Numerical simulations and Rigidity of glasses – II

Matthieu Micoulaut (UPMC)

- ❑ Rigidity transitions and compositional trends
- ❑ Intermediate phases and non-mean field rigidity
- ❑ « *Topological engineering* » (Mauro-Gupta theory)
- ❑ MD based rigidity theory and applications

Optimizing glass = finding anomalies with composition

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Material functionalities from molecular rigidity

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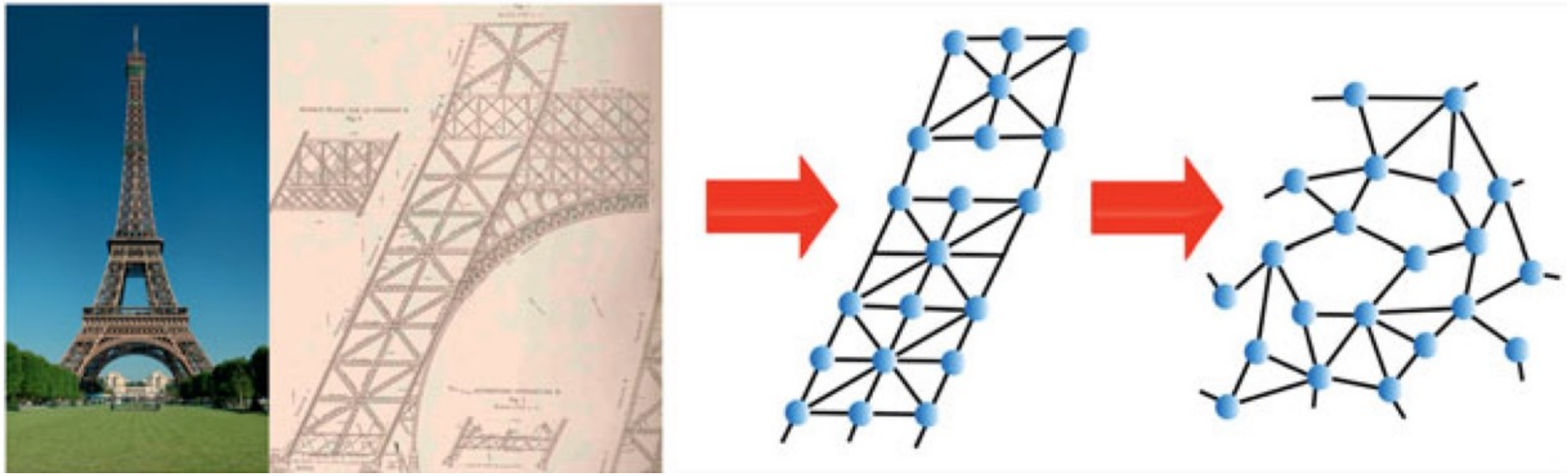
A) Constraint theory

Basic idea: An analogy with mechanical structures (Maxwell)



Mechanical structure

- Nodes
- Bars
- **Tension**

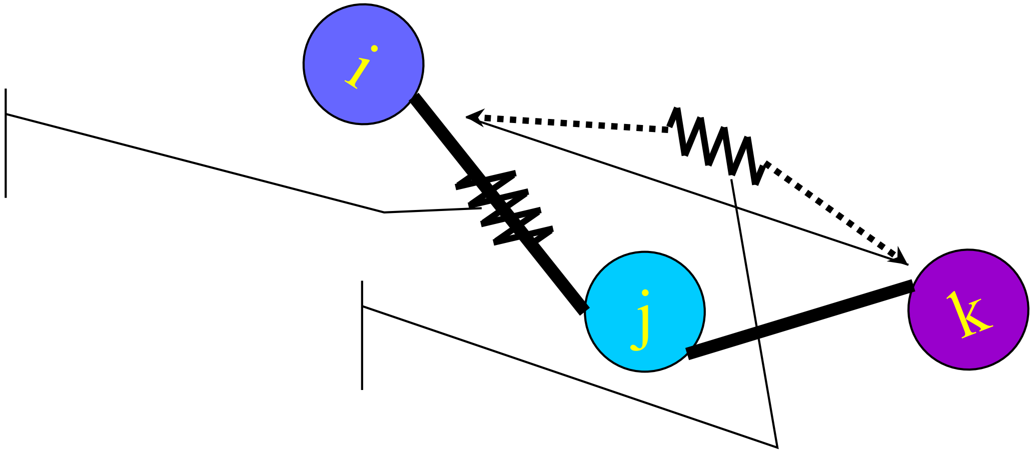
Molecular network (contraint counting)

- Atoms
- Covalent bonds
- **Stretching and bending interactions**

A) CONSTRAINTS AND RIGIDITY TRANSITIONS

1. Enumeration of mechanical constraints

Consider a r-coordinated atom



Stretching constraints α_{ij}

r/2

Bending constraints β_{ijk}

2r-3

- If r=2, there is only one angle.

Each time, one adds a bond, one needs to define 2 new angles

- We consider a system with N species of concentration n_r.

The number of constraints per atom is :

$$n_c = \frac{\sum_{r\geq 2}^{N} n_r(\frac{r}{2} + (2r-3)}{\sum_{r\geq 2}^{N} n_r}$$

J.C. Phillips, JNCS 1979

- ☐ We introduce the network mean coordination number

$$\bar{r} = \frac{\sum_{r\geq 2}^{N} r n_r}{\sum_{r\geq 2}^{N} n_r}$$

e.g. accessed from the Bhatia-Thornton pair distribution function $g_{NN}(r)$

- ☐ Then n_c can be simply rewritten as :

$$n_c = \frac{\sum_{r\geq 2}^{N} n_r(\frac{r}{2}+(2r-3)}{\sum_{r\geq 2}^{N} n_r}=(\frac{\bar{r}}{2} + (2\bar{r} - 3))$$

- ☐ Invoking the Maxwell stability criterion for **isostatic** structures n_c=D=3

we find a stability criterion for:

$$n_c = (\frac{\bar{r}}{2} + (2\bar{r} - 3))=3$$

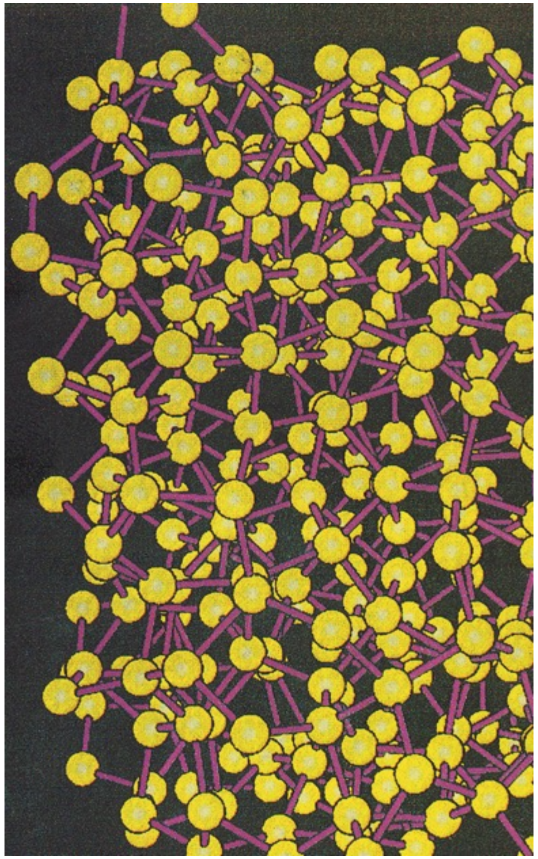
or :

$$\boxed{\boldsymbol{\bar{r} = \frac{12}{5} = 2.4}}$$

- ☐ Networks with n_c<3 are underconstrained (flexible). With n_c>3, they are overconstrained

- ☐ Important quantity: number of floppy (deformation) modes : f=3-n_c

A) CONSTRAINTS AND RIGIDITY TRANSITIONS



2. Rigidity transition:

☐ Amorphous silicon and harmonic potential

$$V = \frac{\alpha}{2}(\Delta l)^2 + \frac{\beta l}{2}(\Delta\theta)^2$$

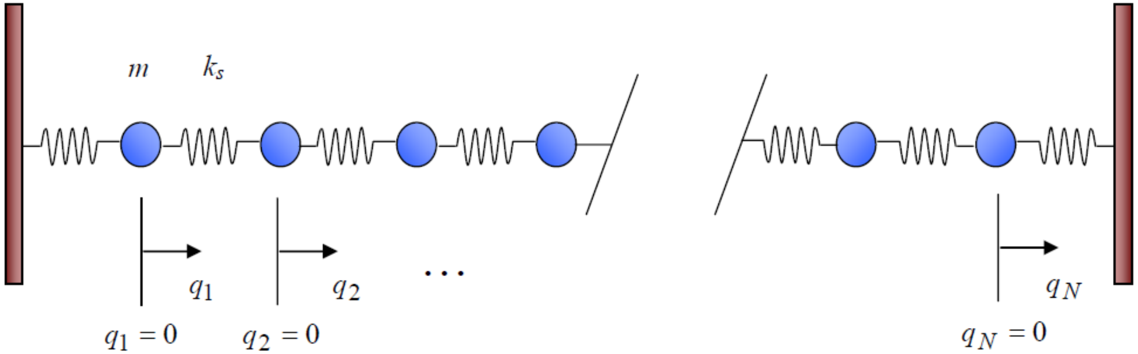
Stretching **Bending**

☐ **RANDOM** Bond depletion (<r> decreases) on a-Si.

☐ Calculation of the eigenmodes (vibrational frequencies) of the system

☐ Example of simple eigenmode calculation:

the linear chain



- Force acting on spring j: $F_j = -k_s\left(q_j - q_{j-1}\right) - k_s\left(q_j - q_{j+1}\right)$
- Newton’s law gives: $\ddot{q}_j - \tilde{\omega}^2\left(q_{j-1} - 2q_j + q_{j+1}\right) = 0$

  with frequencies $\tilde{\omega}^2 = k_s / m$

- Normal mode solution : $q_j = q_{0,j} e^{i\Omega t}$

$$\Omega^2 q_{0,j} + \tilde{\omega}^2\left(q_{0,j-1} - 2q_{0,j} + q_{0,j+1}\right) = 0$$

which actually reduces the problem to an **eigenvalue (Ω) problem**:

$$\begin{pmatrix} 2\tilde{\omega}^2 - \Omega^2 & -\tilde{\omega}^2 & 0 & 0 & \\ -\tilde{\omega}^2 & 2\tilde{\omega}^2 - \Omega^2 & -\tilde{\omega}^2 & 0 & \\ 0 & -\tilde{\omega}^2 & 2\tilde{\omega}^2 - \Omega^2 & -\tilde{\omega}^2 & \cdots \\ 0 & 0 & -\tilde{\omega}^2 & 2\tilde{\omega}^2 - \Omega^2 & \\ & & \vdots & & \end{pmatrix} \begin{pmatrix} q_{0,1} \\ q_{0,2} \\ q_{0,3} \\ q_{0,4} \\ \vdots \end{pmatrix} = 0$$

- **More general**: normal modes=eigenvalues Ω of the dynamical matrix

2. Rigidity transition:

- ☐ Thorpe (1983) found that bond depleted a-Si with mean coordination number <r> < 2.385 contain **zero frequency normal (floppy) modes** Ω.

- ☐ Their number **f** (rank of the Ω=0 block of the dynamical matrix) scales as

$$\boxed{f = 3 - N_c = 6 - \frac{5}{2} < r >}$$

- ☐ **Flexible to rigid elastic phase transition**
  - ➢ Control parameter <r>
  - ➢ Order parameter f

- ☐ Power-law $C_{ij}=(<r>-2.4)^p$ (p=1,5) in the stressed rigid phase. Elastic phase transition.

- ☐ Isostatic glass n_c=3 is at the R transition

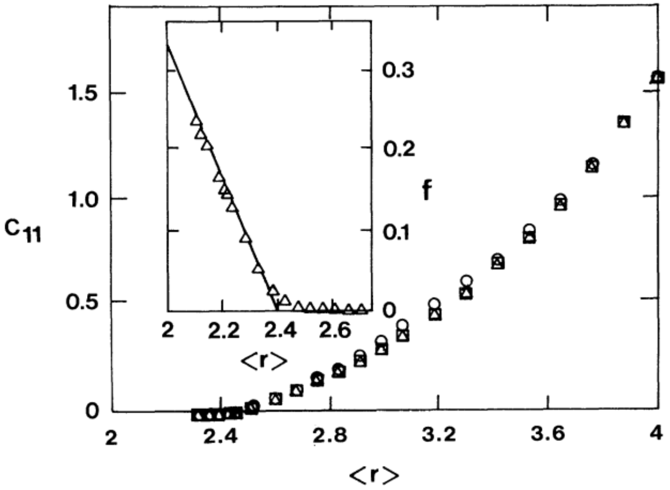


FIG. 1. Elastic modulus C_{11} with $\beta/\alpha=0.2$ in units where $\alpha=4a$ and as a function of the mean coordination $\langle r\rangle$. The three symbols are for three different series of random networks. The inset shows the number of zero-frequency modes f (averaged over three networks) compared to the result of the mean-field theory [Eq. (3)] shown by a straight line.

He and Thorpe, PRL 1985

Examples of application:

☐ **Ge_xSe_{1-x} glasses**:
Ge is 4-fold and Se is 2-fold.

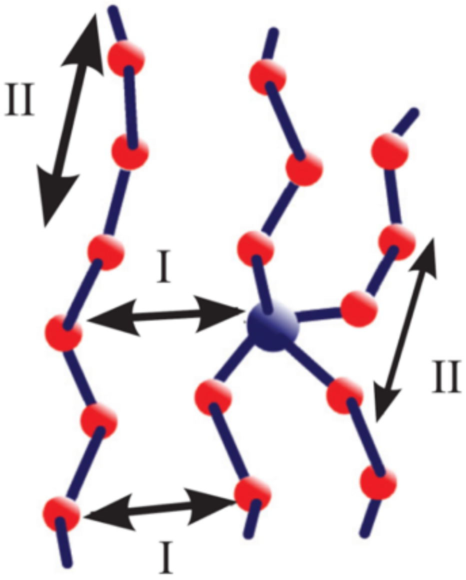
- Ge has 2r-3=5 BB and r/2=2 BS constraints
- Se has 1 BB and 1 BS constraint

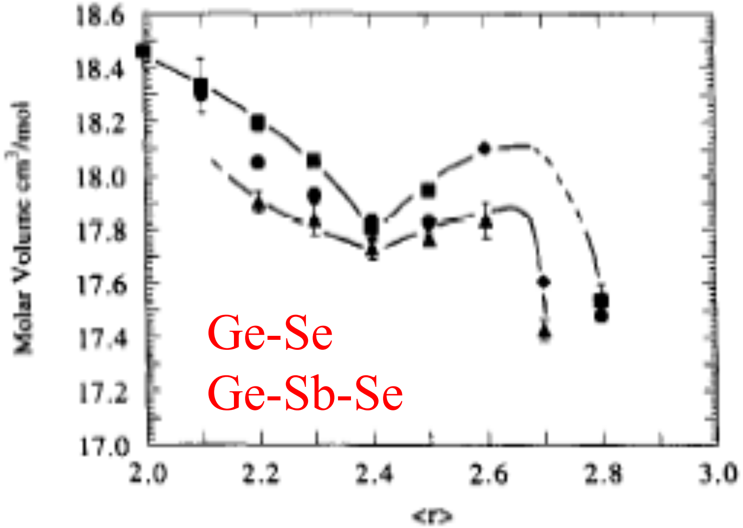
- nc=2(1-x)+7x=2+5x
- Stability criterion for n_c=3 i.e. for x=0.2

- Mean coordination number at 20% Ge

$$\bar{r} = r_{Ge}x + r_{Se}(1-x) = 4x + 2(1-x) = 2.4$$

$Ge_{20}Se_{80}$=$GeSe_4$ glasses are isostatic





Varshneya et al. JNCS 1991

Playing with numbers…can be a dangerous game !

Chalcogenide network glasses

r(Se)=2 , r(Ge)=4

Ge_xSe_{1-x}

Ge-Sb-Se, Ge-As-Se, etc…

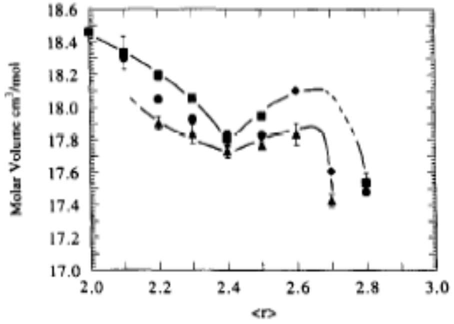


Fig. 6. Dependence of molar volume on ⟨r⟩ for binary Ge–Se and ternary Ge–Sb–Se systems. The molar volume at room temperature for the binary and ternary are represented by ■ and ▲, respectively. The molar volume values for the binary glasses given by Ota et al. [11] are represented by ● and those for the ternary glasses given by Savage et al. [23] are represented by ♦. The curves are drawn as a guide to the eye. The maximum measured error is 0.5%.

1979-2000: Anomalies at <r>=2.4

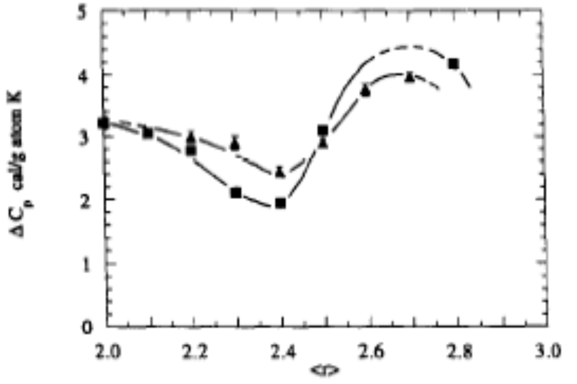


Fig. 10. ΔC_p versus ⟨r⟩ for binary Ge–Se and ternary Ge–Sb–Se systems. The ΔC_p values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 1.8%.

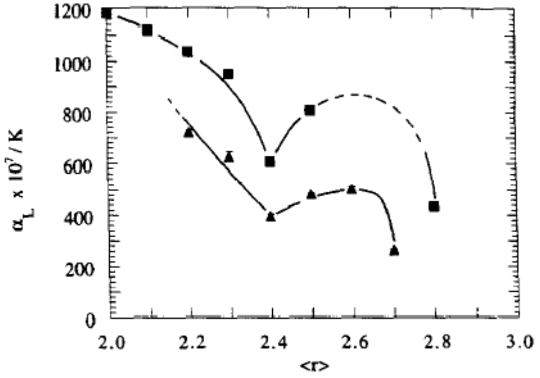
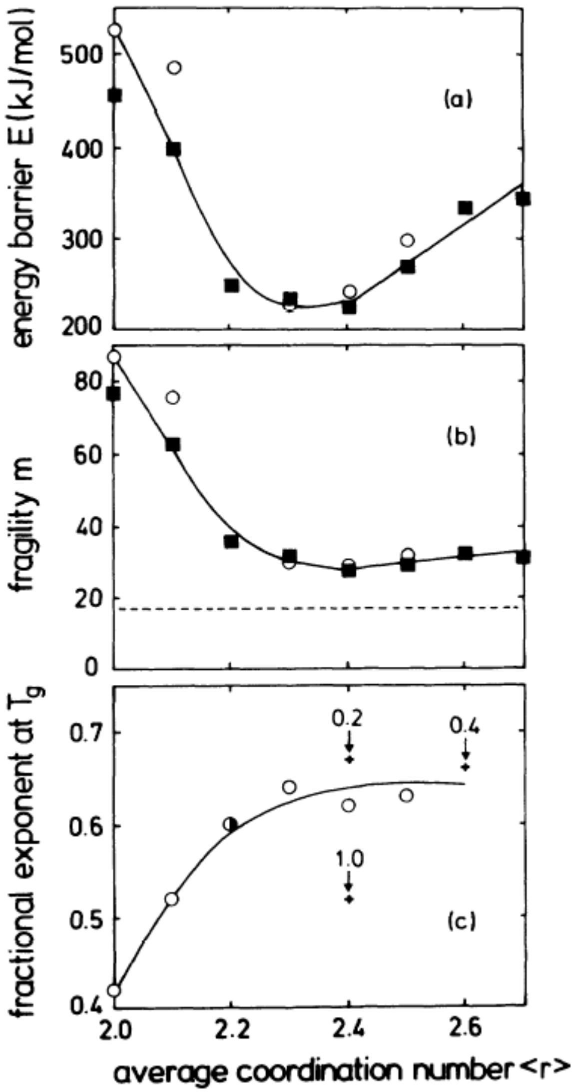


Fig. 4. Liquid state thermal expansion coefficient, α_L, versus ⟨r⟩ for the binary Ge–Se and ternary Ge–Sb–Se systems. The α_L values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 3.5%.

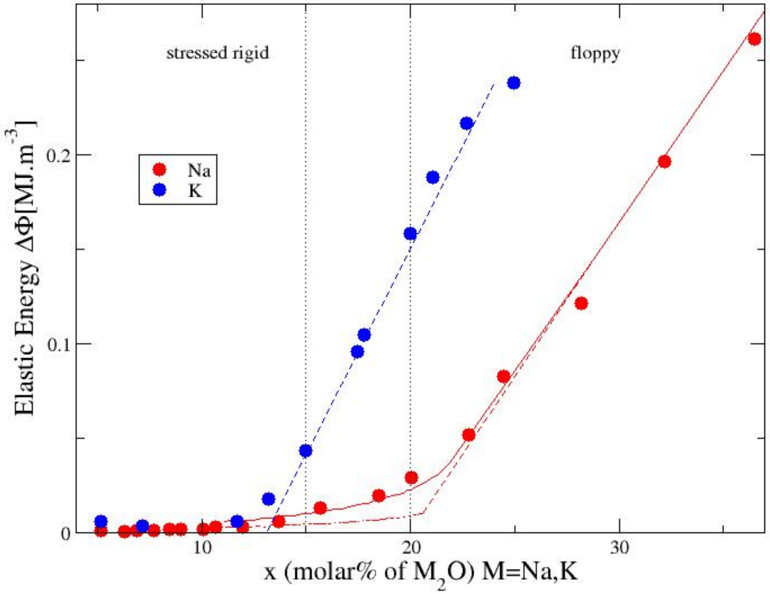


Boehmer and Angell, PRB 1994

Varshneya et al., JNCS 1991

SiO_2-Na_2O

SiO_2-K_2O

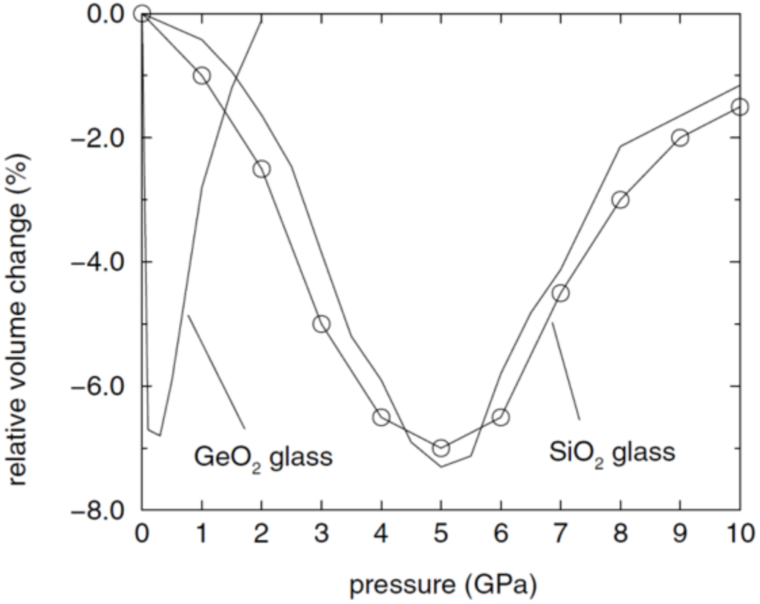


Binary oxides : (1-x)SiO_2-xNa_2O

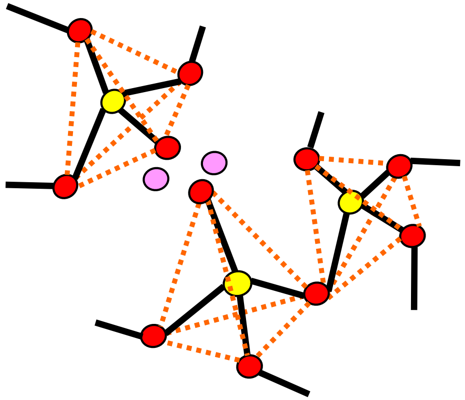
☐ *Depolymerization* with addition of Na. r(Q^4)=4 , r(Q^3)=3,

☐ Silica and germania: **rigidity under pressure** under pressure

Micoulaut, Am. Mineral. 2008
Vaills et al. JPCM 2005

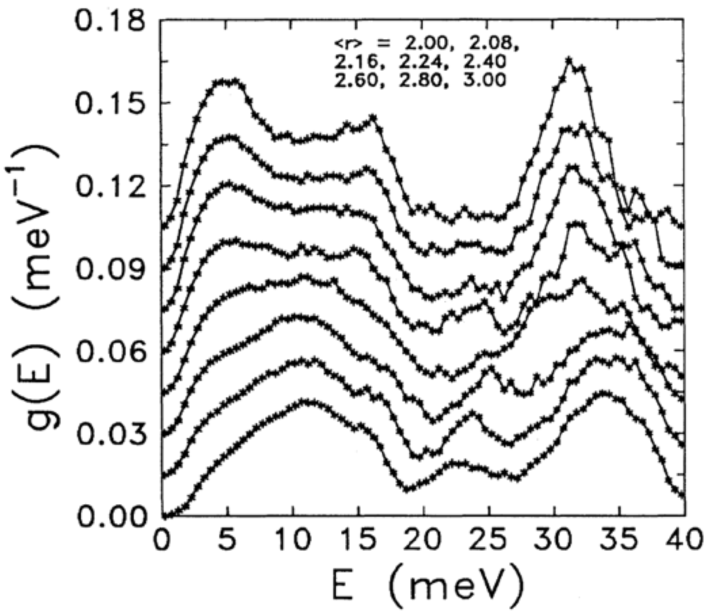


Trachenko et al., PRL 2005



Phillips-Thorpe rigidity theory … a survey

- Raman vibrational thresholds at $<r>_c$
- Minimum in activation energy for stress relaxation at $<r>_c$ (Ge-As-Se)
- Network packing. Molar volumes become minimum (Ge-Se)
- Minimum in activation energy for viscosity (Ge-As-Se)
- Insulator-Metal transition pressures change régime



Kamitakahara et al. PRB 44, 94 (1991)

BUT…

- Is it too simple ? Or simply elegant ?
  - simplified interactions
  - restricted to chalcogenides ?
  - are bond depleted networks realistic ?

- «*Horizontal axis*» theory

- VDOS nightmare
  - survival of floppy modes at high <r>

- **T=0 theory**

- E(floppy)=4 meV

- weak evidence for anomalies in C_{11}, C_{44}

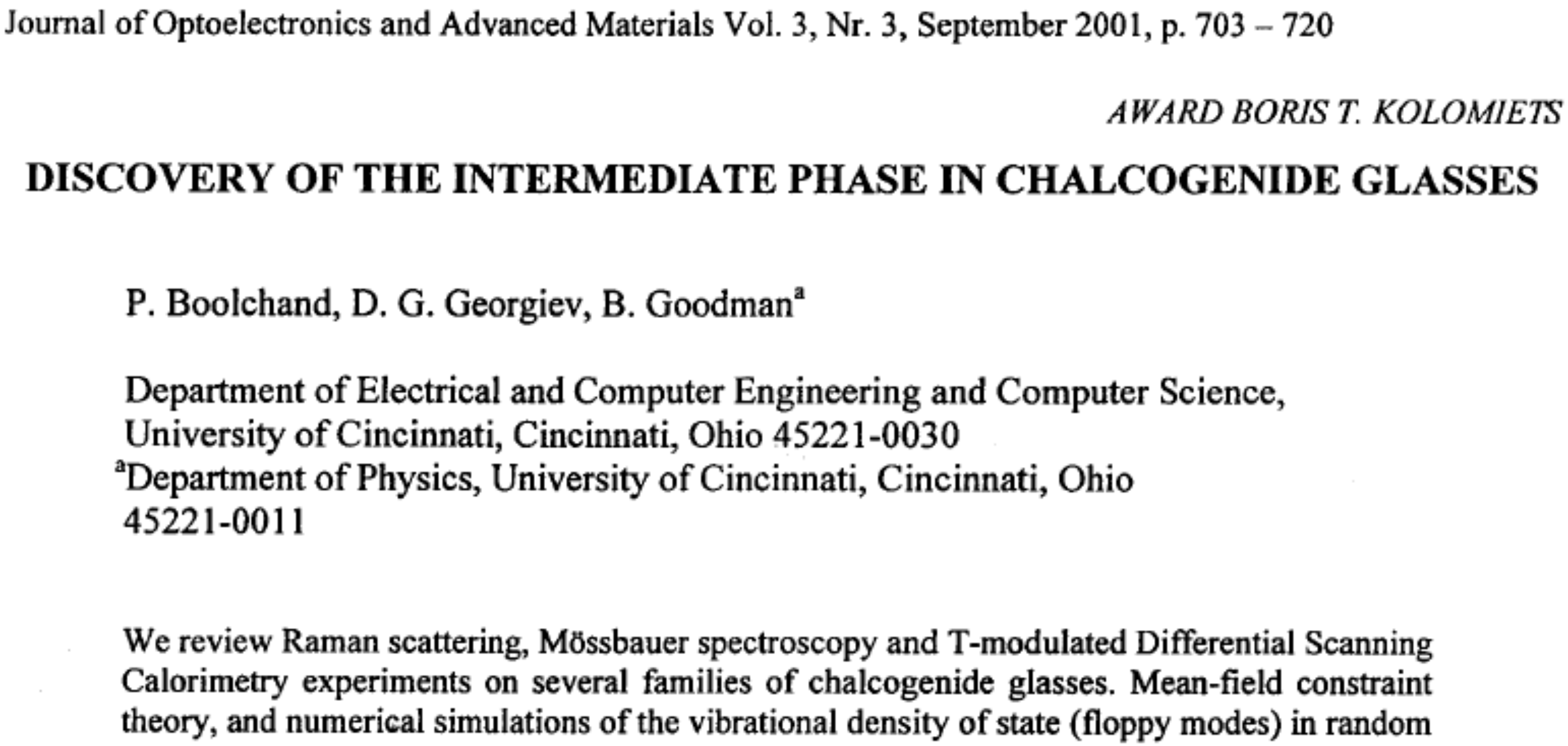
- Connection with MD ?

