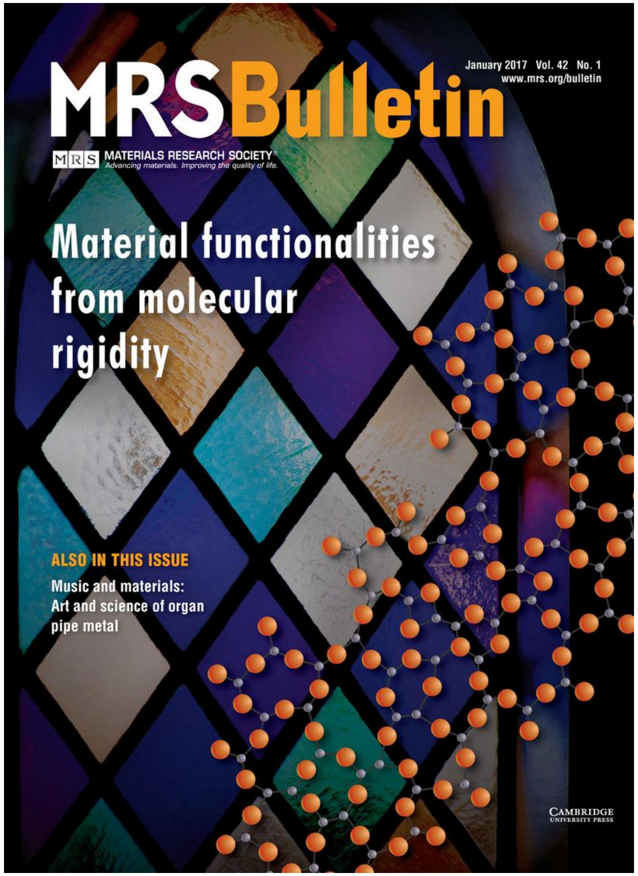
Modélisation des propriétés thermodynamiques par une approche topologique

Matthieu Micoulaut (UPMC)

- Rigidity transitions and compositional trends
- « *Topological engineering* » (Mauro-Gupta)
- MD based rigidity and applications
- Non mean-field effects

Optimizing glass = finding anomalies with composition



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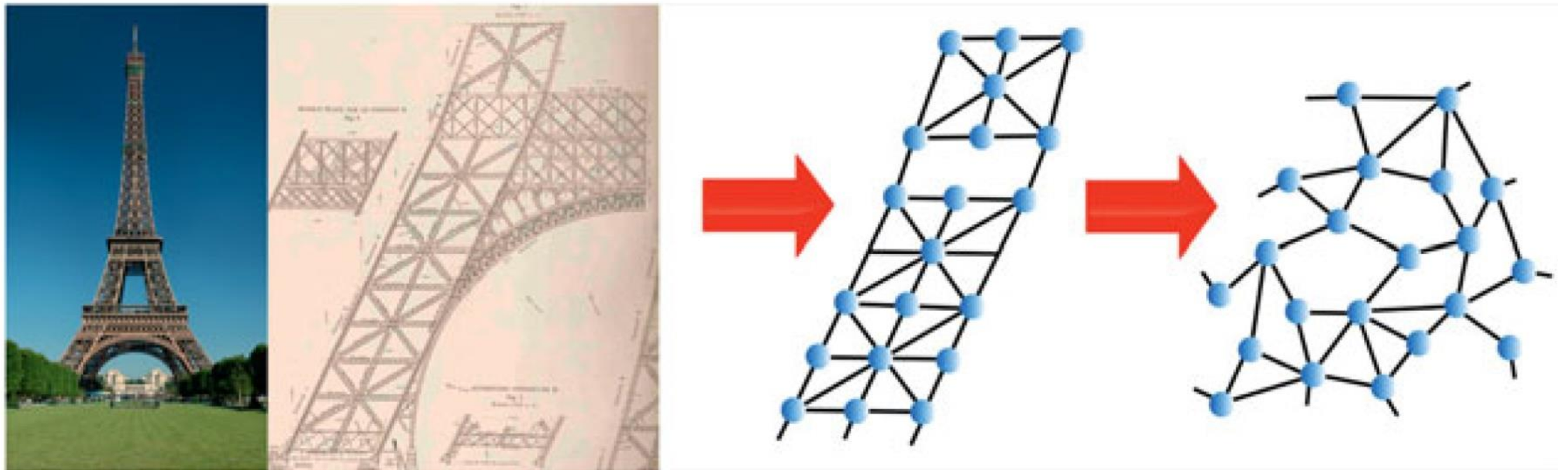
A) Constraint theory

Basic idea: An analogy with mechanical structures (Maxwell)



Mechanical structure

- Nodes
- Bars
- **Tension**

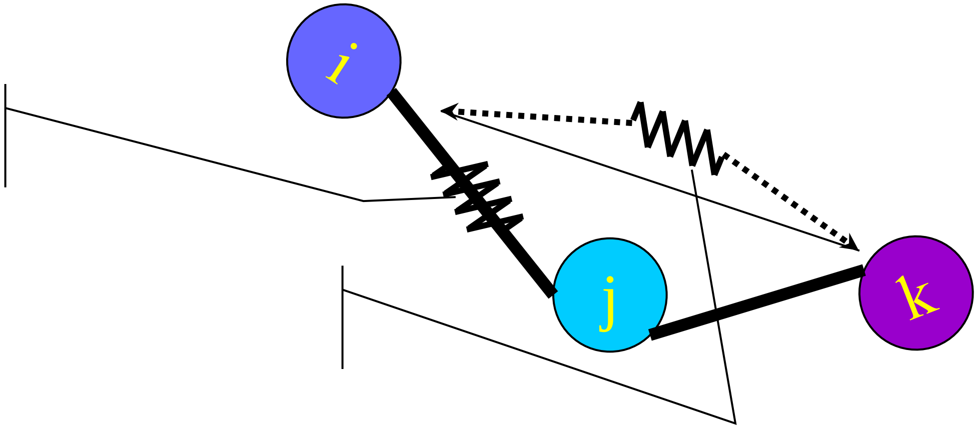
Molecular network (contraint counting)

- 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 :

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

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

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

Rigidity transition

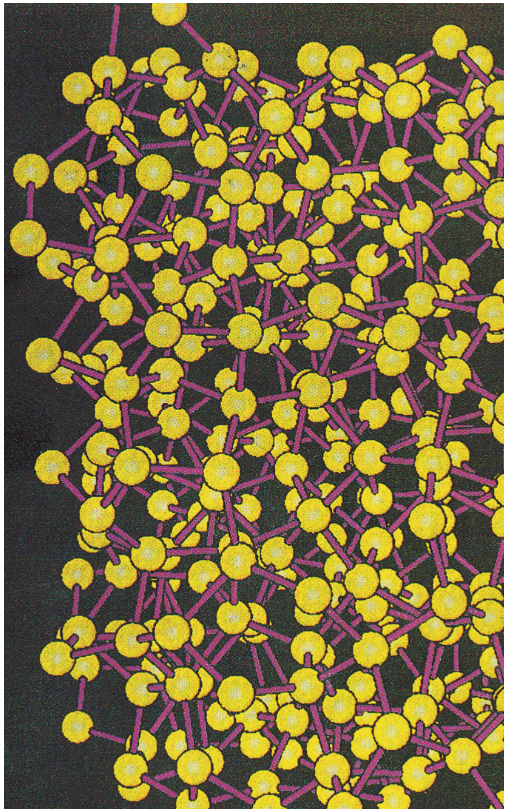
A) CONSTRAINTS AND RIGIDITY TRANSITIONS

2. Rigidity transition:

- Amorphous silicon and harmonic potential

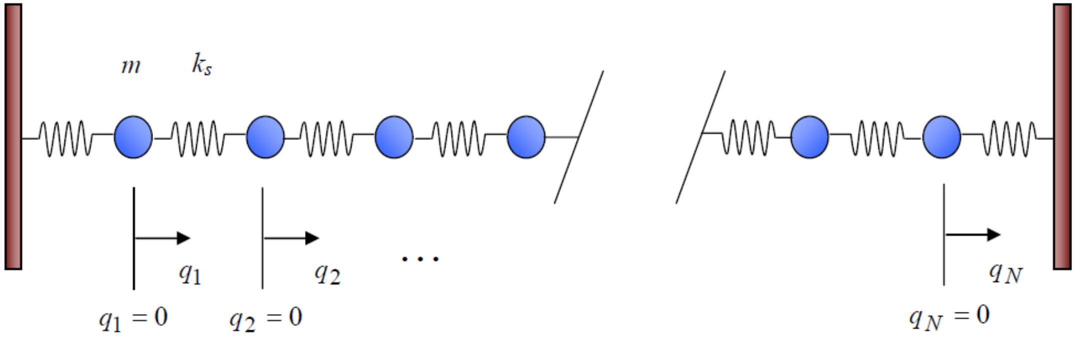
$$V = \frac{\alpha}{2}(\Delta l)^2 + \frac{\beta l}{2}(\Delta \theta)^2$$

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: $F_j = -k_s(q_j - q_{j-1}) - k_s(q_j - q_{j+1})$

- ☐ Newton's law gives: $\ddot{q}_j - \tilde{\varpi}^2(q_{j-1} - 2q_j + q_{j+1}) = 0$

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

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

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

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

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

- ☐ **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

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

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

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

- Isostatic glass n_c=3 is at the R transition

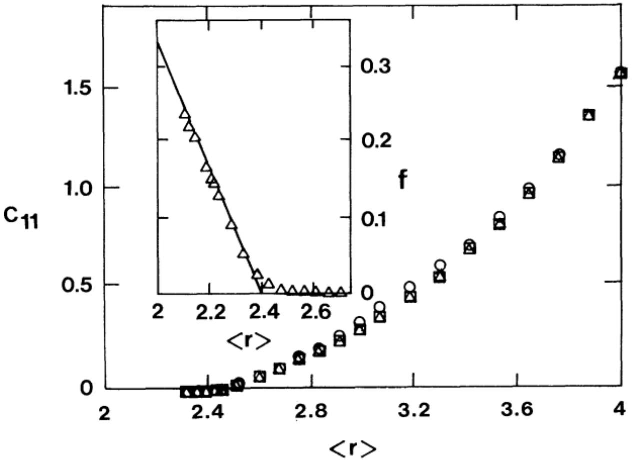


FIG. 1. Elastic modulus C_{11} with $\beta/\alpha = 0.2$ in units where $\alpha = 4a$ and as a function of the mean coordination $\langle r \rangle$. The three symbols are for three different series of random networks. The inset shows the number of zero-frequency modes f (averaged over three networks)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

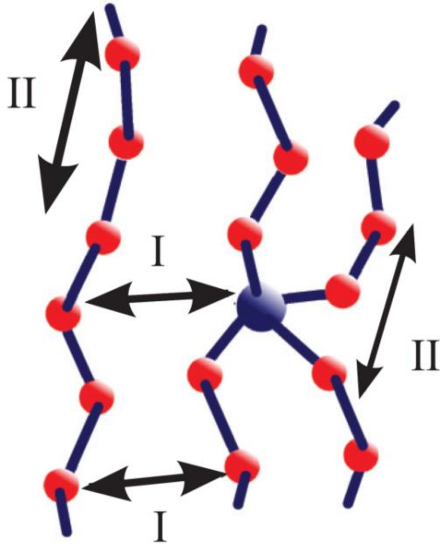
- Ge has 2r-3=5 BB and r/2=2 BS constraints
- Se has 1 BB and 1 BS constraint

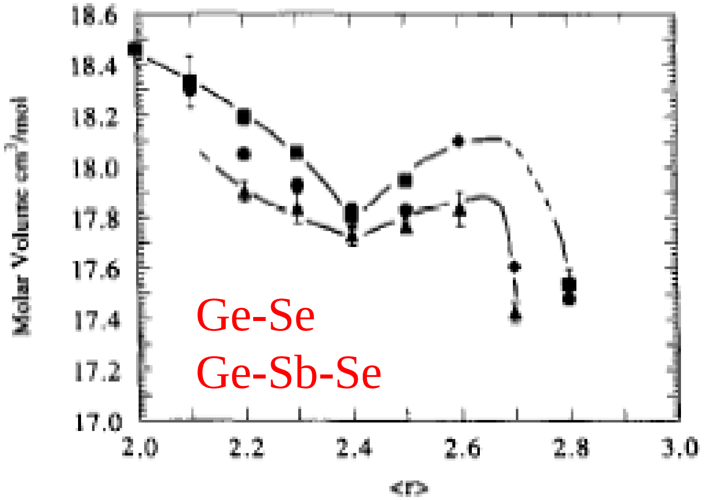
- nc=2(1-x)+7x=2+5x
- Stability criterion for $n_c=3$ i.e. for x=0.2

- 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…

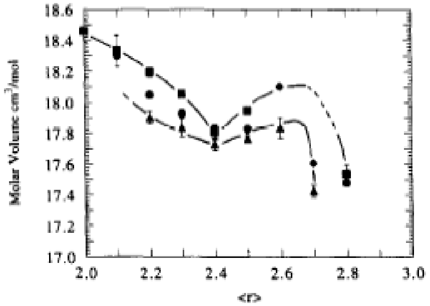


Fig. 6. Dependence of molar volume on ⟨r⟩ for binary Ge–Se and ternary Ge–Sb–Se systems. The molar volume at room temperature for the binary and ternary are represented by ■ and ▲, respectively. The molar volume values for the binary glasses given by Ota et al. [11] are represented by ● and those for 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%.

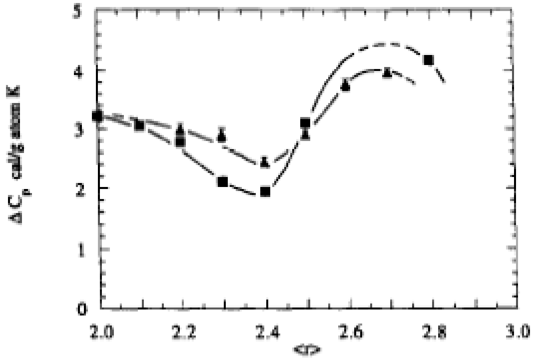


Fig. 10. ΔC_p versus ⟨r⟩ for binary Ge–Se and ternary Ge–Sb–Se systems. The ΔC_p values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 1.8%.

