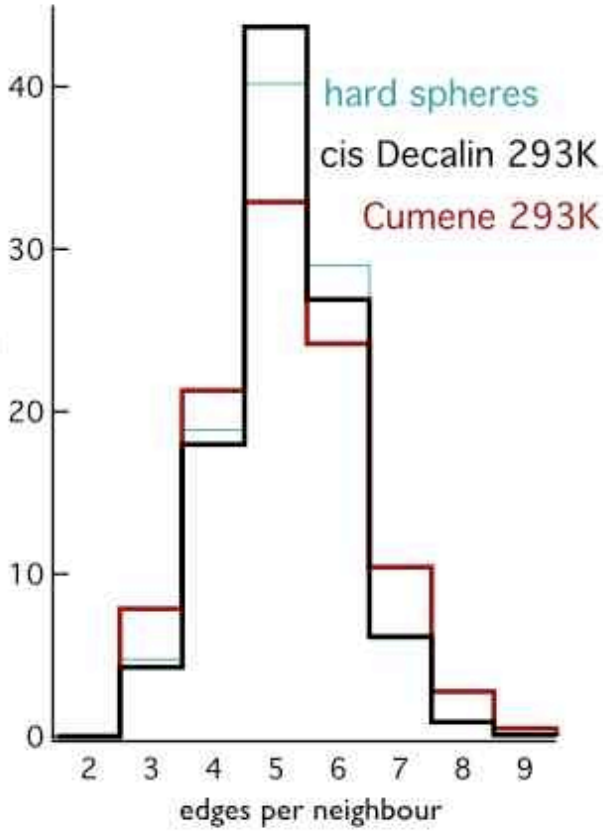



Decalin

cis



Cumene

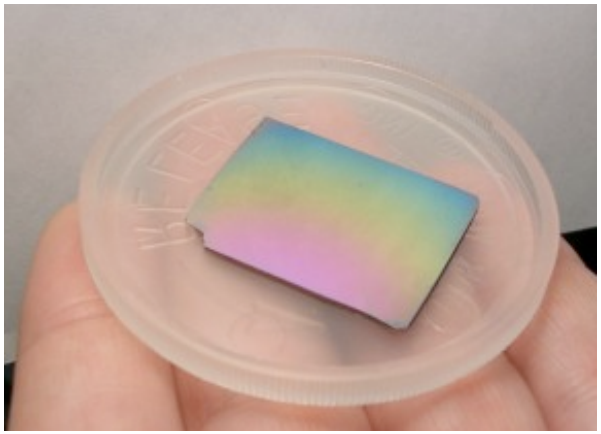



Neighbour geometry:

The neighbour geometry for Decalin is relatively close to the geometry of the model of randomly close packed hard spheres.

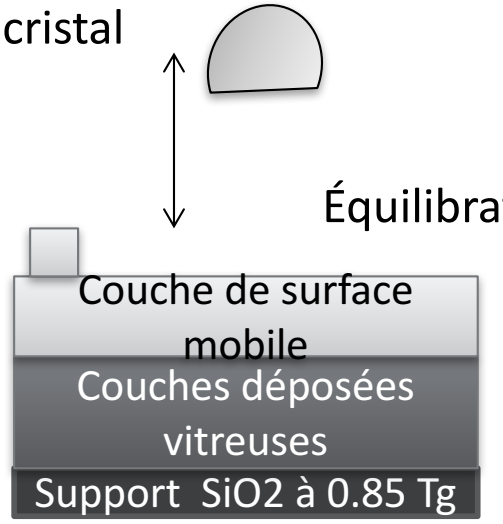
The ability to form a glass comes from the strong correlations between first neighbors and Interpenetrating aggregates in the high viscous regime (T<T*).

# Formation d'un verre stable



T du substrat = proche de 0.85 Tg
avec une vitesse de dépot de 0.2 nm/s
jusqu'à une épaisseur de 10-15nm jqà 600nm

Creuset contenant quelques mg de cristal

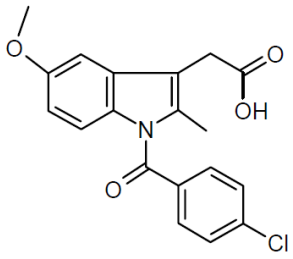


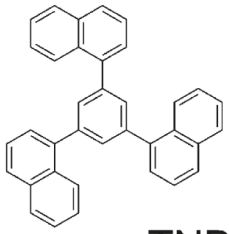

Enceinte à 10-8 torr

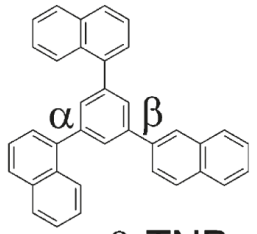
**Empilement très efficace**
**Haute densité**

**Très différent des techniques de trempe par déposition de vapeur avec un substrat à T<<Tg**

indomethacin (IMC, Tg~315 K)
trisnaphthylbenzene (TNB, Tg~348 K)



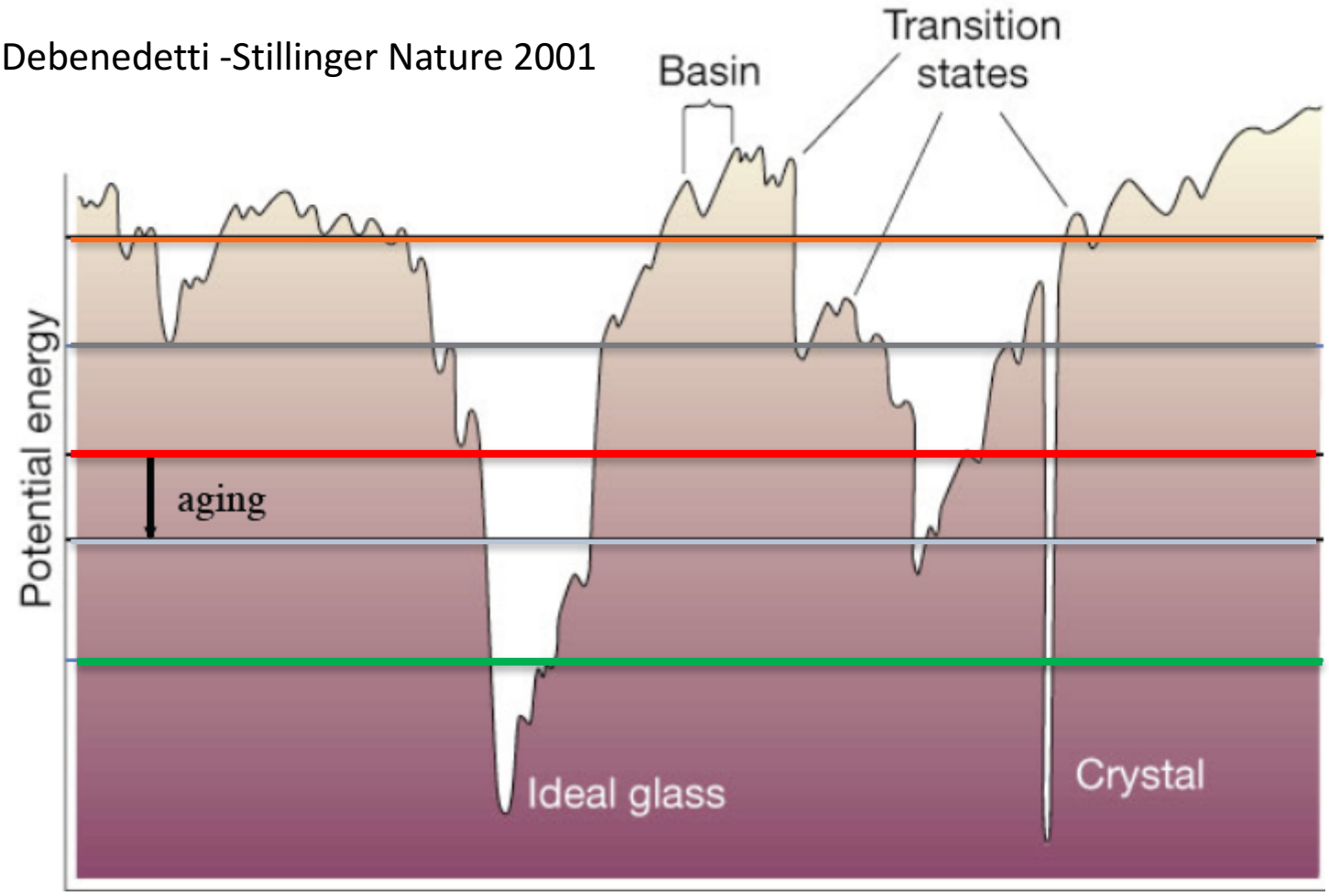


α,α,α-TNB



α,α,β-TNB

# Schematic representation Potential energy landscape

Debenedetti -Stillinger Nature 2001




Tc (MCT)