B. INTERMEDIATE PHASE

Experimentally

Picture of rigidity transitions has been changed in depth during the last decade.

Calorimetric measurements (modulated DSC)



Journal of Optoelectronics and Advanced Materials Vol. 3, Nr. 3, September 2001, p. 703 – 720

AWARD BORIS T. KOLOMIETS

DISCOVERY OF THE INTERMEDIATE PHASE IN CHALCOGENIDE GLASSES

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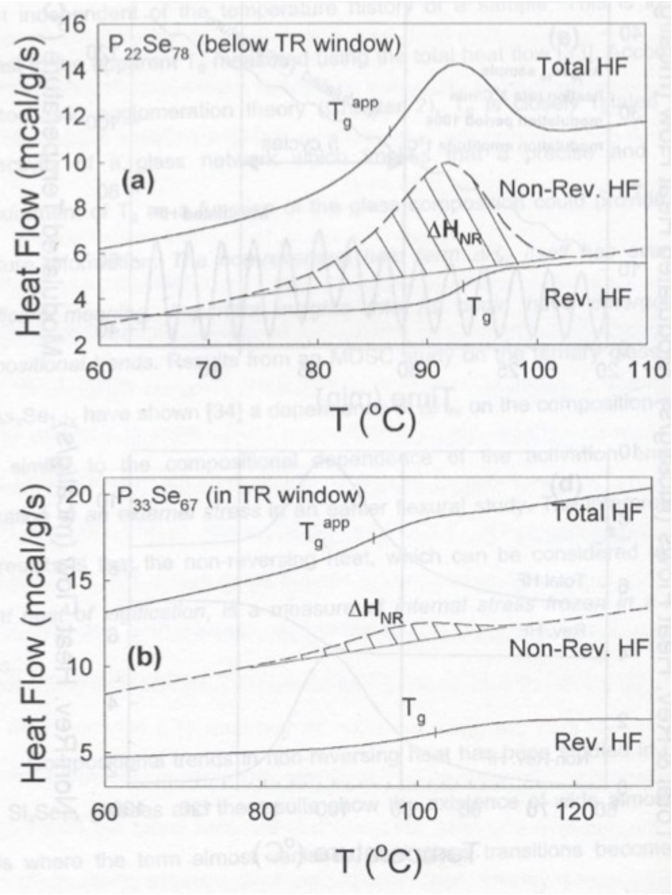
45221-0011

We review Raman scattering, Mössbauer spectroscopy and T-modulated Differential Scanning Calorimetry experiments on several families of chalcogenide glasses. Mean-field constraint theory, and numerical simulations of the vibrational density of state (floppy modes) in random

B. INTERMEDIATE PHASE

Modulated DSC and reversibility windows



Georgiev et al. PRB (2003)

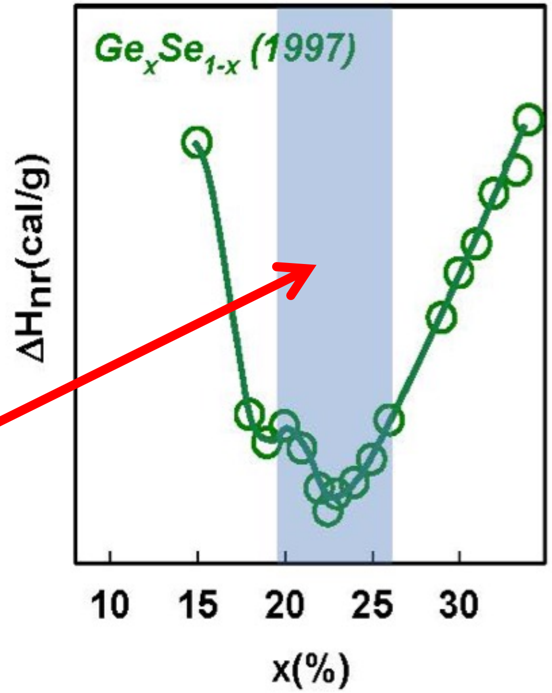
❑ Use of modulated differential scanning calorimetry (MDSC) across the glass transition

$$\dot{H}_T = \dot{H}_{rev} + \dot{H}_{nonrev}$$

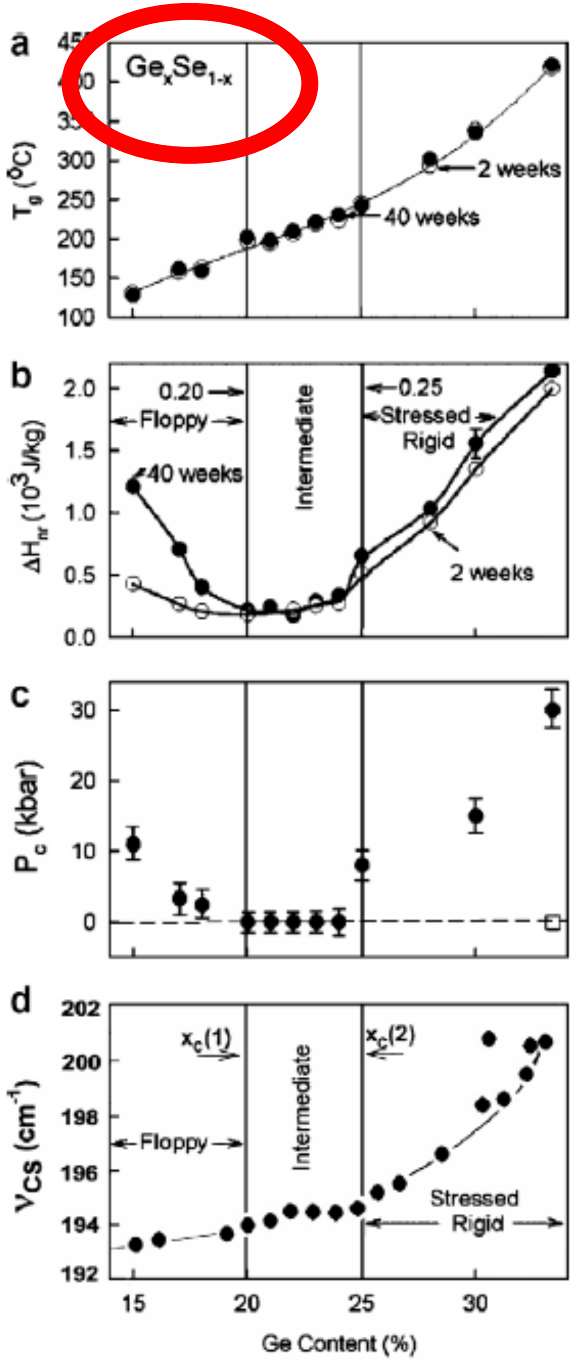
❑ Allows for the definition of 2 heat flows

- Reversible (ΔC_p)
- Non-reversible

Non-reversing enthalpy (ΔH_{nr})



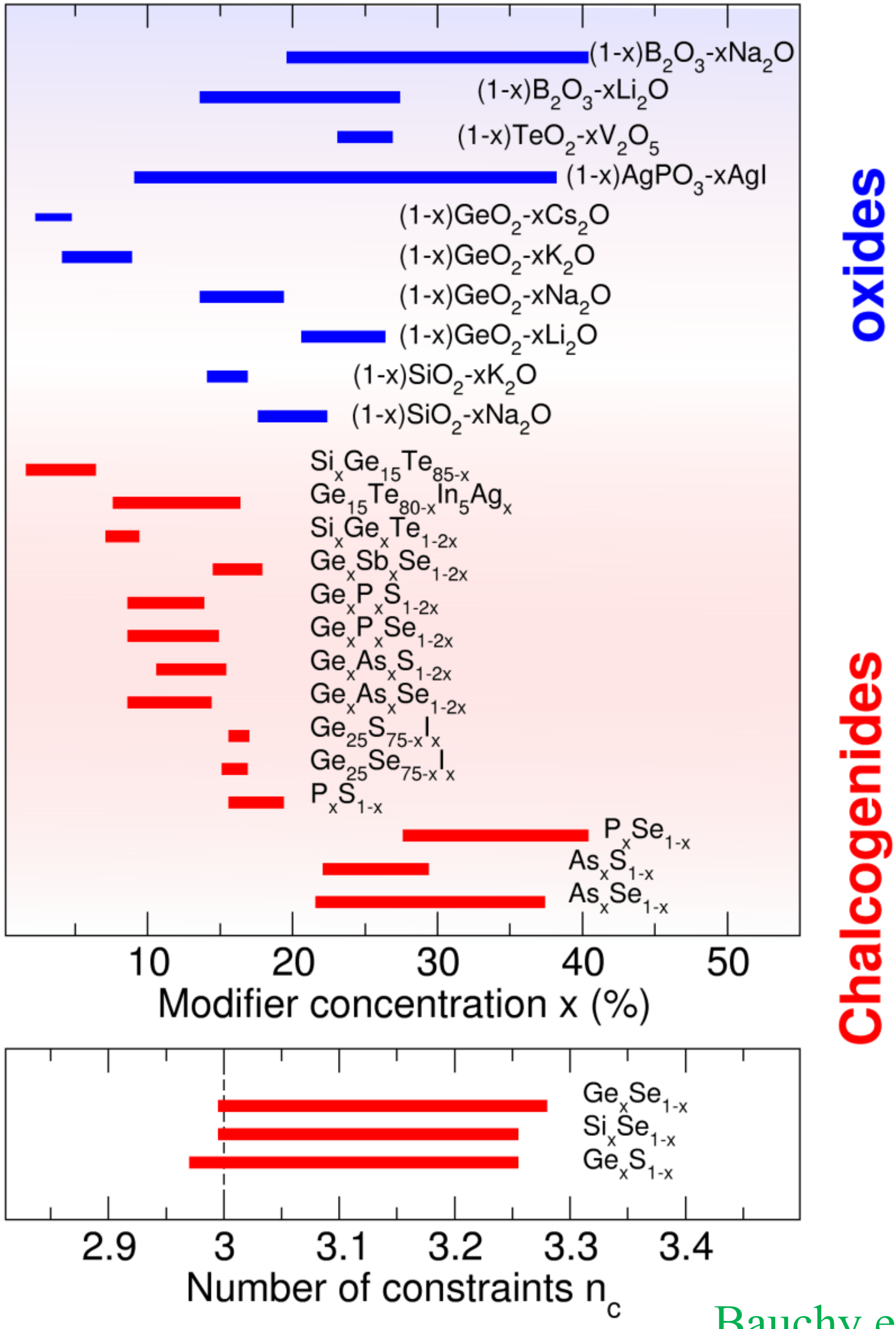
Reversibility window



Wang et al., PRB 2005

Remarkable properties for selected glass compositions

- ❑ Since the RW is found between the flexible and the stressed rigid phase, it is also often called the « Intermediate phase ».
- ❑ **Non-mean field phase** otherwise one would have the single <r>=2.4 transitions.
- ❑ Central idea: stress avoidance under increasing cross-linking density. **Network self-organization Adaptation, optimization,…**
- ❑ Nearly vanishing of ΔH_{nr} at Tg
- ❑ Stress free character (P_c minimum, Raman)
- ❑ Vibrational thresholds (Raman, IR)
- ❑ **Generic (chalcogenides, oxides)**



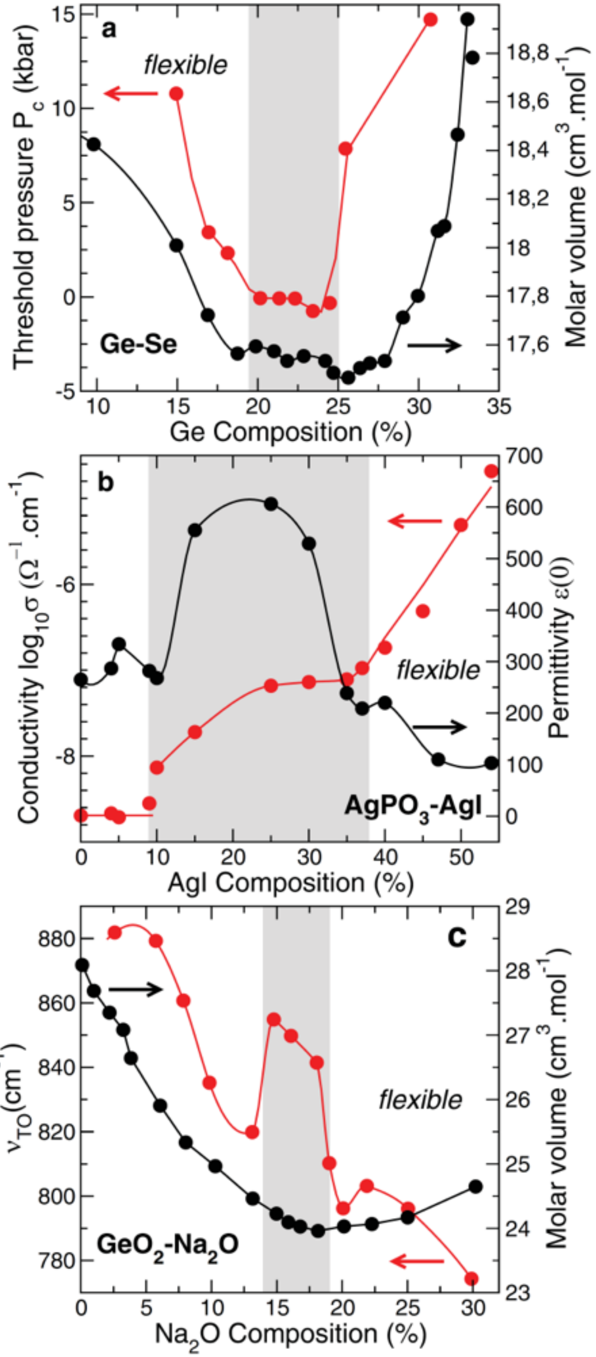
Bauchy et al. Nature Comm. **6**, 6398 (2015)

A subject which has not been without controversy…

"*Marginality of non-reversible component of complex heat flow in MDSC experiments does not necessary reflect self-organized intermediate phase.*"
PSS 2011

« *However, that (mDSC) measurement might also be subjected to a large experimental uncertainty.*"
PRB 2009

"*The observation of the reversibility window might be an experimental artifact.*"
PRB 2009



Micoulaut, Bauchy, PSS 2013

Why has the RW been missed before ?

Three experimental conditions have to be met

Senapati, JNCS 1991

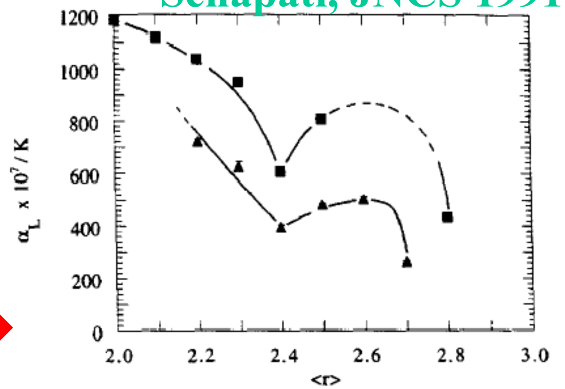
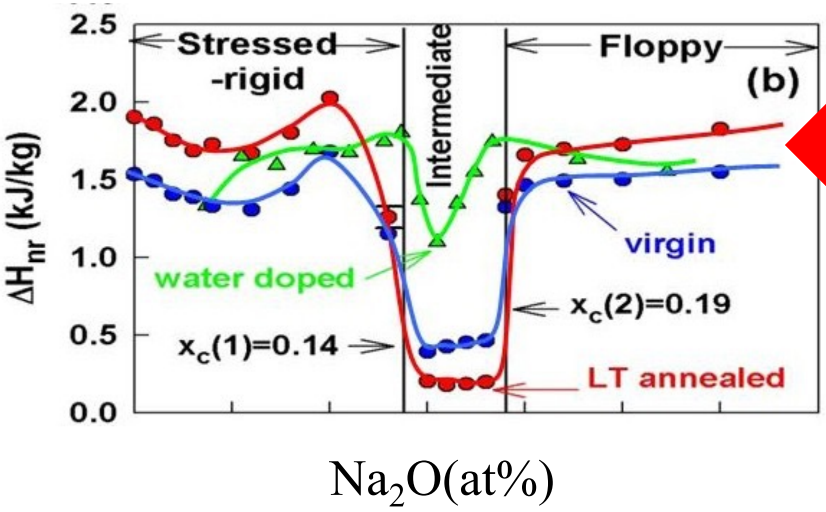


Fig. 4. Liquid state thermal expansion coefficient, α_L, versus $\langle r \rangle$ for the binary Ge–Se and ternary Ge–Sb–Se systems. The α_L values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 3.5%.

Tiny compositional changes



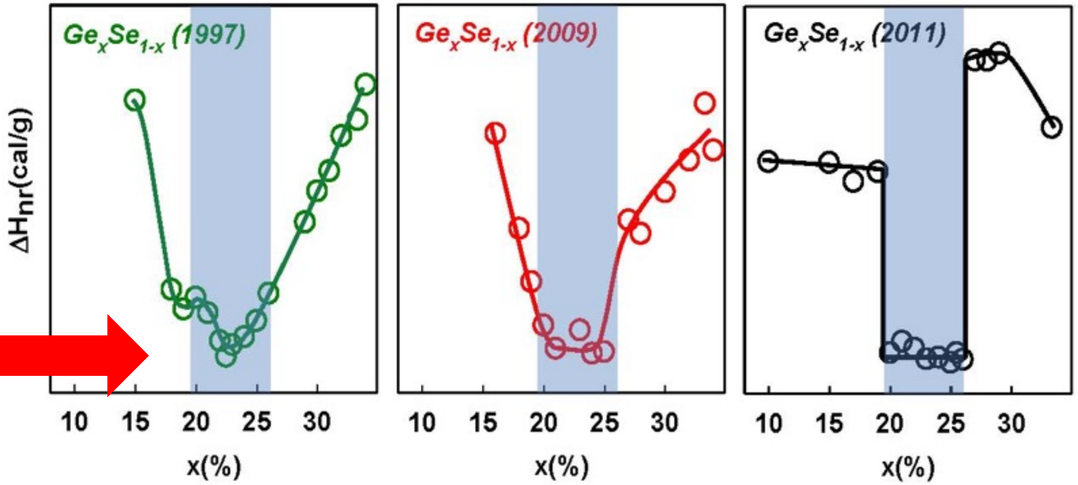
Sample purity (dryness)

Bhosle et al., IJAGS 2012

Homogeneity

Alloying time+

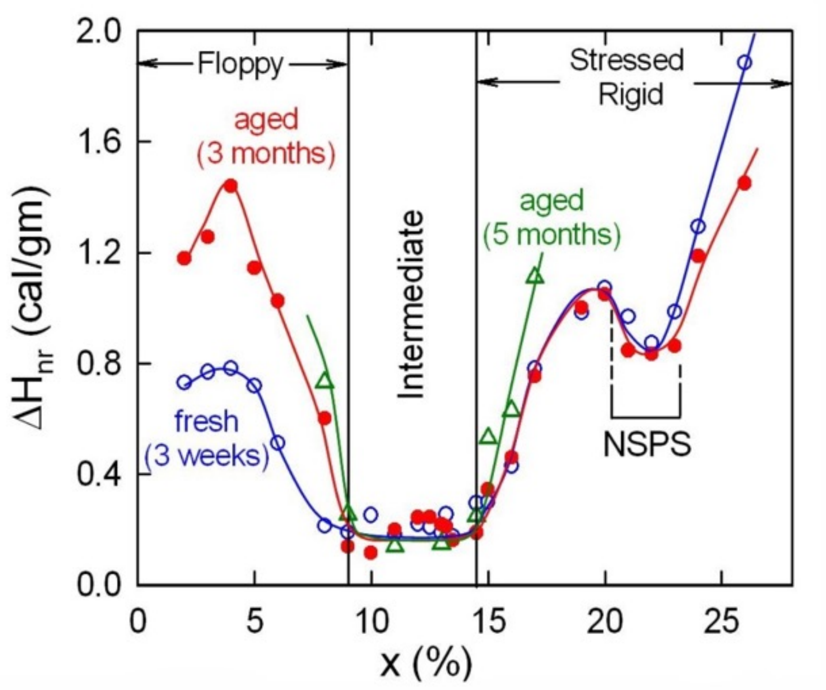
Raman profiling



Ageing

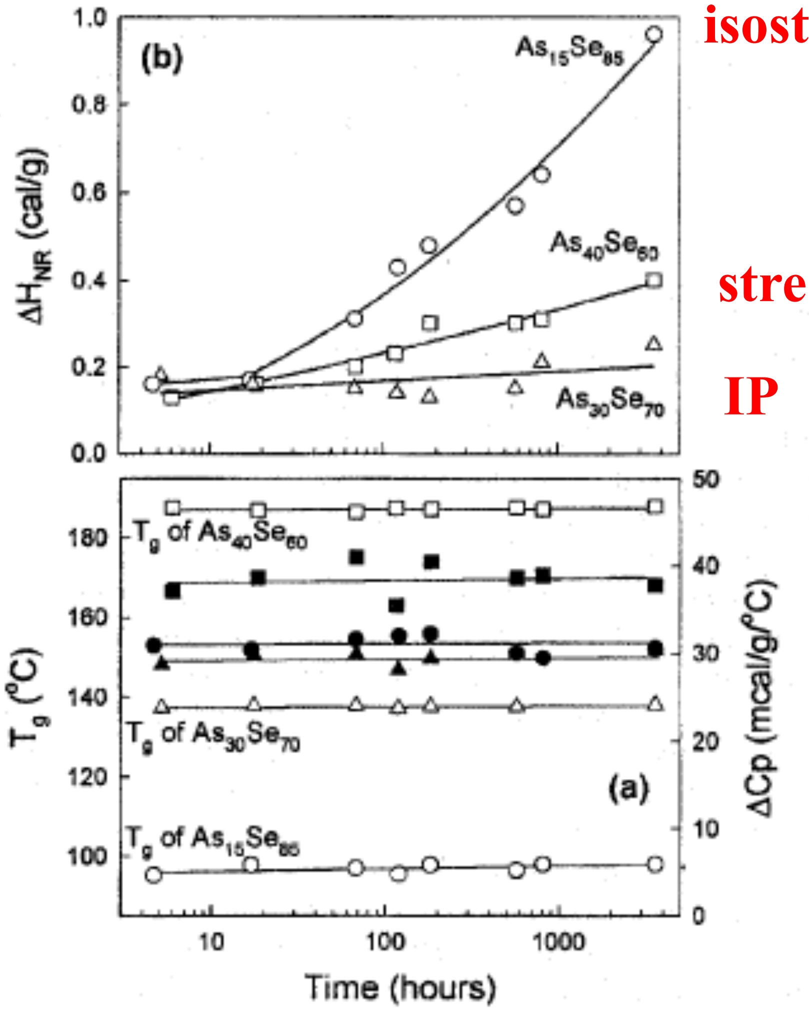
Not « no ageing » but « weak ageing »

$P_xGe_xSe_{1-2x}$



Chakravarthy et al. JPCM (2005)

As_xSe_{1-x}



isostatic

stressed

IP

Georgiev et al. JOAM (2003)

Fragility and relaxation

- ☐ Intermediate phase melts display anomalous relaxational properties.
  - ➢ the smallest measured fragilities (M=15). Silica (SiO_2) has M=20-28
  - ➢ Minimum in Kohlrausch exponent β.
  - ➢ Jump distances in solid electrolytes

Micoulaut et al. PRB 2009

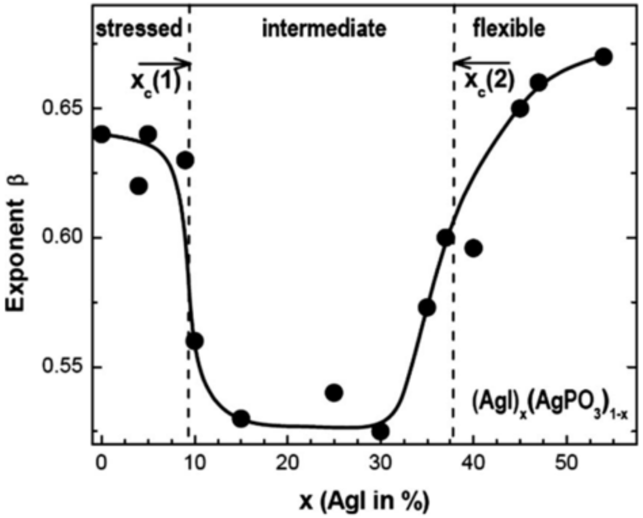
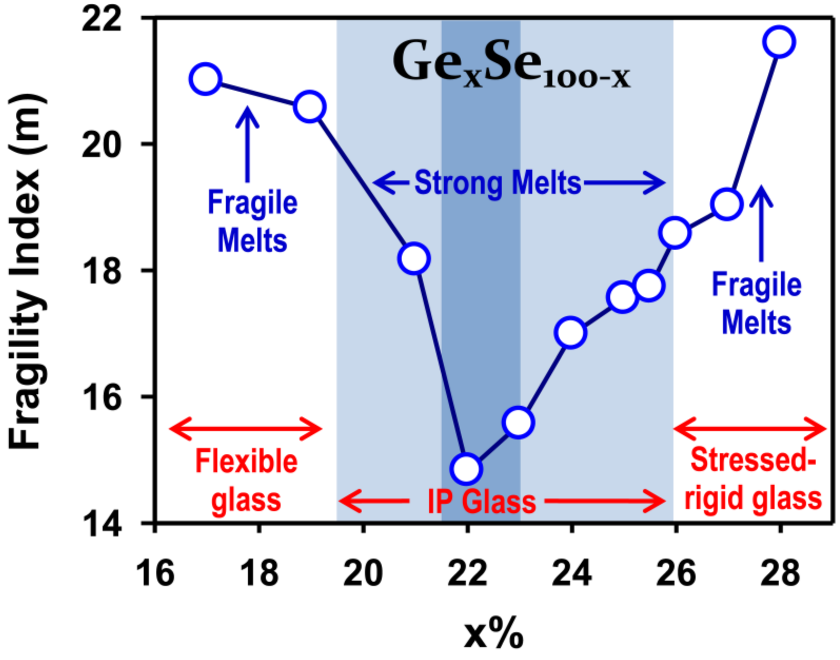
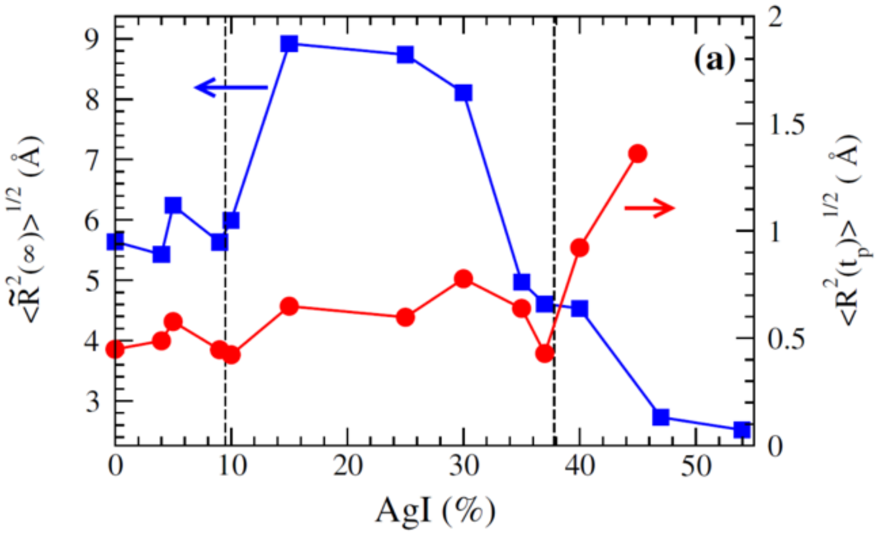


FIG. 6. Variations in the Kohlrausch stretched exponent $\beta(x)$ as a function of the AgI concentration x in $(AgPO_3)_{1-x}$-$(AgI)_x$ glasses.



Gunasekera et al. JCP 2013



Micoulaut, Malki, PRL 2010

B. INTERMEDIATE PHASE

Theory beyond the mean-field estimate ?