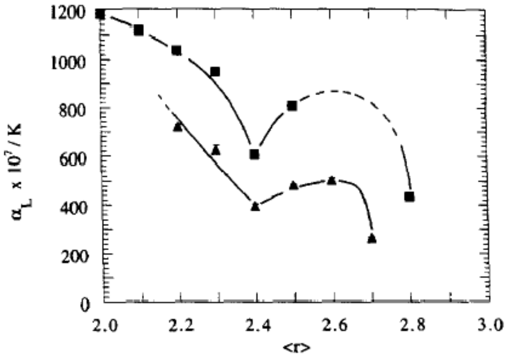
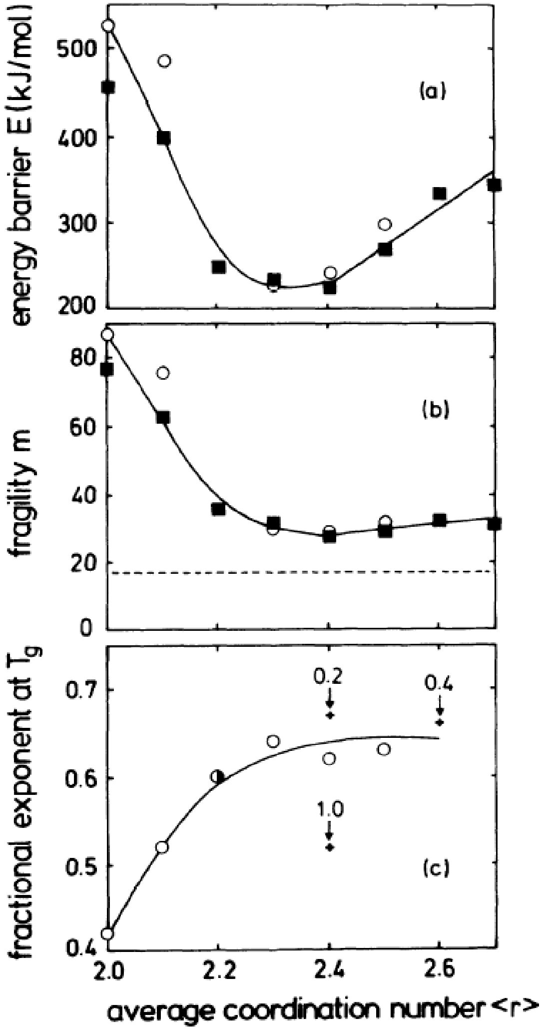


Fig. 4. Liquid state thermal expansion coefficient, α_L, versus ⟨r⟩ for the binary Ge–Se and ternary Ge–Sb–Se systems. The α_L values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 3.5%.



Boehmer and Angell, PRB 1994

Varshneya et al., JNCS 1991

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:

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

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

- 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:

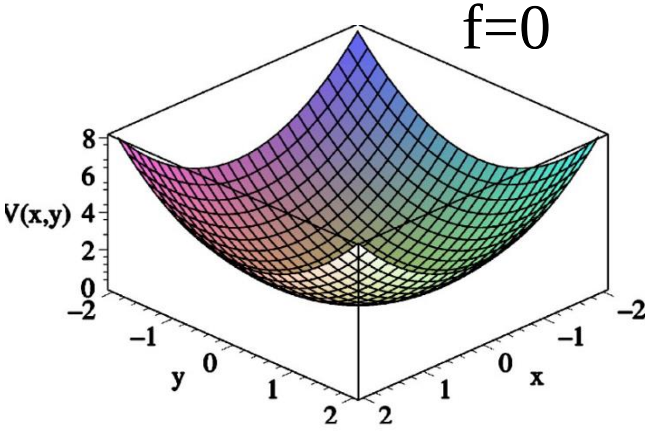
- For a given inherent structure (local minimum of the PES), the number of channels is given by *f*.

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

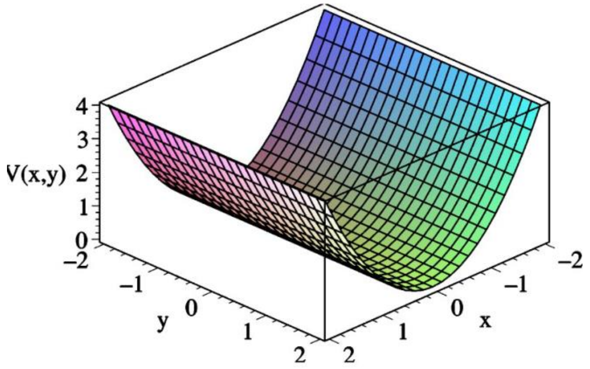
- At fixed volume, $\Omega(E,V,N)$ is proportional to the area defined by the surface f constant E. $S=k_B\ln\Omega$

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

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:

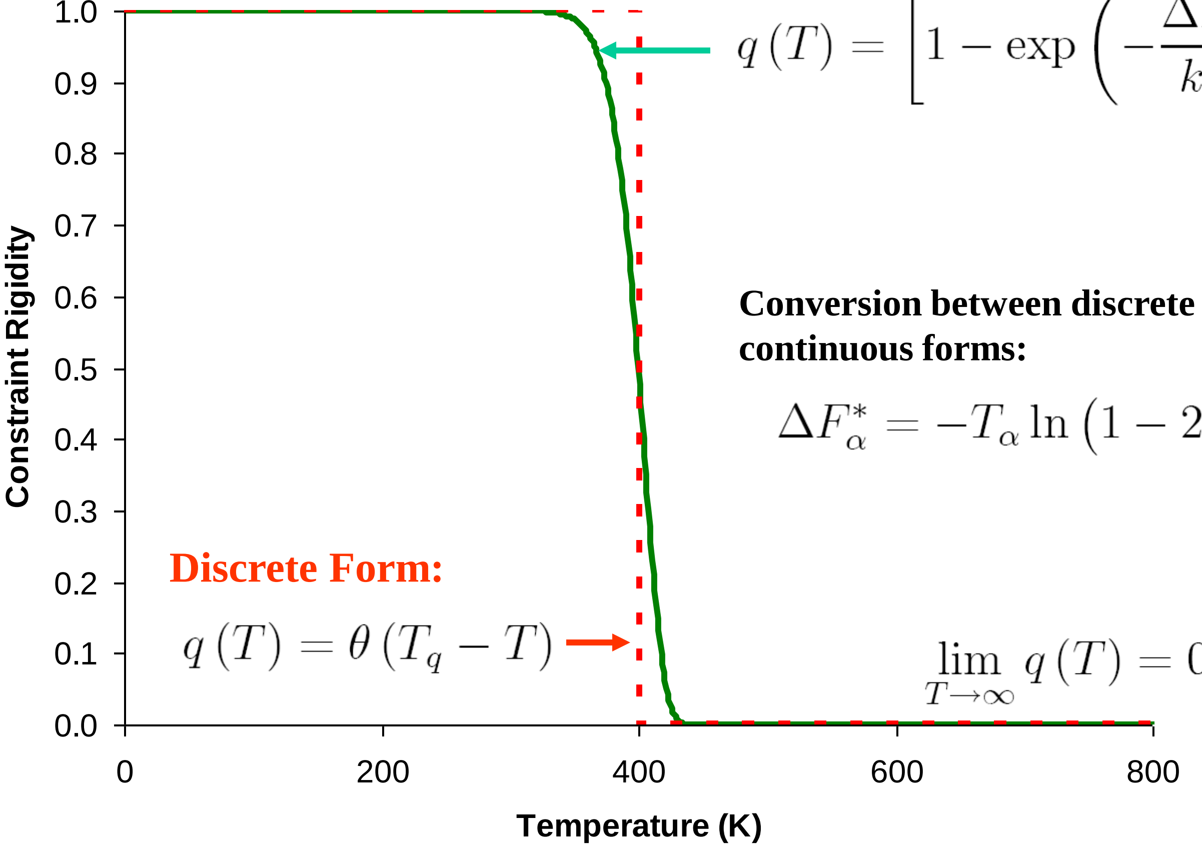
$$n\left(T,x\right)=\sum_{i}N_{i}\left(x\right)\sum_{\alpha}w_{i,\alpha}q_{\alpha}\left(T\right)$$

- 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)

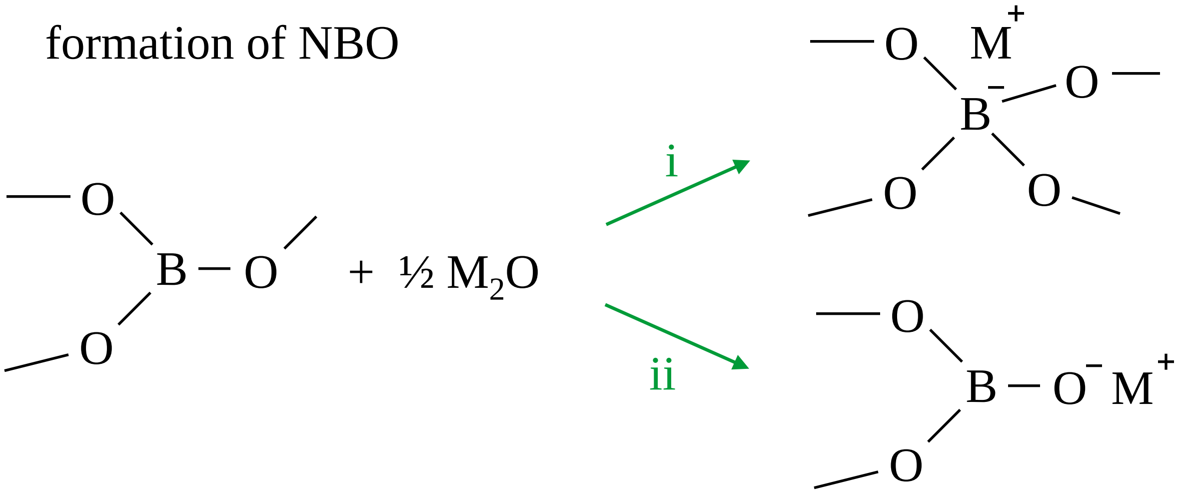
4. Connect the change in degrees of freedom ($f = d - n$) with change in specific property of interest

D) Temperature dependent constraints

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

- ☐ Applied to borate glasses $Na_2O\text{-}B_2O_3$

- ☐ 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

<u>Step 1</u>: Model the local structure as a function of composition

☐ Complete statistics

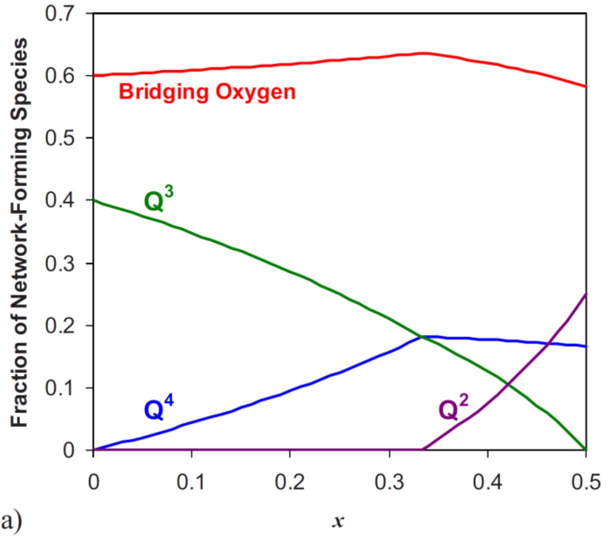
x>0.33 $$N_2(x) = \frac{3(3x-1)}{5(1-x)} \qquad N_3(x) = \frac{1-2x}{1-x} \qquad N_4(x) = \frac{3-4x}{5(1-x)}$$

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).