Trempe rapide

**Tg (100s)**

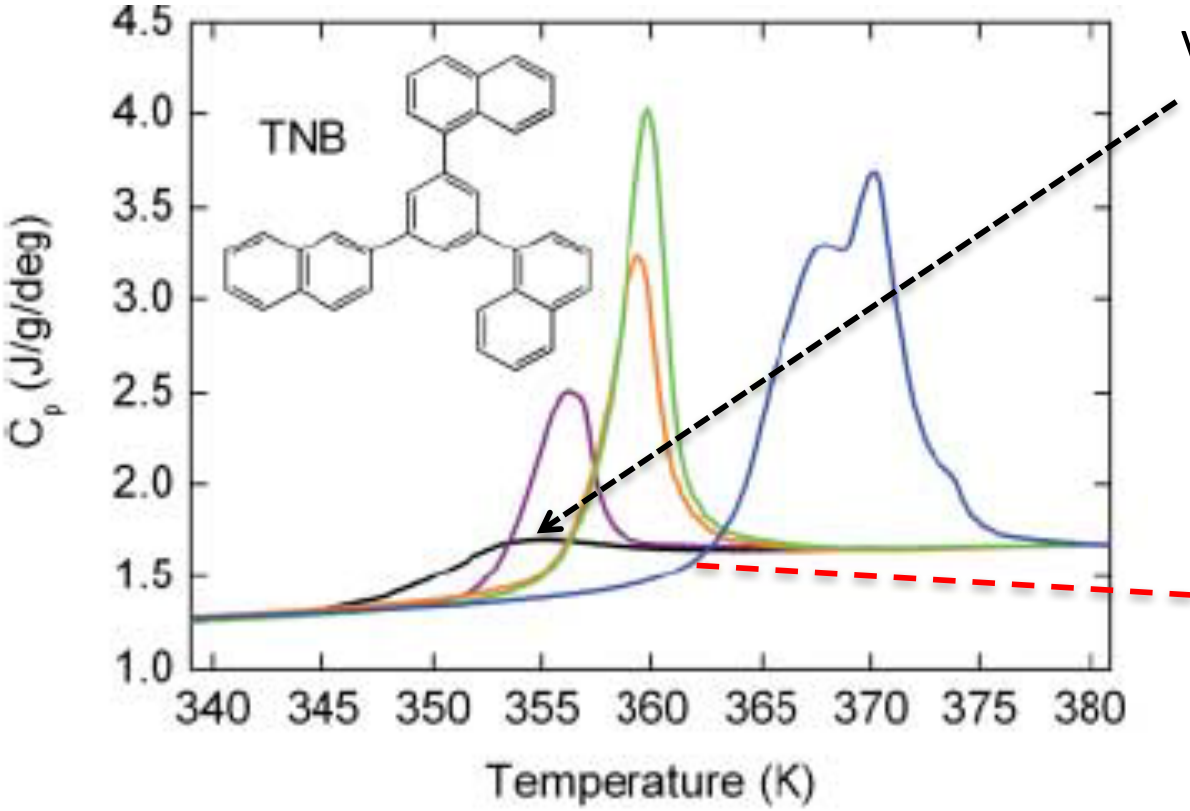
**Vieillissement Sous Tg**

**Déposition à 0.85 Tg**

**Offre la possibilité de découvrir les parties les plus basses de ce paysage et approcher un possible verre idéal**

Sans compter les applications technologiques

# Signature calorimétrique Cp par DSC TNB




Verre ordinaire cooling à 40K/mn

**Verre vieilli à 296K pdt 174 jours**

**328K 9**

**328K 15**

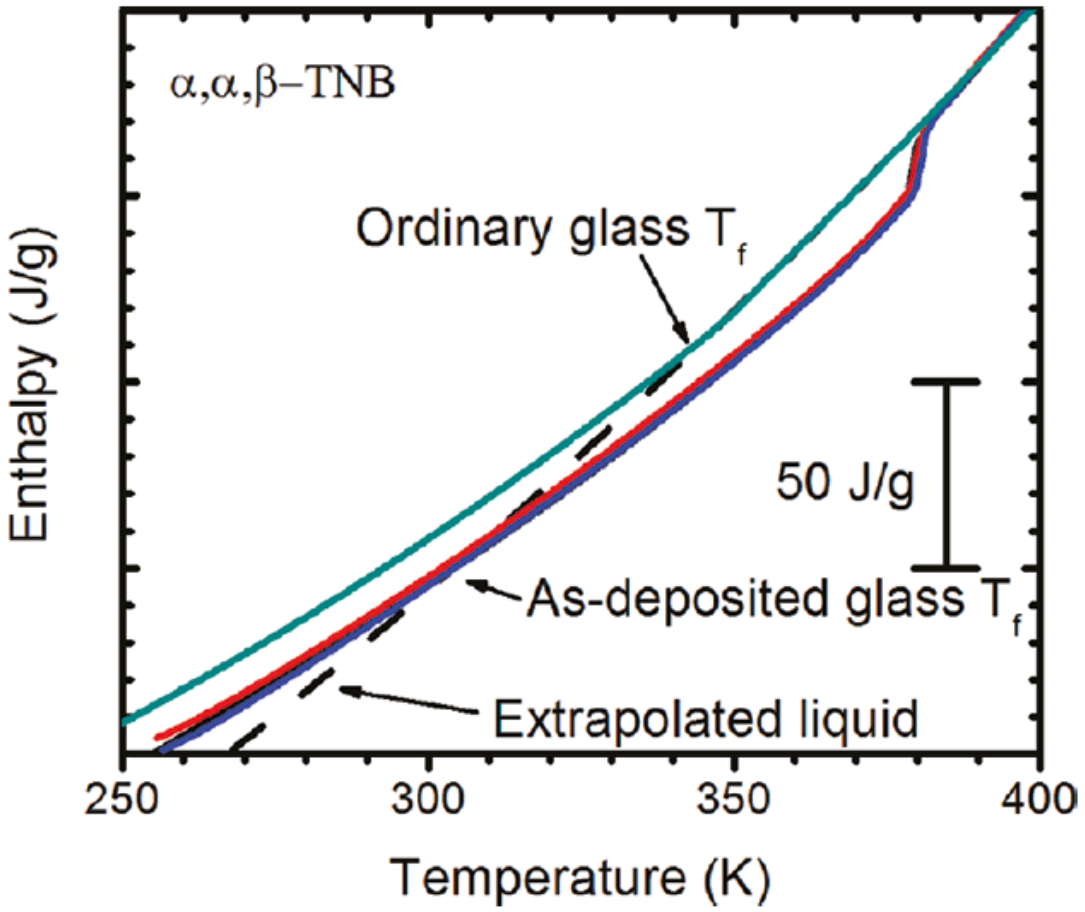
**TNB Physical Vapor Deposition**
**à 296K à 5nm/s**
**Onset à 363K**

363K est la T nécessaire pour activer la mobilité des molécules , indiquant que

le verre PVD est beaucoup plus stable cinétiquement

.