- ☐ **Obvious link with the mean-field rigidity transition (<r>=2.4)**

- ☐ **Central idea:** Self-organization or stress avoidance

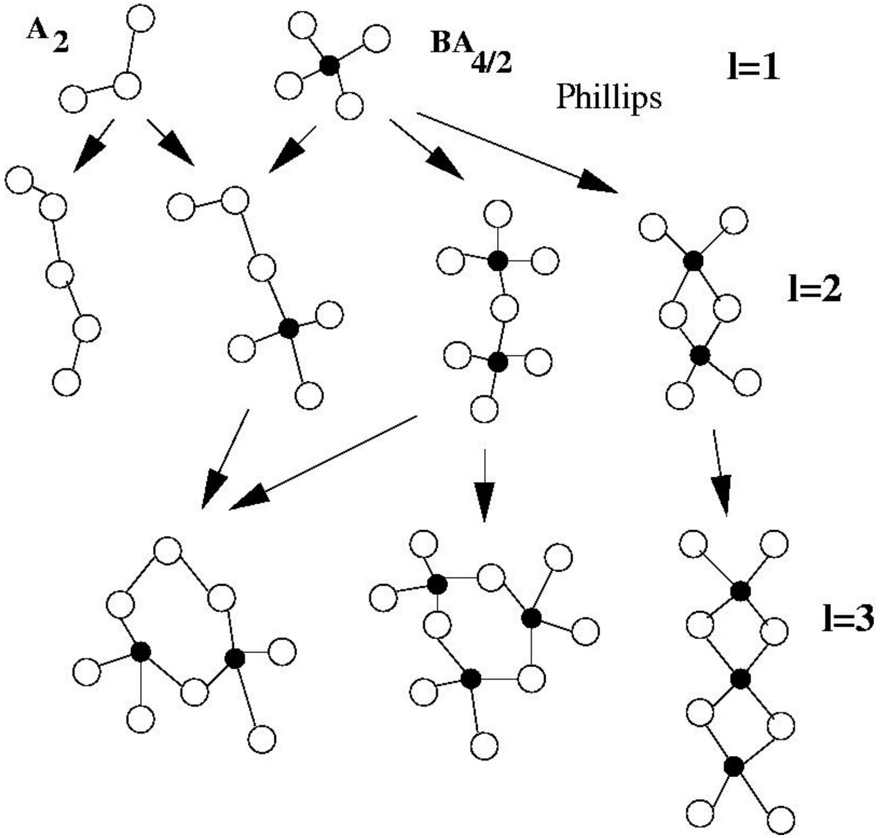
- ☐ **Strategies**
  - ☐ Lattice models : Normal mode analysis of self-organized networks
    Thorpe (2000), Mousseau (PRE 2006), Wyart (PRL 2013)

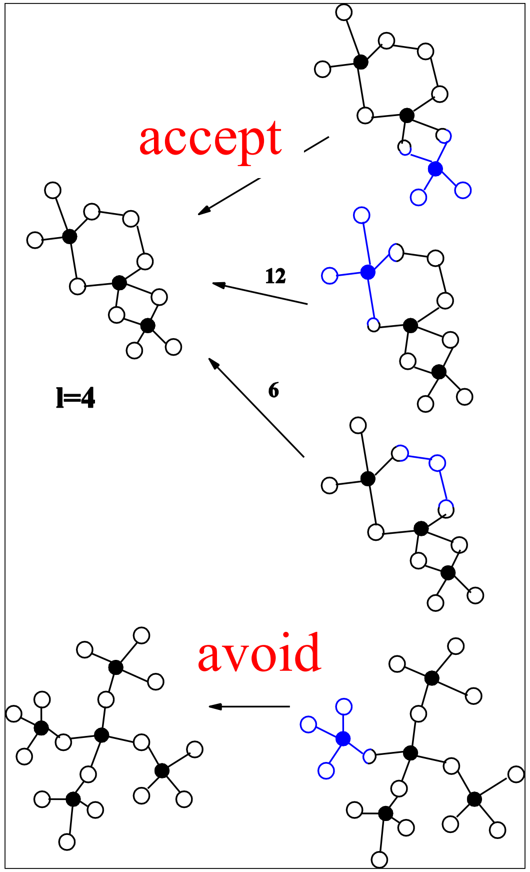
  - ☐ Cluster expansions
    Micoulaut (2003)

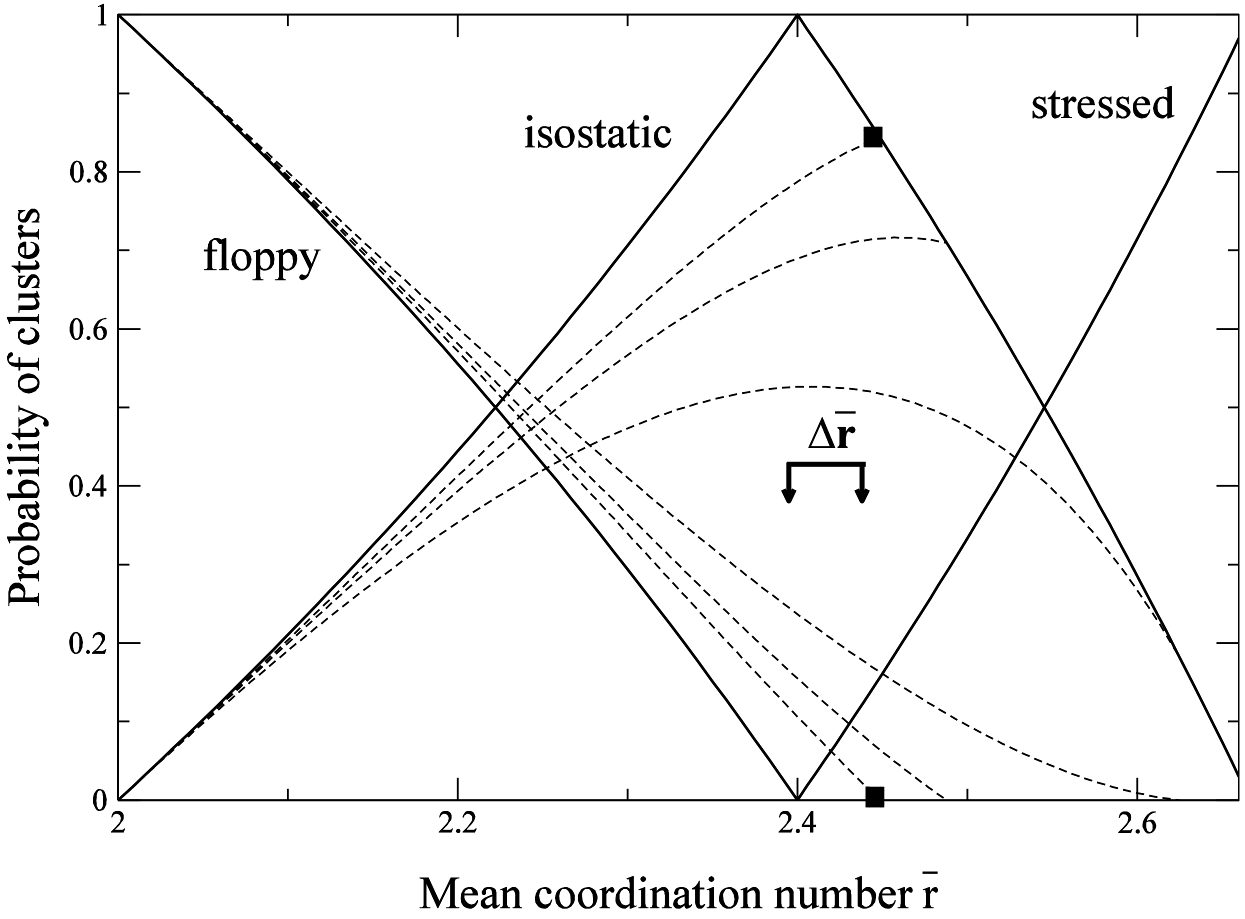
  - ☐ MD simulations
    See below

CLUSTER EXPANSIONS

- Build size increasing bond models (clusters) and use constraint counting algorithms.
- The basic level (the local structure) gives the mean-field result






floppy
isostatic
stressed
$\Delta\bar{r}$
Probability of clusters
0
0.2
0.4
0.6
0.8
1
2
2.2
2.4
2.6
Mean coordination number $\bar{r}$

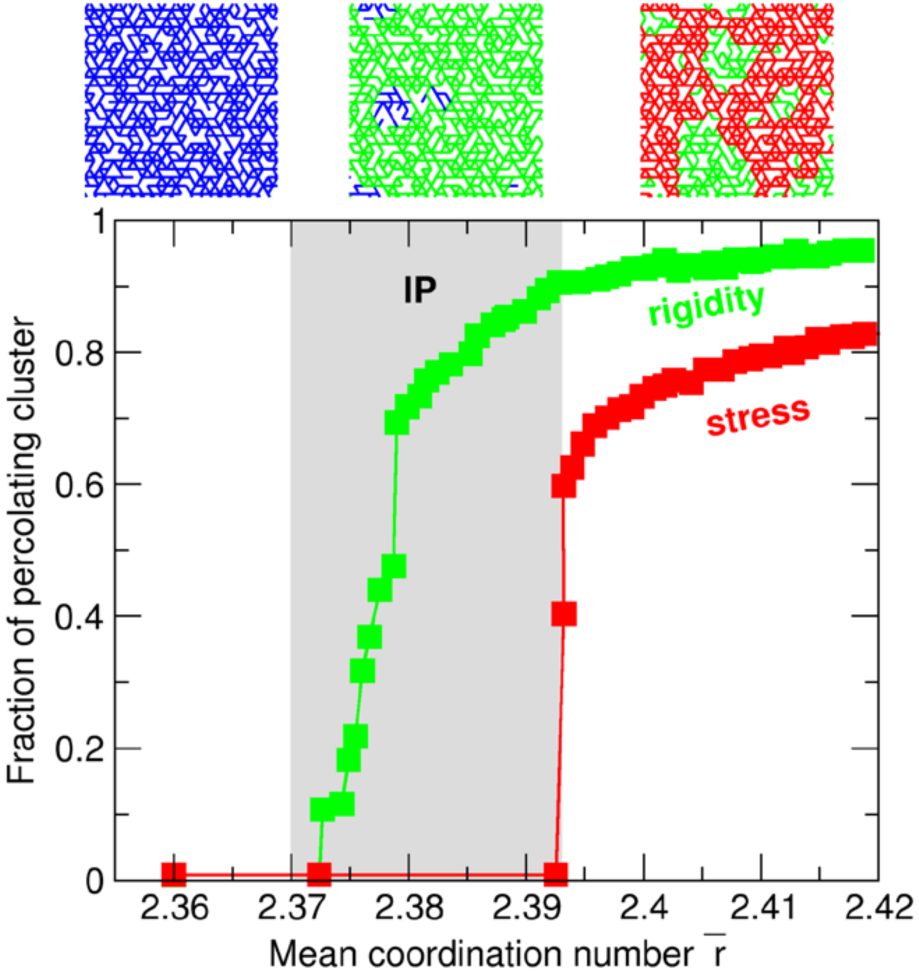
LATTICE MODELS

Analogy with simulations on triangular networks

- Single RT: Bonds removed randomly+eigenmode analysis.
- Decomposition of the network into rigid clusters + determination of all stressed rigid regions.
- **Self-organization**: bonds added in a flexible region of the network are accepted only if this leads to isostatically rigid clusters (and not stressed rigid).
- **Two transitions**: rigidity and stress. Both coalesce in random networks
- Temperature effect

  Brière et al. PRE 2006

  Le and Wyart, PRL 2013



Thorpe et al. JNCS 2000

C) Constraints and thermodynamics

- Hamiltonian of a system containing f floppy modes with zero frequency energy:

$$H = \sum_{j=1}^{3N} \frac{P_j^2}{2m} + \sum_{j=1}^{3N(1-f)} \frac{1}{2} m\omega_j^2 Q_j^2$$

- Out of which can be calculated a partition function:

$$Z = \int \cdots \int \prod_{j=1}^{N} dP_j dQ_j e^{-H/kT}$$

$$= \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \prod_{j=1}^{3N(1-f)} \left(\frac{2\pi kT}{m\omega_j^2}\right)^{1/2}$$

- Floppy modes are cyclic variables of H

- Provides a **channel in the potential energy** landscape (PES) since the energy does not depend upon a change in a floppy mode coordinate

Naumis, PRB 2000, 2005

Constraints and thermodynamics:

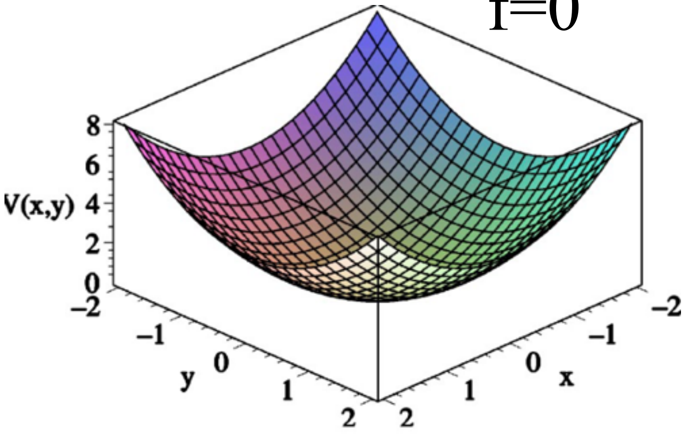
☐ For a given inherent structure (local minimum of the PES), the number of channels is given by *f*.

☐ Entropy due to floppy modes (available phase space to visit).

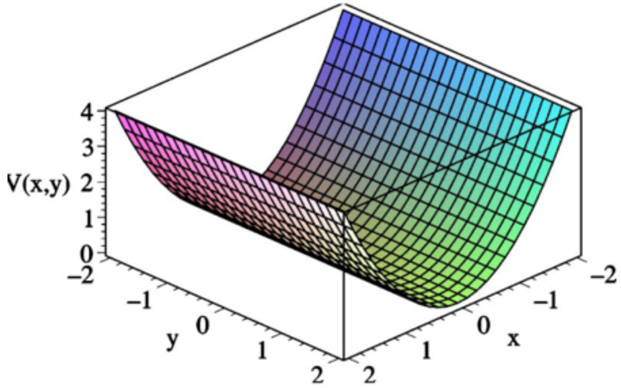
☐ At fixed volume, Ω(E,V,N) is proportional to the area defined by the surface f constant E. $S=k_B \ln\Omega$

$$\boxed{S \approx f\,3Nk_B \ln(V/V_0)}$$

f=0



f non zero



Naumis, Phys. Rev. E71, 026114 (2005).

D) Temperature dependent constraints

Basics

- ☐ Gupta & Mauro (2009) generalization of the Phillips approach by inclusion of temperature-dependent constraints:

$$n\left(T,x\right)=\sum_{i}N_i\left(x\right)\sum_{\alpha}w_{i,\alpha}q_{\alpha}\left(T\right)$$

- ☐ Required parameters:
  - ☐ $N_i(x)$: mole fraction of each network-forming species i
  - ☐ $w_{i,\alpha}$: number of α-type constraints for each species i
  - ☐ $q_{\alpha}(T)$: temperature-dependent rigidity of constraint α

Gupta & Mauro, *J. Chem. Phys.* 130, 094503 (2009)

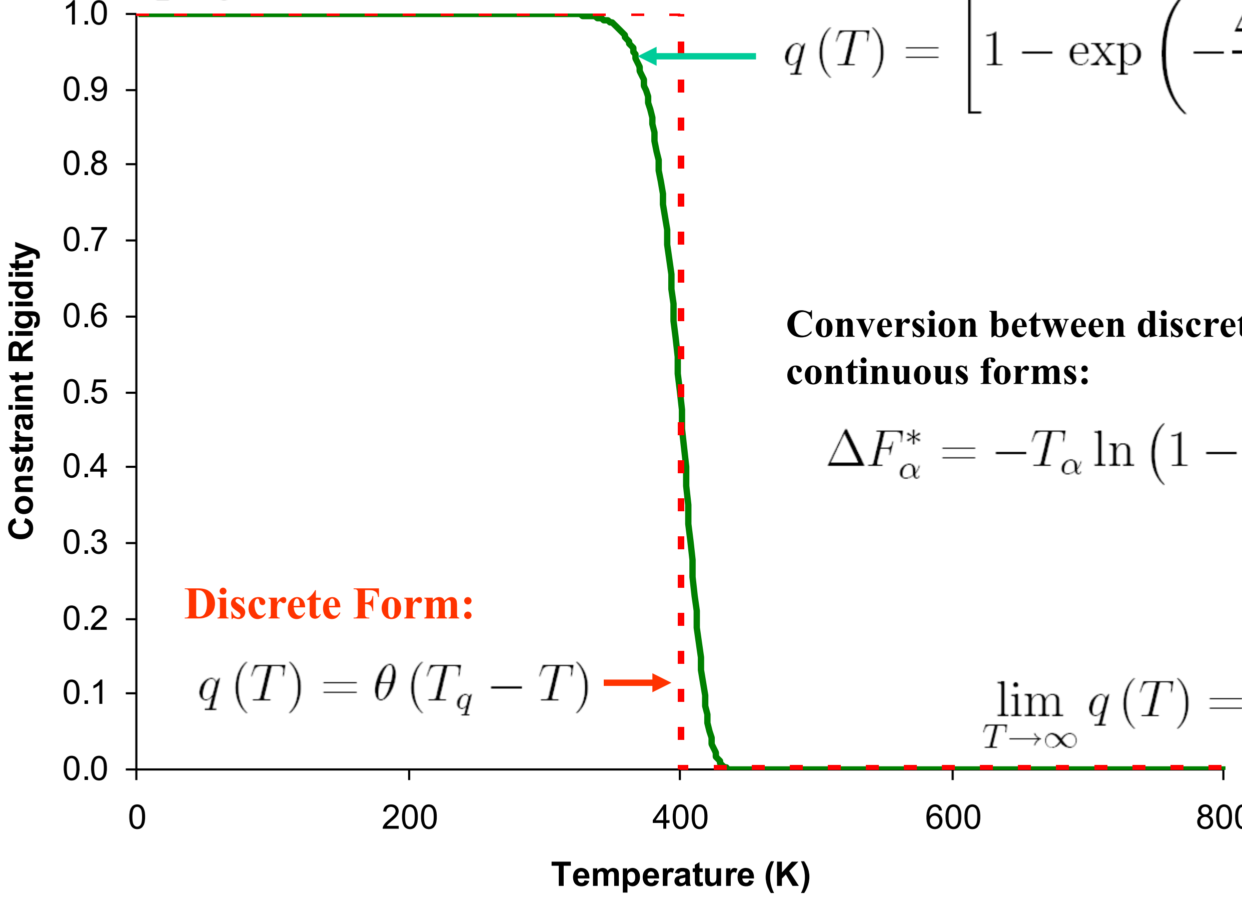
Mauro, Gupta, Loucks, *J. Chem. Phys.* 130, 234503 (2009)

$q_\alpha(T)$: temperature-dependent rigidity of constraint α

$$\lim_{T\to 0} q\left(T\right) = 1$$

Continuous Form:

$$q\left(T\right) = \left[1 - \exp\left(-\frac{\Delta F^*}{kT}\right)\right]^{\nu t_{obs}}$$



Conversion between discrete and continuous forms:

$$\Delta F_\alpha^* = -T_\alpha \ln\left(1 - 2^{-1/\nu t_{obs}}\right)$$

Discrete Form:

$$q\left(T\right) = \theta\left(T_q - T\right)$$

$$\lim_{T\to\infty} q\left(T\right) = 0$$

D) Temperature dependent constraints

Steps

1. Identify and count the number of network-forming species as a function of composition

2. Identify and count the number of constraints associated with each of those species

3. Rank the constraints in terms of their relative strength (onset temperature)

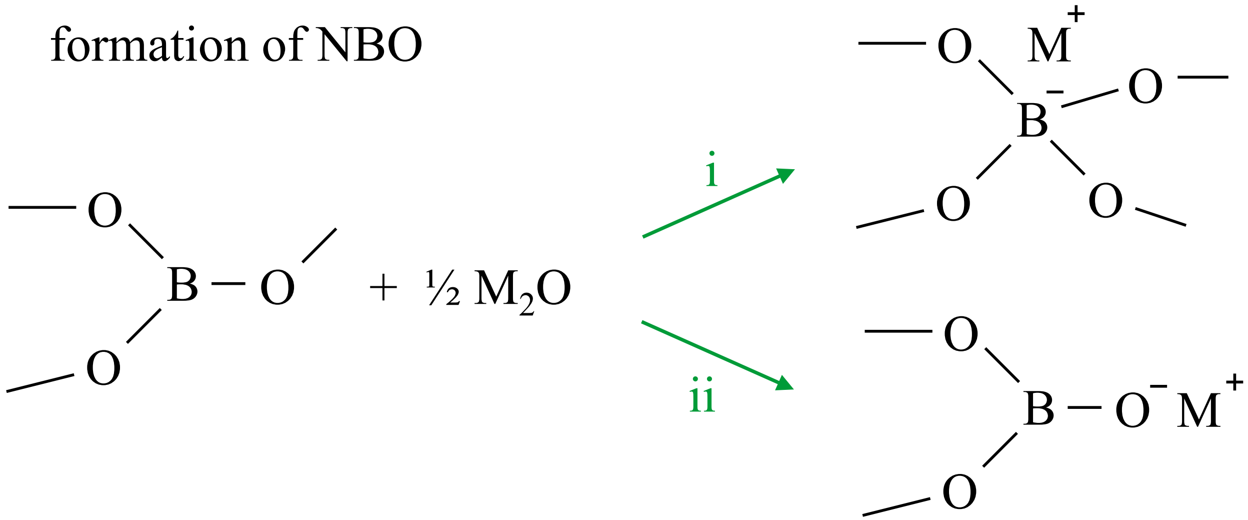
4. Connect the change in degrees of freedom ($f = d - n$) with change in specific property of interest

D) Temperature dependent constraints

Step 1: Model the local structure as a function of composition

- ☐ Applied to borate glasses Na_2O-B_2O_3

- ☐ Addition of modifier oxide to B_2O_3 can cause
  - ➢ boron coordination change
  - ➢ formation of NBO



- ☐ Remember of simple bond models for alkali borates for x>0.33

$$N_2(x) = \frac{3(3x-1)}{5(1-x)} \qquad N_3(x) = \frac{1-2x}{1-x} \qquad N_4(x) = \frac{3-4x}{5(1-x)}$$

D) Temperature dependent constraints

Step 1: Model the local structure as a function of composition

☐ Complete statistics

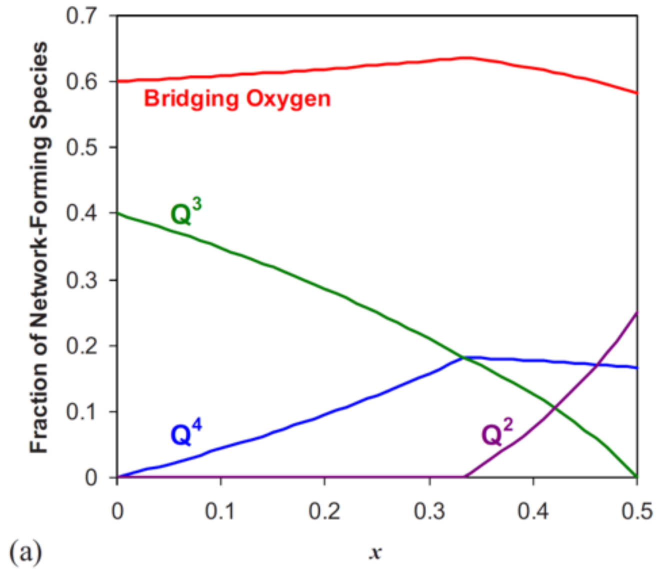
x>0.33 $$N_2(x) = \frac{3(3x-1)}{5(1-x)} \qquad N_3(x) = \frac{1-2x}{1-x} \qquad N_4(x) = \frac{3-4x}{5(1-x)}$$

x<0.33 $$N_3(x) = 1 - R = 1 - \frac{x}{1-x} = \frac{1-2x}{1-x}$$

$$N_4(x) = R = \frac{x}{1-x}$$

☐Can sometimes be re-expressed in terms of bonding oxygens (those participating to the network connectivity, i.e. N_B=4 on a B4).

$$N(Q^4) = \begin{cases} \dfrac{2x}{5-4x}, & x \le \dfrac{1}{3}, \\ \dfrac{6-8x}{31-38x}, & \dfrac{1}{3} < x \le \dfrac{1}{2}, \end{cases} \qquad N(\mathrm{O^B}) = \begin{cases} \dfrac{3-2x}{5-4x}, & x \le \dfrac{1}{3}, \\ \dfrac{21-28x}{31-38x}, & \dfrac{1}{3} < x \le \dfrac{1}{2}, \end{cases}$$



Mauro et al. JCP 2009

D) Temperature dependent constraints

Step 2: Count constraints on each atom (borates)

- ☐ α: B-O and M^{NB}-O linear (BS) constraints
  - Two α constraints at each oxygen

- ☐ β: O-B-O angular constraints
  - Five β constraints at each Q^4 unit.
  - Three at each Q^3 unit.

- ☐ γ: B-O-B and B-O-$M^{(NB)}$ angular constraints
  - One γ constraint at each bridging oxygen

- ☐ μ: modifier rigidity (due to clustering)
  - Two μ constraints per NBO-forming Na atom

Each involves an onset temperature at which q(T) becomes active for $T<T_{onset}$

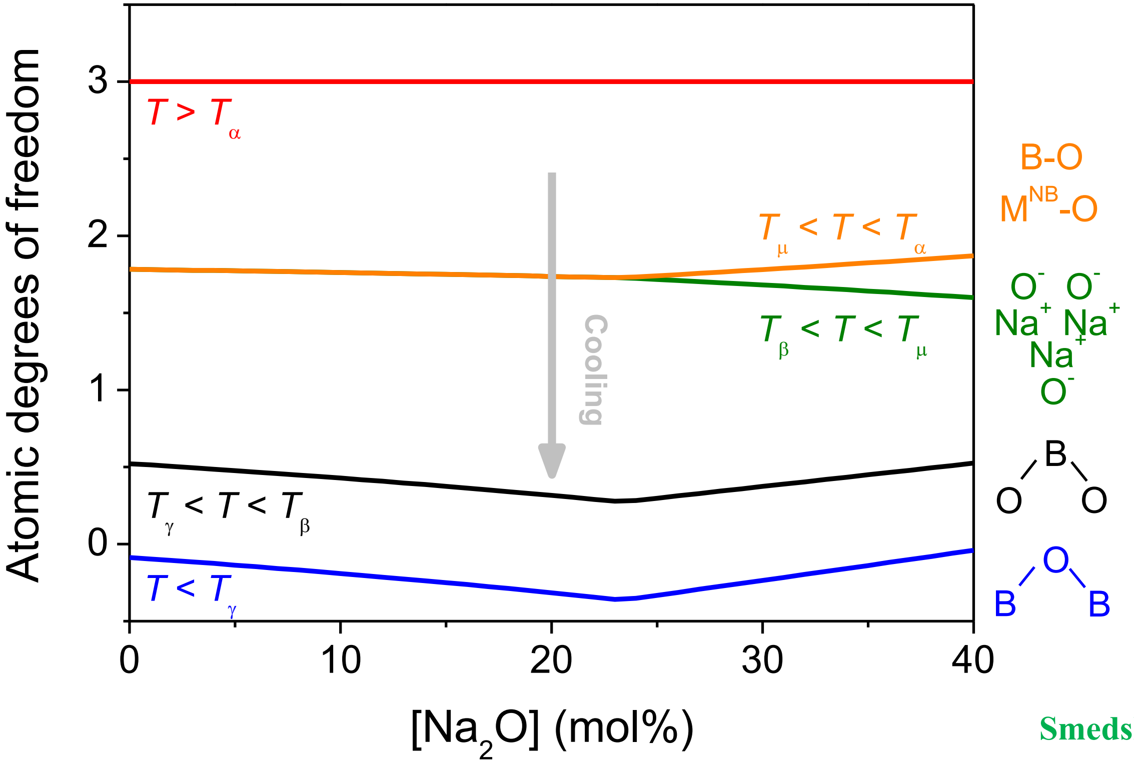
Similar procedure for borosilicates

D) Temperature dependent constraints

Step 3: Ranking of constraints according to temperature

$$T_\gamma < T_\beta < T_\mu < T_\alpha$$

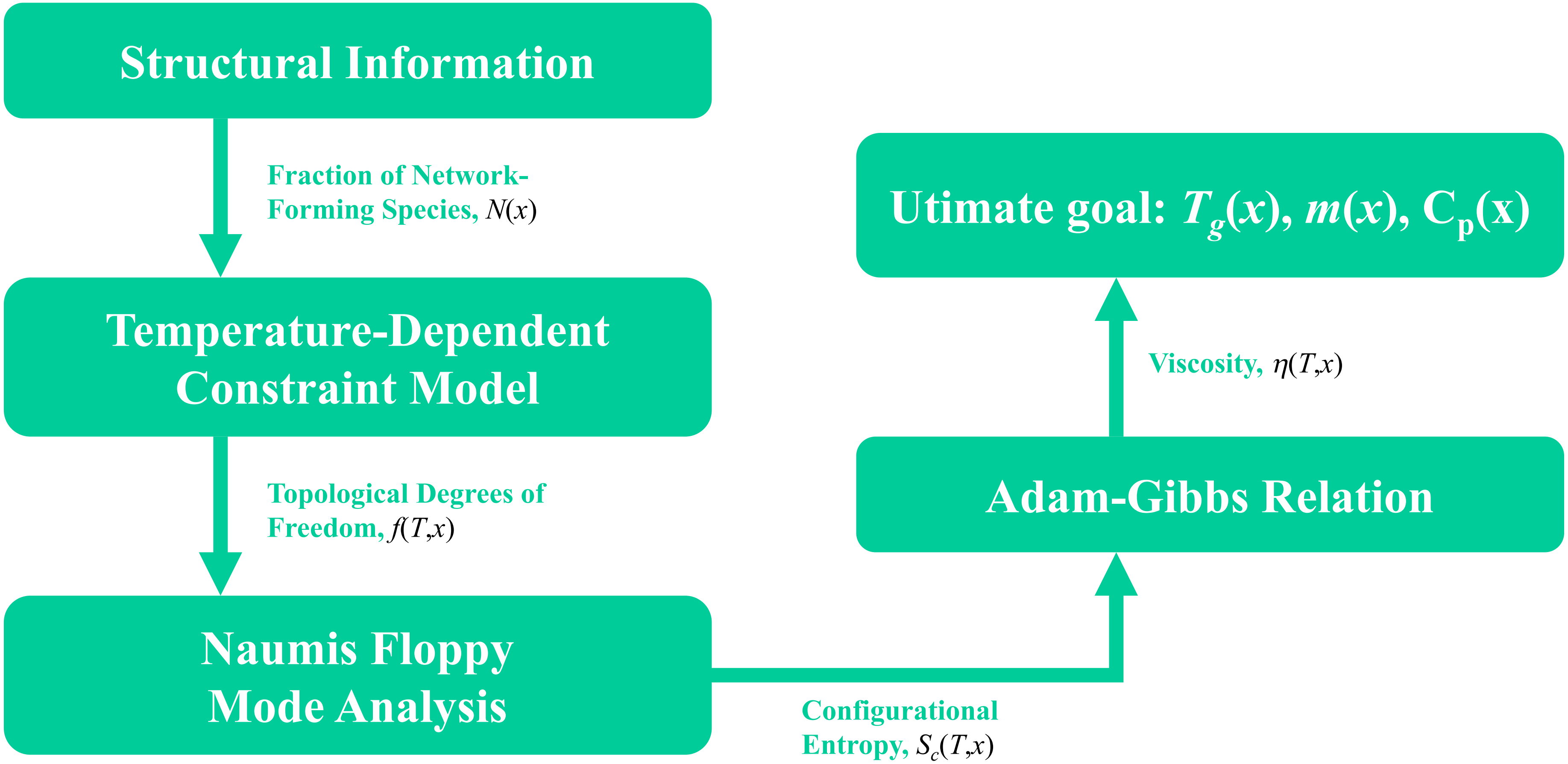
- Constraints become rigid as temperature is lowered
  - Onset temperatures:



Smedskjaer, Mauro, Sen, Yue, *Chem. Mater.* 22, 5358 (2010)

D) Temperature dependent constraints

Step 4: Calculating properties…the roadmap



Structural Information

Fraction of Network-Forming Species, $N(x)$

Temperature-Dependent Constraint Model

Topological Degrees of Freedom, $f(T,x)$

Naumis Floppy Mode Analysis

Configurational Entropy, $S_c(T,x)$

Adam-Gibbs Relation

Viscosity, $\eta(T,x)$

Utimate goal: $T_g(x)$, $m(x)$, $C_p(x)$

D) Temperature dependent constraints

Step 4: Calculating properties

A. Use Adam-Gibbs definition of viscosity

$$\log_{10}\ \eta(T,x) = \log_{10}\ \eta_\infty + \frac{B(x)}{TS_c(T,x)}$$

B. Use the fact that T_g is the reference temperature at which $\eta=10^{12}$ Pa.s. Since η is constant for any composition, we can write:

$$\frac{T_g(x)}{T_g(x_R)} = \frac{S_c[T_g(x_R),x_R]}{S_c[T_g(x),x]}$$

C. Remember that Naumis' model leads to S_c # f (floppy modes).

D. This allows writing:

$$\frac{T_g(x)}{T_g(x_R)} = \frac{f[T_g(x_R),x_R]}{f[T_g(x),x]} = \frac{d-n[T_g(x_R),x_R]}{d-n[T_g(x),x]}$$

D) Temperature dependent constraints

Step 4: Calculating properties

Establishing a new viscosity fitting formula (MYEGA)

$$\log_{10}\eta(T,x) = \log_{10}\eta_\infty(x) + \frac{B(x)}{TS_c(T,x)}$$

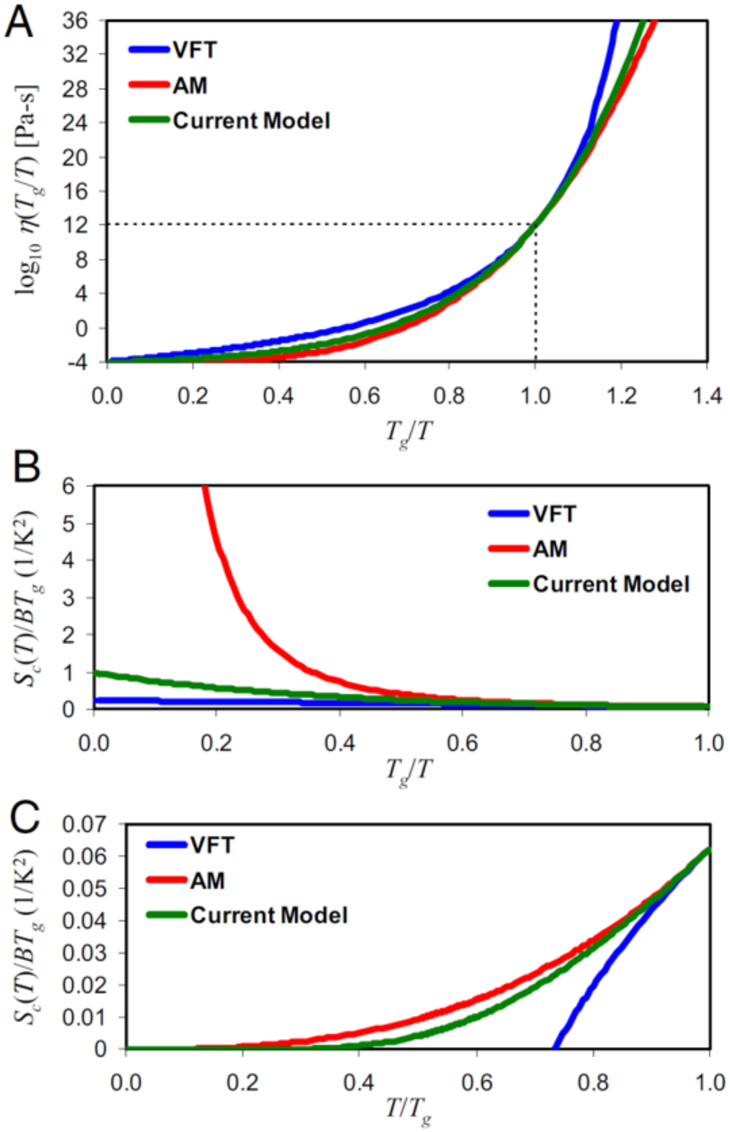
Simple two-state model assuming that f(HT)=3 and f(LT)=0 (no topological degrees of freedom in the glass)

$$f(T,x) = 3\exp\left(-\frac{H(x)}{kT}\right)$$

$$\log_{10}\eta(T,x) = \log_{10}\eta_\infty(x) + \frac{K(x)}{T}\exp\left(\frac{C(x)}{T}\right)$$

$$\log_{10}\eta(T) = \log_{10}\eta_\infty + (12 - \log_{10}\eta_\infty)\frac{T_g}{T}\exp\left[\left(\frac{m}{12-\log_{10}\eta_\infty} - 1\right)\left(\frac{T_g}{T} - 1\right)\right]$$

No divergence found at HT (AM) or at LT (VFT)



Mauro et al. PNAS (2009)

D) Temperature dependent constraints

Step 4: Calculating properties

D. Remember the definition of fragility :

$$m(x) \equiv \left. \frac{\partial \log_{10} \eta(T,x)}{\partial [T_g(x)/T]} \right|_{T=T_g(x)}$$

E. Using Naumis' definition, once more, one obtains:

$$m(x) = m_0 \left(1 + \left. \frac{\partial \ln f(T,x)}{\partial \ln T} \right|_{T=T_g(x)} \right)$$

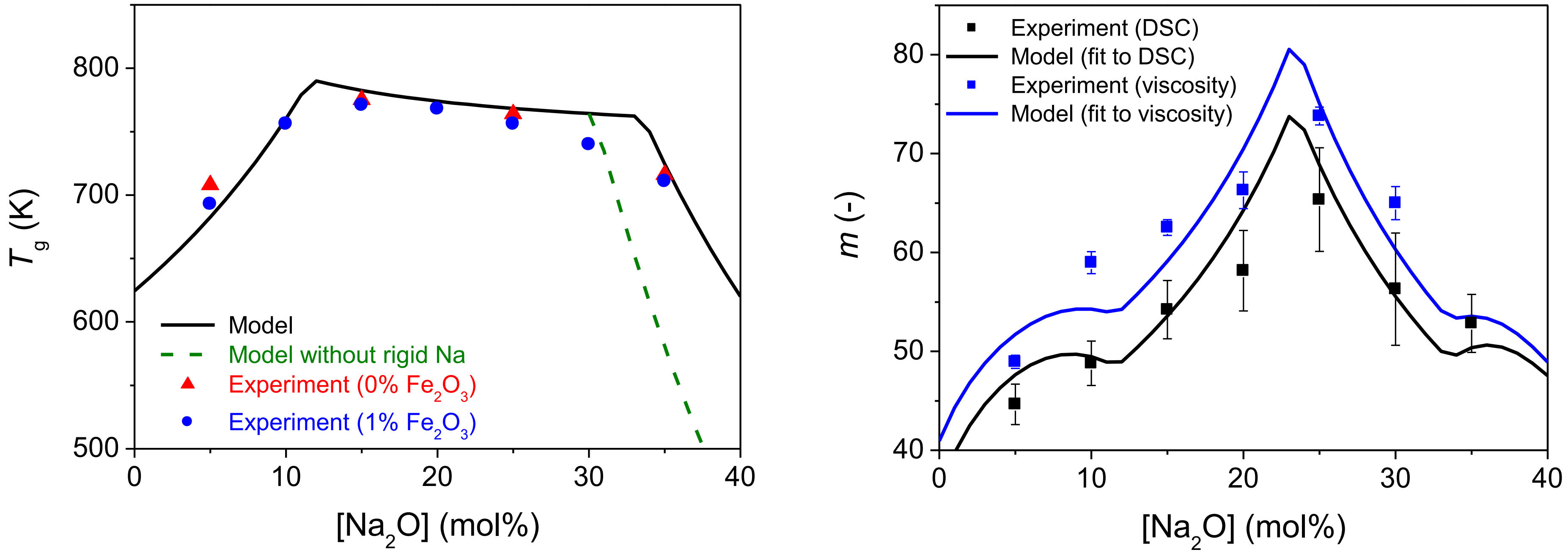
F. Application to sodium borates

$$n(T_g(x),x) = \begin{cases} \dfrac{12-6x}{5-4x}, & x \le \dfrac{1}{3}, \\ \dfrac{96-138x}{31-38x}, & \dfrac{1}{3} < x \le \dfrac{1}{2} \end{cases}$$

$$T_g(x) = \begin{cases} \dfrac{1}{5}\left(\dfrac{5-4x}{1-2x}\right) T_g(0), & x \le \dfrac{1}{3}, \\ \dfrac{1}{11}\left(\dfrac{31-38x}{8x-1}\right) T_g\left(\dfrac{1}{3}\right), & \dfrac{1}{3} < x \le \dfrac{1}{2}, \end{cases}$$

D) Temperature dependent constraints

Results: Fragility and Tg variation of calcium borate glasses

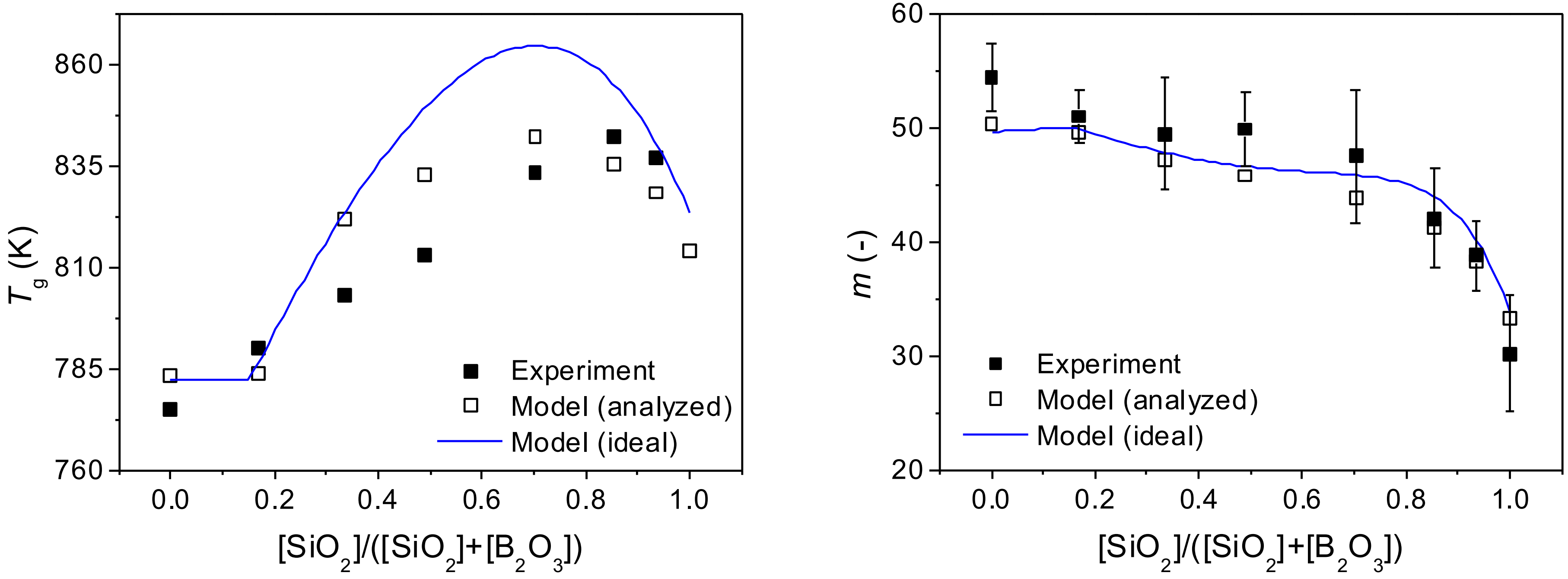


- Na sets up a locally rigid environment, whereas Ca does not
- Prediction of fragility with only one fitting parameter (vt_{obs})

Smedskjaer, Mauro, Sen, Yue, *Chem. Mater.* 22, 5358 (2010)

D) Temperature dependent constraints

Results: Fragility and Tg variation of sodium borosilicate glass

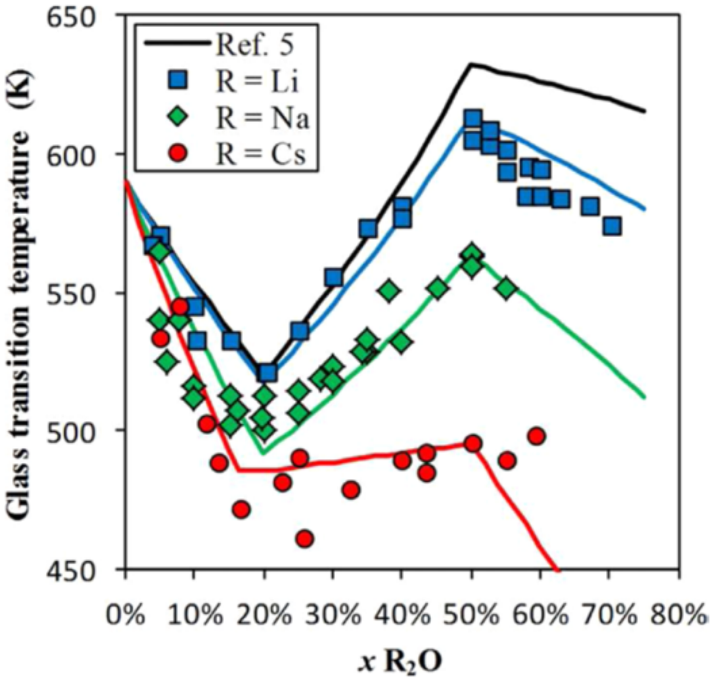


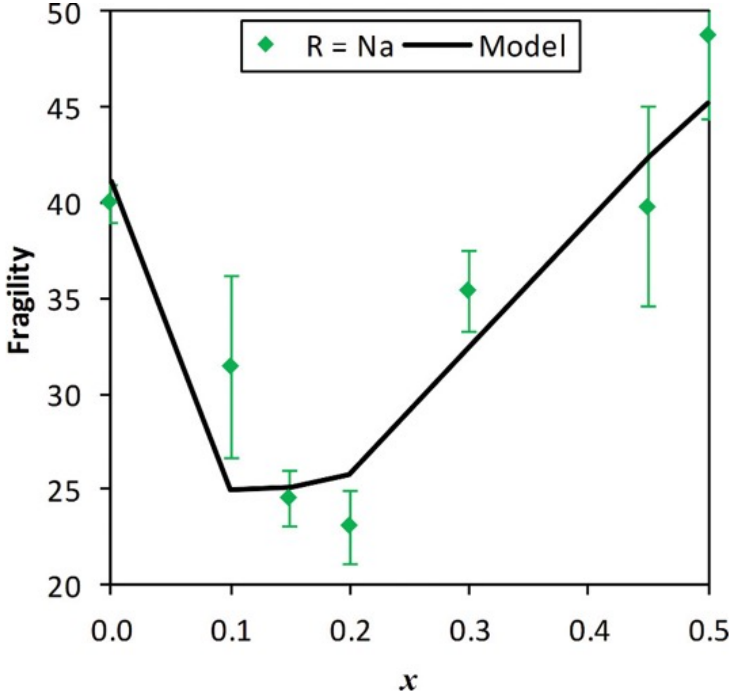
- ❑ T_g of a borate glass can be predicted from that of a silicate glass with $f(x,y,z,T)$ as the only scaling parameter
- ❑ Fragility: onset temperatures $T_{\beta,Si}$ and T_μ are treated as fitting parameters (1425 K)

Smedskjaer et al., *J. Phys. Chem. B* 115, 12930 (2011)

D) Temperature dependent constraints

Results: Tg and fragility variation of alkali phosphate glass





Hermansen et al. JCP 140, 154501 (2014)

Rodrigues et al. *J. Non-Cryst. Solids* **405** 12 (2014)

D) Temperature dependent constraints

Results: Calculating the hardness from constraints

- Idea: critical number of constraints (n_{crit}) must be present for material to display mechanical resistance
  - $n = 2$: rigidity in one dimension (Se)
  - $n = 3$: rigidity in three dimensions (SiO_2)
  - $n = 2.5$: rigid 2D structure (graphene) → n_{crit}

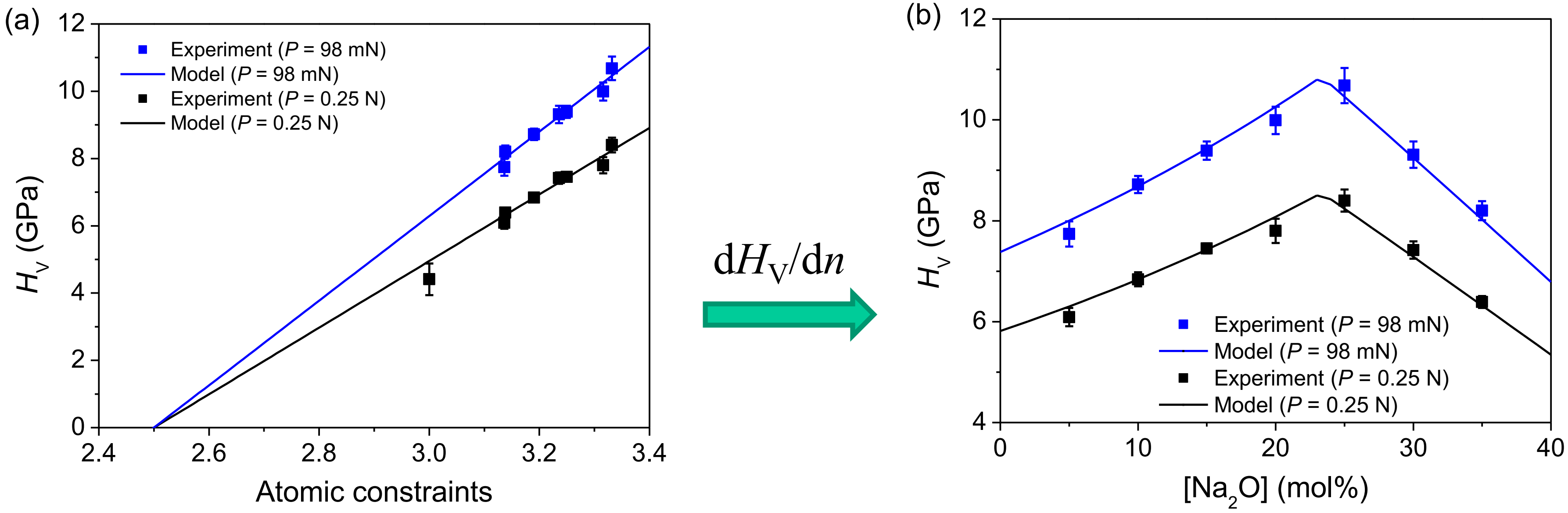
- Proposal: hardness is proportional to the number of 3D network constraints at room temperature

$$
\begin{aligned}
H_V(x, y) &= \left(\frac{dH_V}{dn}\right)[n(x, y) - n_{\mathrm{crit}}] \\
&= \boxed{\left(\frac{dH_V}{dn}\right)}[n(x, y) - 2.5].
\end{aligned}
$$

?

D) Temperature dependent constraints

Results: Hardness H_v in borates and borosilicates

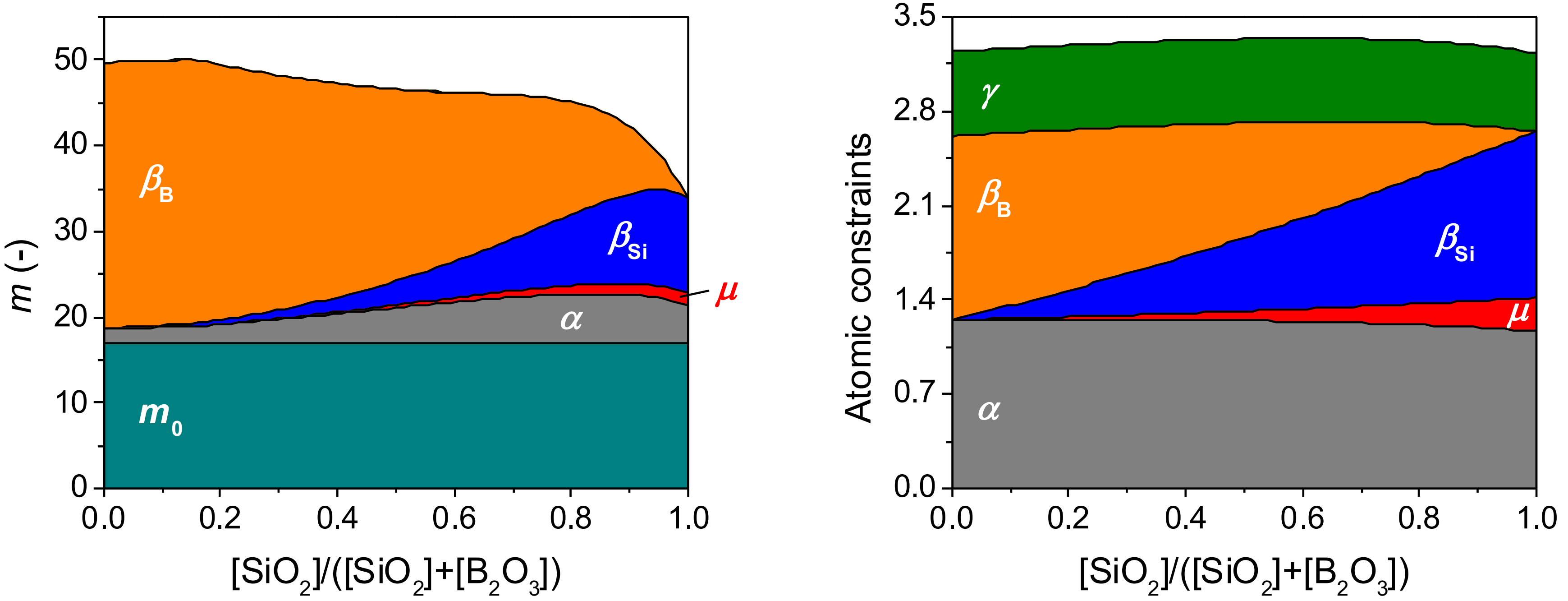


- Glass hardness can be predicted from the average number of room temperature constraints, with only an unknown proportionality constant ($\mathrm{d}H_V/\mathrm{d}n$)

Smedskjaer, Mauro, Yue, *PRL* 105, 115503 (2010)

D) Temperature dependent constraints

Origins of Properties (borosilicates)

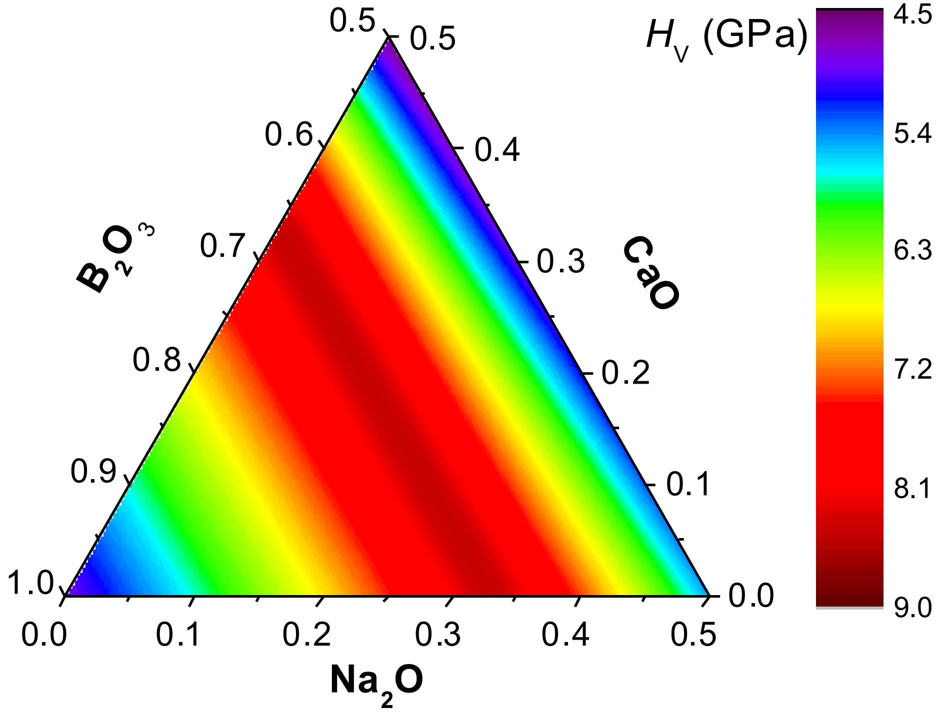


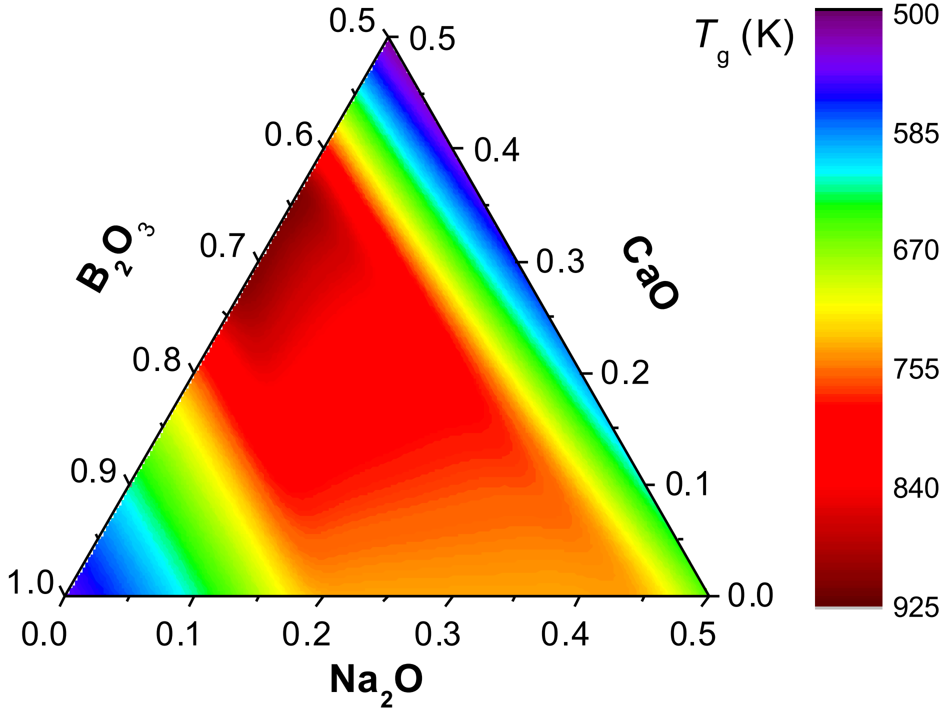
- γ and μ constraints have a negligible impact on fragility, whereas the β_B constraints are the main contributors
- α and γ constraints contribute significantly to hardness

Smedskjaer, Mauro, Youngman, Hogue, Potuzak, Yue, *J. Phys. Chem. B* **115**, 12930 (2011)

D) Temperature dependent constraints

Results: Quantitative designe of glasses (borates)





- ❑ **Topological engineering**: exploring new composition spaces where glasses have not yet been melted
- ❑ Difference in scaling is due to T-dependence of constraints

D. MD BASED RIGIDITY THEORY

1. We start from the estimation of constraints:

$$\boxed{n_c = \frac{\sum_{r\geq 2} n_r \left[r/2 + (2r-3)\right]}{\sum_{r\geq 2} n_r} = \frac{\bar{r}}{2} + 2\bar{r} - 3}$$