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



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 $T<T_{onset}$

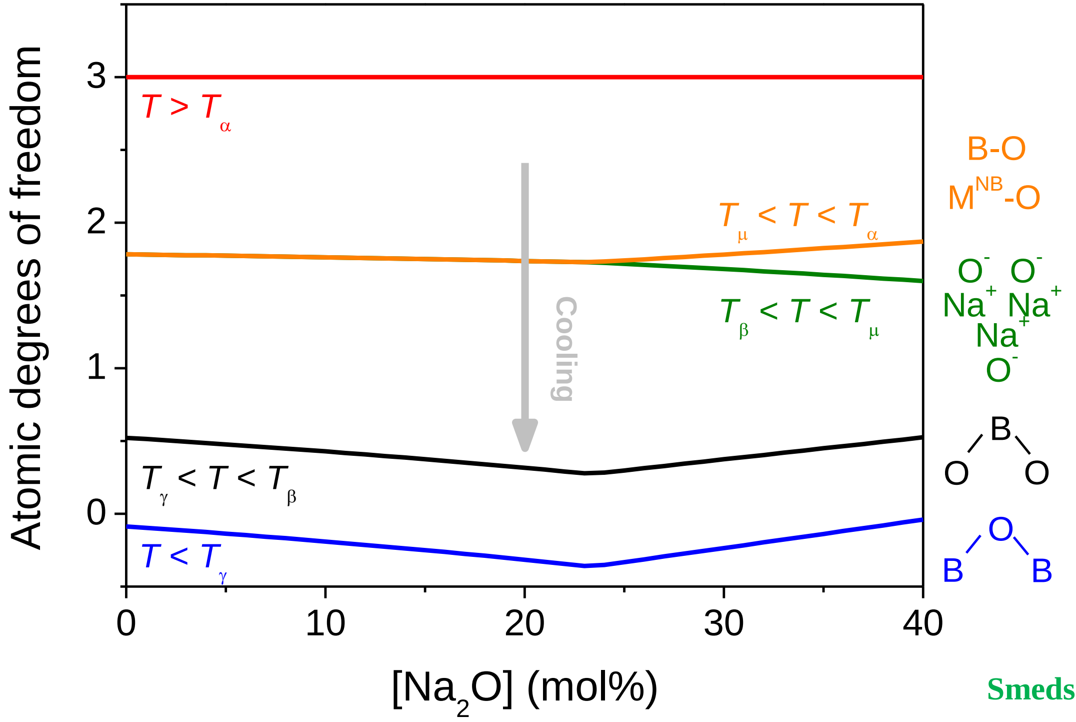
Similar procedure for borosilicates

D) Temperature dependent constraints

<u>Step 3</u>: Ranking of constraints according to temperature

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

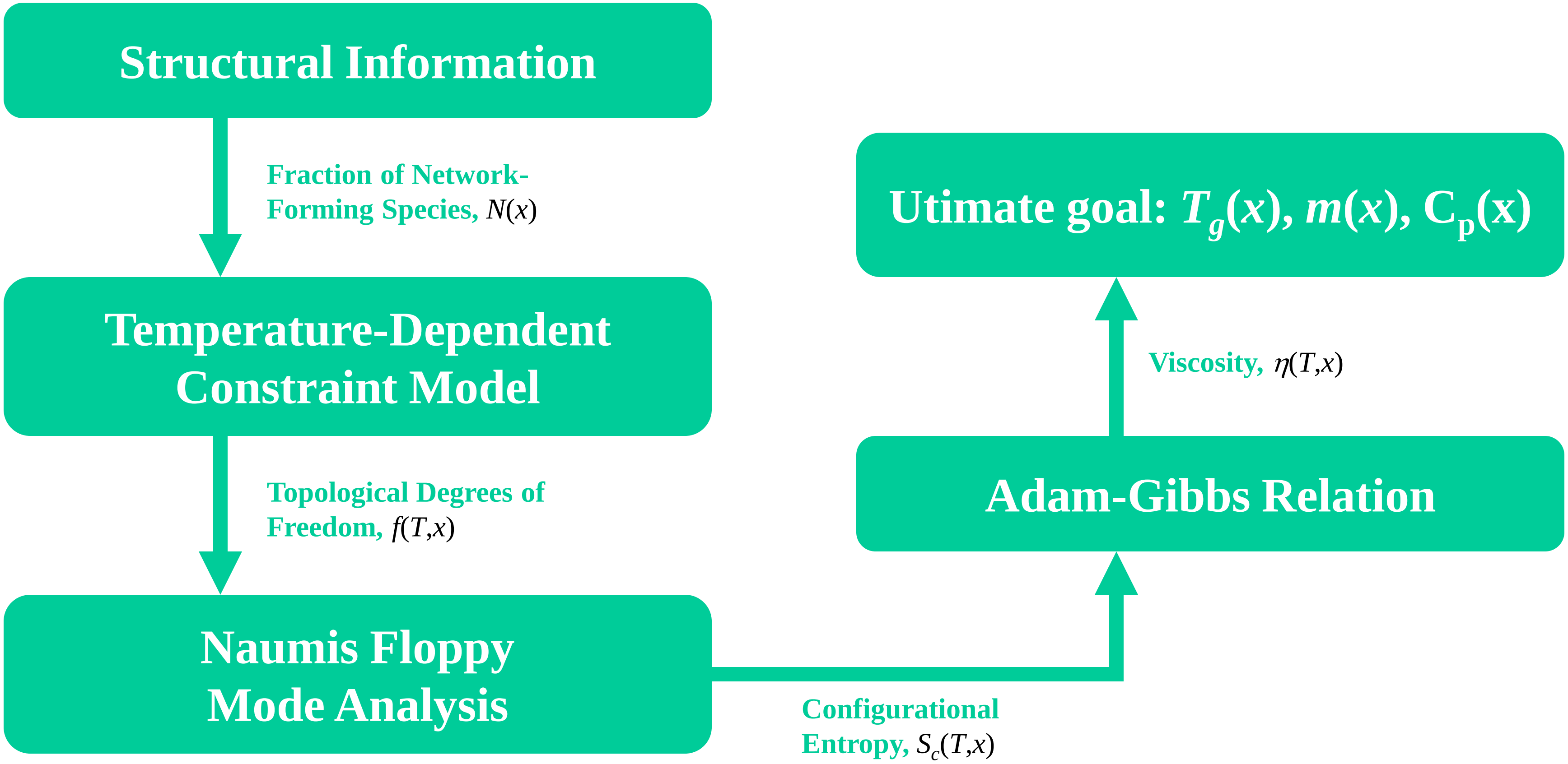
- Constraints become rigid as temperature is lowered
  - Onset temperatures:



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

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:

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

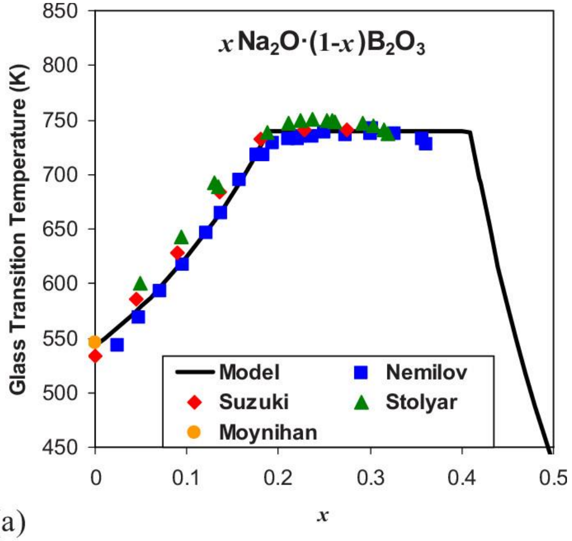
F. Application to sodium borates

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

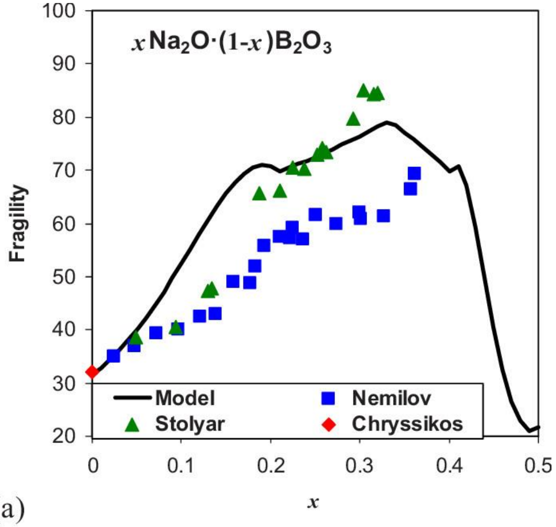
$$T_g(x) = \begin{cases} \dfrac{1}{5}\left(\dfrac{5-4x}{1-2x}\right) T_g(0), & x \leq \dfrac{1}{3}, \\[2ex] \dfrac{1}{11}\left(\dfrac{31-38x}{8x-1}\right) T_g\left(\dfrac{1}{3}\right), & \dfrac{1}{3} < x \leq \dfrac{1}{2}, \end{cases}$$

D) Temperature dependent constraints

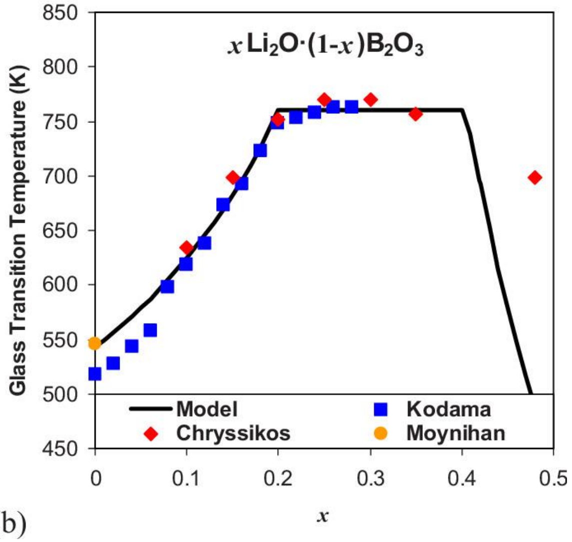
Results: Fragility and Tg variation of sodium borate glass



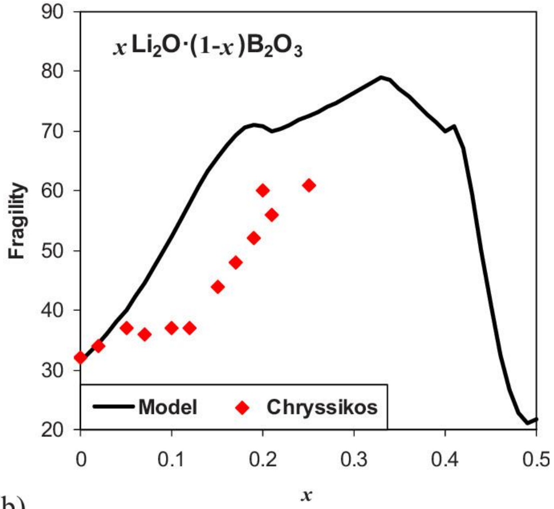
(a)



(a)



(b)

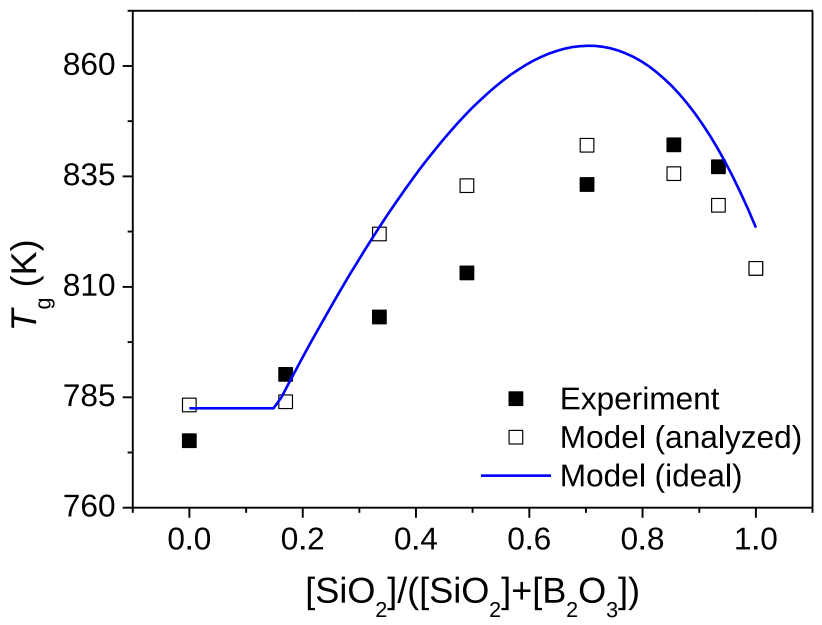


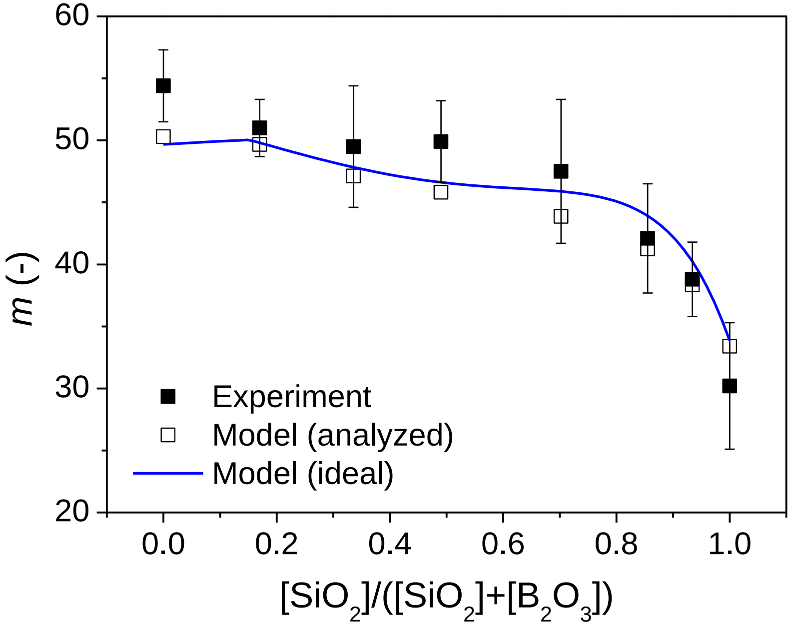
(b)

JCP **2009,** 130,

D) Temperature dependent constraints

Results: Fragility and Tg variation of sodium borosilicate glass



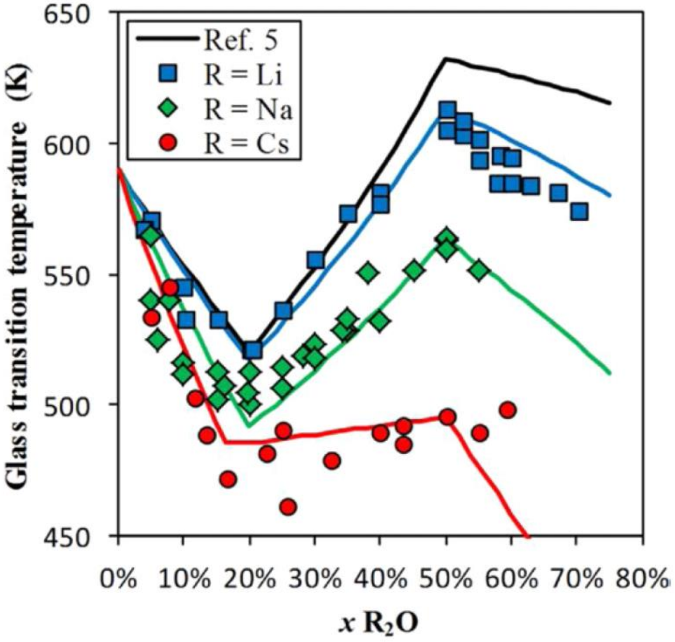


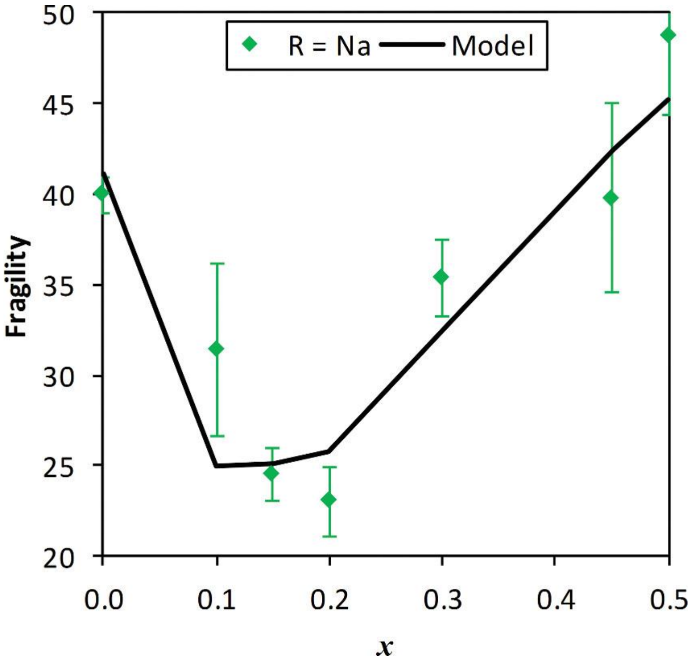
- T_g of a borate glass can be predicted from that of a silicate glass with $f(x,y,z,T)$ as the only scaling parameter
- Fragility: onset temperatures $T_{\beta,\mathrm{Si}}$ and T_μ are treated as fitting parameters (1425 K)

