DECRIRE LA TRANSITION VITREUSE: Simulations moléculaires et approches topologiques

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« Chasseurs d'anomalies »

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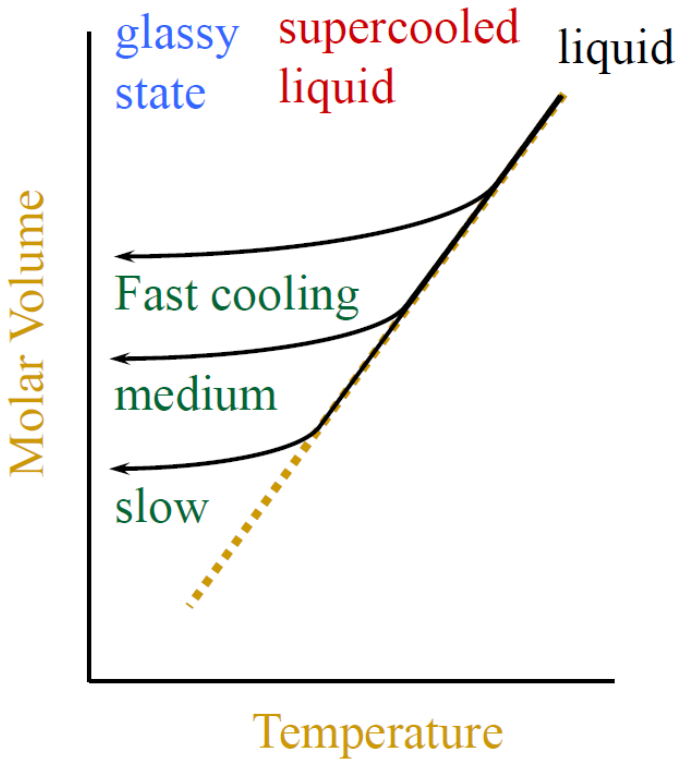
GLASS : an out of equilibrium material

- Faster (slower) cooling freezes glass in at higher (lower) temperature
- Low cooling allows the system to relax more and will lead to structure/properties which may be different.
- Properties of glasses may differ depending on their cooling rate

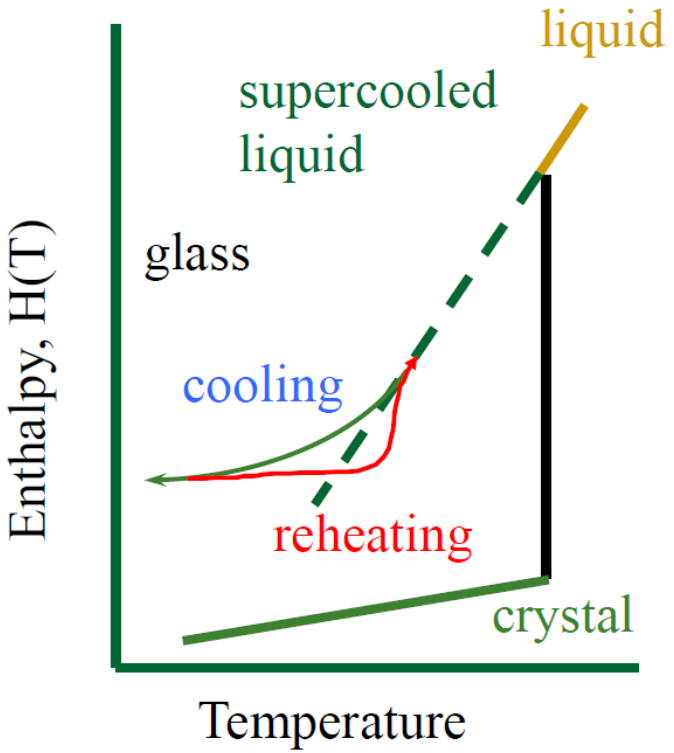


S.W. Martin, IMI Lecture 2010

GLASS : an out of equilibrium material

- With heating, a **hysteresis** loop appears, causing a heat capacity "*overshoot*" at the glass transition, creating a peak.