Questions and limitations

- ☐ **Phase separation ?** Isolated molecular units, As-Ge-S,…

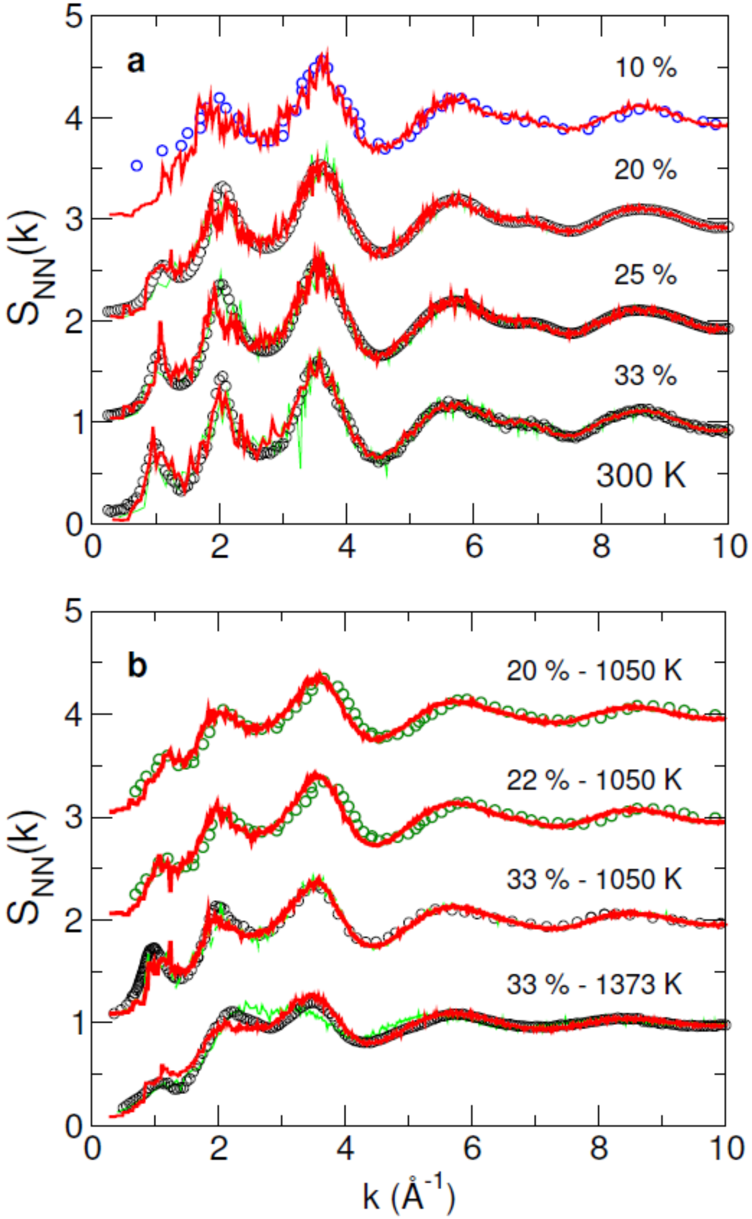
- ☐ **Coordination number, always 8-N ?**
  - CN(Na)=5 in silicates,
  - CN(As)=4 in certain As-Se and P-(Se,S) compositions,…
  - Delocalisation, non-directional (ionic) bonding…

- ☐ **Count all interactions (constraints) ?**
  - Broken Si-O-Na angular constraints in oxides,…
  - Thermally activated broken constraints (Mauro-Gupta)

- ☐ **n_c at all thermodynamic conditions (T,P,x)**

Need to have a good starting MD generated structural model

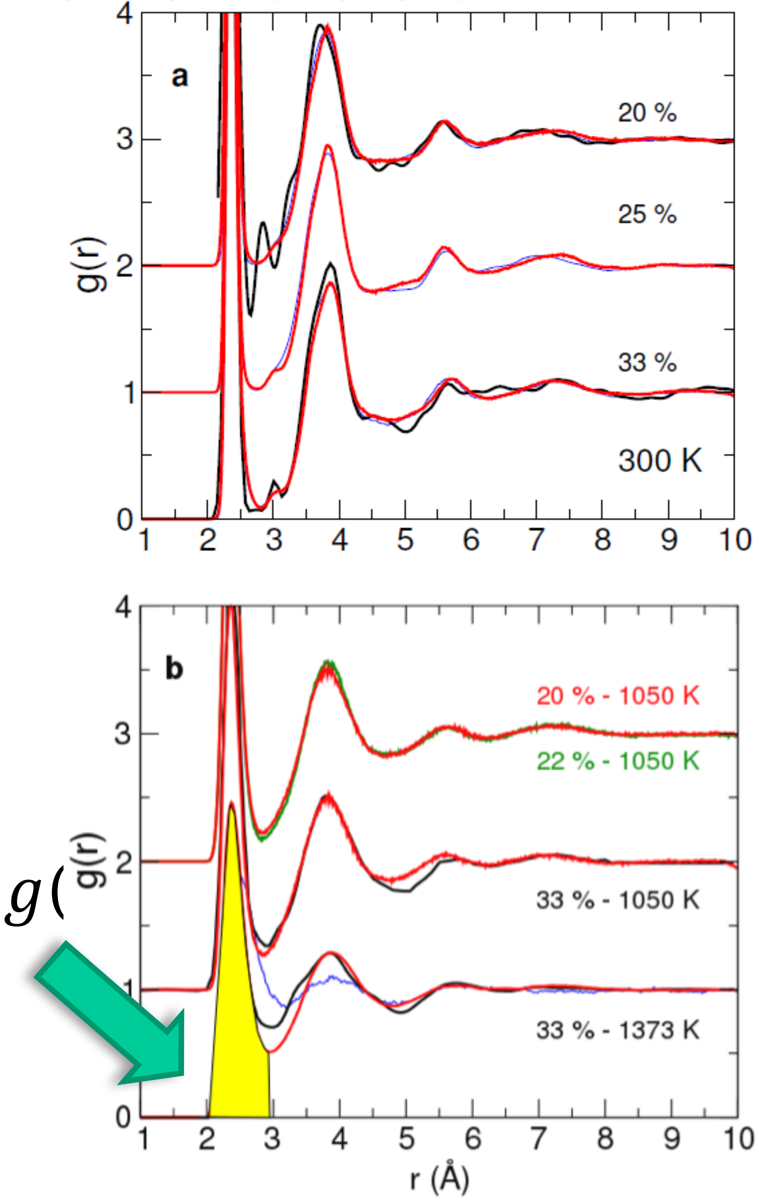
Structure Factors



Ge_xSe_{100-x}

$$CN = \rho 4\pi r^2 \int_0^r g($$

Pair Correlation Functions



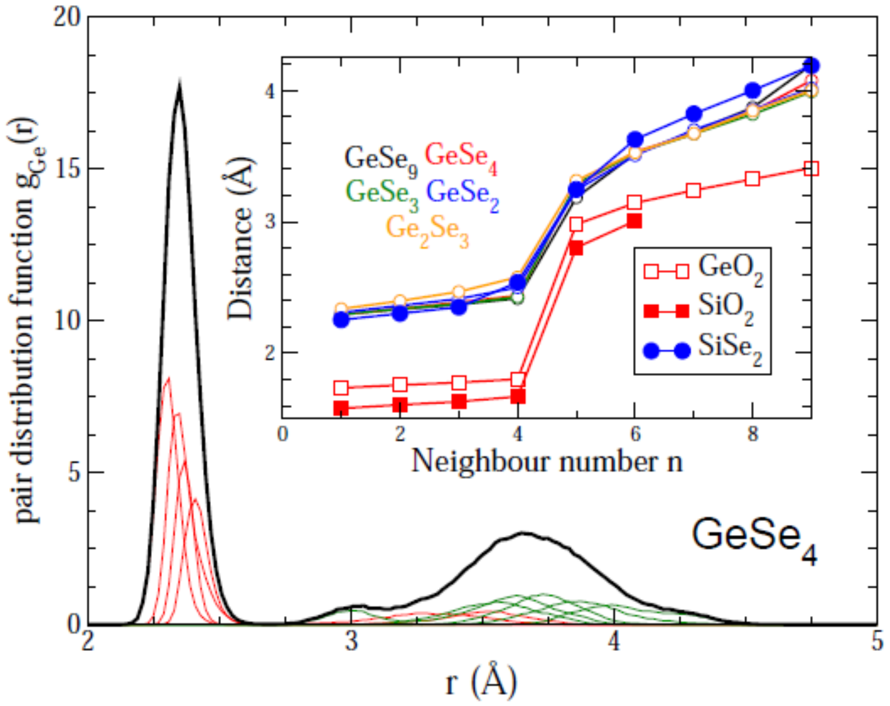
Salmon JNCS 1999 - Rao et al. JNCS 1998- Penfold, Salmon PRL 1991 – Massobrio et al. JPCM 2000, Petri, Salmon, Howells, JPCM 1999, Massobrio et.al PRB 2009, Micoulaut et al. PRB 2009

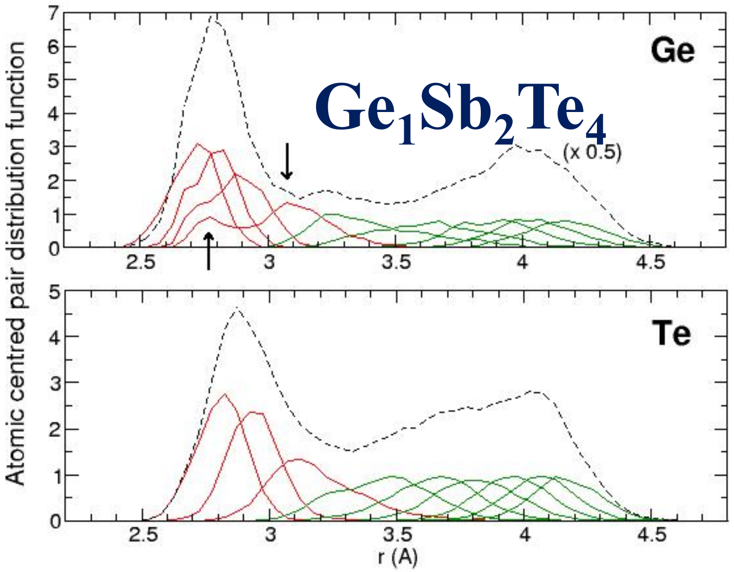
2. General idea:

❑ Generate atomic trajectories for a given system at (x,P,T) using Molecular Dynamics simulations (classical or First Principles)

❑ Compute from these trajectories

1. bond-stretching (# nb of neighbours or neighbor distribution)





Straightforward in oxydes and

4 neighbours around Ge,Si

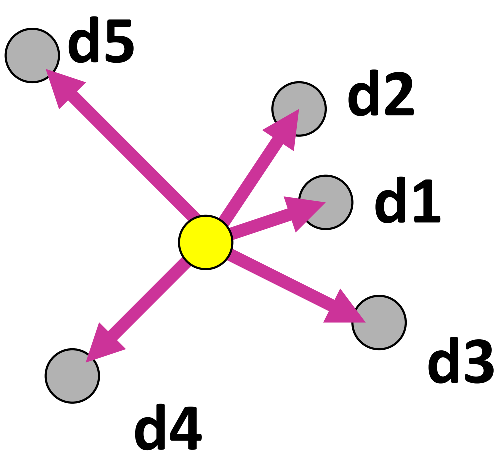
❖ two local environments for Ge

❖ CN(Te) >2

Micoulaut et al. PRB 2010

❑ Compute from these trajectories

1. bond-bending (work on angles)



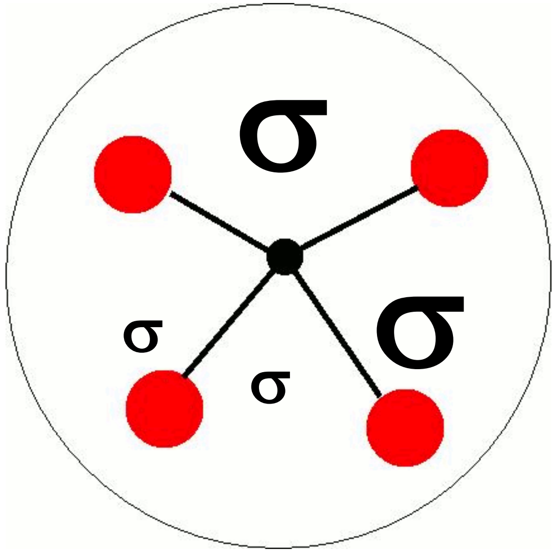
N first neighbor distance distrib.

- N(N-1)/2 bond angles analyzed (102), (103) … (304) … (N-1 0 N)

Peugeot labelling

- Not all are independent !

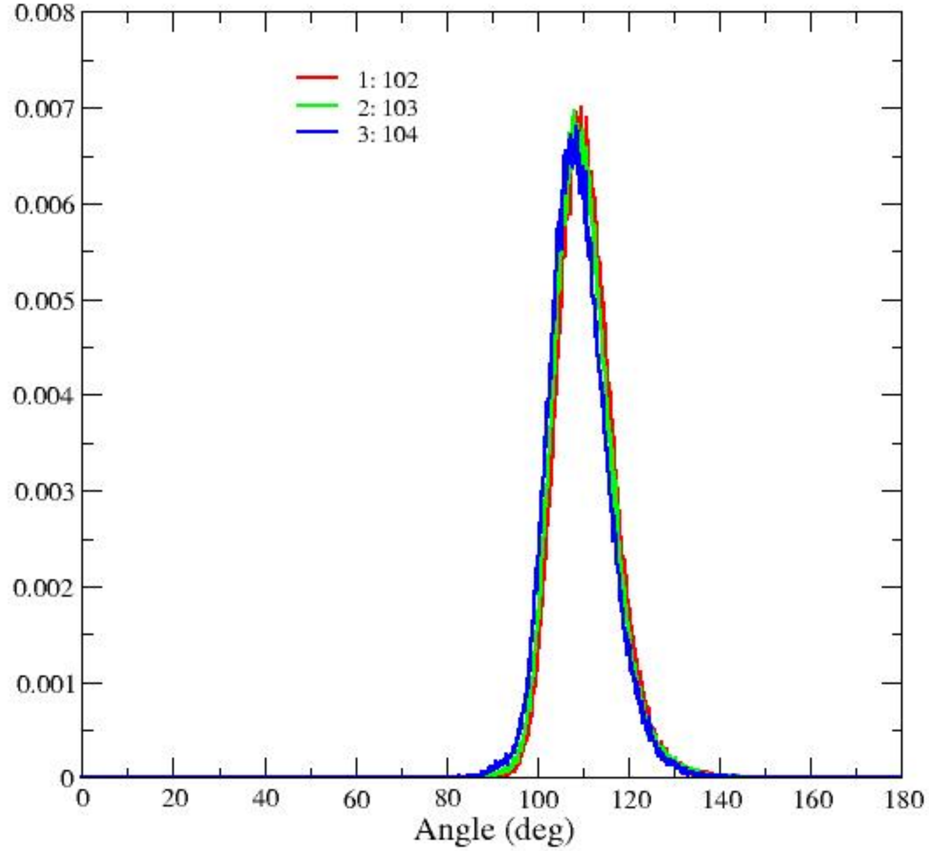
Estimate of bond-bending from <u>partial bond angle distribution (PBAD) $P_i(\theta)$</u>
with i<N(N-1)/2 arbitrary for a given atomic j0k triplet



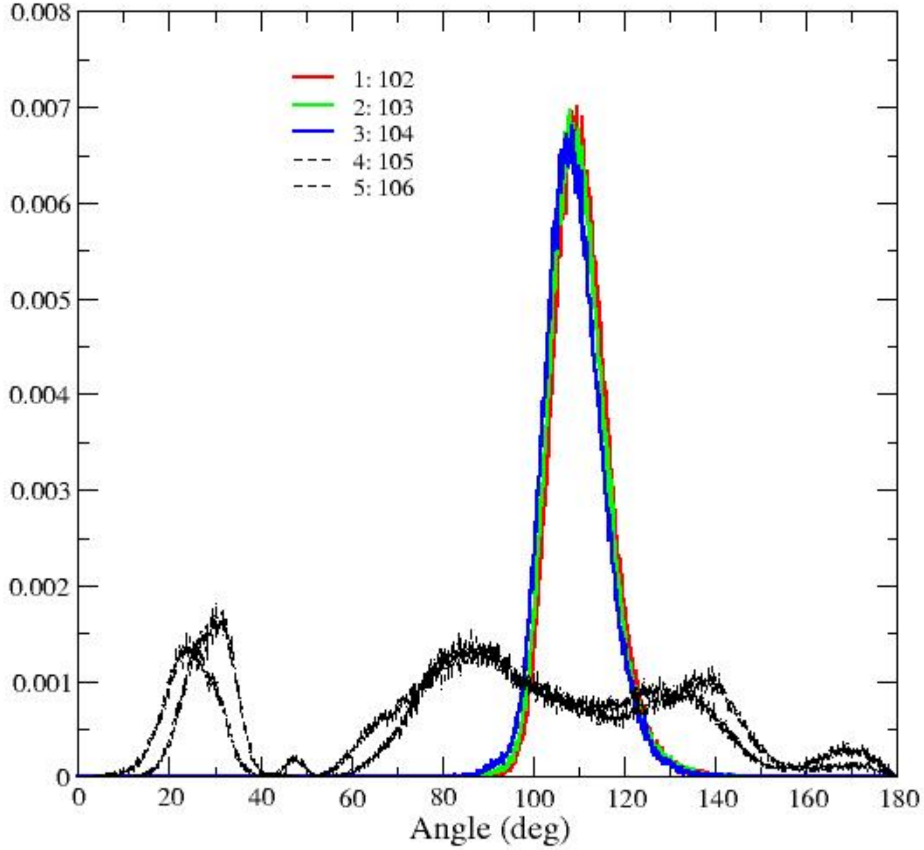
- Splitting the BAD into contributions from neighbours.
- Compute the second moment (σ_i , sometimes fwhm) of each PBA Distribution.

$$\langle {\theta_i}^2 \rangle = \int \theta^2 P_i(\theta) d\theta \qquad {\sigma_i}^2 = \langle {\theta_i}^2 \rangle - \langle \theta_i \rangle^2$$

Ge-centred PBAD in GeO_2 for arbitrary N=6

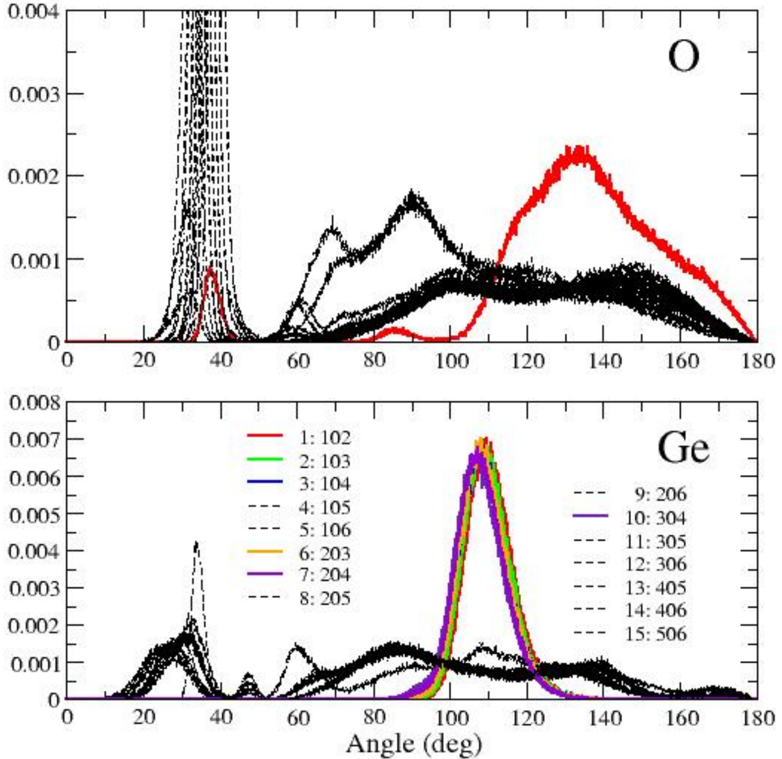


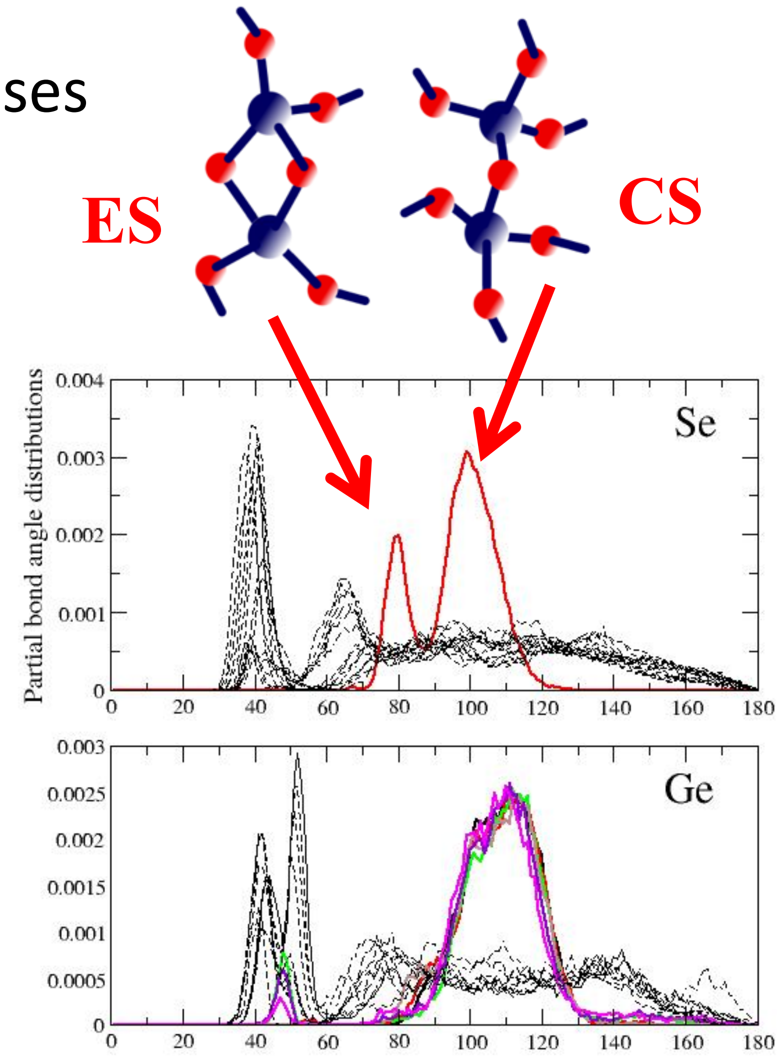
Ge-centred PBAD in GeO_2 for arbitrary N=6



Large $\sigma_{\theta ij}$: broken constraint. Weak restoring force that maintains a mean angle fixed

PBADs for tetrahedral network glasses





GeO_2

Large O-centred angular motion

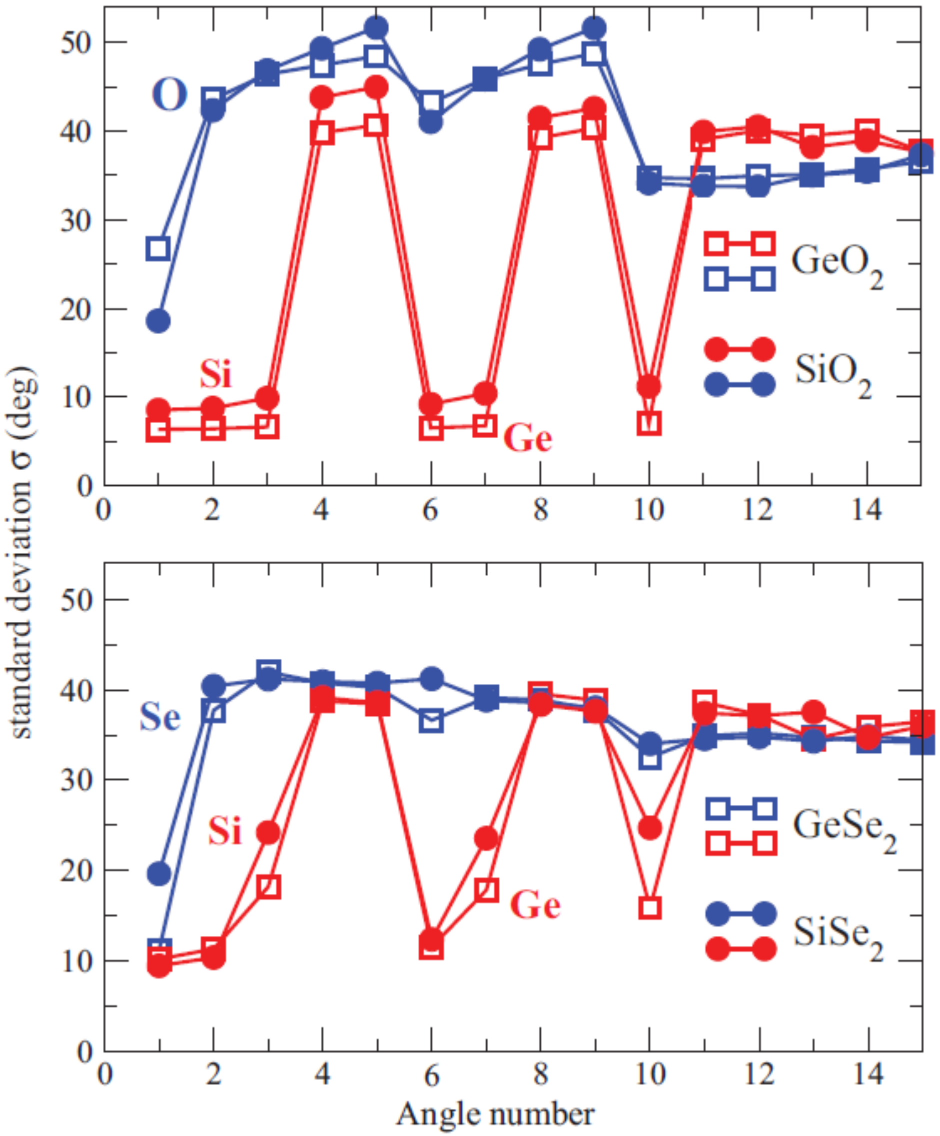
Tetrahedral angle (109°) well defined

$GeSe_2$

Bimodal (ES vs CS) Se-centred distribution

Tetrahedral angle well defined and broader

Standard deviations for tetrahedral network glasses



- **Angular counting from MD matches direct Maxwell counting**

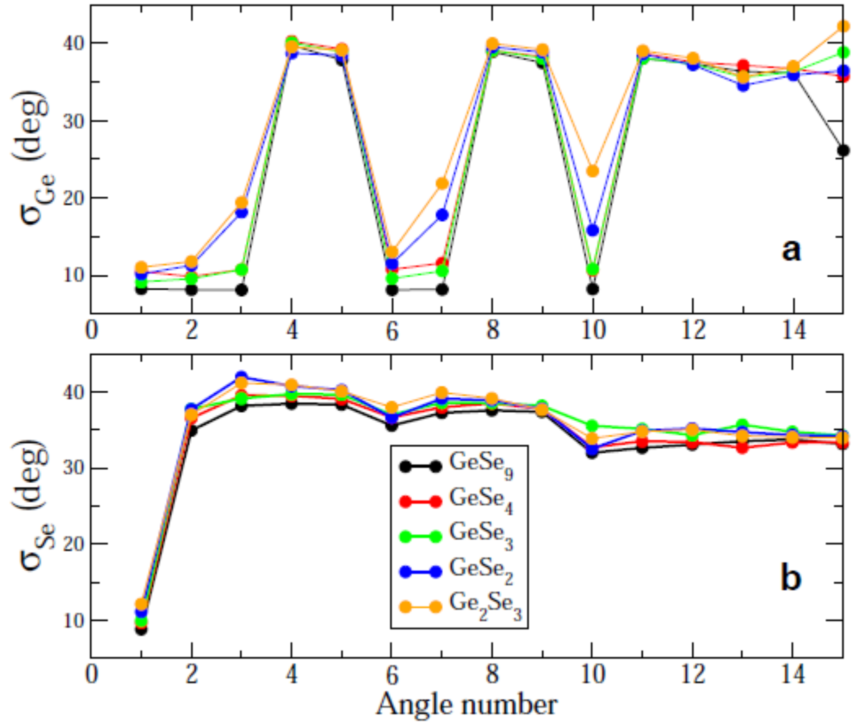
- 6 Ge,Si angles have a low standard deviation (but only 5 independent)

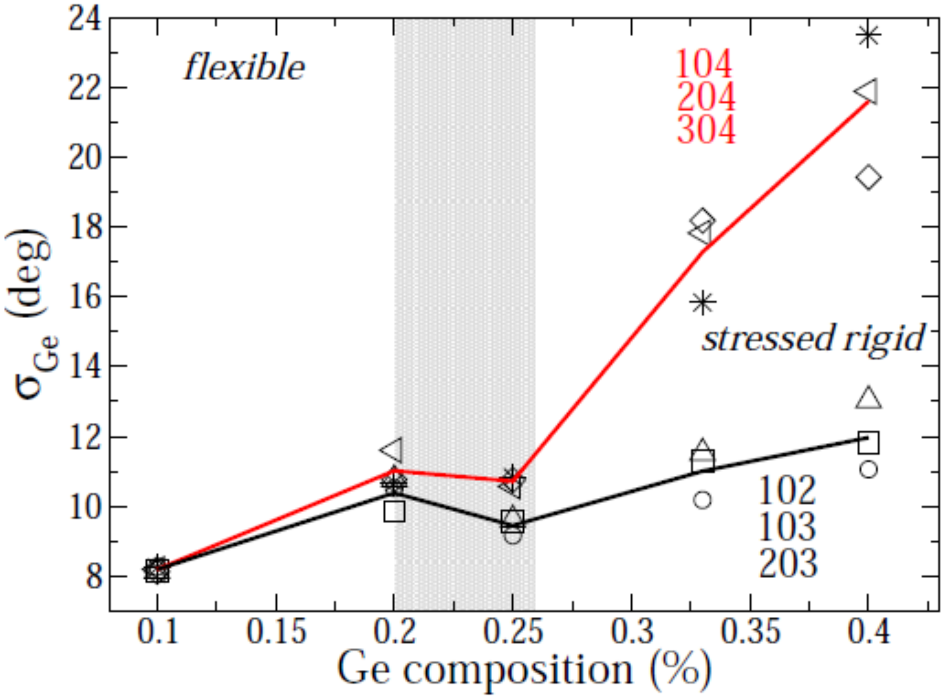
- Equivalent tetrahedral anglular excursion in oxides (rigid tetrahedron).