# Conséquence : calcul de la température fictive à partir de l' enthalpie



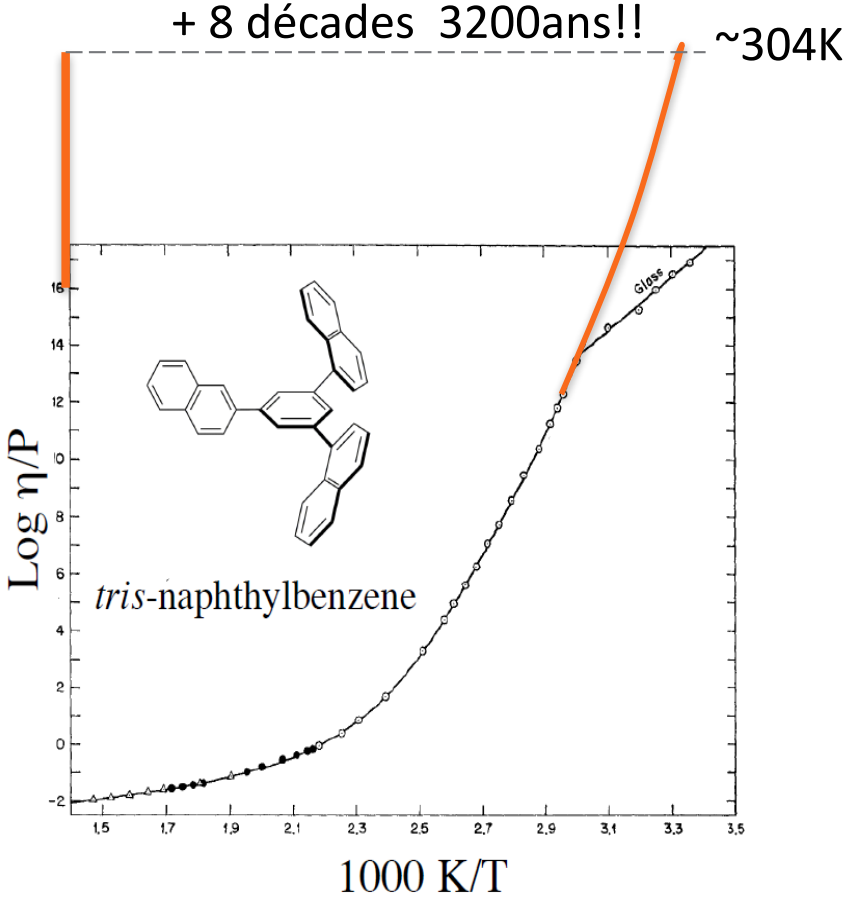

Tf au point de croisement du liquide extrapolé et du PVD verre

**Tf=304K**

**En terme de viscosité η ou τ**

par extrapolation

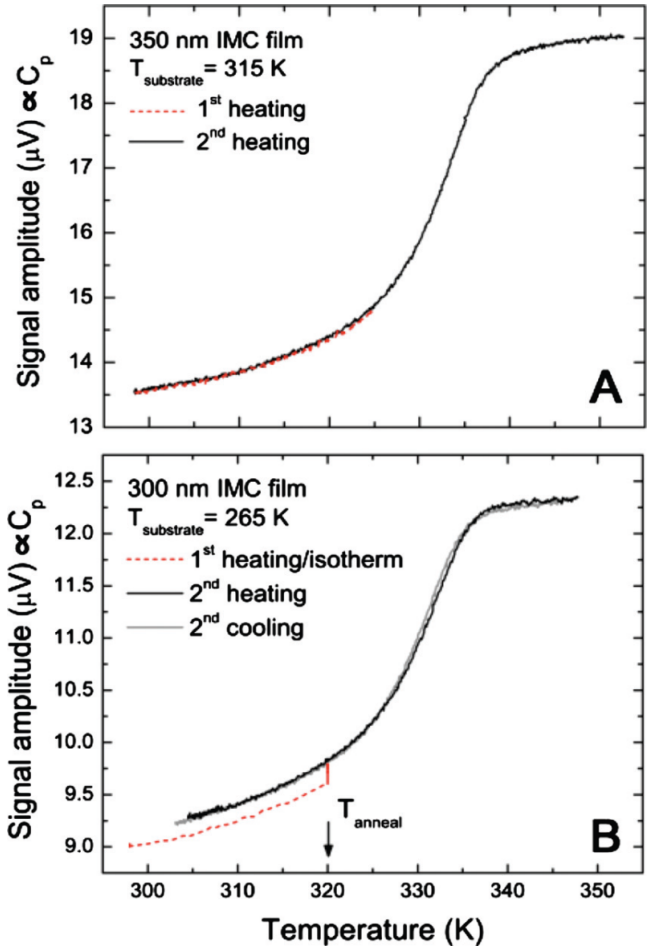
+ 8 décades 3200ans!!