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

D) Temperature dependent constraints

<u>Results</u>: 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}

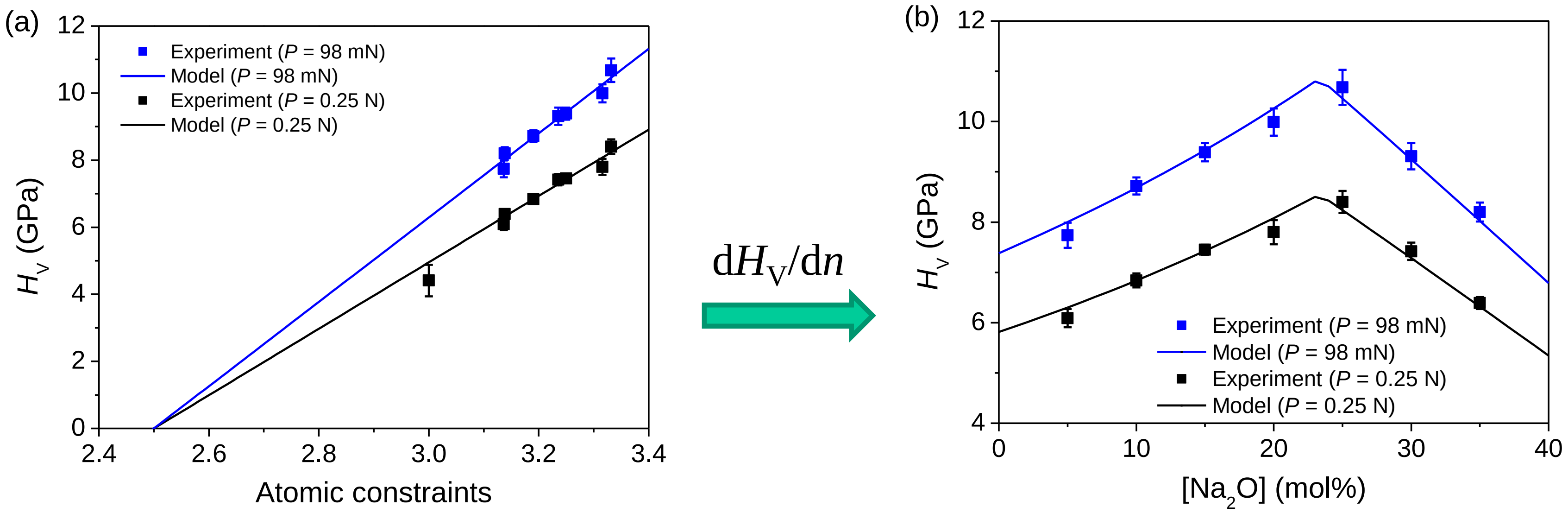
- ❑ Proposal: hardness is proportional to the number of 3D network constraints at room temperature

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

?

D) Temperature dependent constraints

Results: Hardness H_v in borates and borosilicates

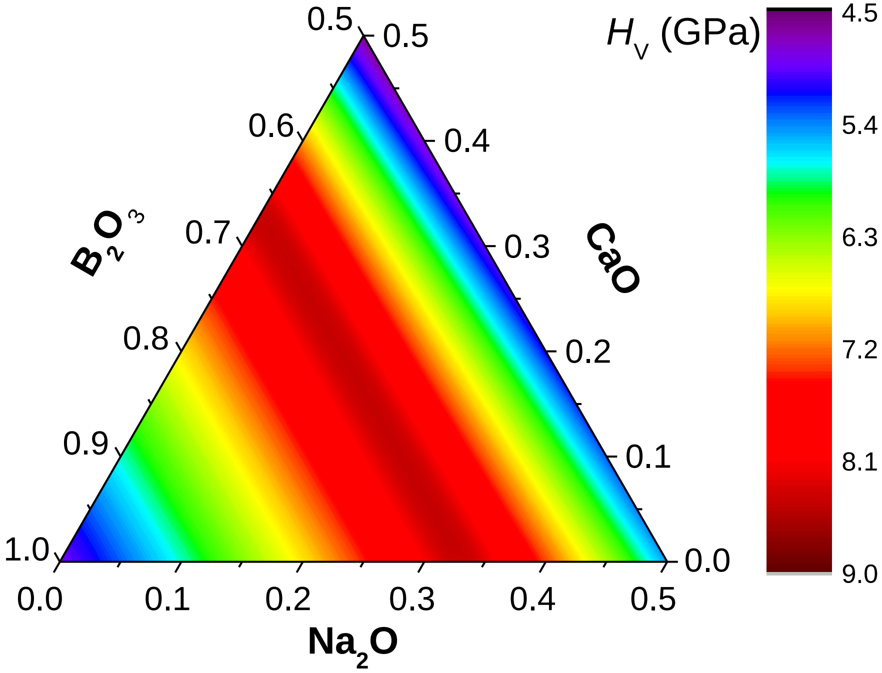


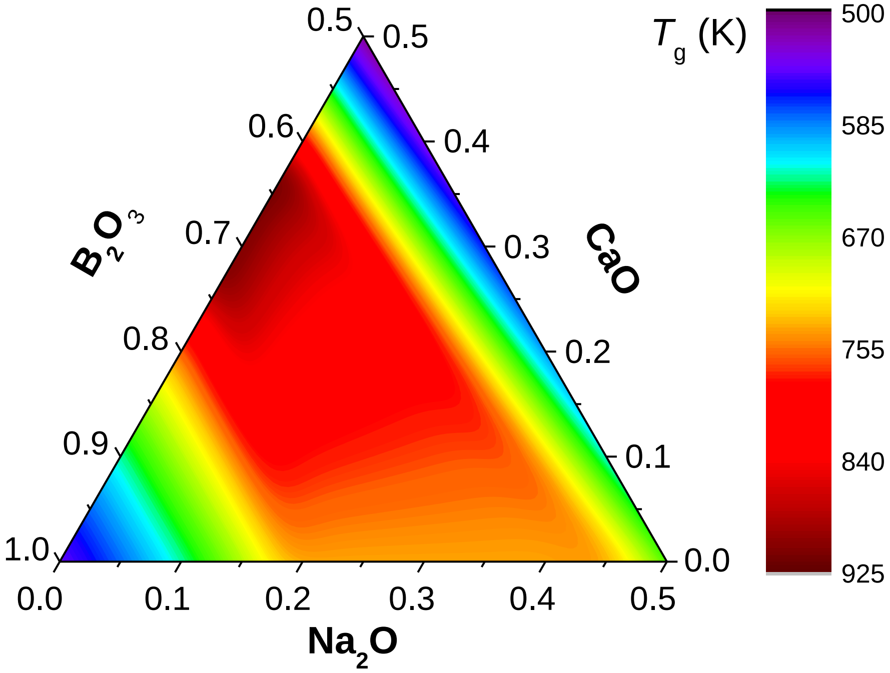
- Glass hardness can be predicted from the average number of room temperature constraints, with only an unknown proportionality constant (dH_V/dn)

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

D) Temperature dependent constraints

Results: Quantitative design 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

C) Temperature dependent constraints

Results: Calculating the specific heat from constraints

- Correlating the kinetic fragility index *m* with thermodynamic property change at T_g

$$\Delta C_\mathrm{p} = C_\mathrm{pl} - C_\mathrm{pg} \cong C_\mathrm{p,conf}$$

$$\Delta C_\mathrm{p}(x,y,z,T) = \left(\frac{\partial H_\mathrm{conf}}{\partial T}\right)_P = \left(\frac{\partial H_\mathrm{conf}}{\partial \ln S_\mathrm{conf}}\right)_P \left(\frac{\partial \ln S_\mathrm{conf}}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H_\mathrm{conf}}{\partial \ln S_\mathrm{conf}}\right)_P \left(\frac{\partial \ln S_\mathrm{conf}}{\partial \ln T}\right)_P$$

  - Adam-Gibbs model →

$$m = m_0\left(1 + \left.\frac{\partial \ln S_\mathrm{conf}(T)}{\partial \ln T}\right|_{T=T_\mathrm{g}}\right)$$

$$\eta = \eta_\infty \exp\left(\frac{B}{TS_\mathrm{conf}}\right)$$

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

C) Temperature dependent constraints

<u>Results</u>: Calculating the specific heat from constraints

$$\Delta C_\mathrm{p}[x,y,z,T_\mathrm{g}(x,y,z)] = \frac{1}{T_\mathrm{g}(x,y,z)}\left(\frac{\partial H_\mathrm{conf}}{\partial \ln S_\mathrm{conf}}\right)_{P,T=T_\mathrm{g}(x,y,z)}\left(\frac{m(x,y,z)}{m_0}-1\right)$$

$$\Delta C_\mathrm{p}[x,y,z,T_\mathrm{g}(x,y,z)] = \frac{S_\mathrm{conf}[x,y,z,T_\mathrm{g}(x,y,z)]}{T_\mathrm{g}(x,y,z)}\left(\frac{\partial H_\mathrm{conf}}{\partial S_\mathrm{conf}}\right)_{P,T=T_\mathrm{g}(x,y,z)}\left(\frac{m(x,y,z)}{m_0}-1\right)$$

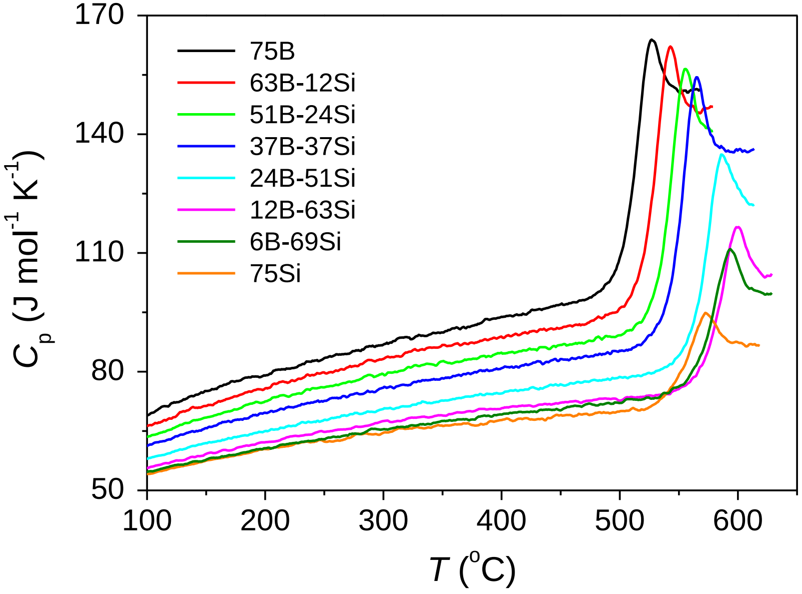
According to temperature-dependent constraint theory, configurational entropy at T_g is inversely proportional to T_g.

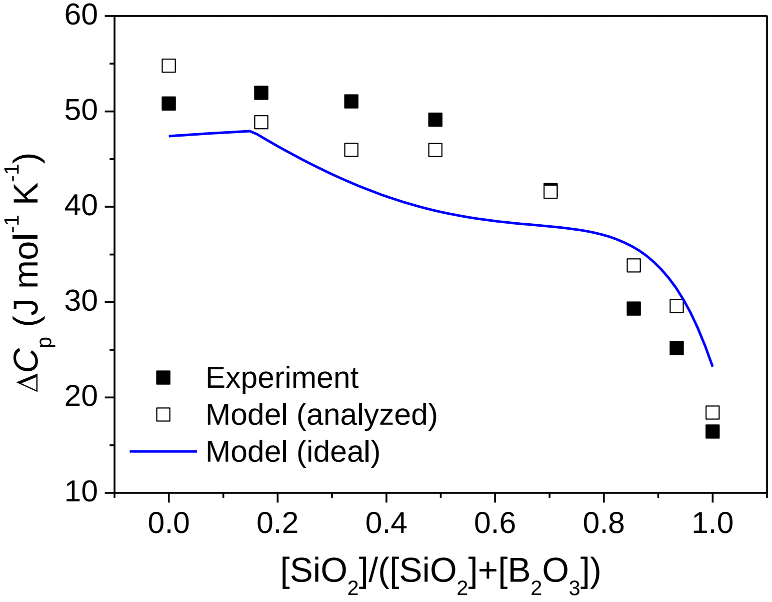
This is a configurational temperature of the glass at T_g. For a normal cooling rate (10 K/min), $T_\mathrm{conf} = T_\mathrm{g}$.

$$\Delta C_\mathrm{p}[x,y,z,T_\mathrm{g}(x,y,z)] = \frac{A((x,y,z)_\mathrm{R})}{[T_\mathrm{g}(x,y,z)]^2}T_\mathrm{conf}(x,y,z)\left(\frac{m(x,y,z)}{m_0}-1\right) = \frac{A((x,y,z)_\mathrm{R})}{T_\mathrm{g}(x,y,z)}\left(\frac{m(x,y,z)}{m_0}-1\right)$$

C) Temperature dependent constraints

<u>Results</u>: Results for the specific heat (borosilicates)





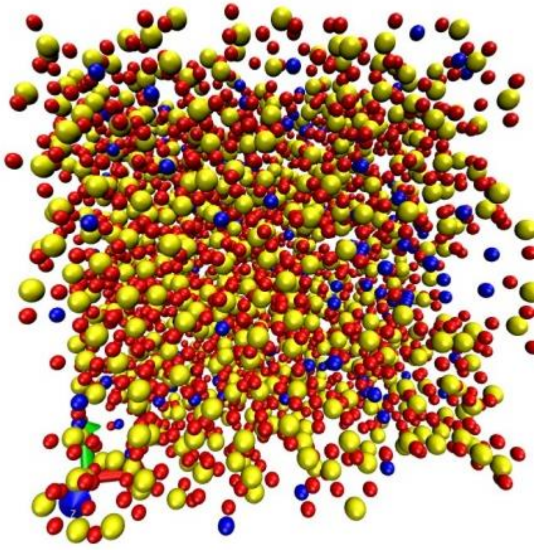
- $\Delta C_p(x,y,z)$ can be predicted with A is the sole fitting parameter (19 kJ/mol)
- Thermodynamic property changes during the glass transition are connected to the kinetic fragility index

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

Constraints/rigidity – Summary

- Powerful and simple tool.
- Builds on a structural model
- Prediction of fragility, Tg, hardness, ΔCp as a function of composition
- Parameters ?