- Increased angular distorsion in chalcogenides (σ is not constant).

- 1 Se angle with a low σ in $GeSe_2$

Standard deviations and rigidity transitions



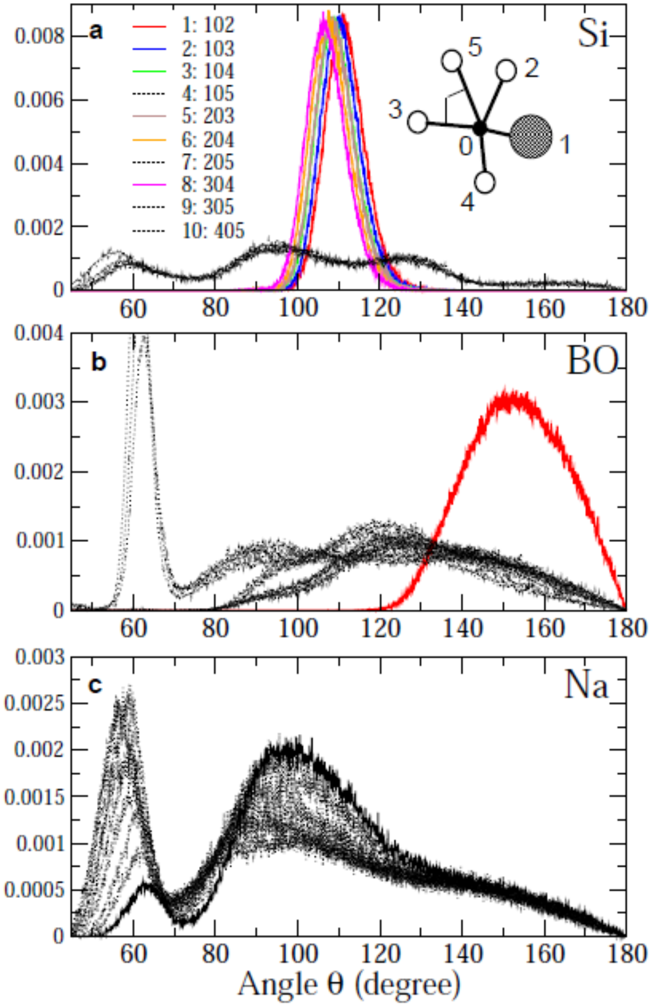


- **Rigidity (increasing Ge) affects mostly the Ge intra-tetrahedral motion.** Stress transition leads to an asymetric intra-tetrahedral angular motion involving the neighbour 4. Weak changes in σ_{Se}

- **Flexible $GeSe_9$ and IP $GeSe_4$ and $GeSe_3$**: similar to oxides: **σ=const, rigid tetrahedra**

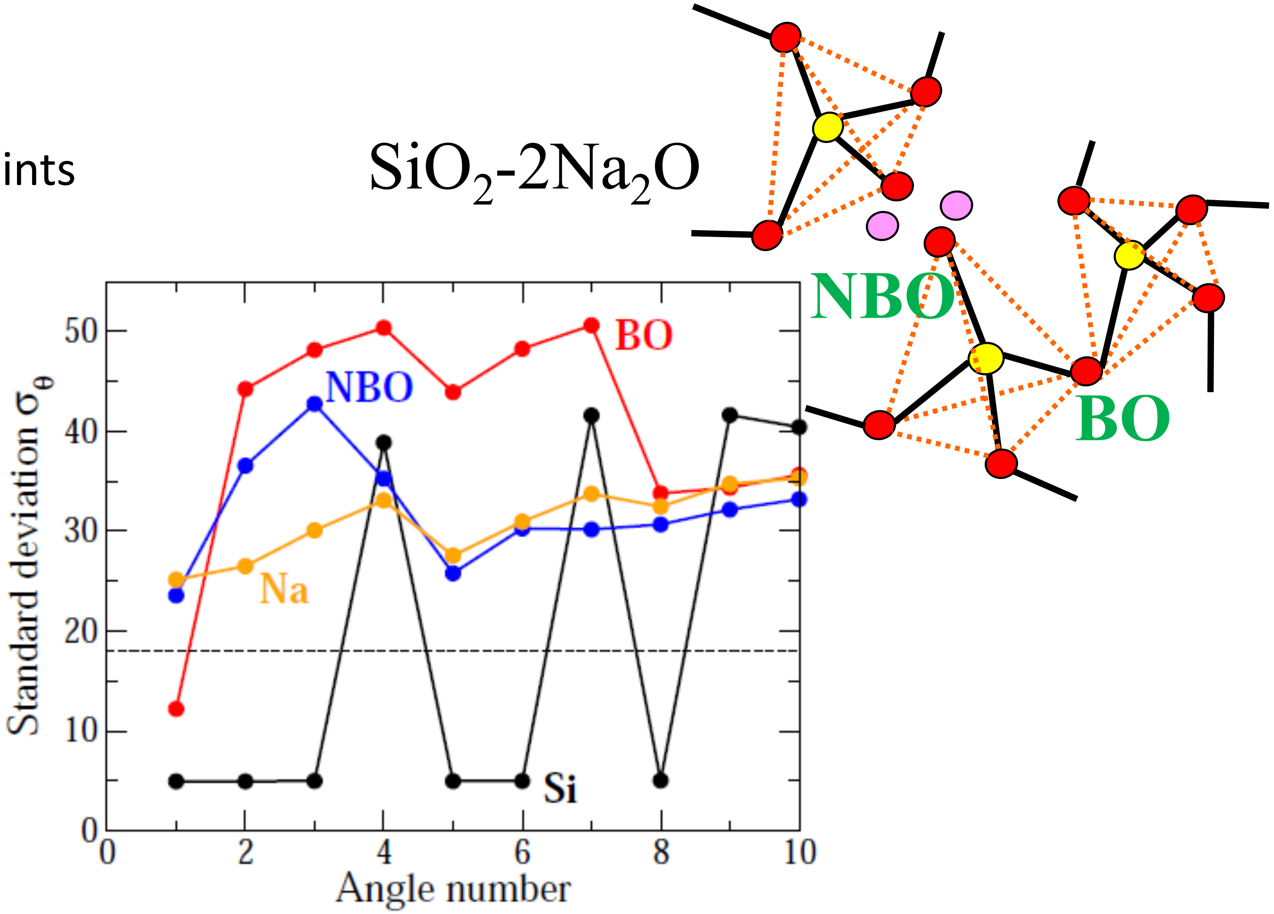
Silicates

Focus on bond-bending constraints



Bauchy et al, JNCS 2011

SiO_2-$2Na_2O$

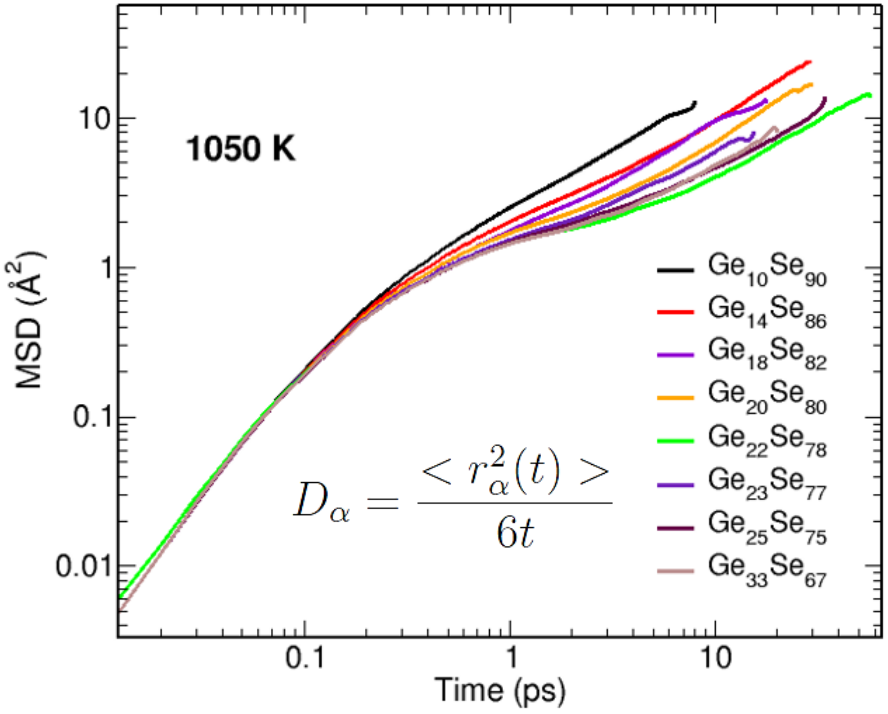


- ☐ Angular constraints are intact <u>only</u> for Si and BO

<u>Clear gap</u> between σ(Si), σ(BO) and σ(Na) and σ(NBO)

Using rigidity and molecular simulations

Ge-Se: Constraints+Dynamics of liquids



$$\langle r_\alpha^2(t)\rangle = \frac{1}{N_\alpha}\langle\sum_{i=1}^{N_\alpha}|\mathbf{r}_i(t)-\mathbf{r}_i(0)|^2\rangle$$

Expectation :

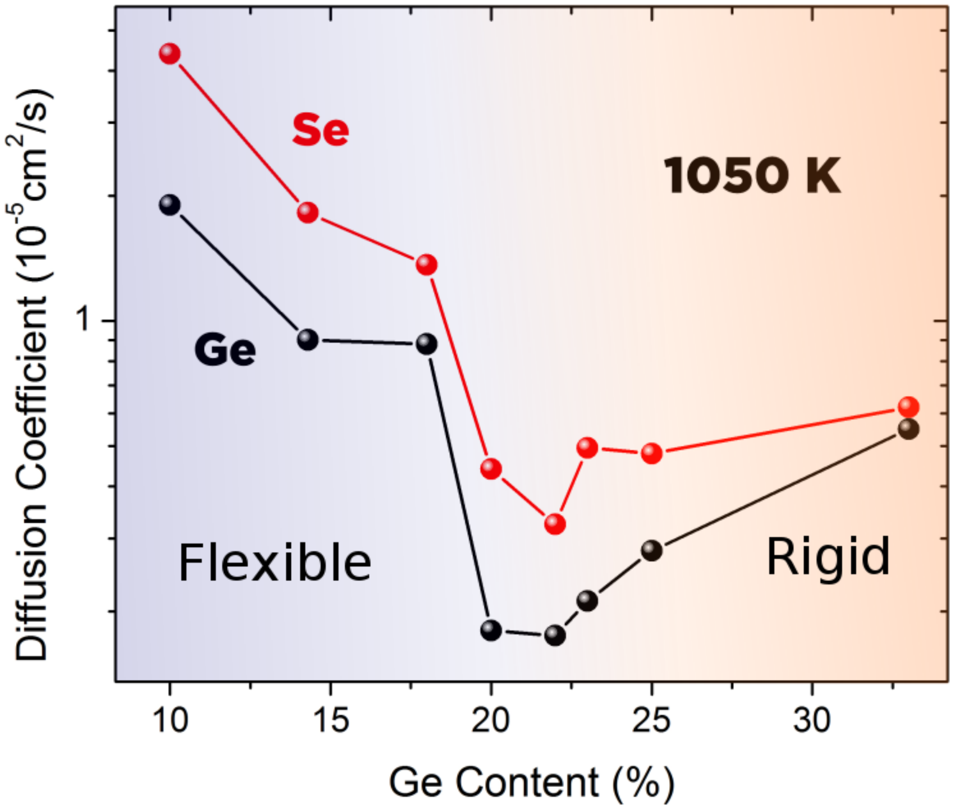
Mobility decreases as Ge

content increases

Non-monotonous Diffusion !

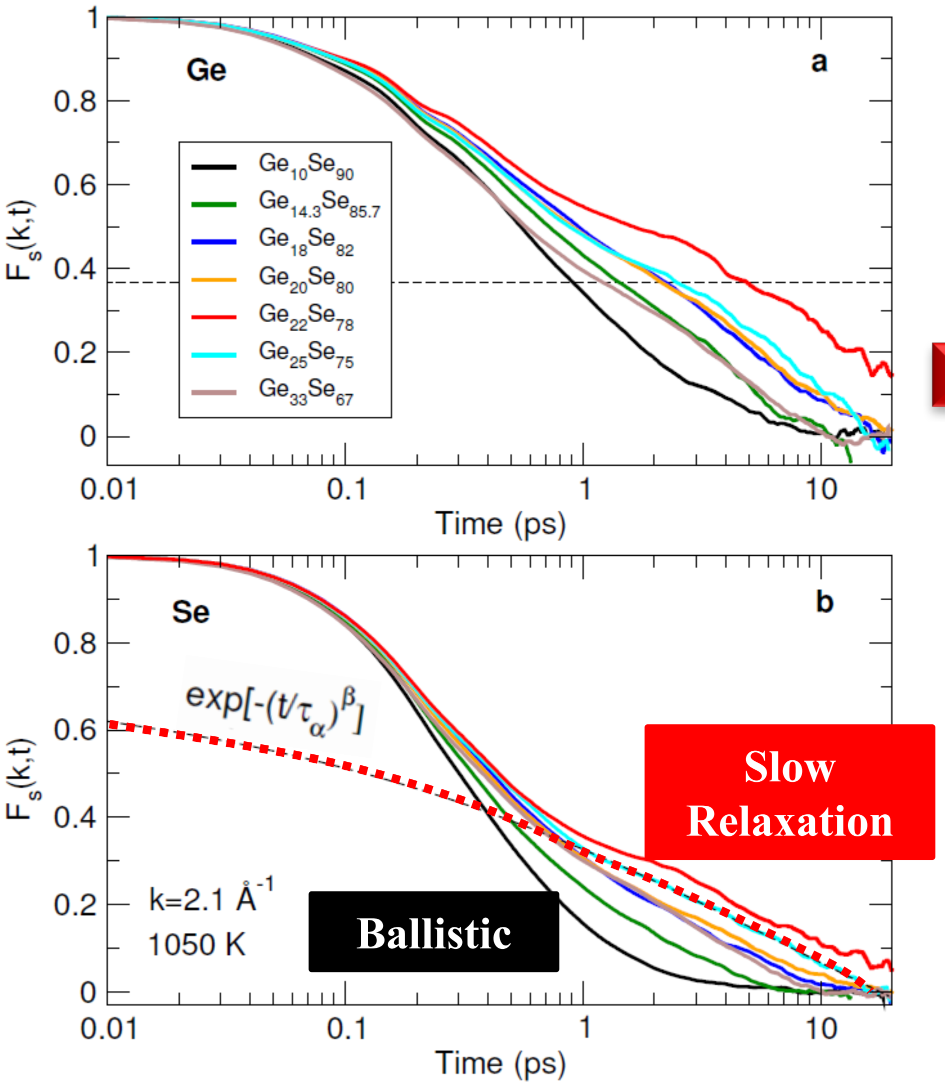
Diffusivity markedly decreases

between 18-22 % Ge



Ge-Se: Constraints+Dynamics of liquids

Intermediate Scattering Factor

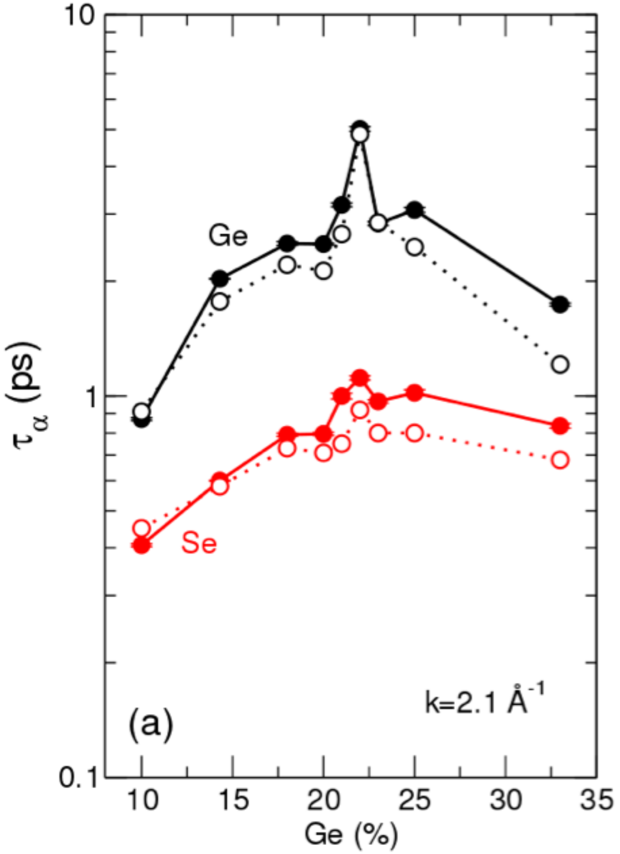


Slow Relaxation

Ballistic

Non-monotononous relaxation processes at 1050 K

$$F_s^\alpha(k,t) = \frac{1}{N_\alpha}\sum_{j=1}^{N_\alpha}\exp(i\mathbf{k}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0)))$$

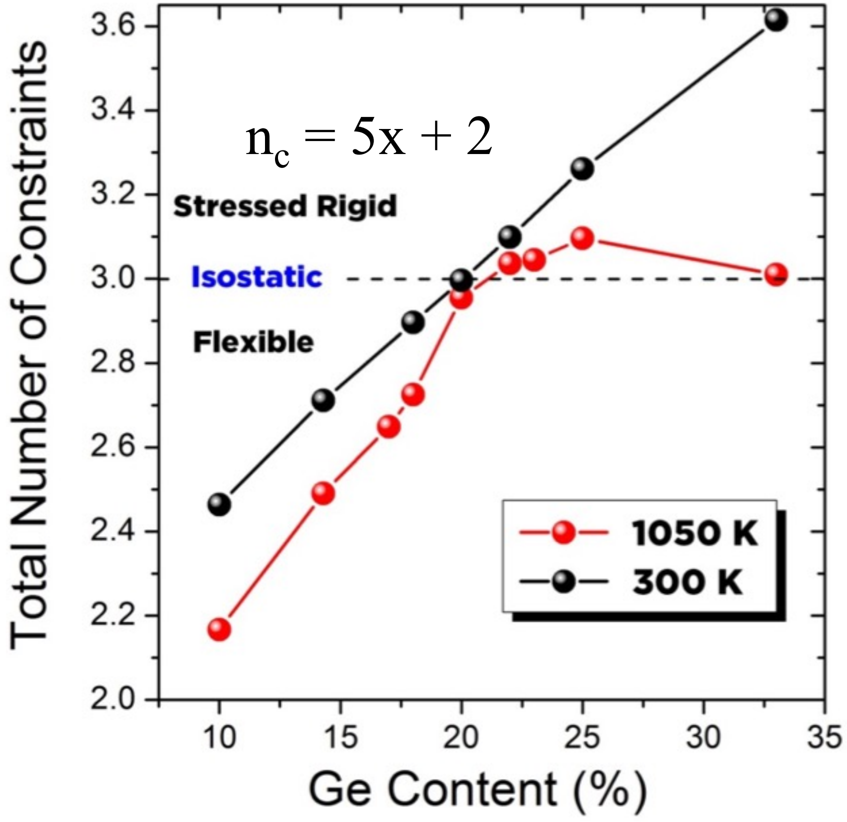


Relaxation times make maximum around rigidity threshold

Ge-Se: Constraints+Dynamics of liquids

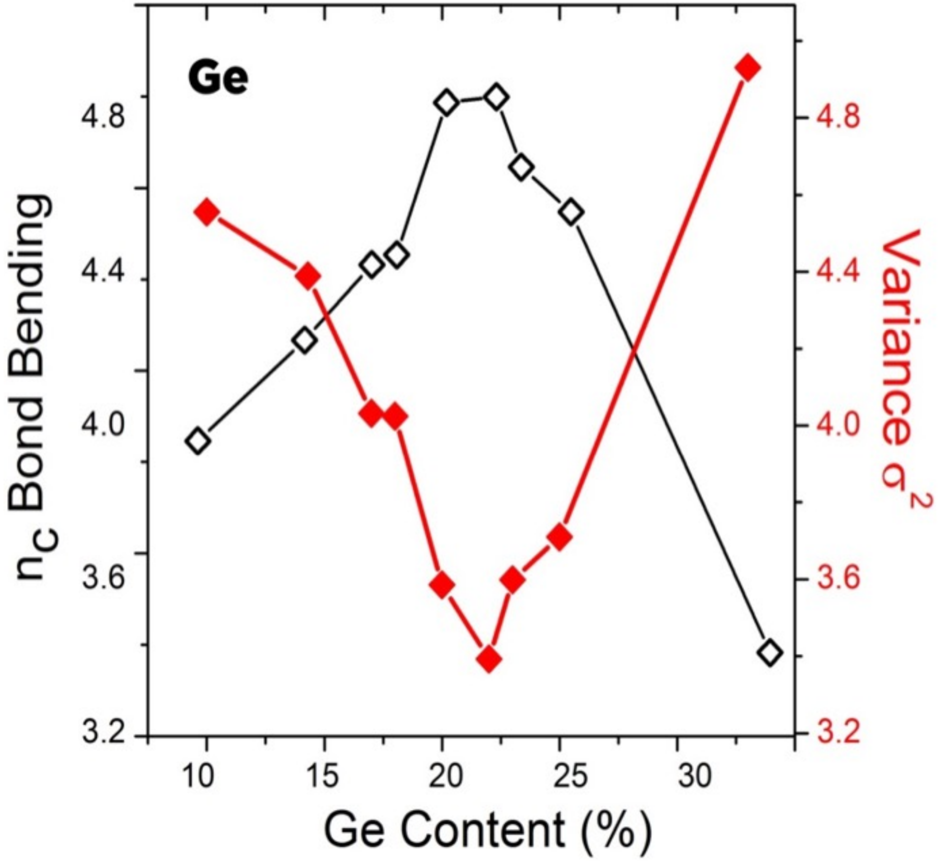
Mean Field prediction is well reproduced

At 300 K but constraints soften at high temperature

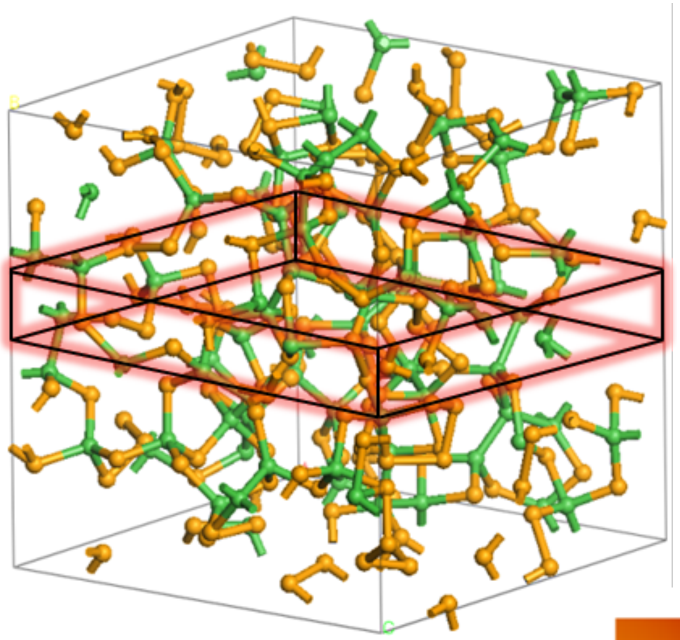


Weak variation of Ge BB at

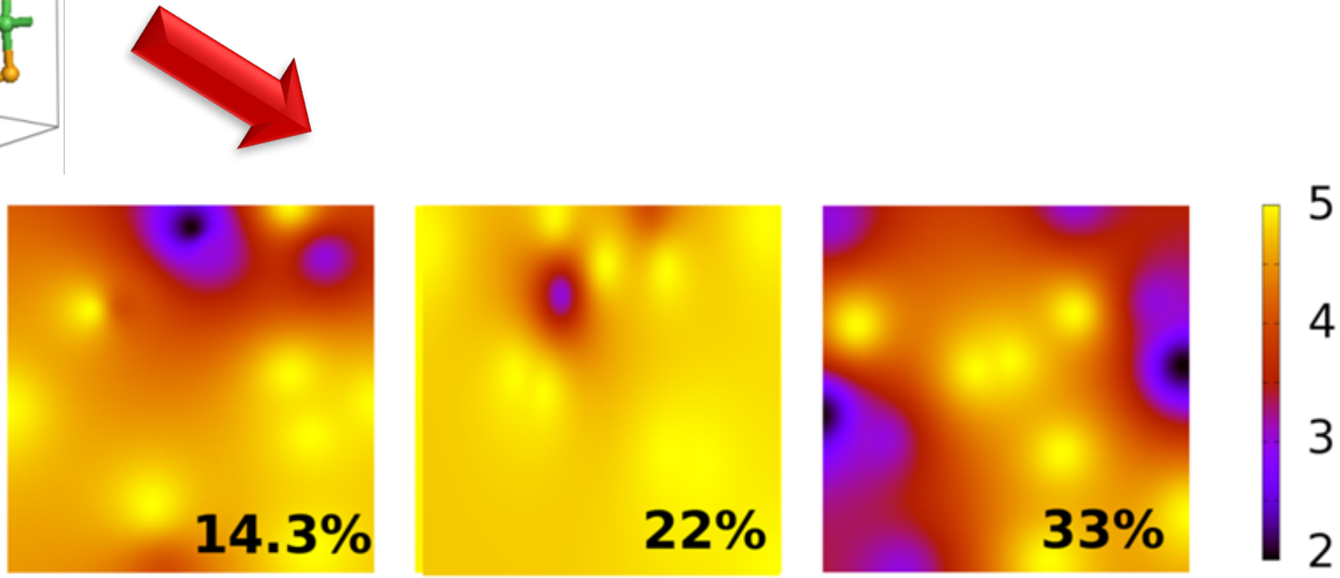
the rigidity transition



Ge-Se: Constraints+Dynamics of liquids



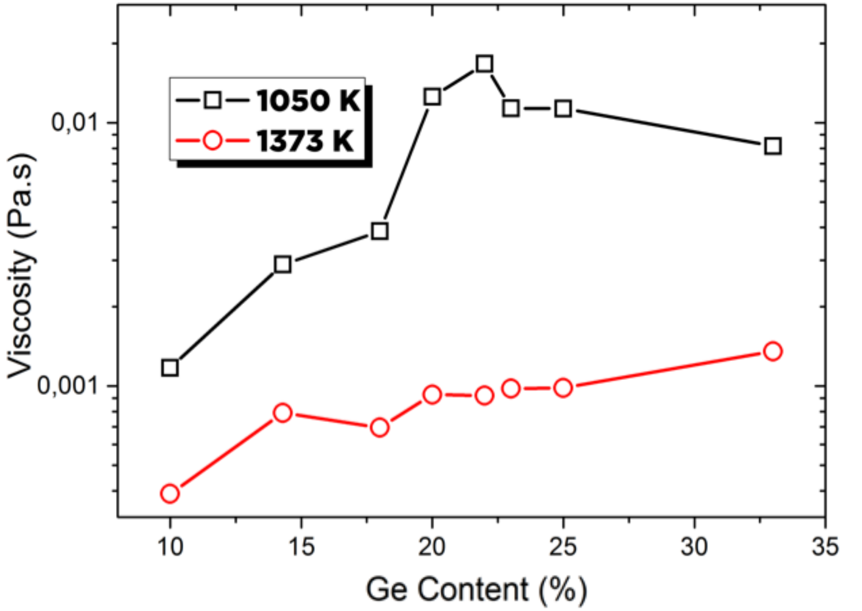
Slabs with 3.4 Å thickness at 1050 K are investigated in terms of spatial distribution of Ge BB constraints.