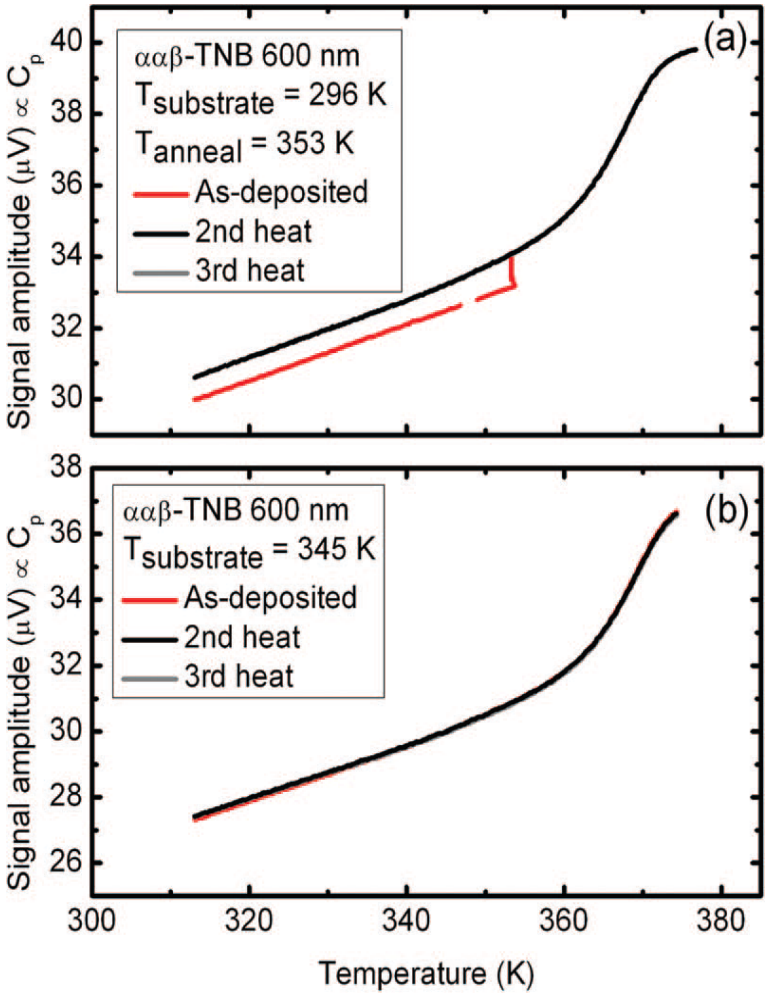

Dawson K, et al J. Phys. Chem. Lett. 2011, 2, 2683–2687

Autres propriétés du VERRE

# Une différence de 4-5% sur la valeur de Cp à 300K dans le verre observé par AC nanocalorimétrie




Kenneth L. Kearns et al, J Chem Phys 2010



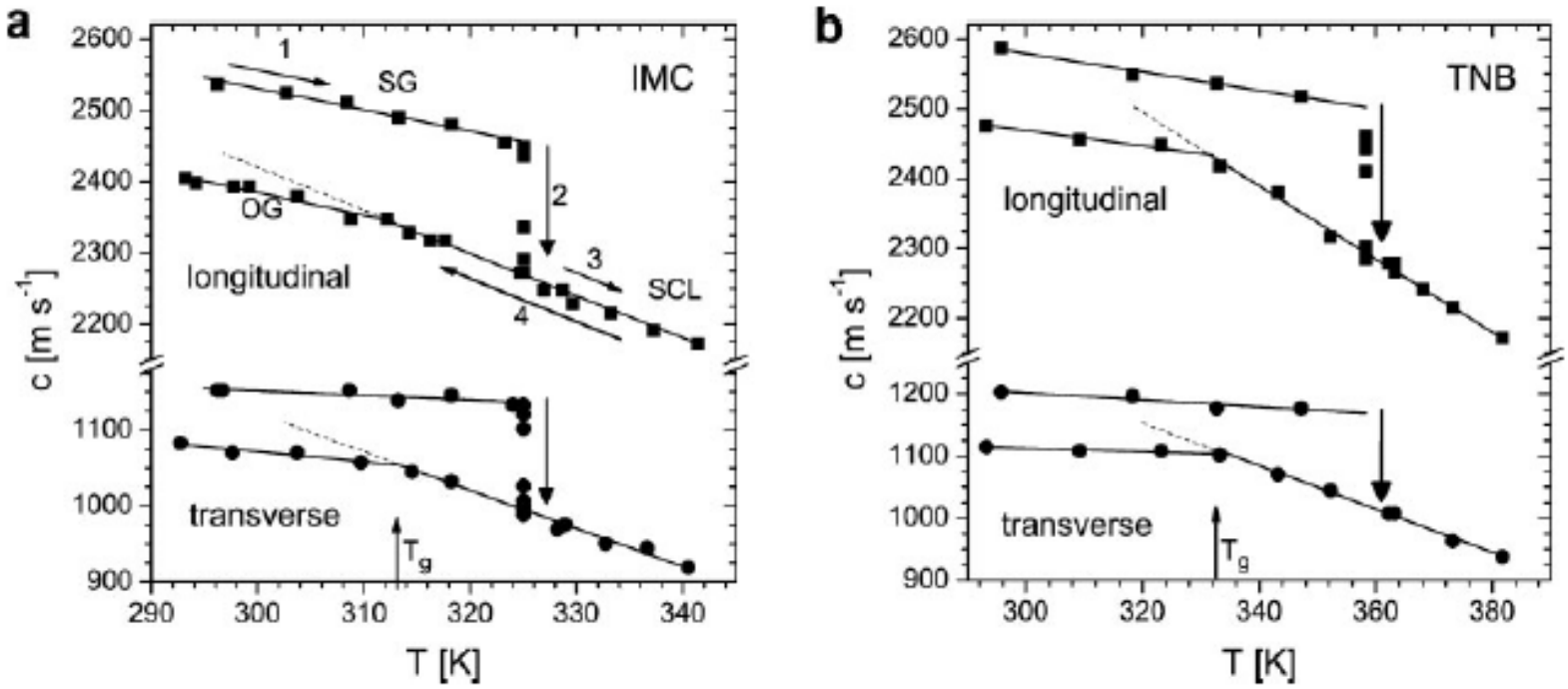

K. Whitaker et al, J Chem Phys 2012

Avec une densification de l'ordre de 1.3% est mesurée par ellipsométrie

Autres propriétés du VERRE

# High-Modulus Organic Glasses Prepared by Physical Vapor Deposition

Kenneth L. Kearns, et al Adv. Mater. 2009, 21, 1




**Longitudinal bulk module M**
**Module de cisaillement G**
**Module de Young E**

} **augmentation de 10% à 19%**

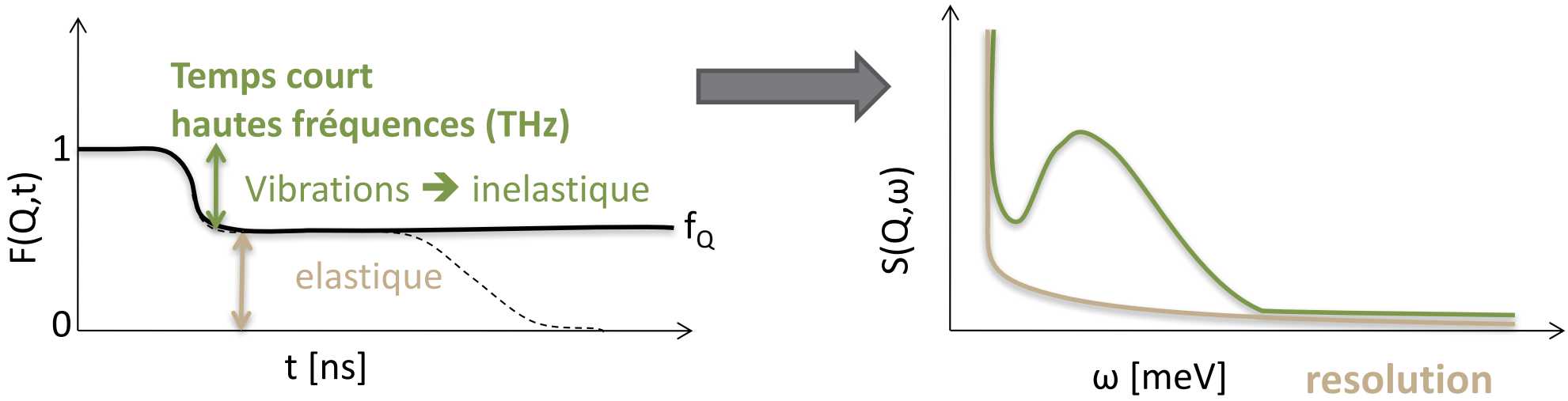
**Alors que par aging, ils ne varient que de .5-3%**

Fréquence de Debye des différents états

$$\omega_D = \left(18\rho\pi^2/(1/c_L^3 + 2/c_T^3)\right)^{1/3}$$

**Autres propriétés du VERRE**

# Verre = photo instantanée du liquide gelé à Tg

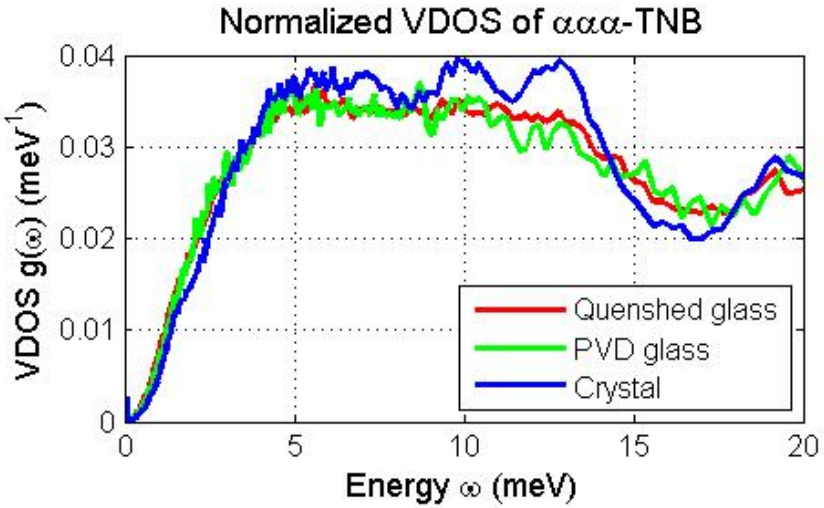


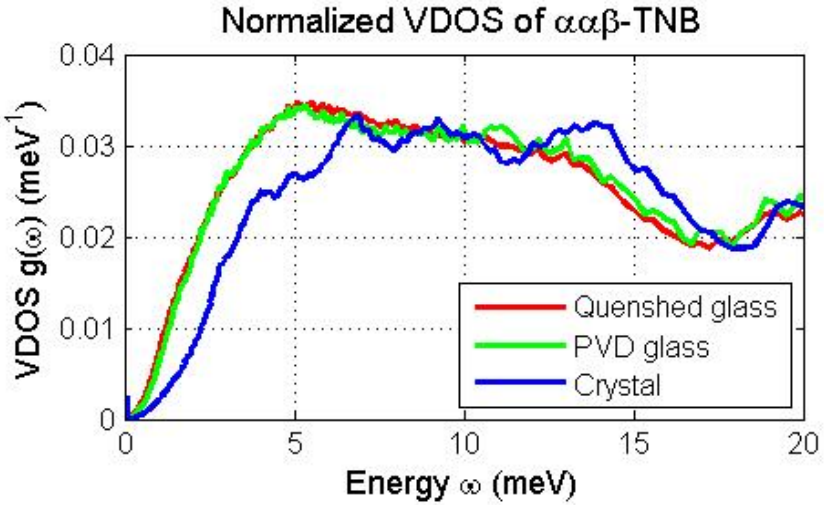

À partir des modes vibrationnelles dans le verre

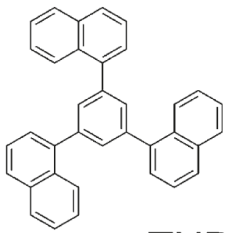
⟹ description de la reponse du verre à de petites pertubations