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) ?**

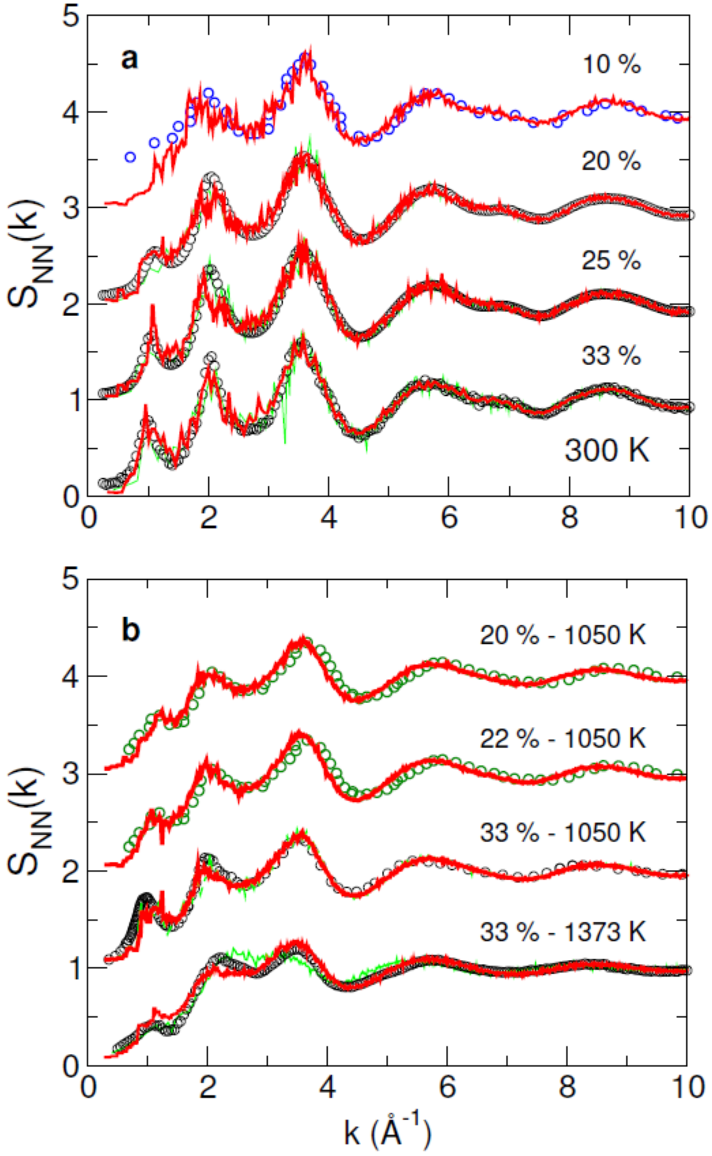
Broken Si-O-Na angular constraints in oxides,...
Thermally activated broken constraints (Mauro-Gupta)

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

Links glass topology with simulations and the statistical physics of liquids

Need to have a good starting MD generated structural model

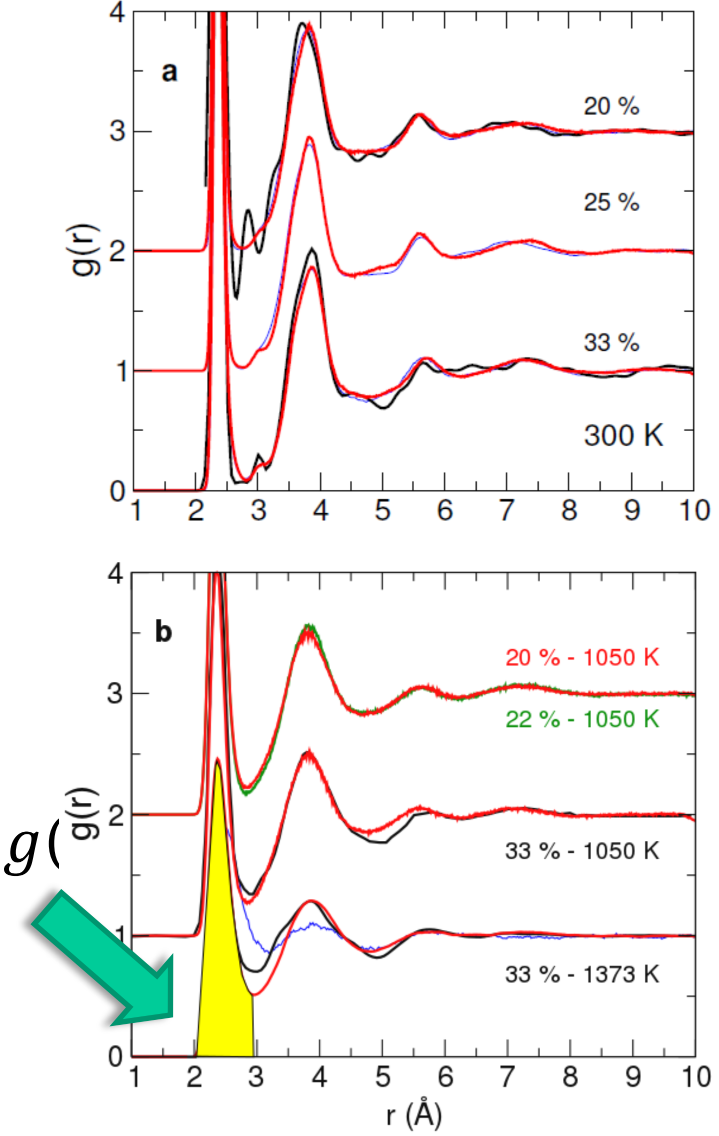
Structure Factors



Pair Correlation Functions

Ge_xSe_{100-x}

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



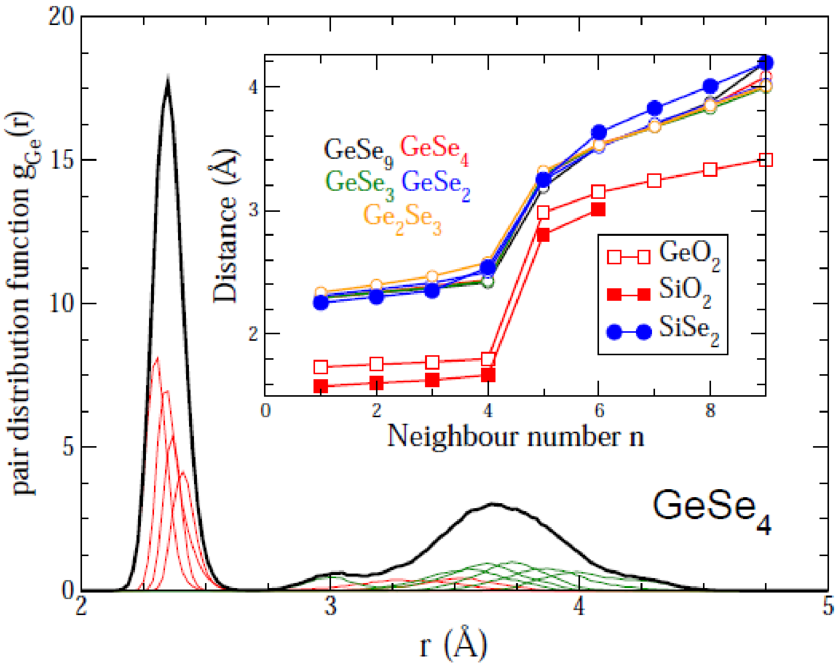
Yildirim, Raty, Micoulaut, Nature Comm. 7, 11086 (2016).

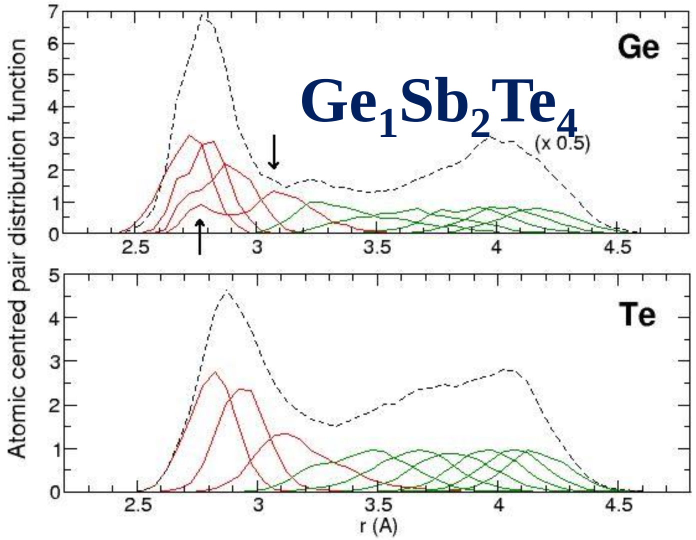
2. General idea:

❑ 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

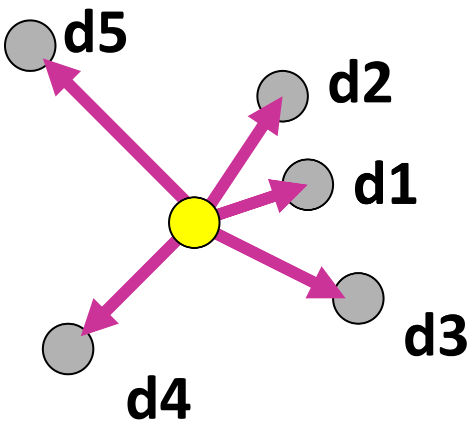
❖ two local environments for Ge

❖ CN(Te) >2

Micoulaut et al. PRB 2010

❑ Compute from these trajectories

1. bond-bending (work on angles)



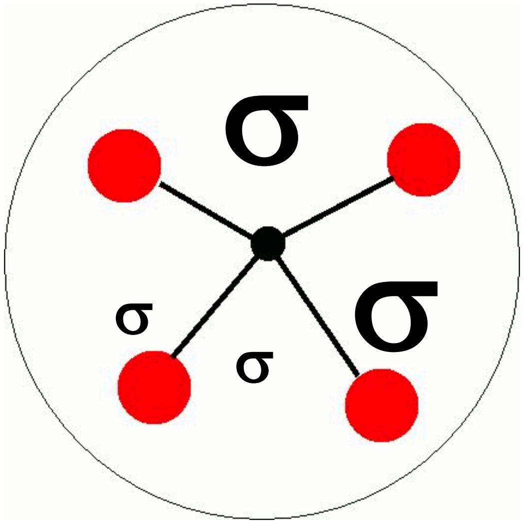
N first neighbor distance distrib.

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



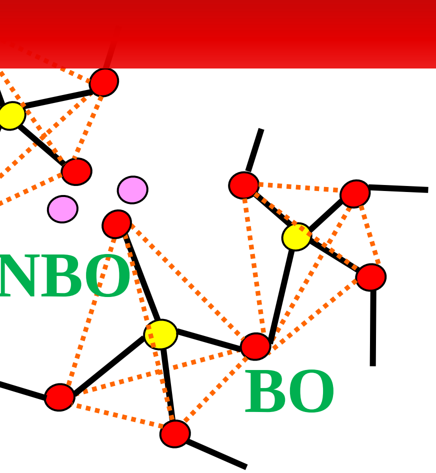
- Splitting the BAD into contributions from neighbours.
- Compute the second moment (σ_ι , sometimes fwhm) of each PBA Distribution.

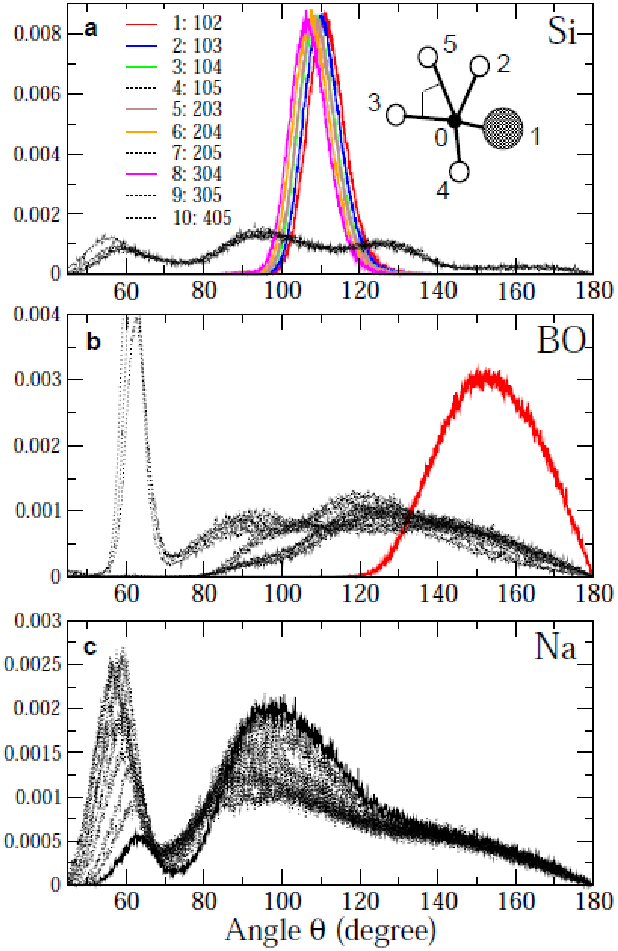
$$\langle {\theta_i}^2 \rangle = \int \theta^2 P_i(\theta) d\theta \qquad {\sigma_i}^2 = \langle {\theta_i}^2 \rangle - \langle \theta_i \rangle^2$$

Constraints+Dynamics of liquids

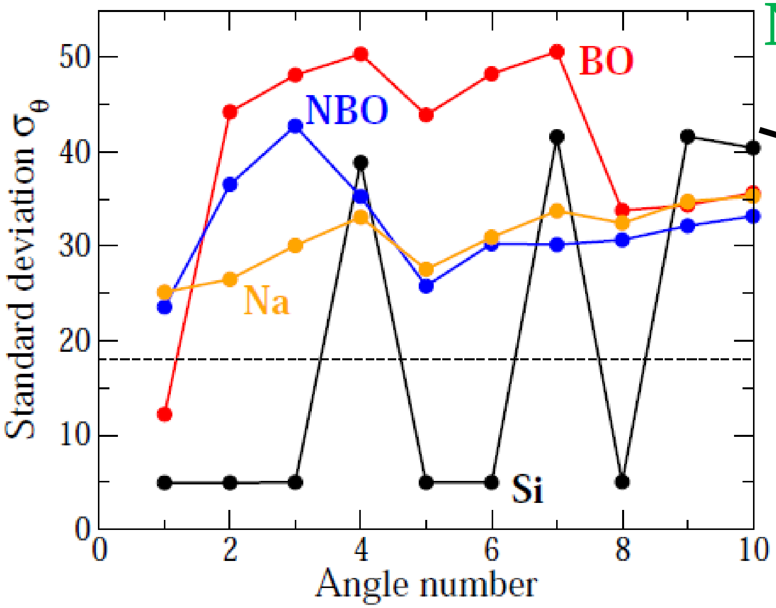
Focus on bond-bending constraints

SiO_2-$2Na_2O$





Bauchy et al, JNCS 2011



- ☐ Angular constraints are intact only for Si and BO

Clear gap between σ(Si), σ(BO) and σ(Na) and σ(NBO)