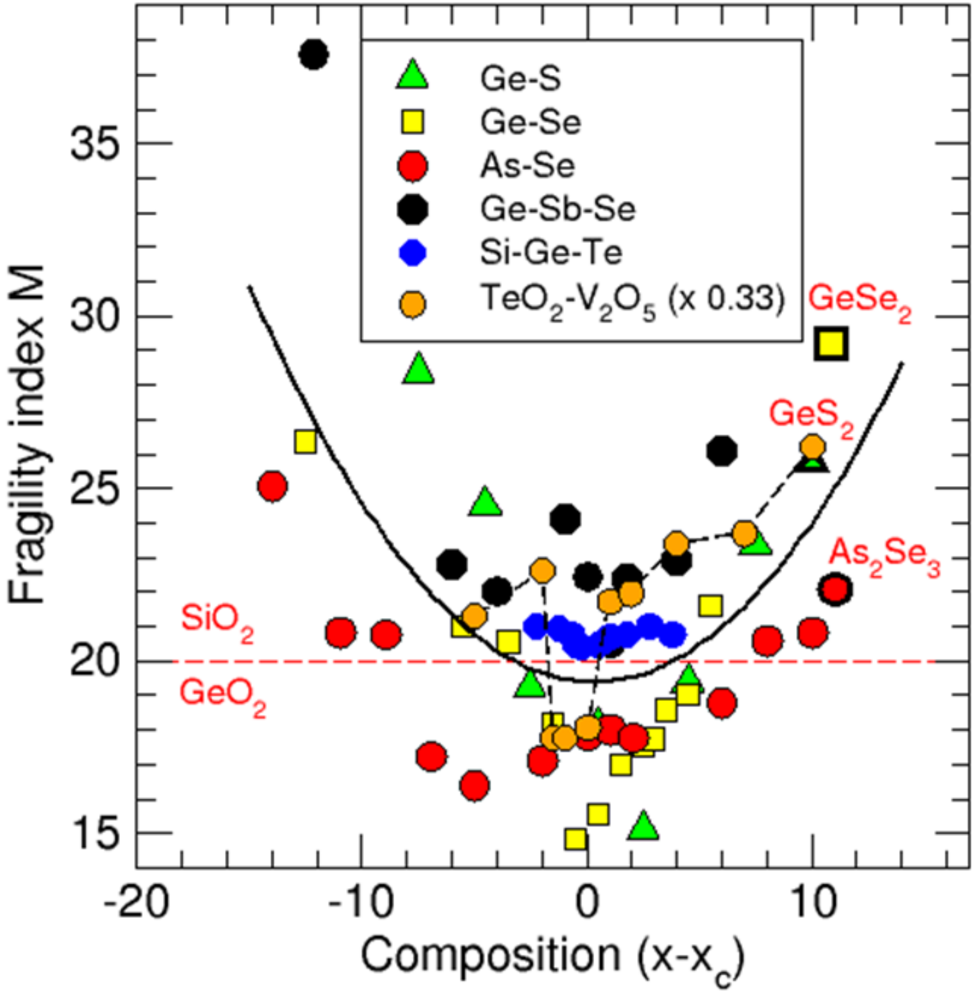


Homogenous distribution of Ge BB constraints at 22 % where the atomic mobility is minimum at 1050 K

Ge-Se: Constraints+Dynamics of liquids

Fragility $$m(x) = \frac{\partial \log \ \eta(T,x)}{\partial (T_g(x)/T)}\Big|_{T=T_g}$$

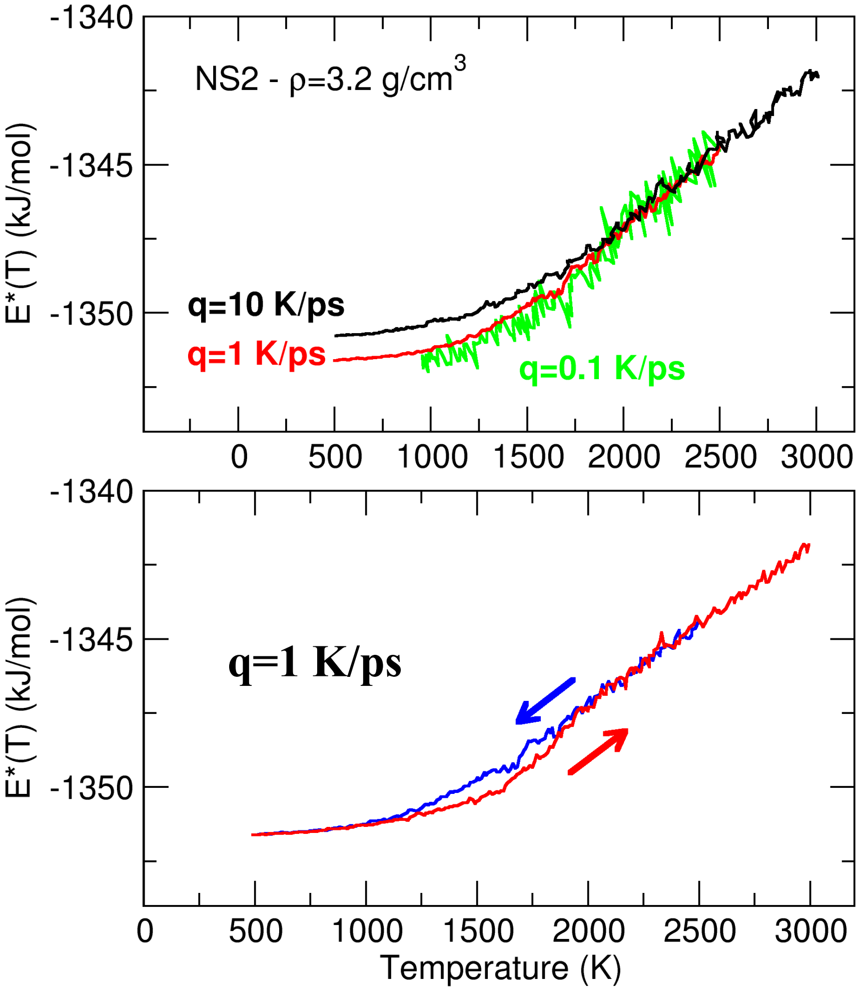




Fragilities of many glassy network forming melts show a global minima when scaled to isostatic composition

Reversibility in glasses

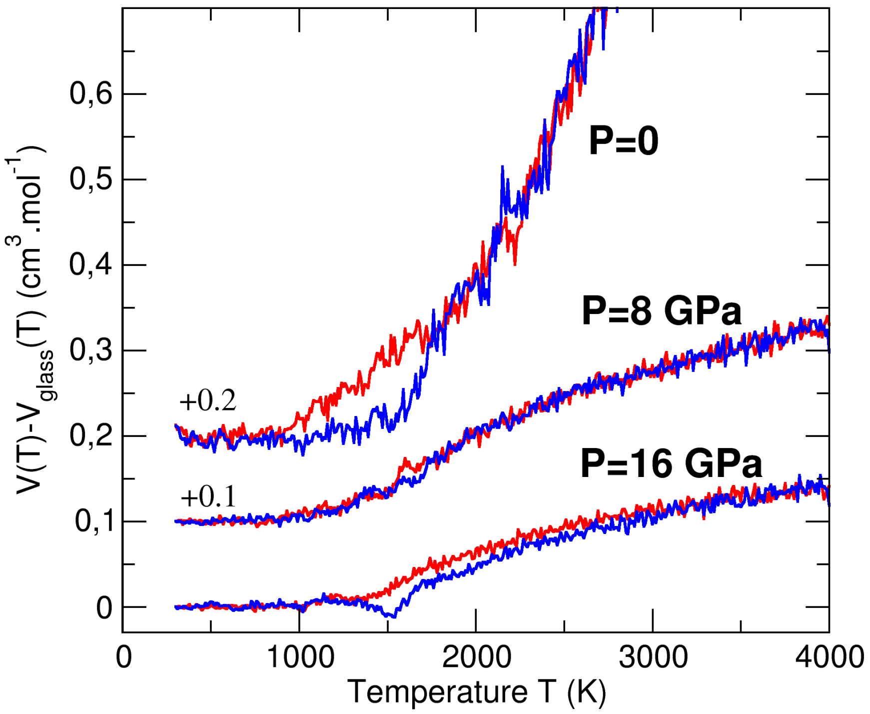
Liquid-glass transition of NS2 liquids

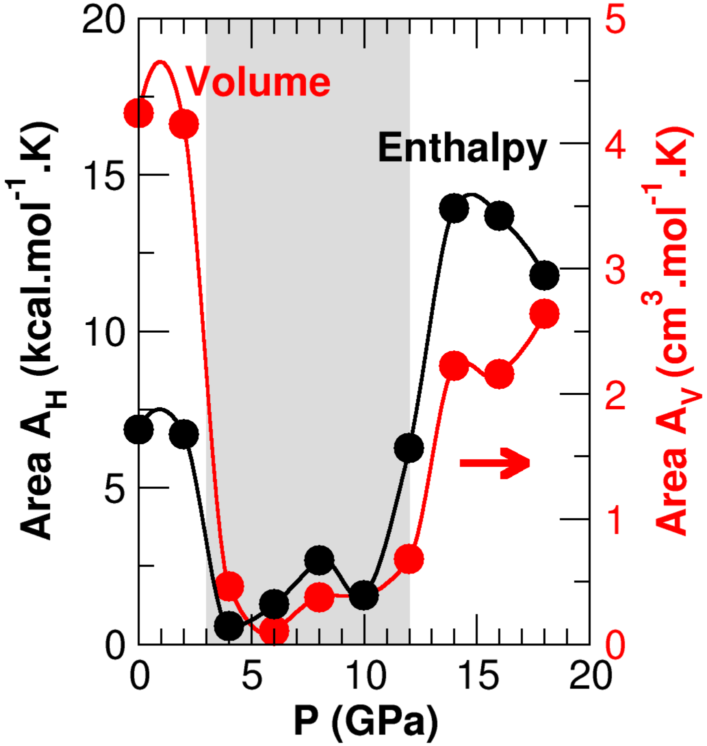


- Reproduction of the glass transition phenomenology
- **Cooling:** faster cooling ($q=dT/dt$) freezes glass in at higher temperature
- Well defined fictive temperature
- With **heating**, a hysteresis loop is found, and originates a heat capacity "*overshoot*" at the glass transition.

Reversibility in glasses

Tg cooling-annealing cycle in NPT





- ☐ Same anomalies in NPT Ensemble. Volume recovery for selected pressures.
- ☐ Enthalpy minimum in a pressure window found between ~3 GPa < P < 12 GPa.

Reversibility in glasses

Link with transport properties: diffusion and viscosity

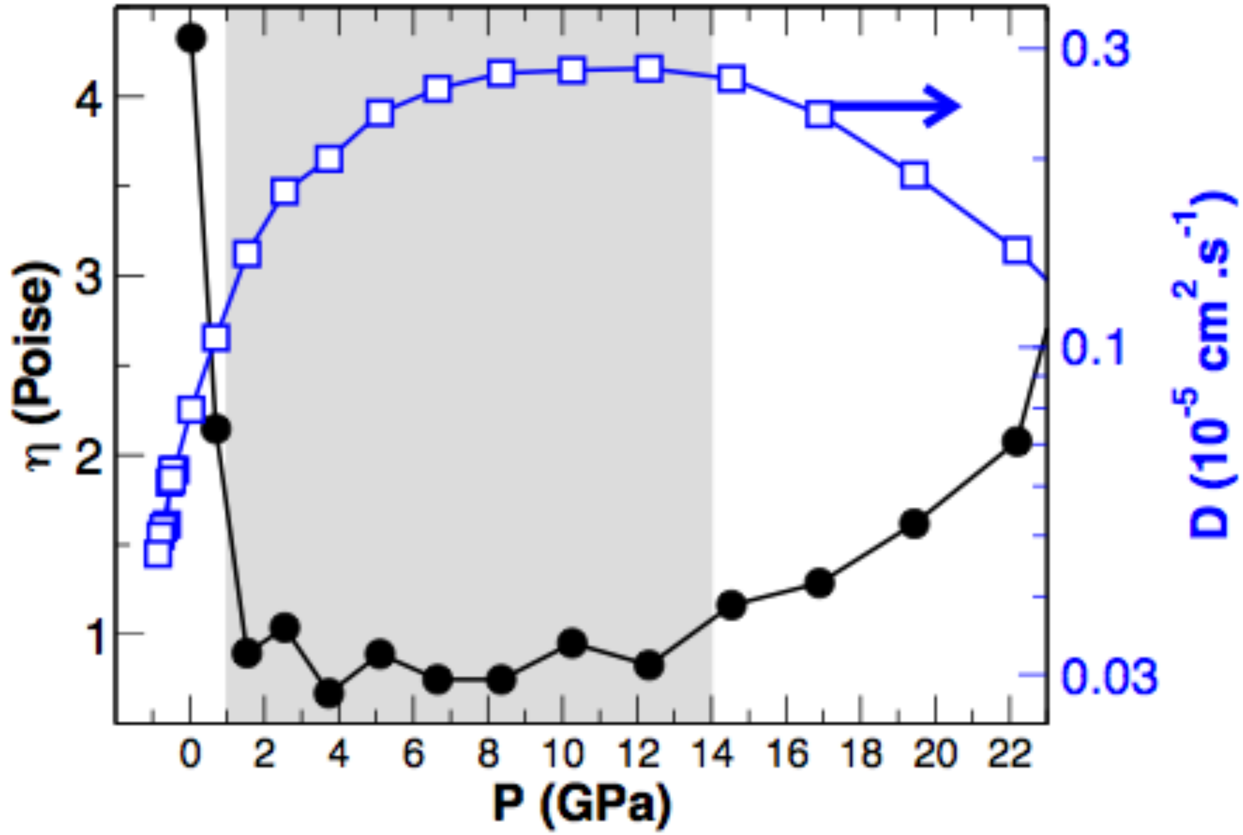
Diffusion (msd) and viscosity (Green-Kubo, Stress auto-correlation)

- In the pressure window (2000K) :

- minimum of viscosity
- maximum of O/Si diffusion

- Similar features (diffusivity anomaly as in d-SiO_2 or d-H_2O, **Debenedetti et al. , Nature (2000)**

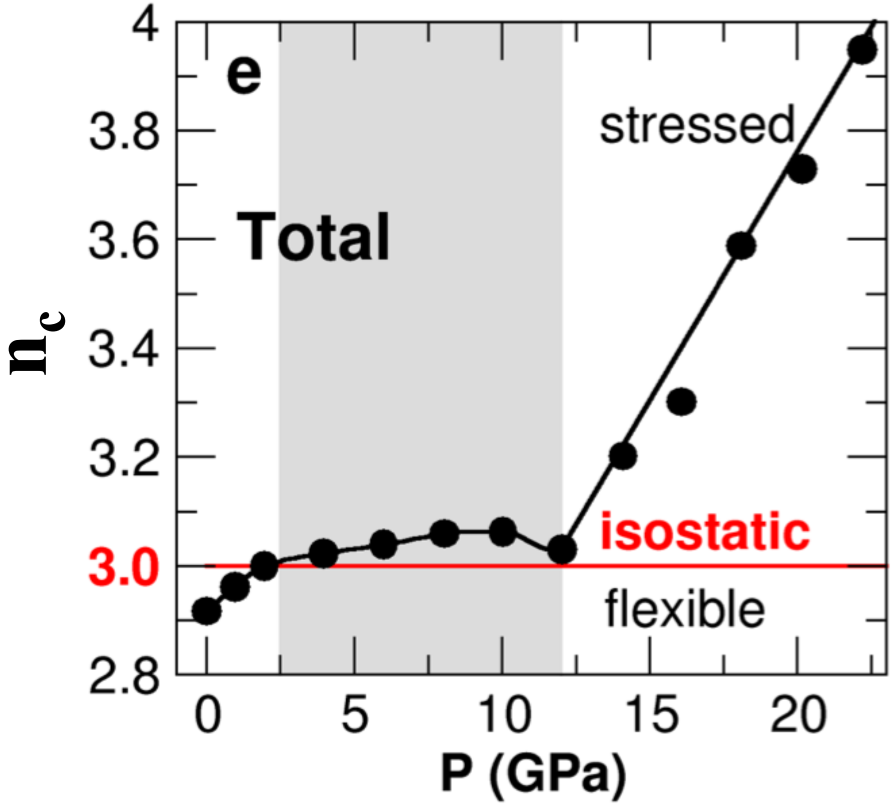
- Ease of diffusion (i.e. relaxation) related to reversibility.



M. Bauchy, M. Micoulaut, Phys. Rev. Letters 110, 095501 (2013).

Reversibility in glasses

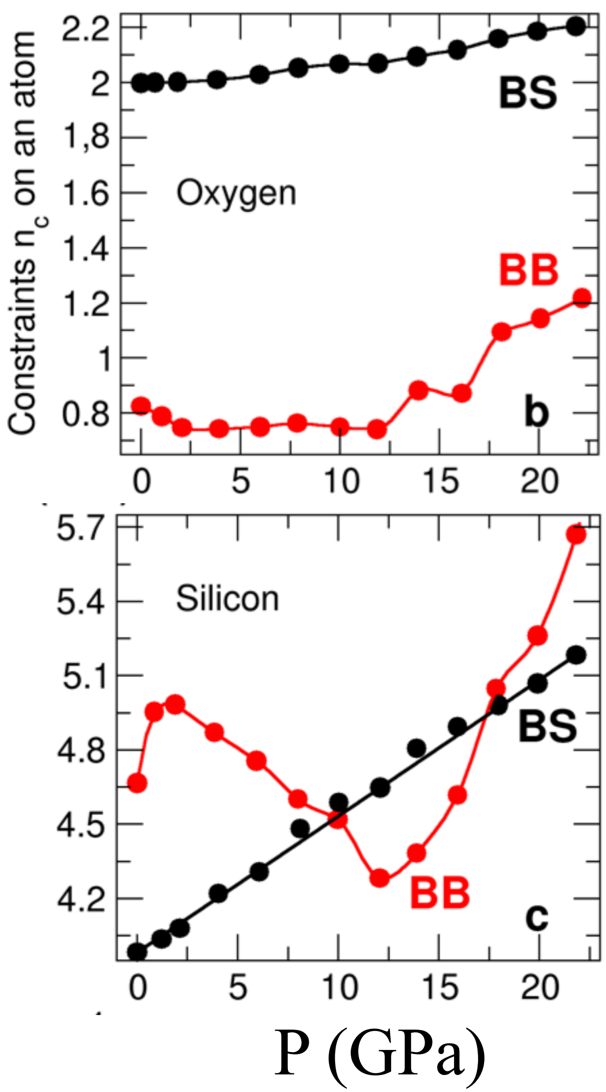
Effect of rigidity



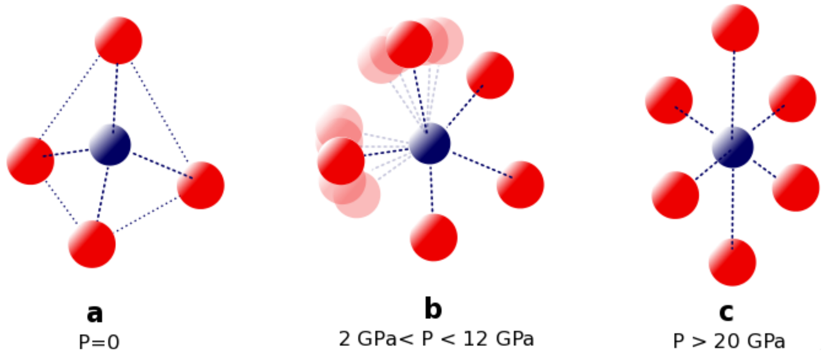
- ❑ At P=0, the NS2 glass is flexible (Rigid to Flexible transition for 20% Na_2O)
- ❑ In the Pressure window, saturation of n_c to a limiting value nc ~3.
- ❑ Isostatic character of the network

Reversibility in glasses

Effect of rigidity



- ☐ **Detail:** With increase of pressure, stretching constraints (BS) and stress increase.
- ☐ Linked with increase of Si and O coordination.
- ☐ Softening of the bending (BB) constraint to avoid pressure-induced stress.



- ☐ Network adaptation only possible up to a certain point.

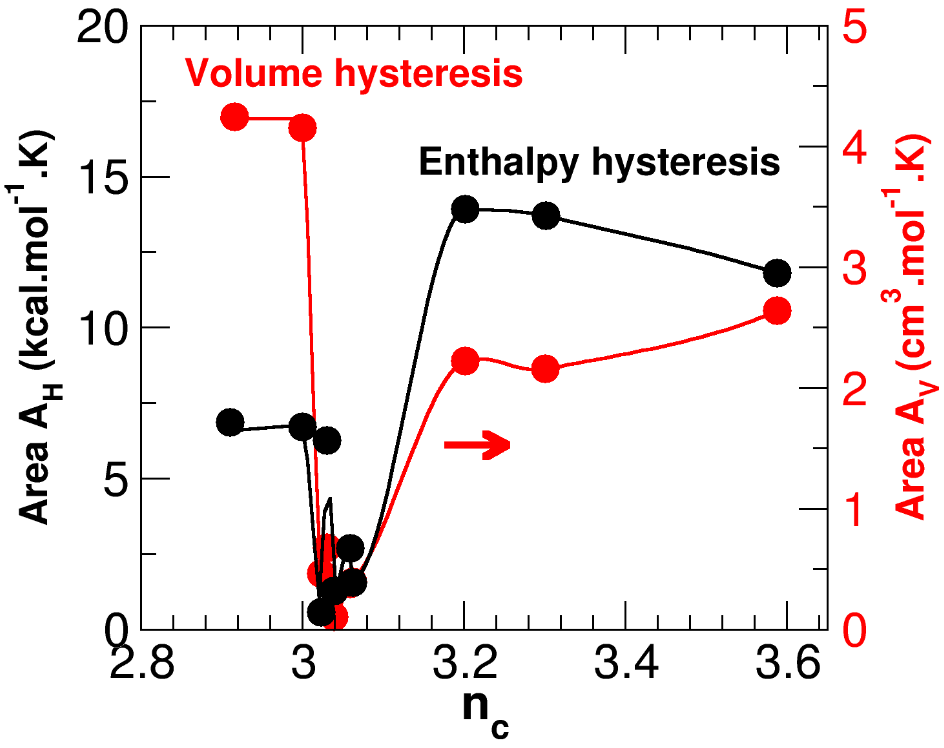
The reversibility of the glass transition, and the underlying anomalies are driven by the adaptive isostatic nature of the base network.

Reversibility in glasses

- ☐ Isostatic (n_c=3) glass transitions display an ease to reversibility.

Reversibility: at a fixed cooling/heating rate, the energy/volume hysteresis is minimum.
OPTIMAL RELAXATION

- ☐ Thermal anomalies are linked with anomalies in transport in the liquid and with structural anomalies in the glass.



- ☐ Upon increasing stress, the system adapts to maintain as long as possible the isostatic character of the network.

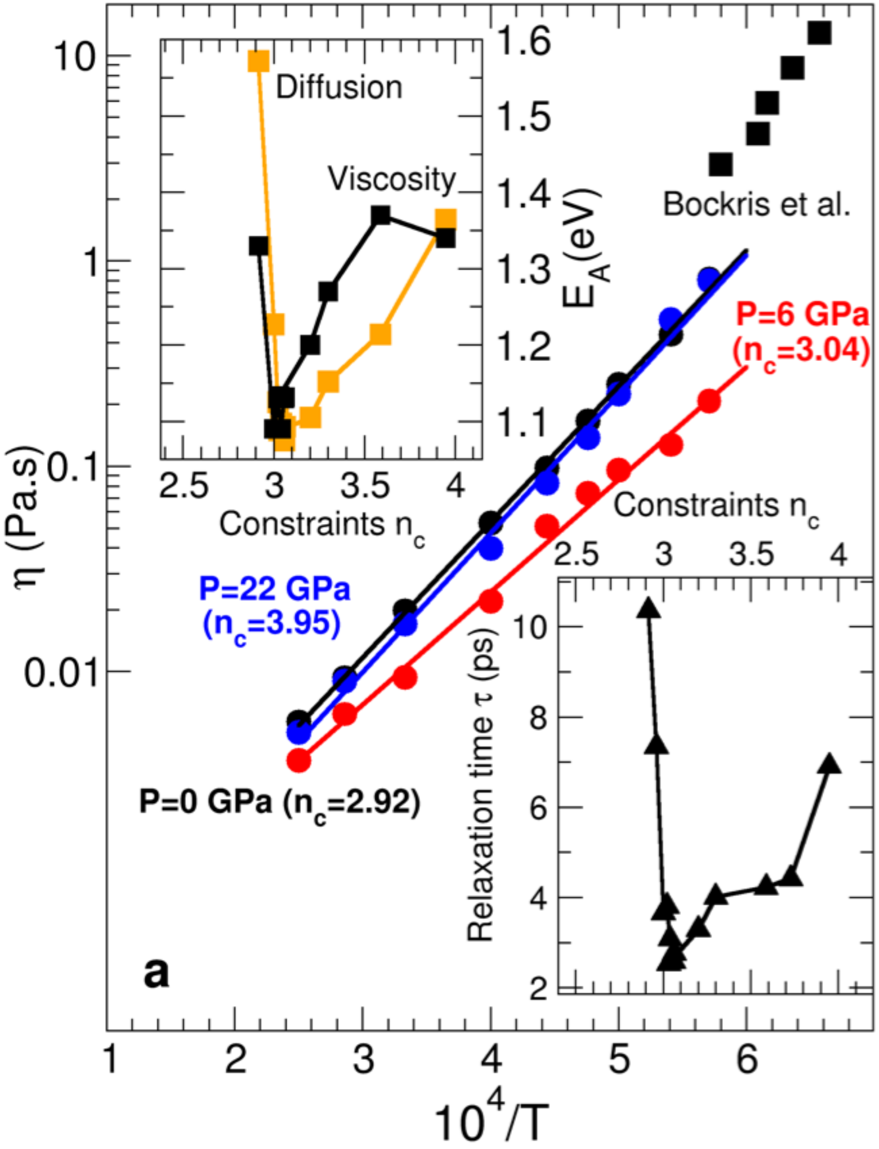
Reversibility in glasses

- ❑ Enhanced ease for relaxation (minimum of the activation energies for (D,η)) for nc~3

(in the pressure window 3 < P < 12 GPa).

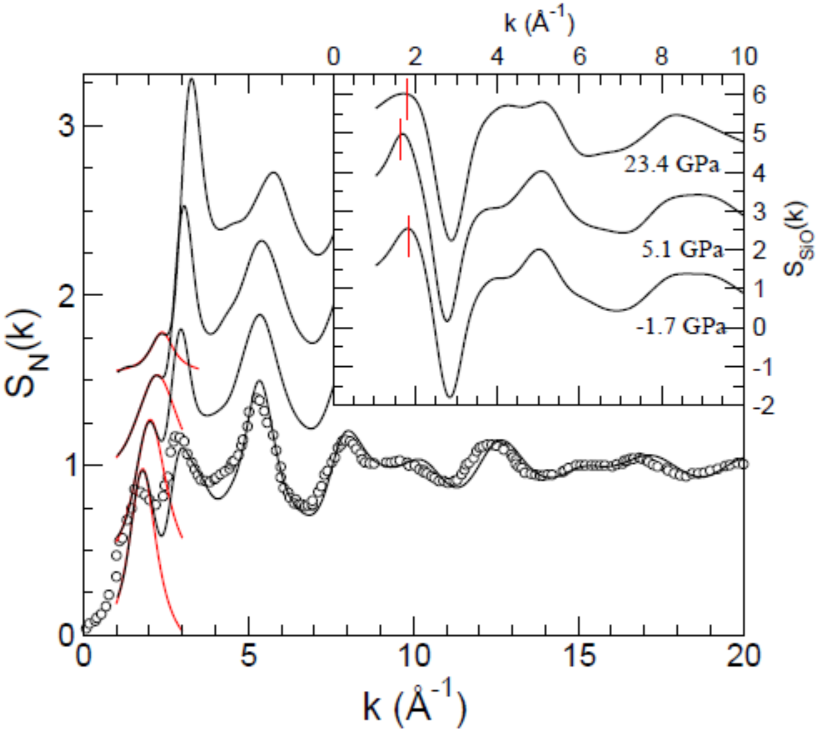
- ❑ Relaxation time also minimizes

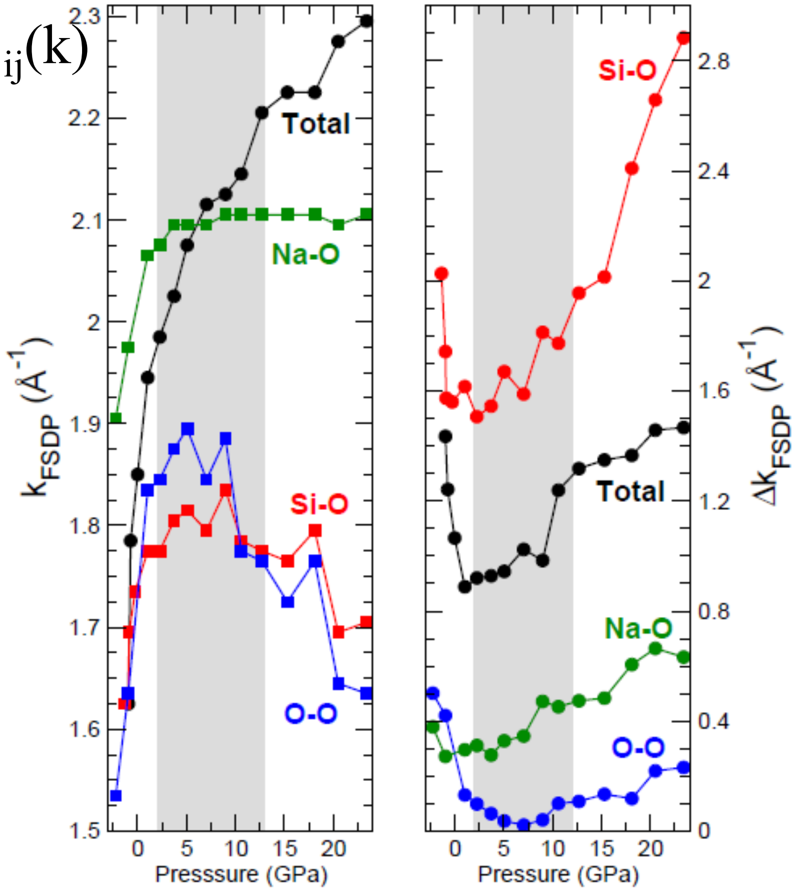
- ❑ Enhanced relaxation



Reversibility in glasses

- **Link with structure**
- First sharp diffraction peak (FSDP) of partial $S_{ij}(k)$



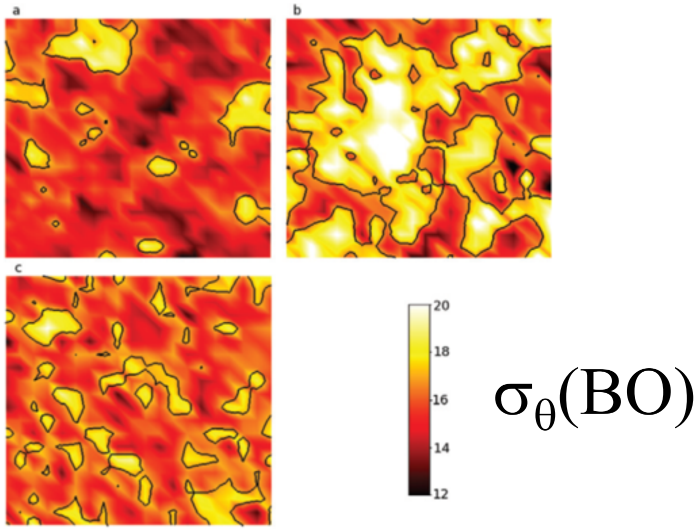


- Correlation lengths are minimal
- Coherence length (Sherer equation)
are maximal : IP has large domain sizes
- Also obtained in As-Se glasses

Micoulaut et al. 250, 976 (2013)
Bauchy et al. PRL110, 095501 (2013)
Bauchy et al. PRL 110, 165501 (2013)

Reversibility in glasses

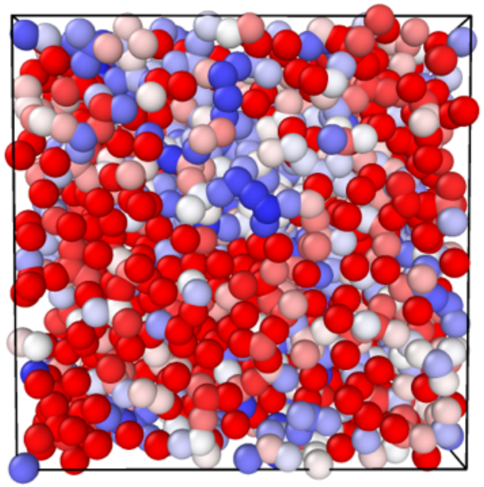
Are these constraints homogeneously distributed ?