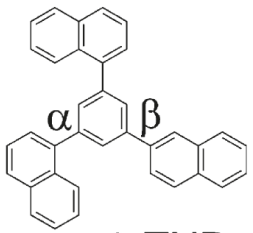
Pour les systèmes désordonnés, ces modes établissent une relation entre le désordre structural et la dynamique collective

# Calcul de la VDOS à partir de S(Q,ω)

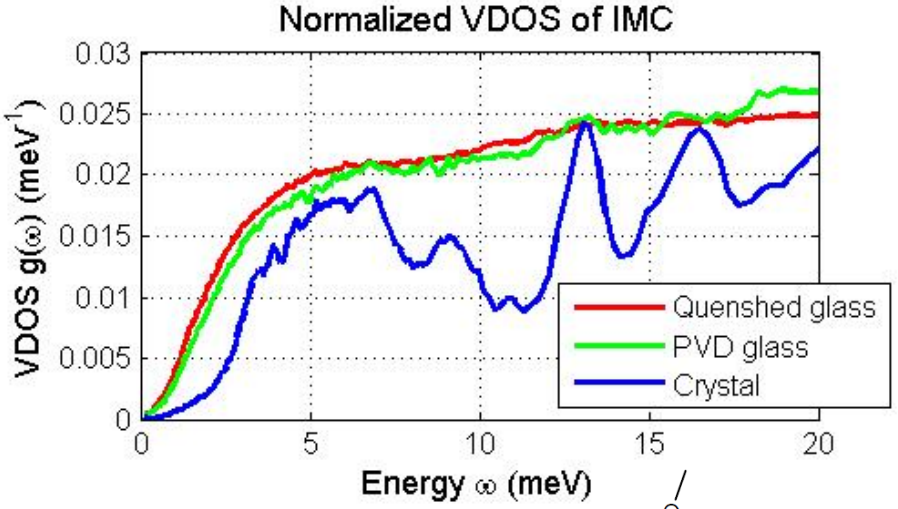


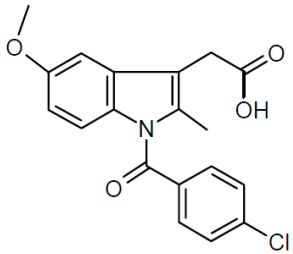





α,α,α-TNB



α,α,β-TNB




Des différences moins marquées
à basses fréquences, mais bien présentes

Systèmes moléculaires complexes avec
des modes intramoléculaires à basse freq.

# Analyse de la VDOS

à partir des déplacements des particulesd'un systeme soumis à une contrainte

→ Informations sur les ihomogénéités de l'amorphe,

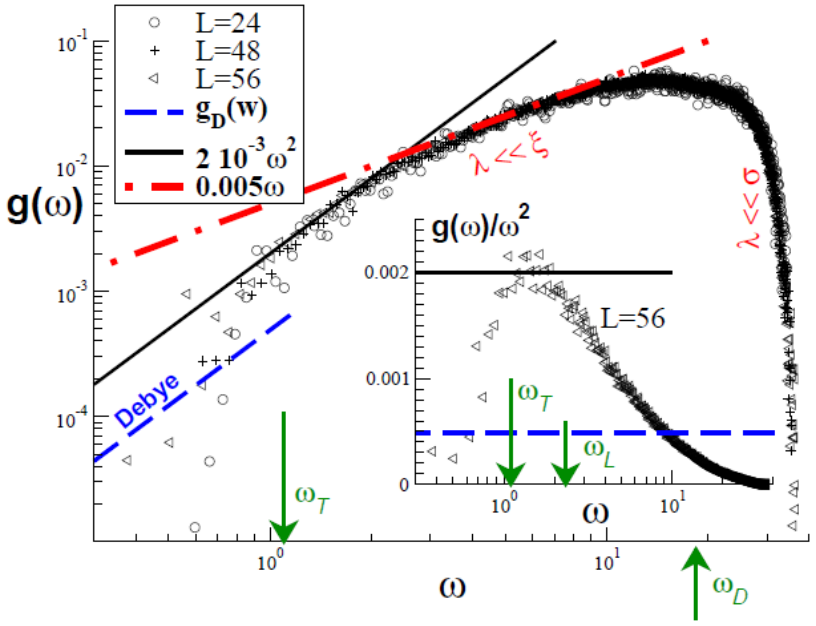
Toute deviation à une dcontrainte uniforme définit des déformations non affines

cross over entre un **comportement élastique continu (Debye)**
et un **régime de déplacement non affine**

Léonforte et al PRE 2004, 2005

$w^2$

$w^1$

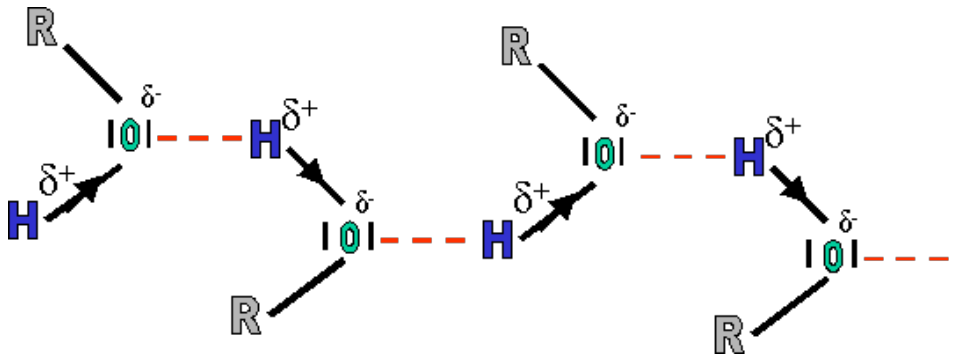


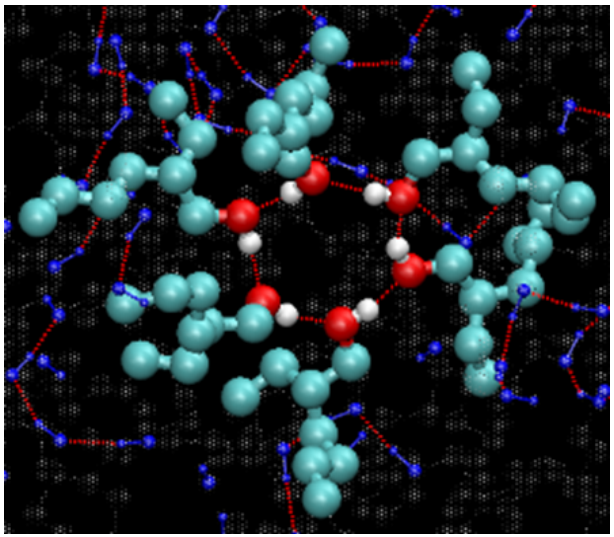

**'hétérogénéités élastiques' de plus petites tailles dans les verres stables**

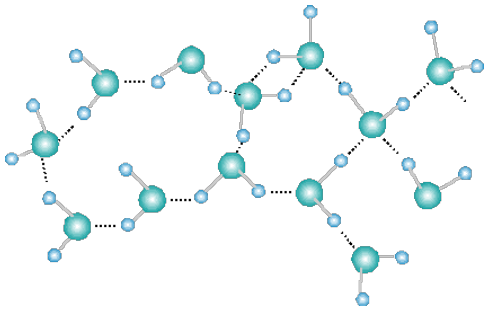
# Networks of molecular liquids ?