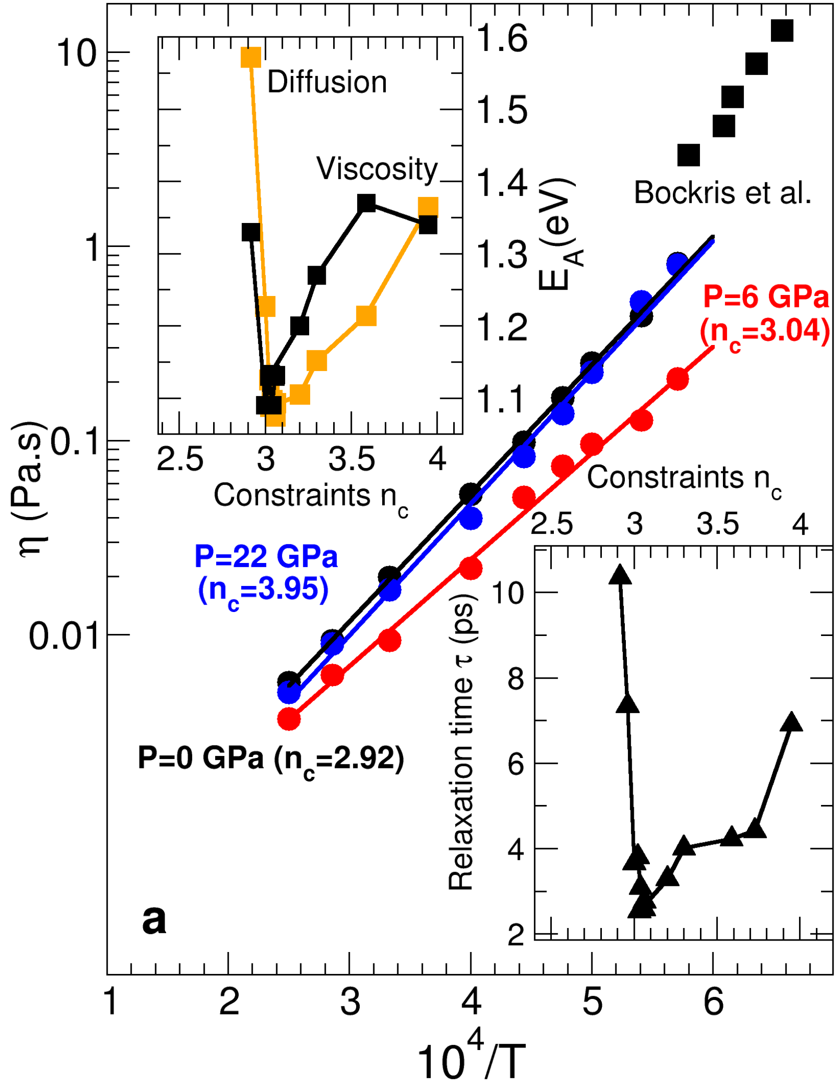
Constraints+Dynamics of liquids

Separate calculation of dynamic/thermodynamic properties and constraints

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

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

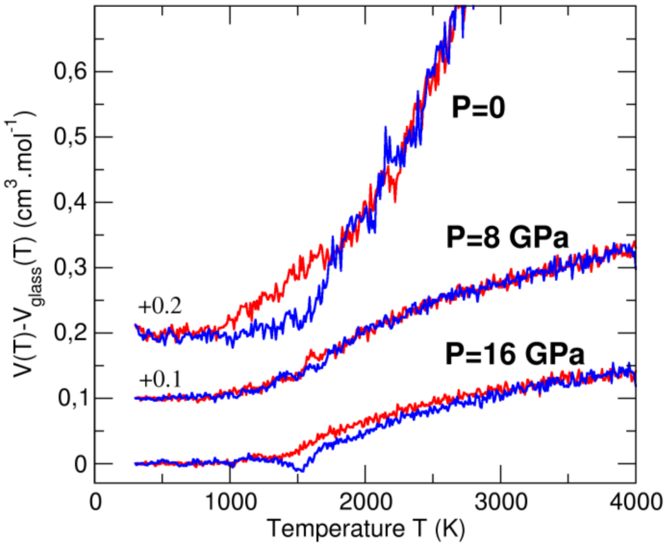
- Enhanced relaxation, relaxation time also minimizes



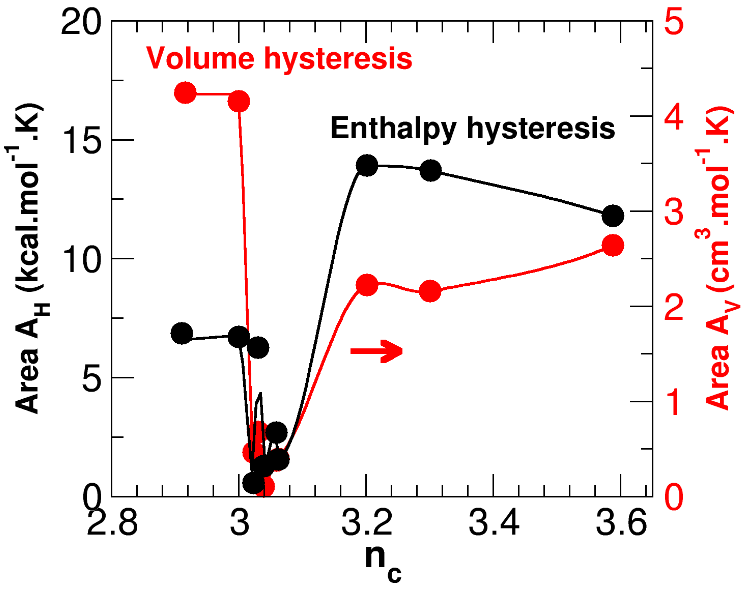
Bauchy, Micoulaut, Nature Comm. 6, 6398 (2015)

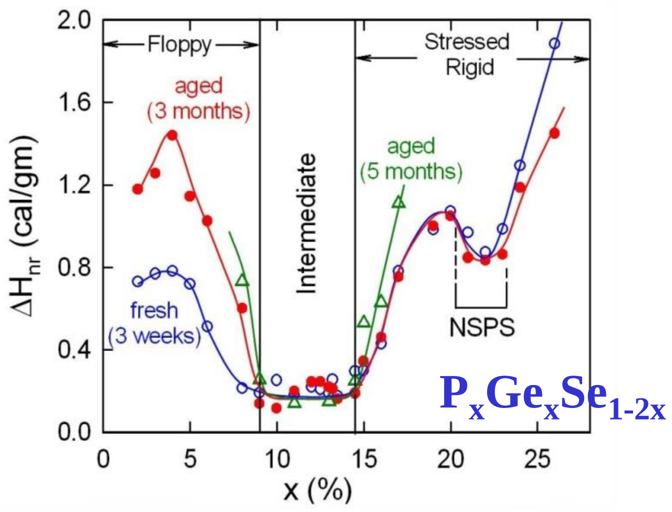
Constraints+Dynamics of liquids

Glass reversibility



- ☐ Isostatic (n_c=3) glass transitions display an ease to reversibility at the glass transition.
- ☐ Thermal anomalies are linked with anomalies in transport in the liquid and with structural anomalies in the glass.

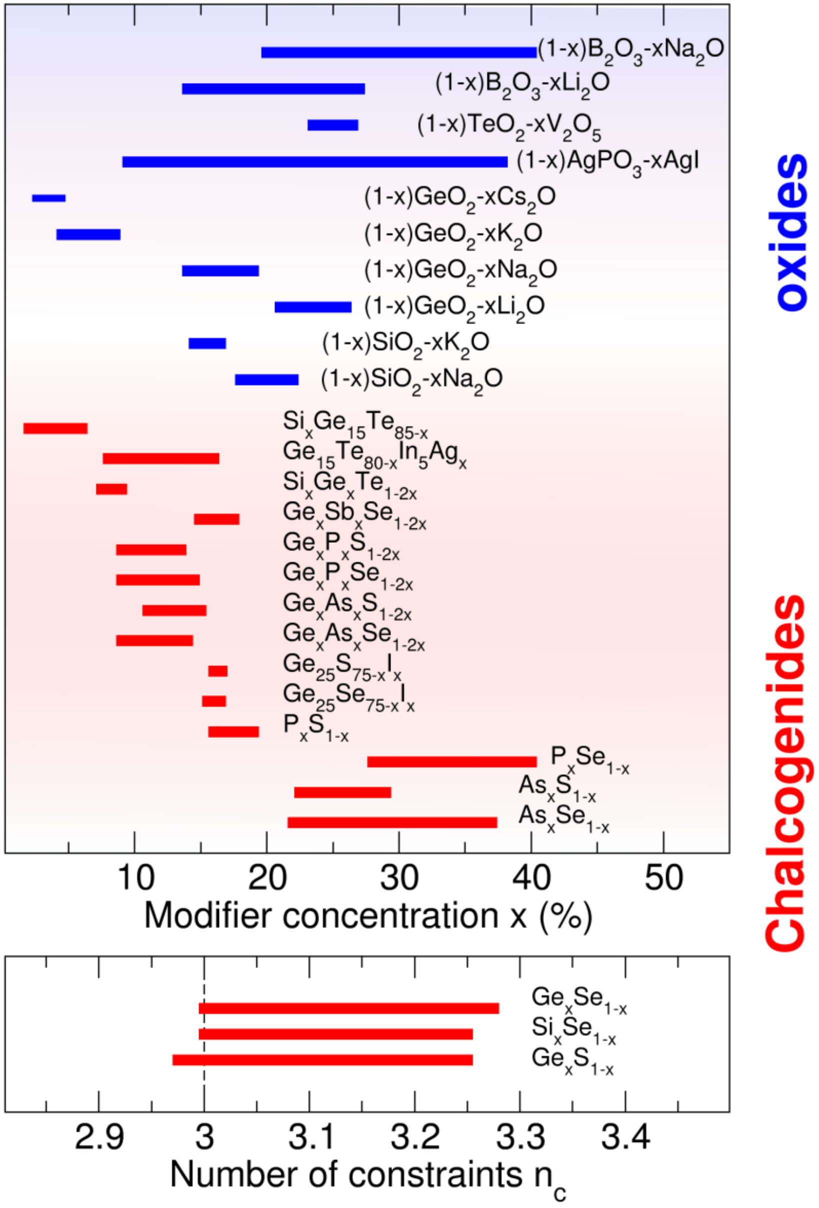


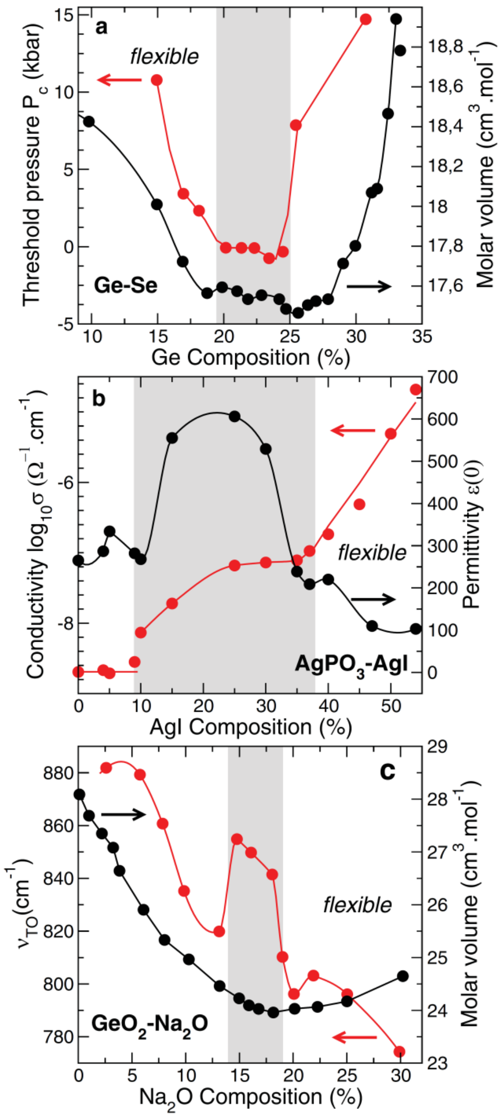


$P_xGe_xSe_{1-2x}$

Chakravarthy et al. JPCM (2005)

Constraints+Dynamics of liquids





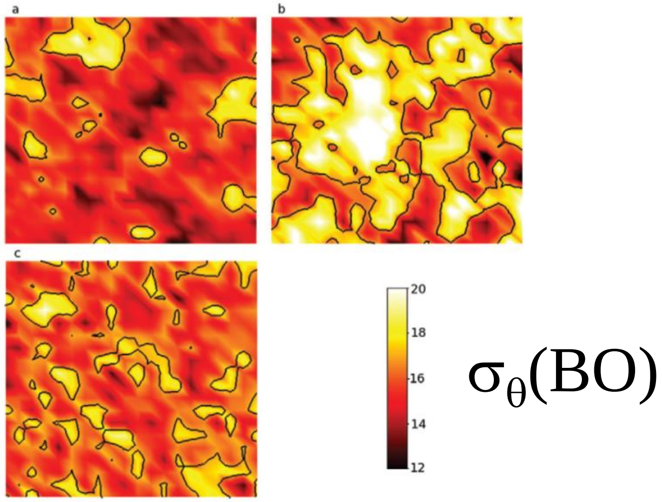
Micoulaut, Bauchy, PSS 2013

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

Constraints+Dynamics of liquids

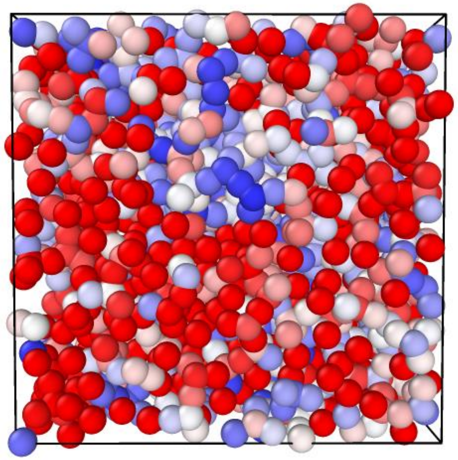
Are these constraints homogeneously distributed ?