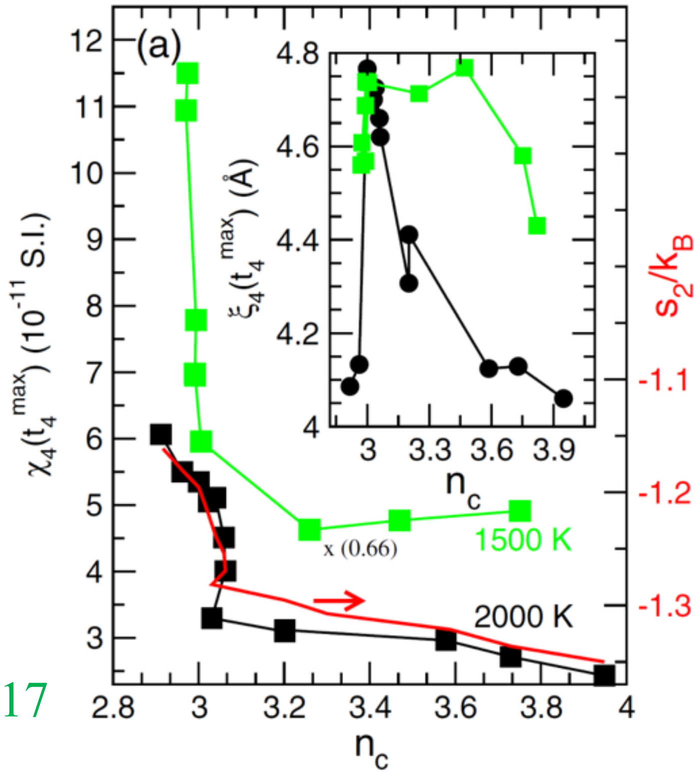
Bauchy et al. EPL 2013

Do they impact more subtle aspects of dynamics ?

Dynamic heteroegenities



Micoulaut et al. PRL 2017



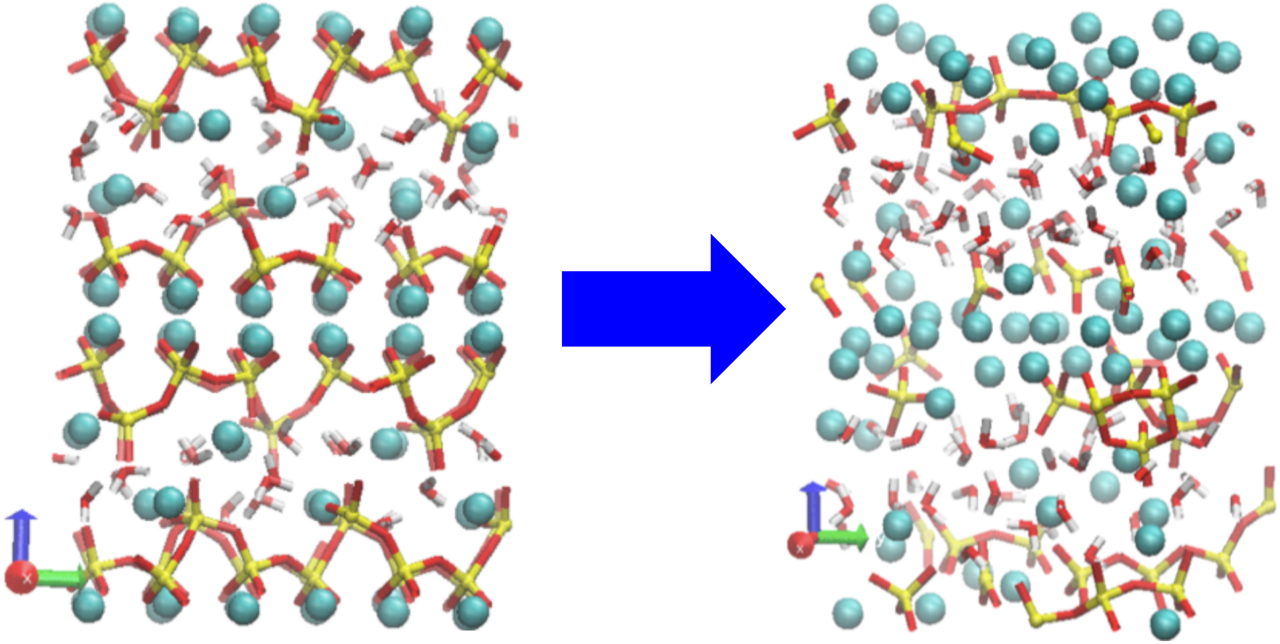
Rigidity transition in cement

Extending the rigidity theory to complex materials

C-S-H cement models

150 different samples
with varying Ca/Si ratio
:
From 1.09 to 2.05

Around 500 atoms
ReaxFF potential
(reaction with water)



Ca/Si = 1.09

Ca/Si = 1.89

Crystalline

Amorphous

M. Pellenq et al. JCP 2005
Bauchy et al. JCP 140, 214503 (2014)

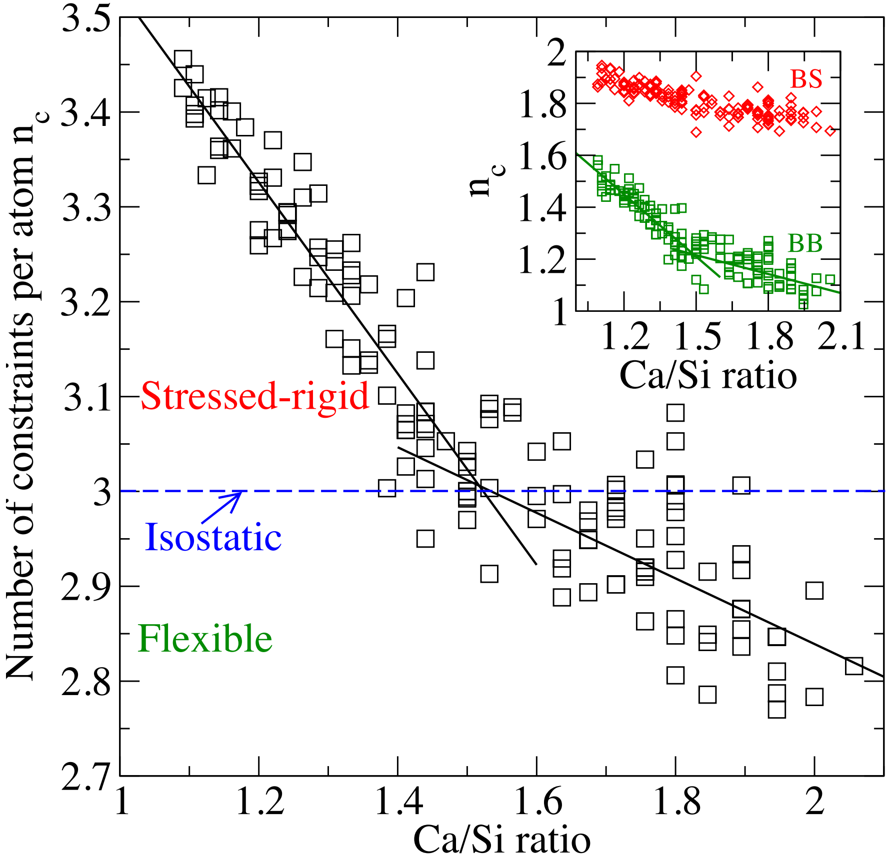
Rigidity transitions in cement

- Rigidity transition at Ca/Si = 1.5 (isostatic)

- Rigid at low Ca/Si ratio
- Flexible at high Ca/Si ratio

- Change of the slope at the rigidity transition

- Transition mostly driven by bond-bending constraints

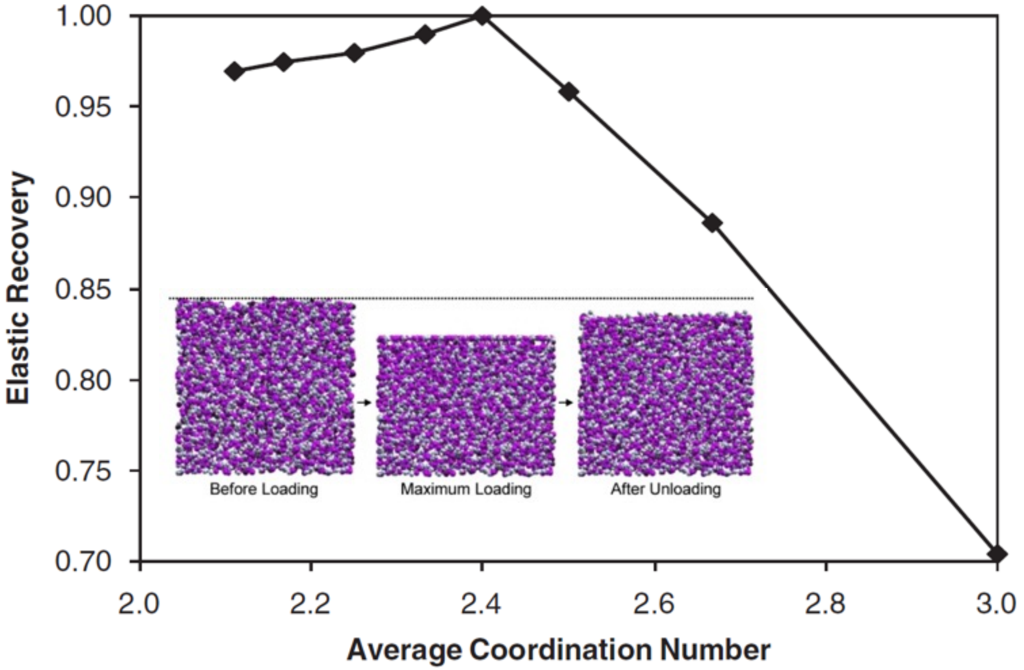


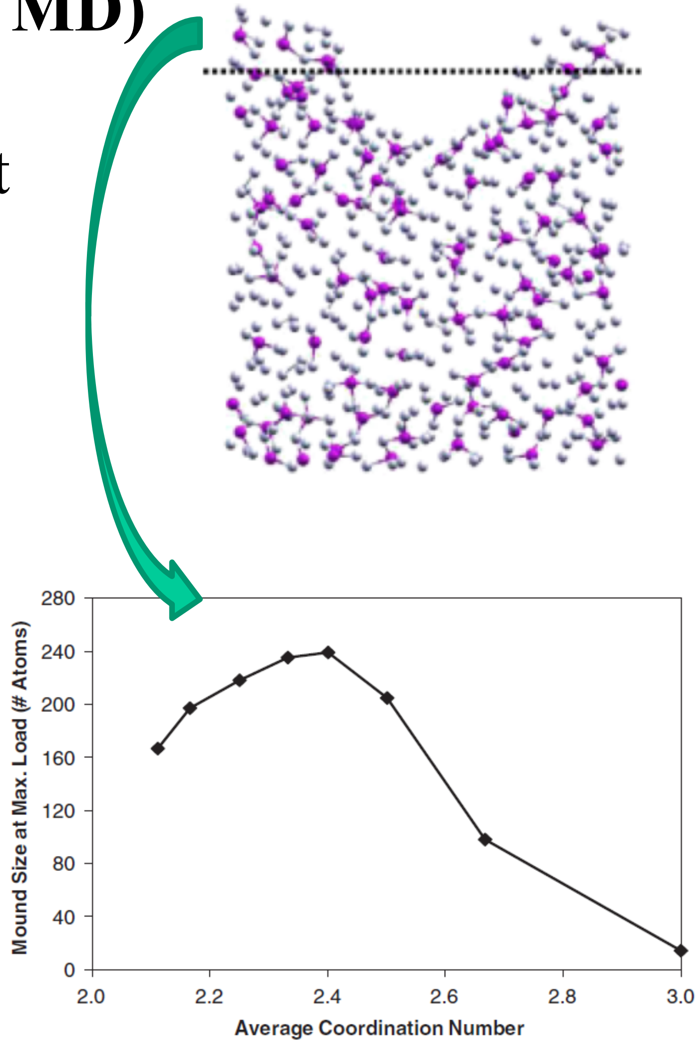
Mechanical properties and rigidity

Mechanical behaviour of Ge-Se (classical MD)

Nanoindentation as a function of Ge content
Loading and unloading

Anomalies found for isostatic glasses



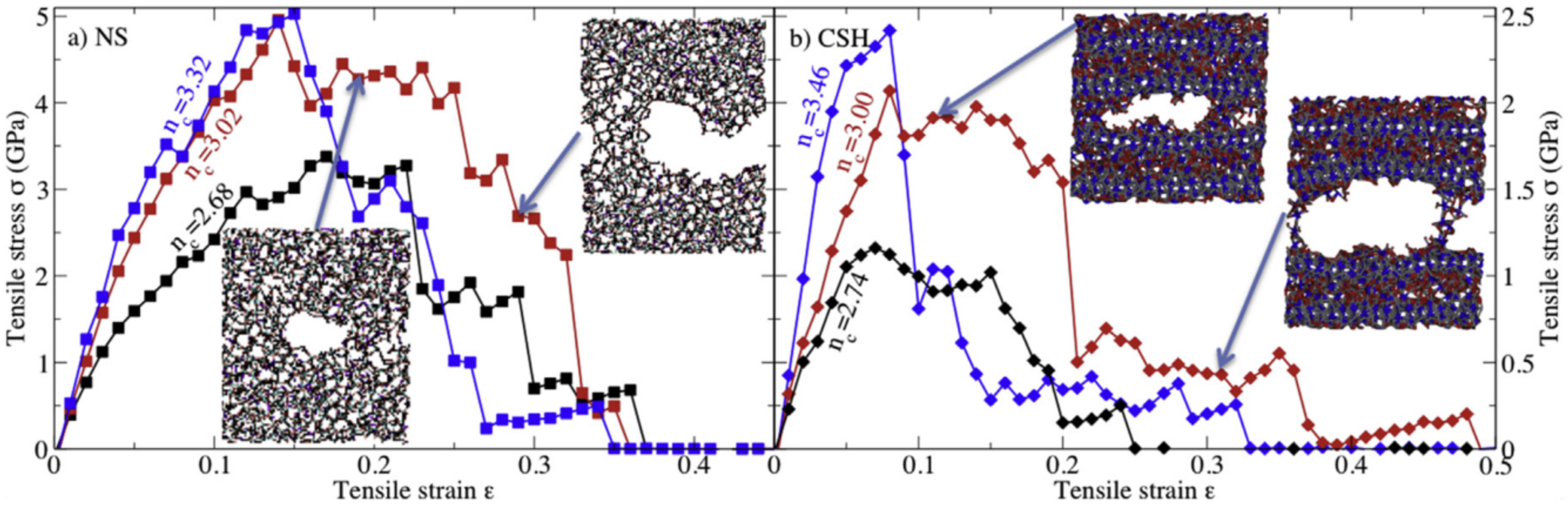


Mauro and Varshneya, J.Am. Ceram. Soc. 90, 192 (2007).

Mechanical properties and rigidity

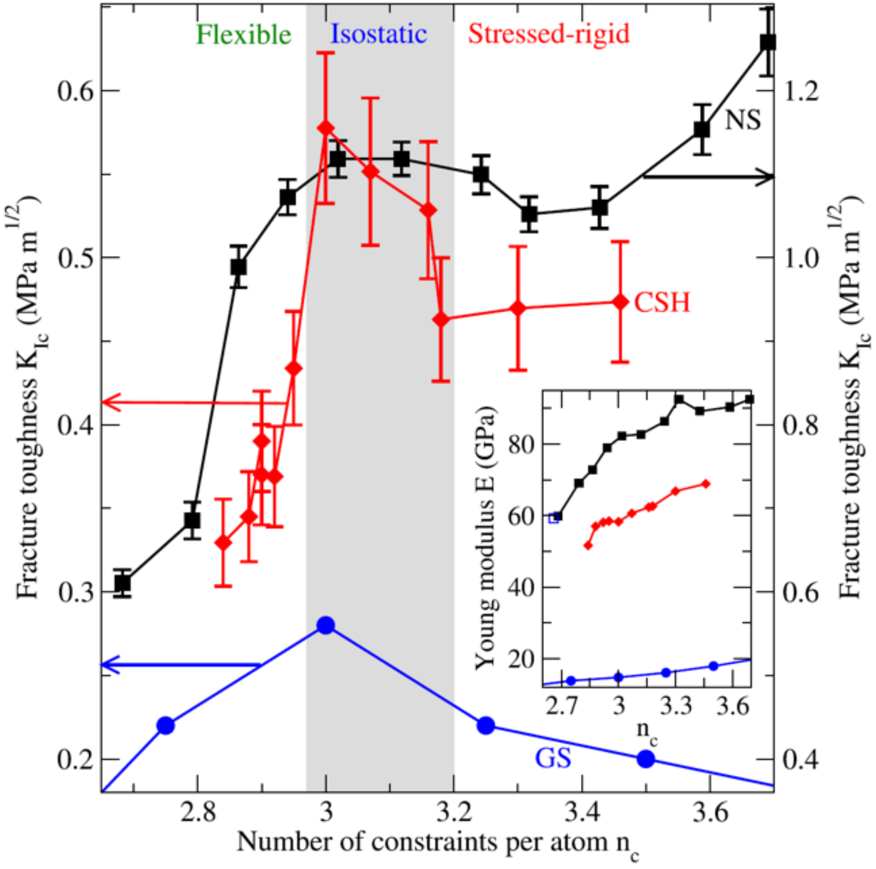
Mechanical behaviour contrasted to n_c

- Rigidity status (n_c) is controlled by pressure
- Application to NS2 and CSH (cement)
- Numerical tensile experiments



Bauchy et al. Acta Mater. 121, 234 (2016)
Bauchy et al. PRL 114 (2015) 125502

Fracture toughness and rigidity



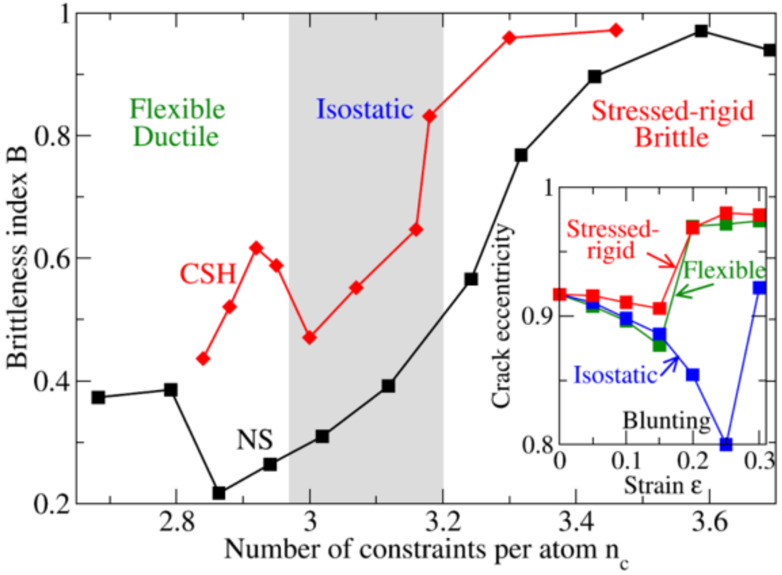
Données GS:
Guin et al. J.AM.Ceram. Soc (2002)

Isostatic systems

- Maximum fracture toughness
- Rigidity transition coincides with a ductile-to-brittle transition.

$$B = 2\gamma_S/G_C,$$

- Network is rigid but free of eigen-stress and features stress relaxation through crack blunting, resulting in optimal resistance to fracture.

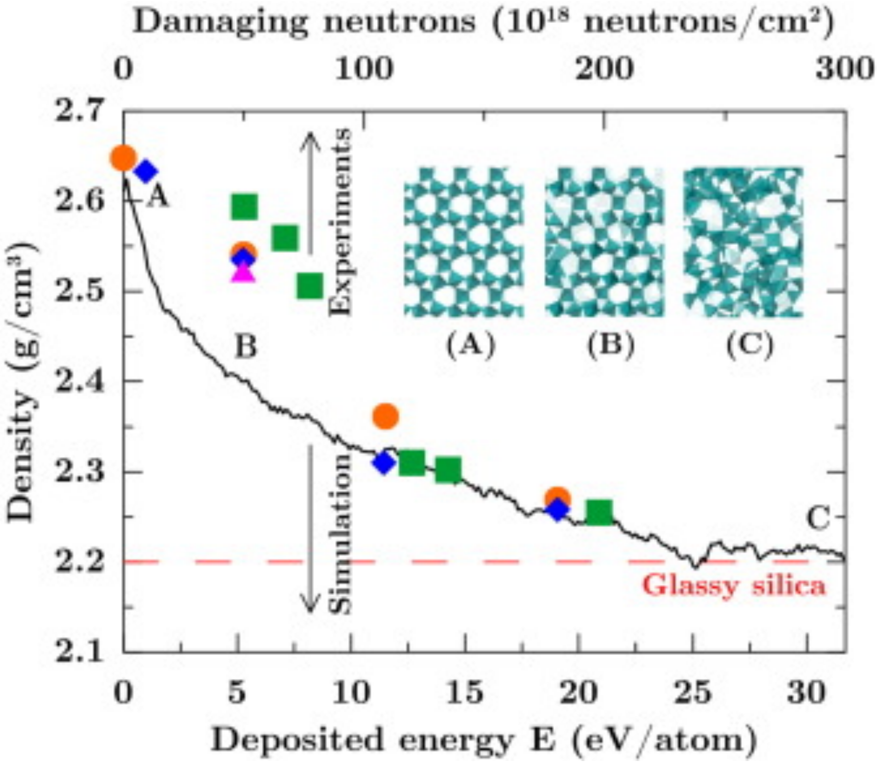


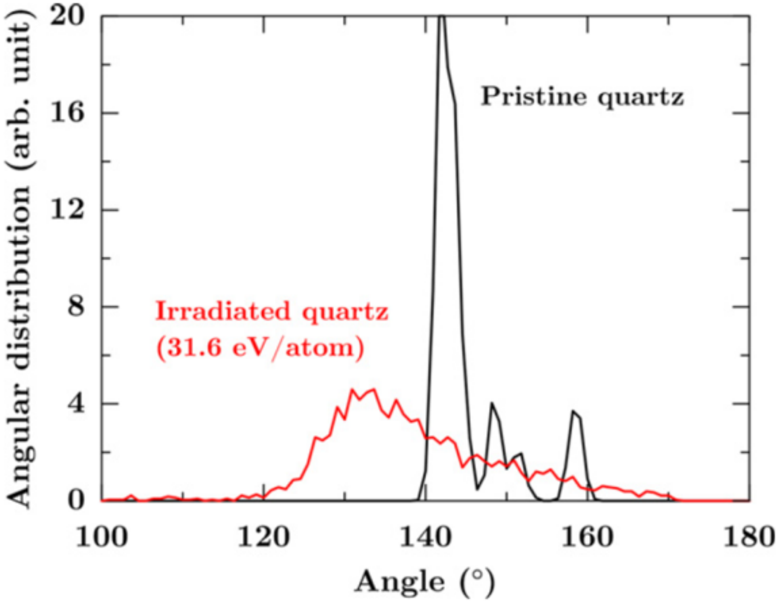
Irradiation in quartz

Irradiation-induced damage in quartz investigated from rigidity theory

- MD simulations of quartz by high energy ballistic (irradiation) motion

  v_O linked with deposited energy E (strategy **J.M. Delaye, JNCS 2001**)
- MD based constraint counting
- Relating MD calculated properties to n_c.



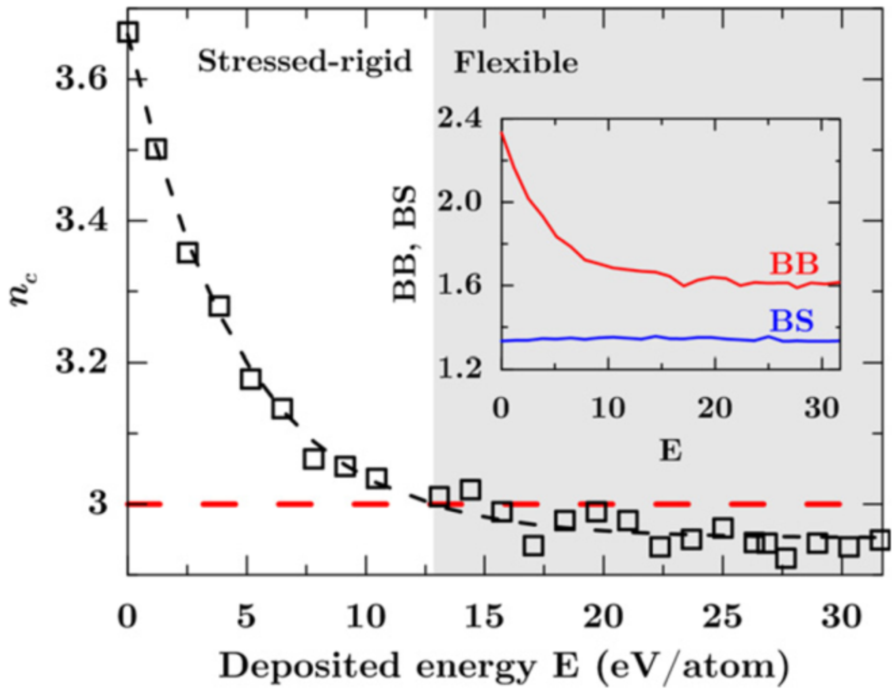


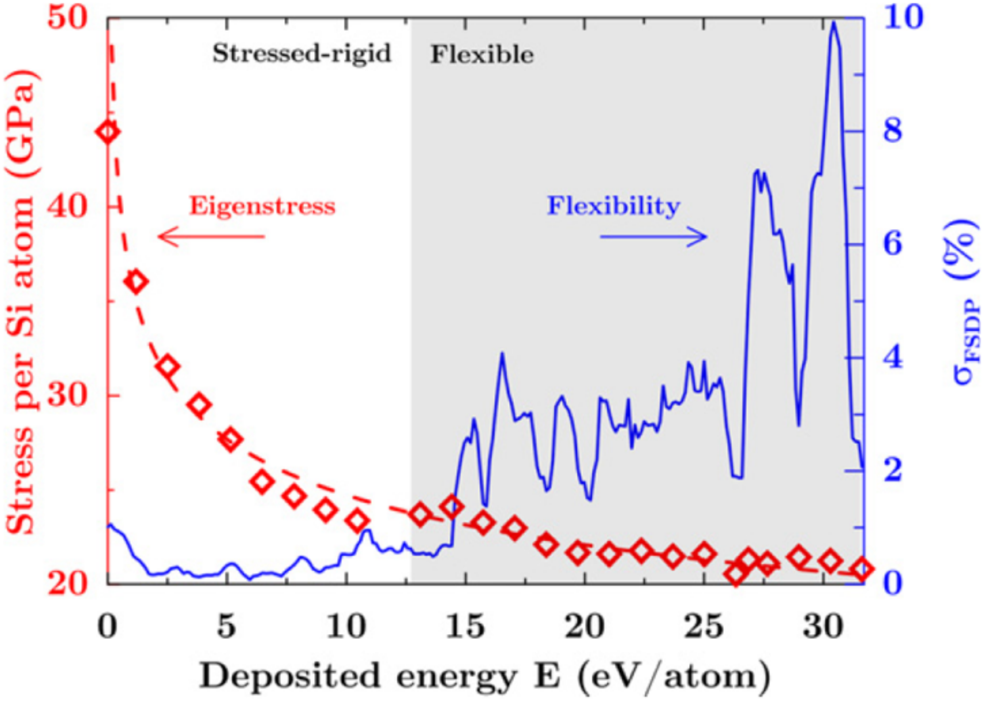
Wang et al. JNCS 463 (2017) 25

Irradiation in quartz

Evidence of a rigid-to-flexible rigidity transition

- Arises from the simultaneous loss of atomic eigenstress and onset of network flexibility
- Link with structural signatures (FSDP)





Wang et al. JNCS 463 (2017) 25

Conclusion:

- ❑ Rigidity transitions provide an interesting framework for the understanding of compositional trends in glasses

- ❑ Optimizing properties from the inspection of anomalous behaviors (maxima and minima)

- ❑ Various means can serve to bring a complex system from flexible to rigid
  Composition, pressure, irradiation, ion strengthening,…

- ❑ Adaptative isostatic window (a thermodynamic phase ?) with surprising properties (highly debated research). Design new applications ?
  - ➢ Weak ageing phenomena. Stable glasses.
  - ➢ Space-filling tendencies, Fragility anomalies (not always,…)
  - ➢ **Experimental challenge (sample preparation)**

- ❑ MD based constraint theory leads to an atomic scale insight and links with various properties (transport, structure, mechanics, conduction,…)

M. Micoulaut, Advances Phys. X (2016). Open