## Role of Hydrogen Bonds

## Auto-association of alcohols



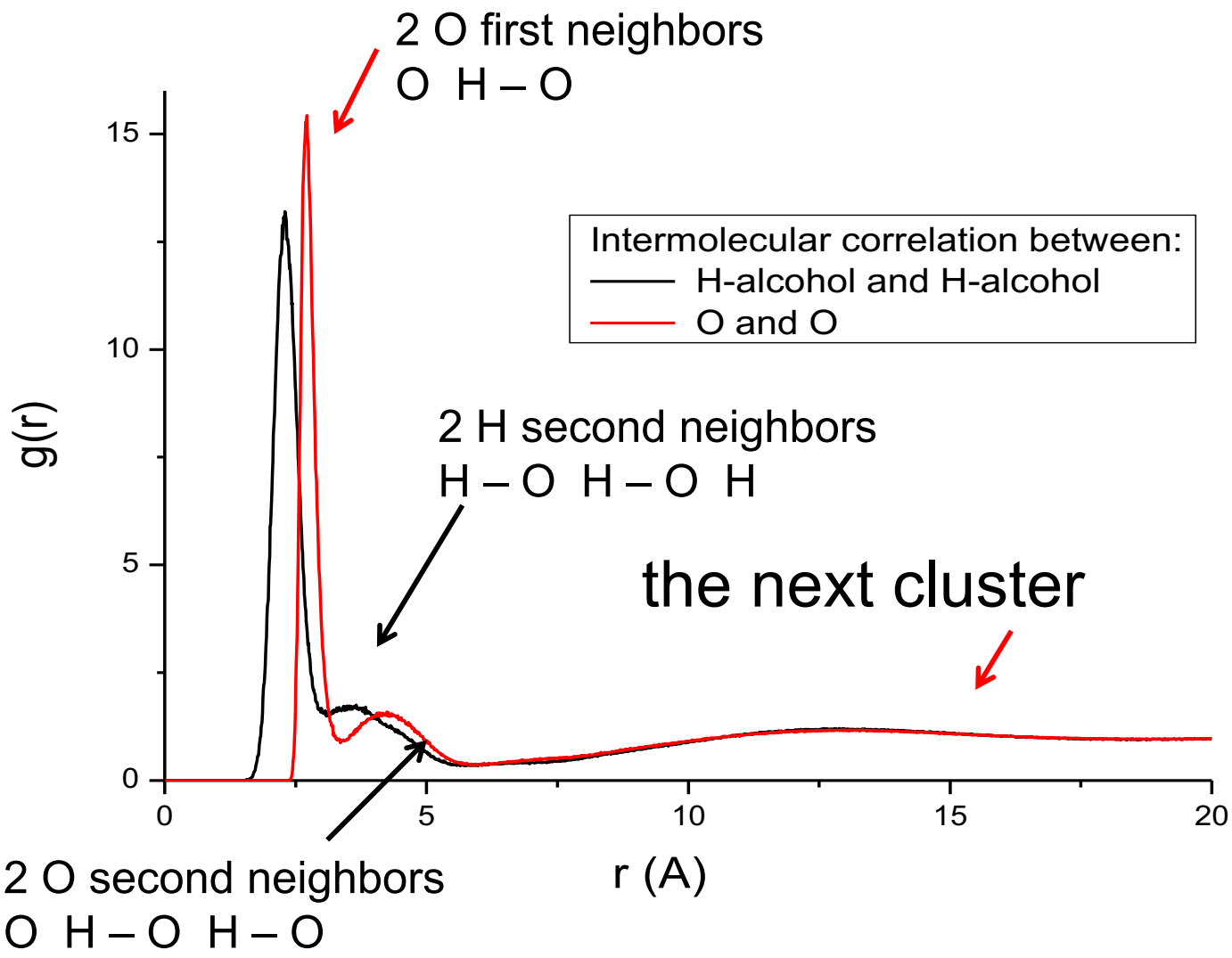



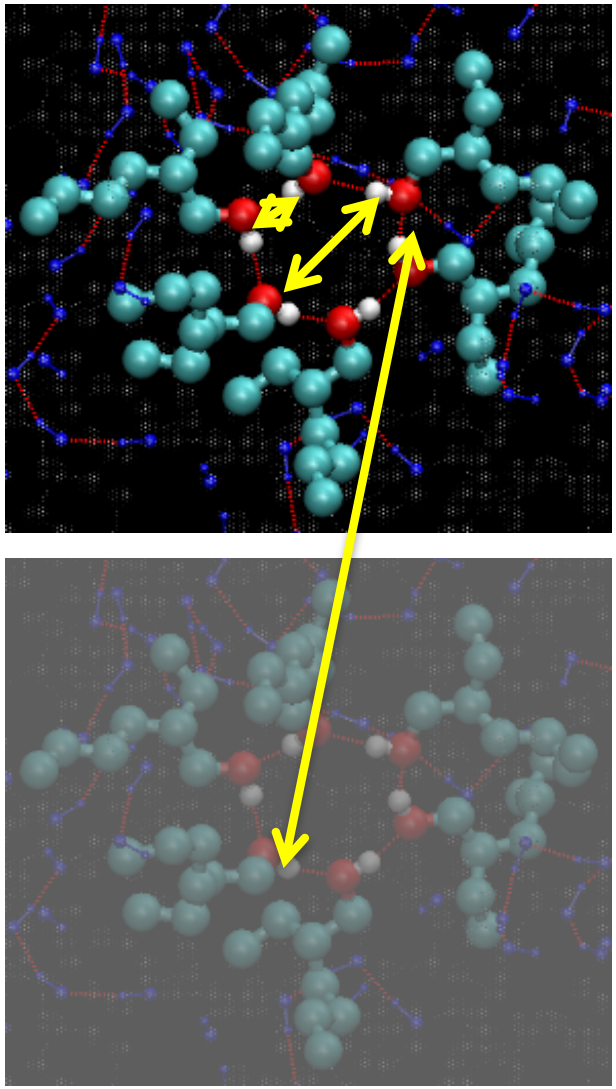


water : 17 cristalline phases

# **1ethyl 2hexanol** MD analysis 300K: Partial radial distribution function involving O -H atoms

**Evidence of various length scales, showing cluster formation**



# 1ethyl 2hexanol  static structure factor at Patm

Same remarkable feature: a well defined prepeak

Fully deuterared sample
Elastic neutron scattering

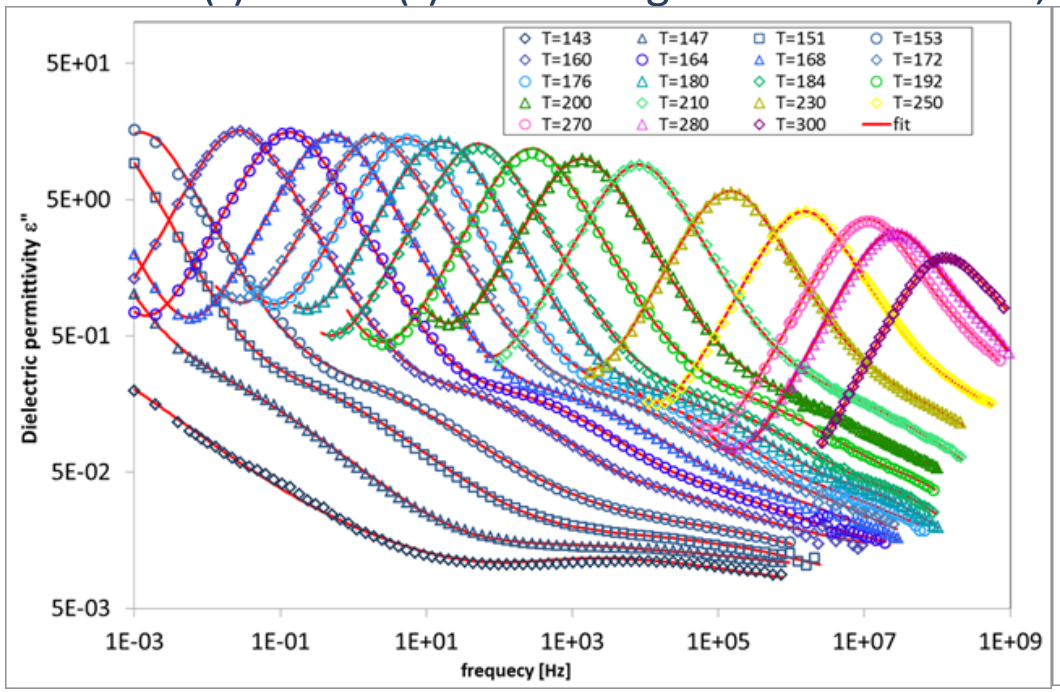
Fully hydrogenated
Xray scattering

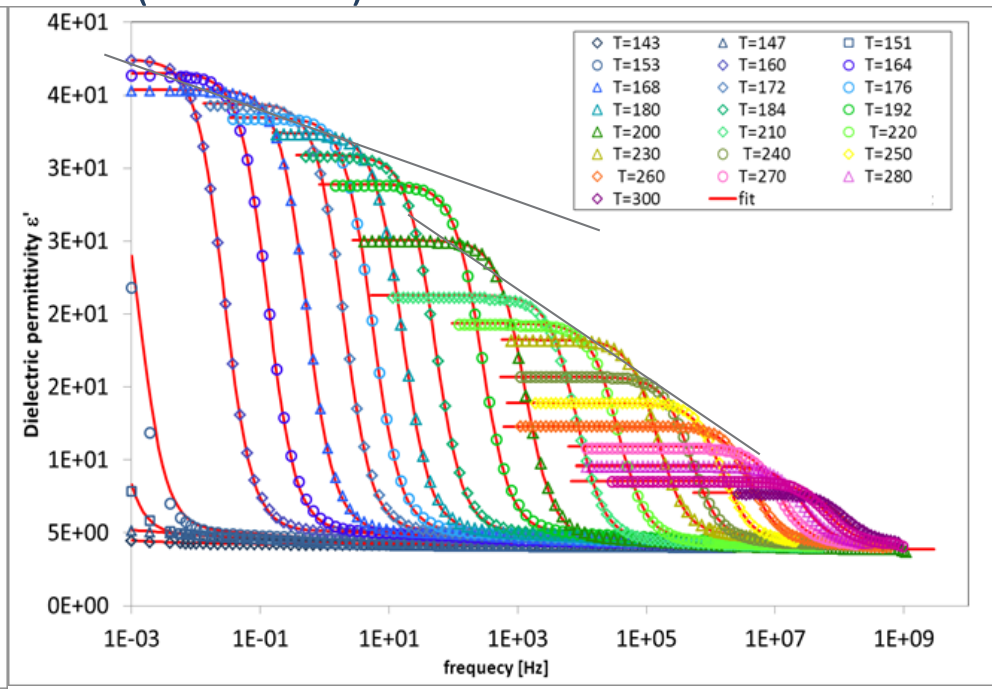
# Case of 1ethyl 2hexanol dielectric spectra

**Prior work by Richert and Böhmer over the last  years**

The largest ratio $\tau_D/\tau_\alpha$