Bauchy et al. EPL 2013

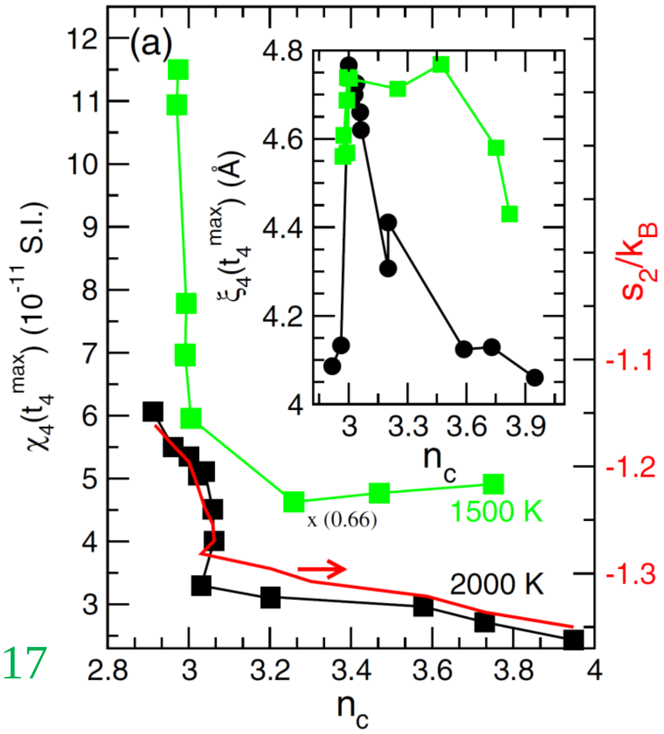


Do they impact more subtle aspects of dynamics ?

Dynamic heteroegenities



Micoulaut et al. PRL 2017



Constraints+Dynamics of liquids

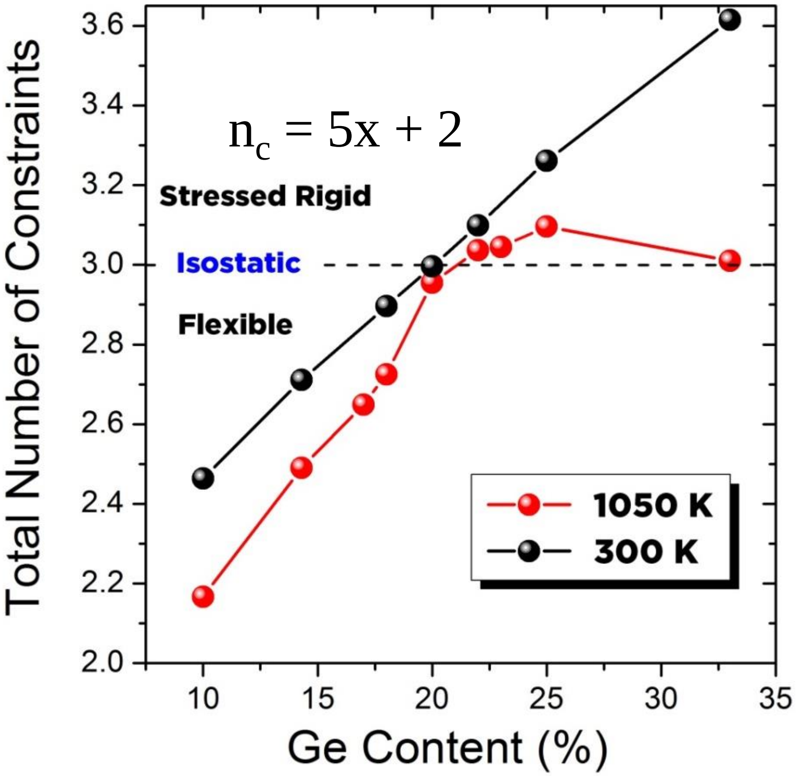
Mean Field prediction is well reproduced

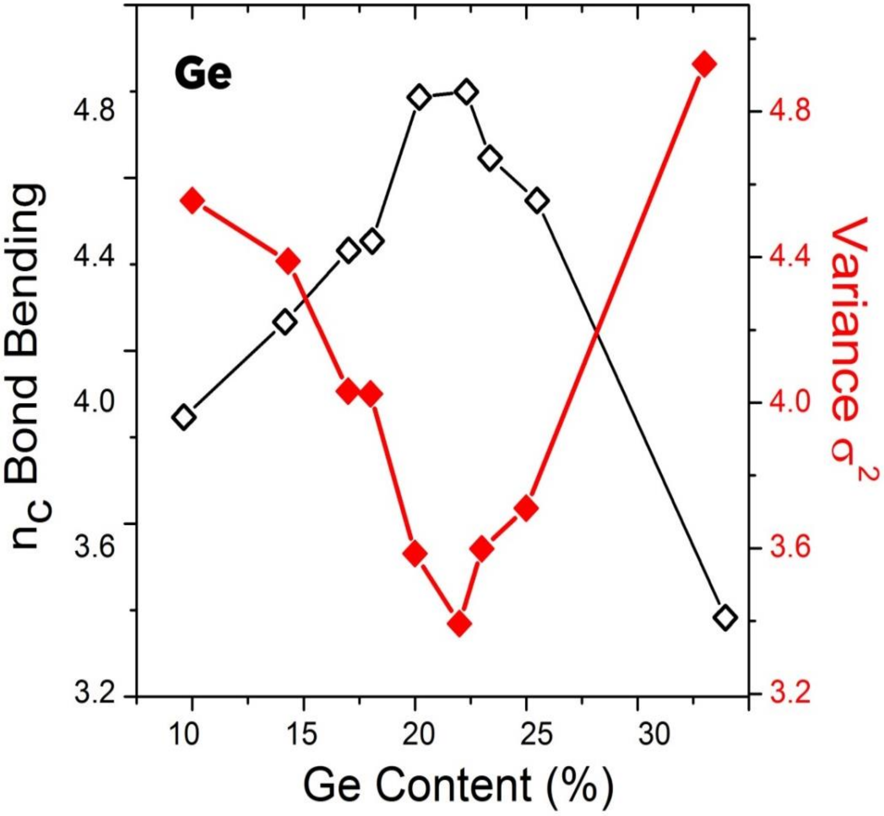
At 300 K but constraints soften at high

temperature

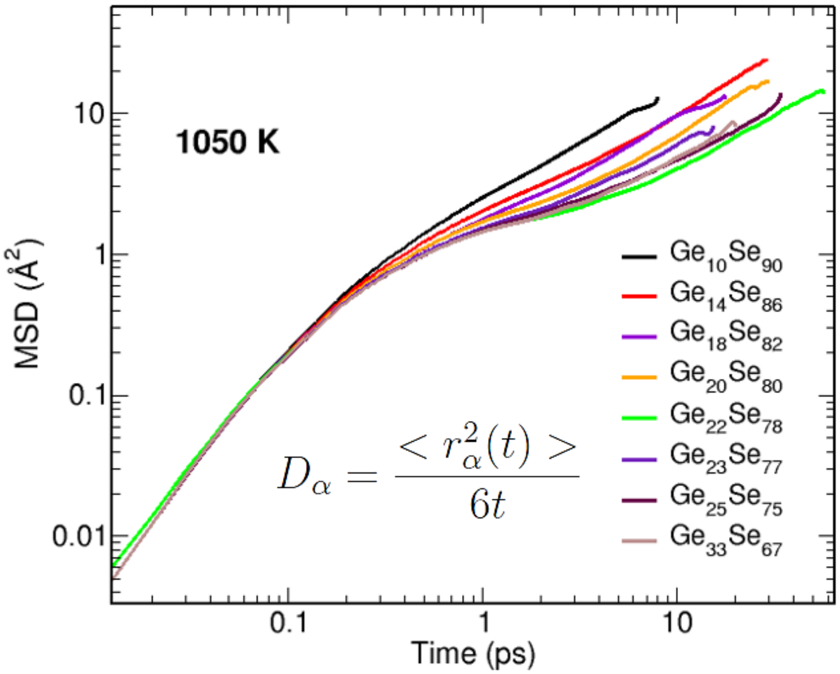
Weak variation of Ge BB at

the rigidity transition





Constraints+Dynamics of liquids



$$D_\alpha = \frac{< r_\alpha^2(t) >}{6t}$$

Non-monotonous Diffusion !

Diffusivity markedly decreases

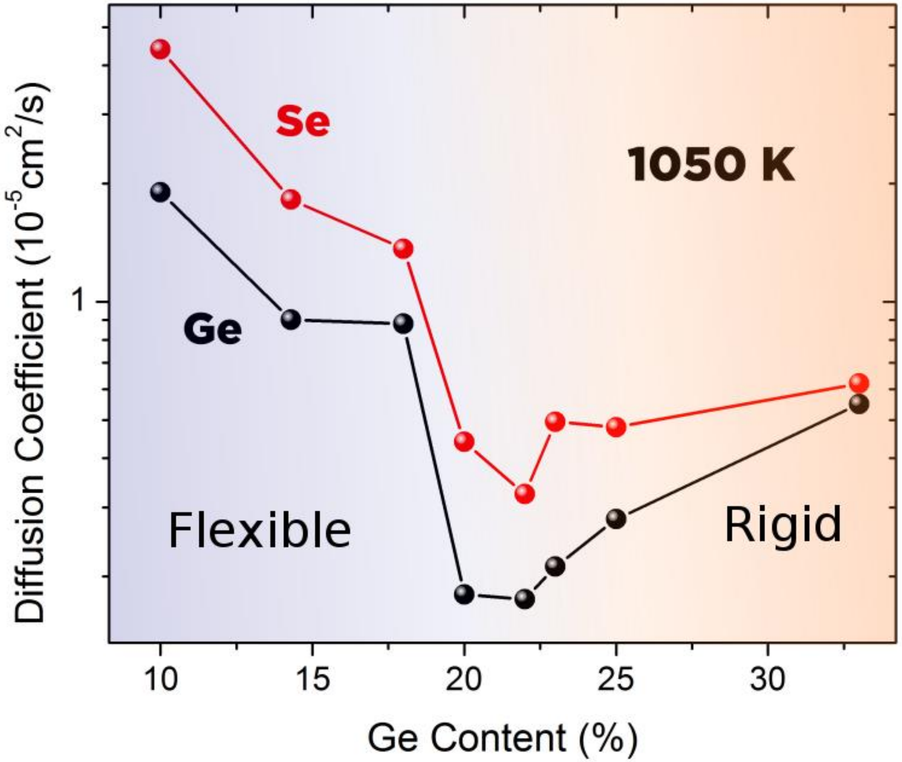
between 18-22 % Ge

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

Expectation :

Mobility decreases as Ge

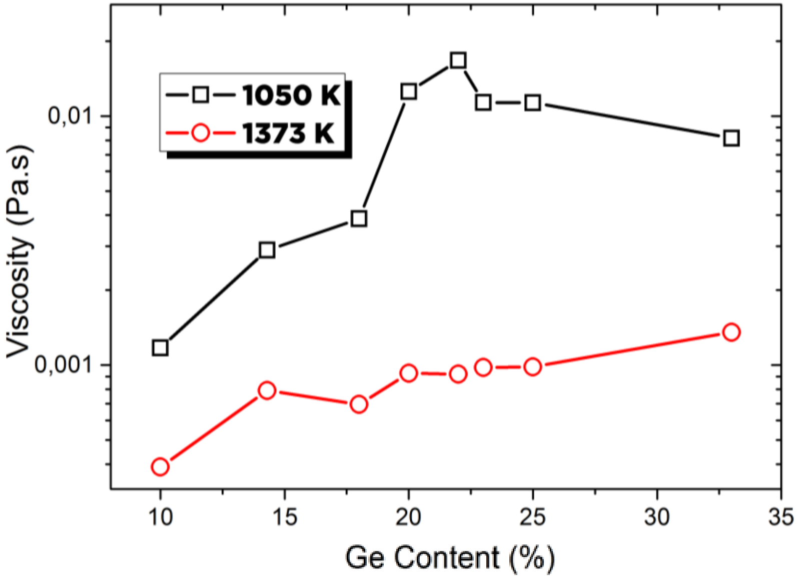
content increases

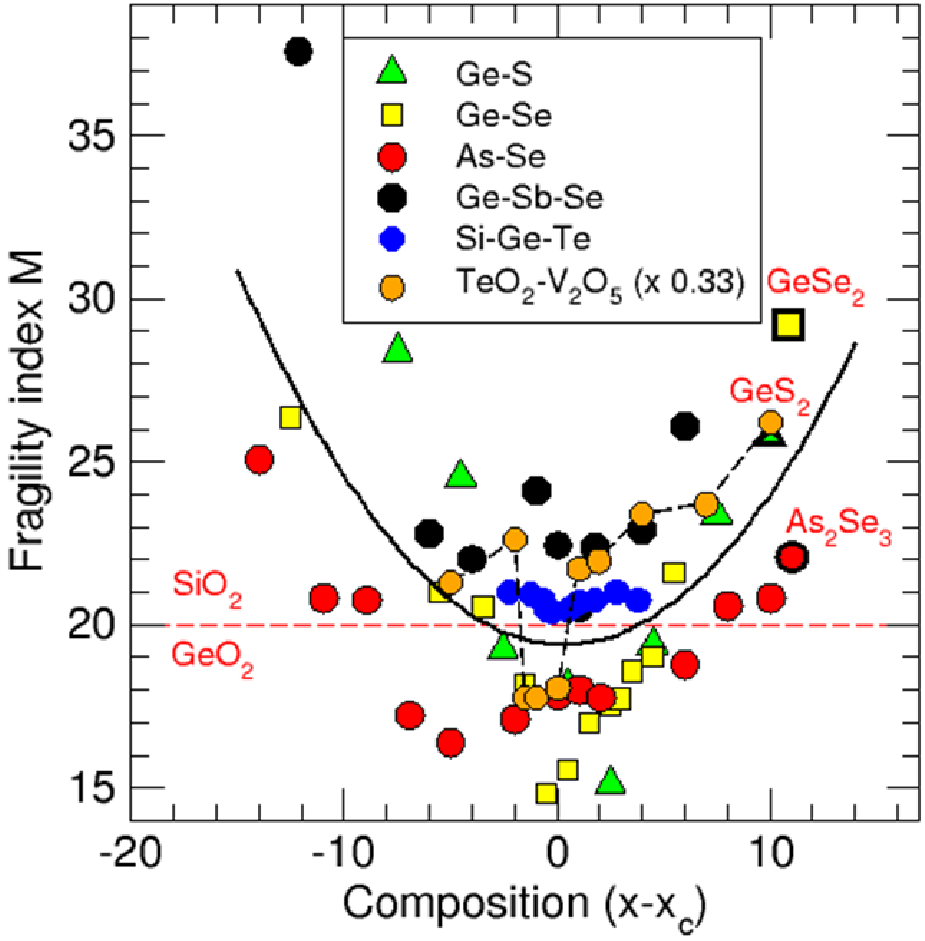


Constraints+Dynamics of liquids

Fragility

$$m(x) = \left.\frac{\partial \log\ \eta(T,x)}{\partial (T_g(x)/T)}\right|_{T=T_g}$$