$\varepsilon''(f)$ and $\varepsilon'(f)$ over a large T and ω domain, Patm ( this work)



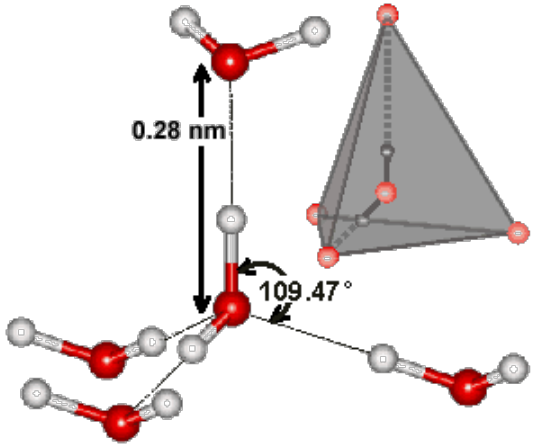

↓ mHz

↓ GHz

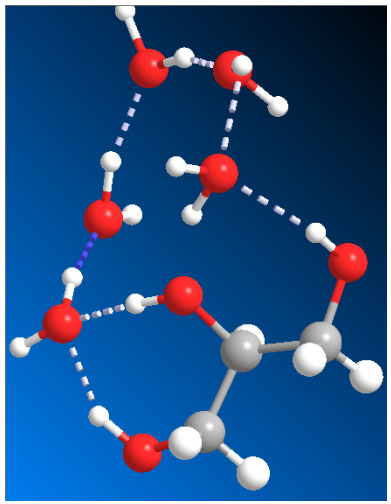
$$g_K = \frac{1}{\mu^2}\frac{9\varepsilon_0 k_B T}{N}\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2}$$

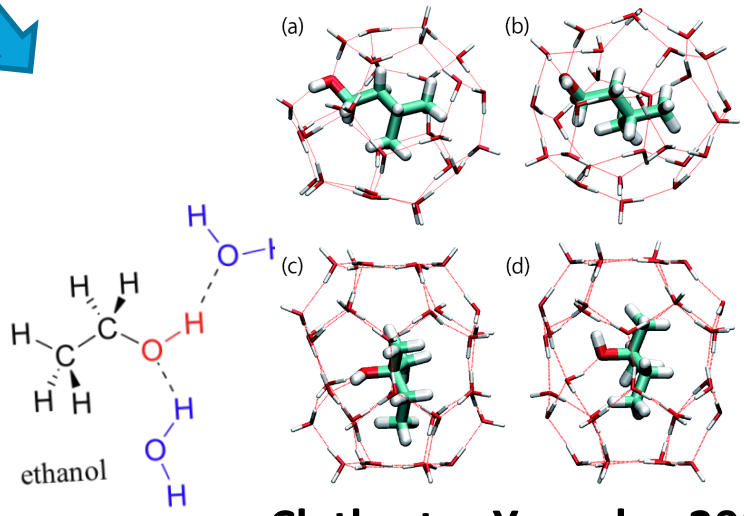
# Role of Hydrogen Bonds in solutions
# Water + alcohol, aminoacids…

lower hydrophobicity
better to delay nucleation
and retard growth,
working by
disrupting the water
hydrogen bond network,




higher hydrophobicity
strengthens local water
structure
control of hydrate formation

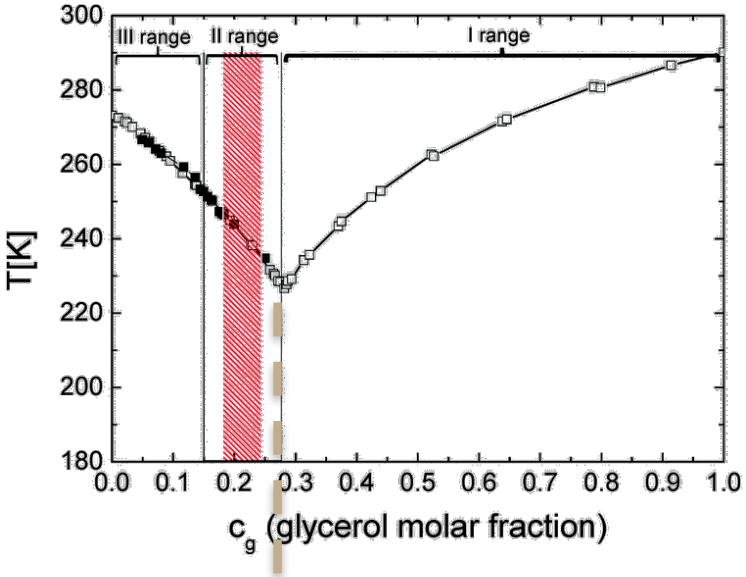





**Clathrates Yasuoka, 2015**

# Water + glycerol phase diagram
# case 1 : strongly hydrophilic alcohol

**Inaba (2007)**



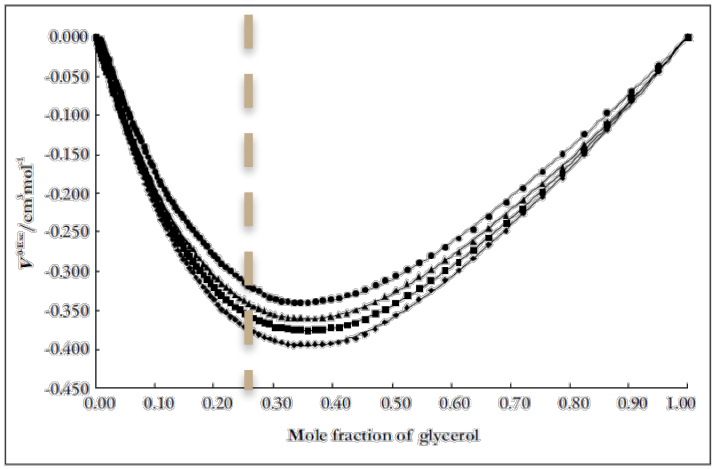
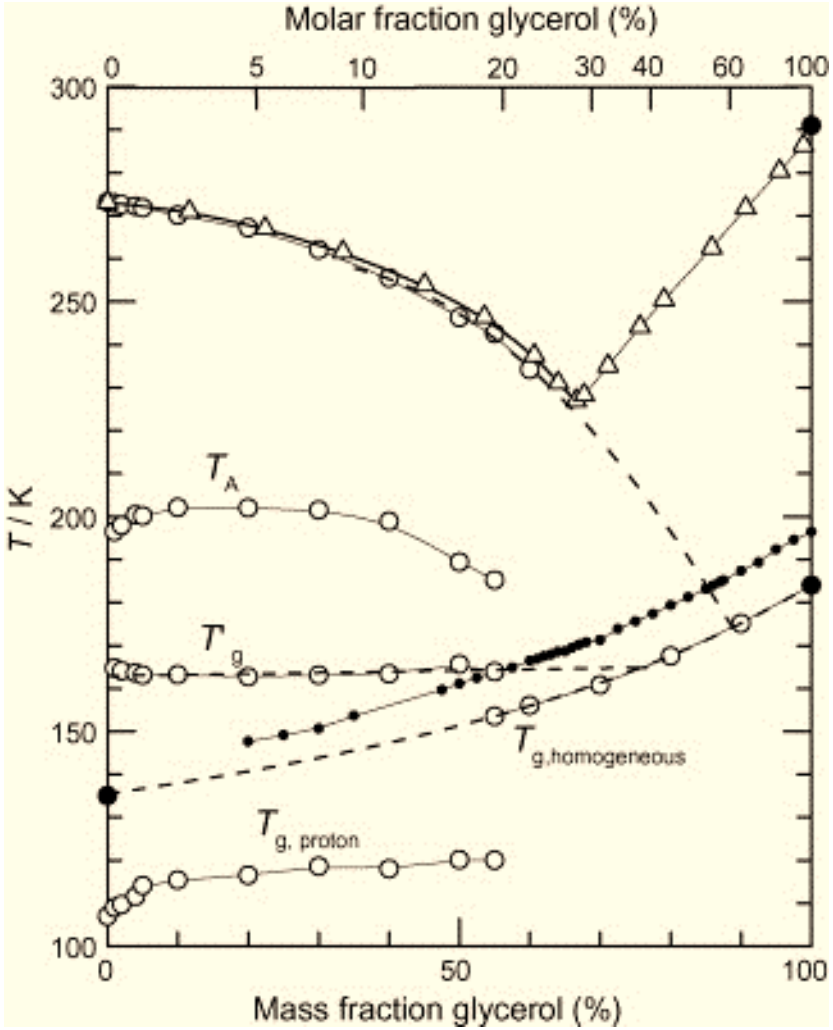
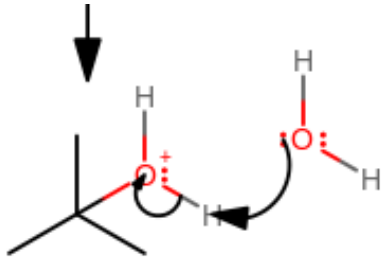



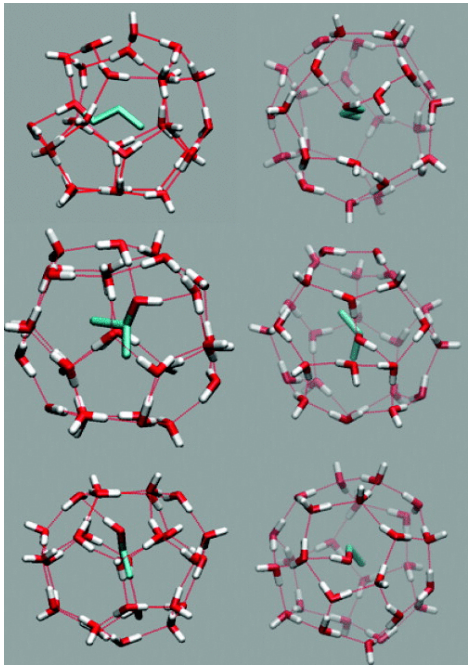

Figure 1. Excess molar volumes of glycerol + water mixtures at several temperatures. (♦): 288.15 K; (■): 293.15 K; (▲): 298.15 K; (●): 303.15 K.

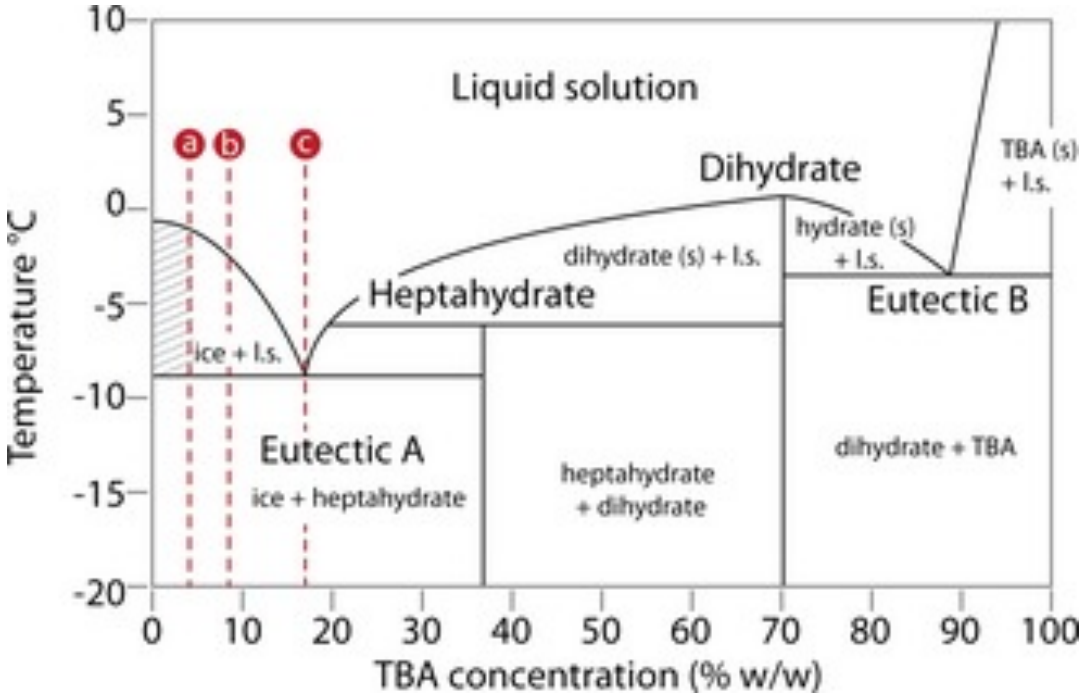



**Tanaka (2012) mais dans Nat mat**

# Water + monoalcohol phase diagram
# case 1 : partly hydrophobic alcohol






**Clathrates**

**GT is a combination of cooperative effects and local, molecular ones.**

**The local structure is distinct from that of the crystal**

the molecular details play a fundamental role in its dynamics ( de Gennes, Narrowing, rigid vs flexible)

The high T behavior, the ability to form a glass etc.... results from the combination of

- **the strength of the intermolecular interactions,** attraction, dispersion
- **the shape of the molecule,**
- **the short-range (spatial) correlations associated with the local arrangement of the molecules in the liquid.**

The simplest system that forms a glass is a **molecule**, with a reduced number of partial contributions to S(Q), a simplified the shape keeping intrinsic and self generated disorder.

It presents a low activation energy at high Temperature and very high fragility.
No increase in static correlation length while dynamical ones varie by a factor of 3 to 4.