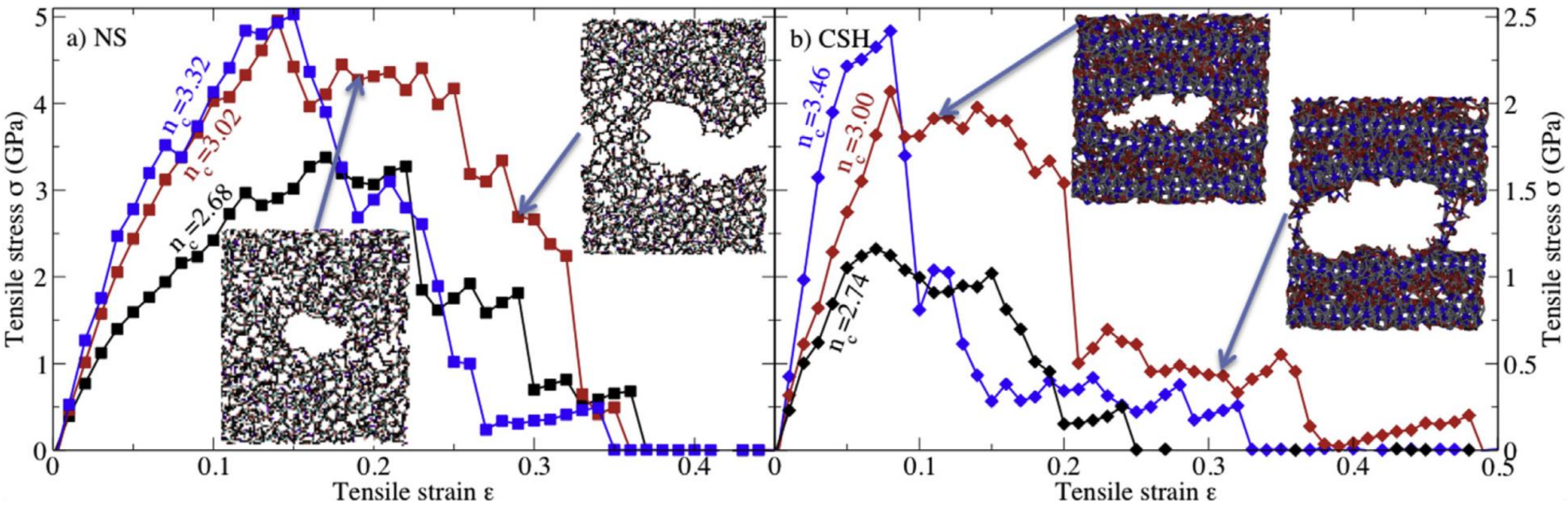
Fragilities of many glassy network forming melts show a global minima when scaled to isostatic composition

Yildirim, Raty, Micoulaut, Nature Comm. 7, 11086 (2016).

Mechanical properties and rigidity

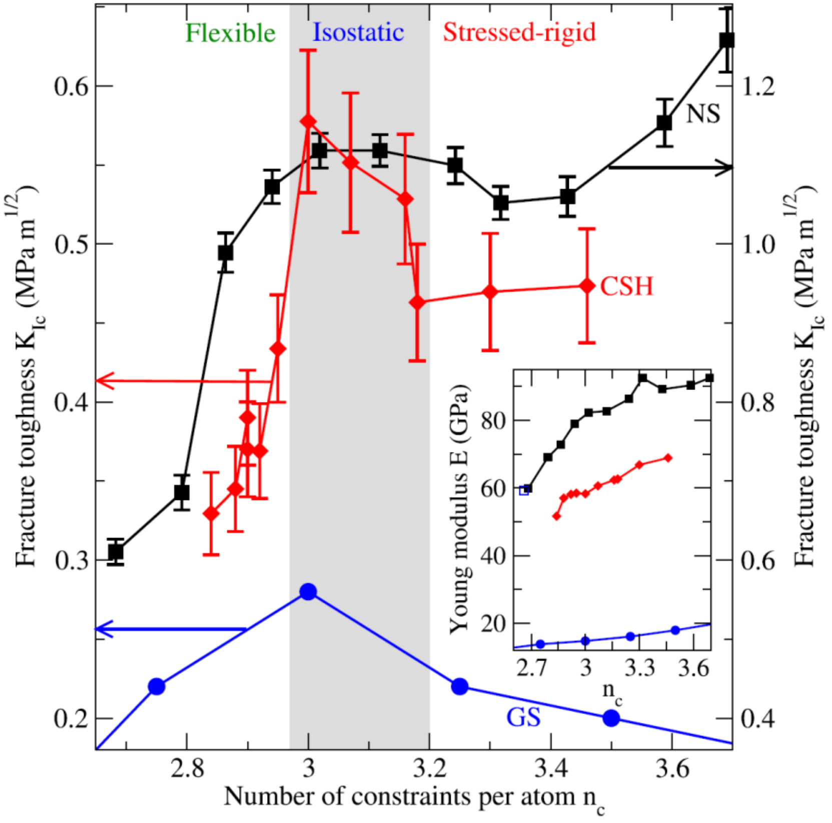
Mechanical behaviour contrasted to n_c

- 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

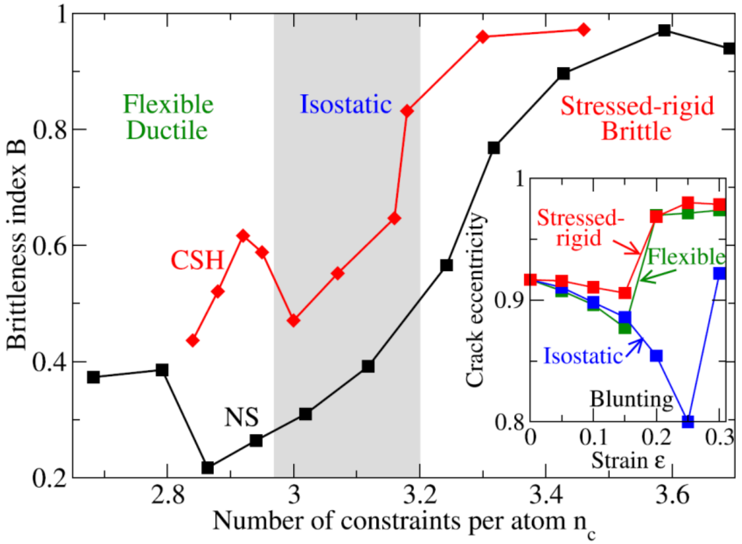


Isostatic systems

- 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.

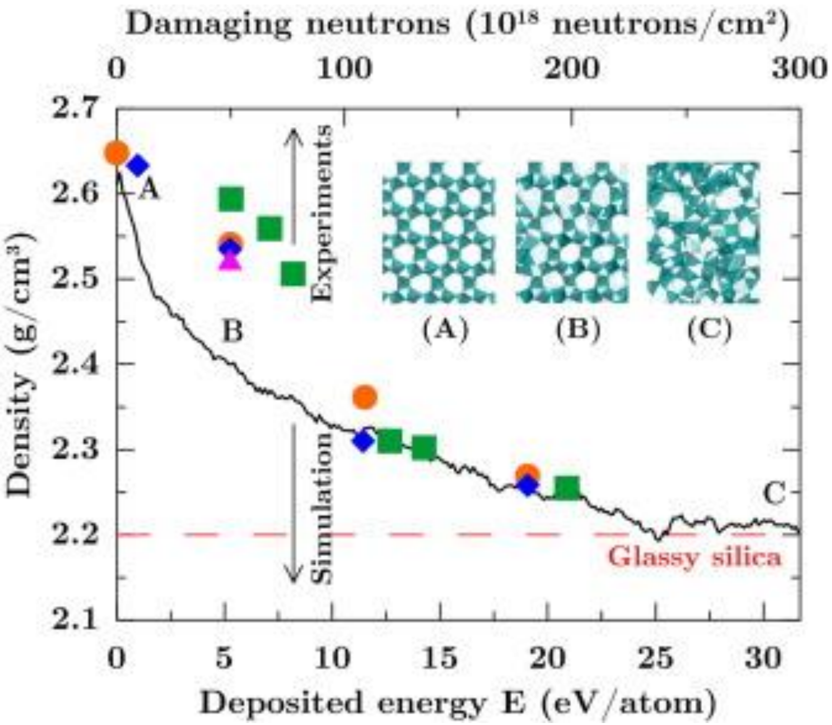


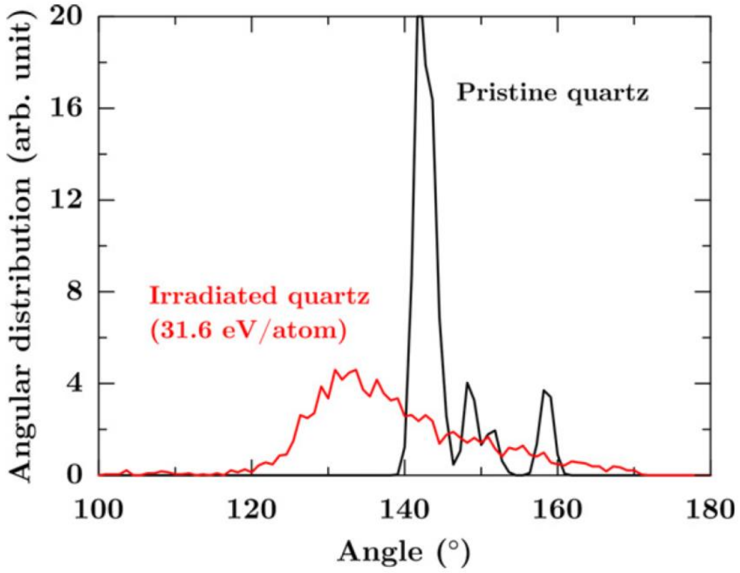
Données GS:
Guin et al. J.AM.Ceram. Soc (2002)

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.



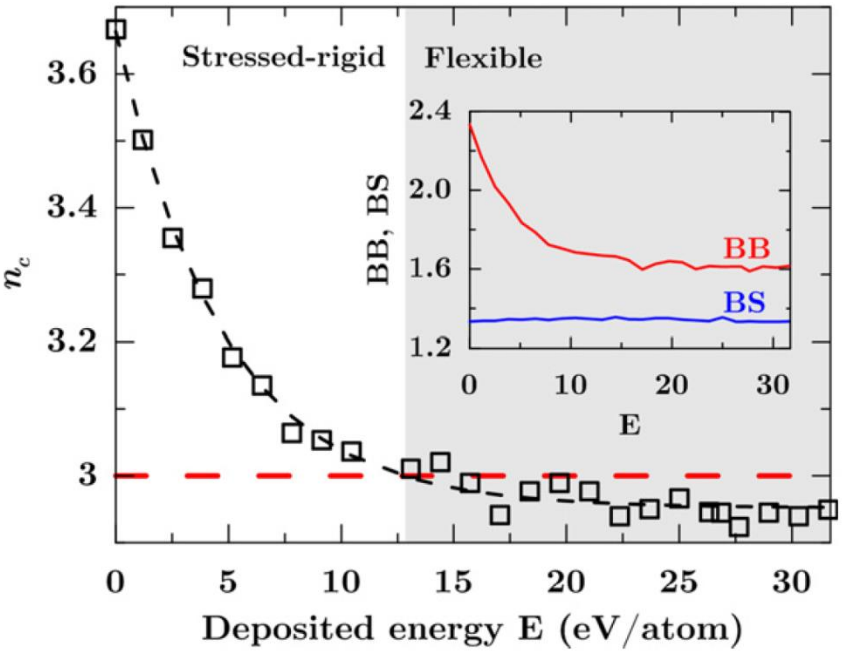


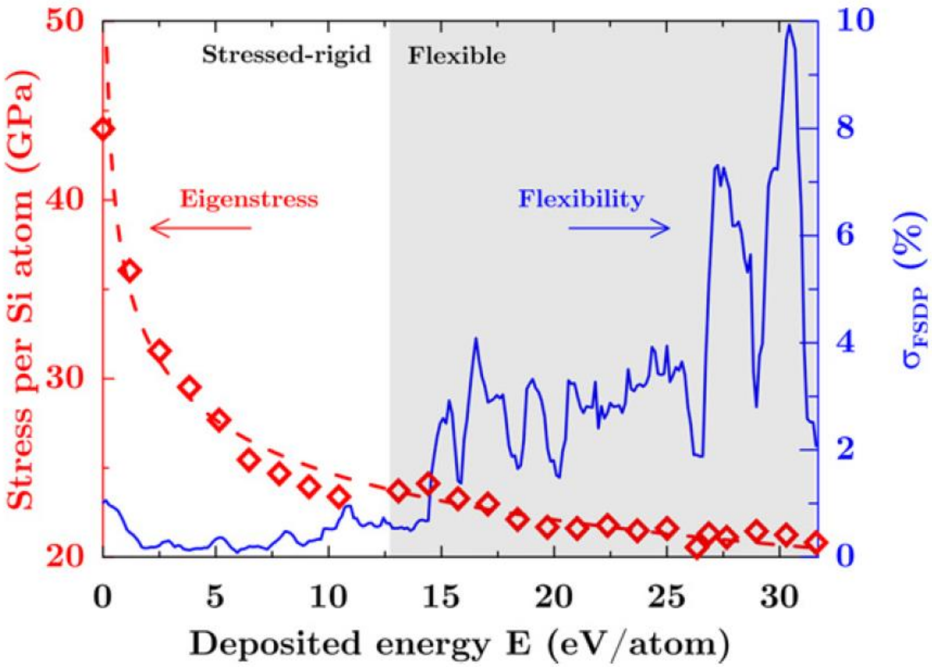
Wang et al. JNCS 463 (2017) 25

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,…

- Models (Mauro-Gupta) permit to capture salient features of thermodynamic properties with composition.

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

M. Micoulaut, Advances Phys. X 1, 147 (2016).