- The overshoot in the heat capacity curve (or the area of the cycle) is a direct manifestation of the relaxation.



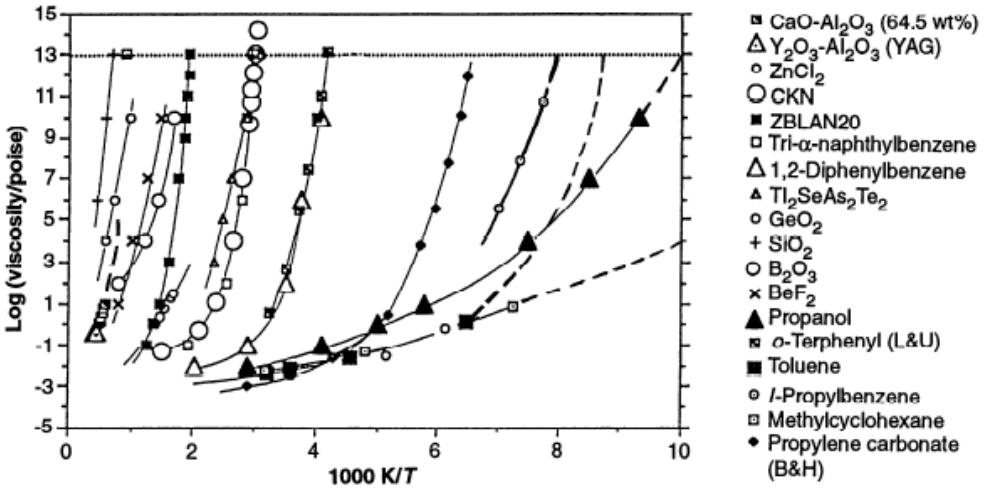
S.W. Martin, IMI Lecture 2010

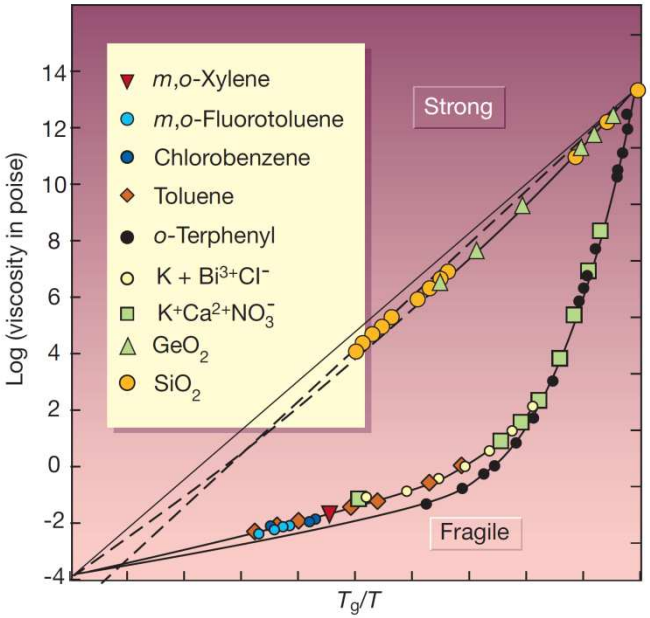
GLASS : an out of equilibrium material

- Dramatic temperature behaviour
- Viscous slowing down with temperature decrease
- Relaxation time to equilibrium diverges

$$M = \left[\frac{d \log_{10} \eta}{d\left(\frac{T_g}{T}\right)} \right]_{T=T_g}$$

Fragility index





Theory tools

- Intermediate scattering function $F_s(k,t)$
- Mean square displacement and beyond (diffusivity)
- Dynamic heterogeneities
- Energy landscapes

Most of these methods (if not all) use molecular dynamics simulations

- Local atomic probe
- Numerical validation of statistical models or concepts

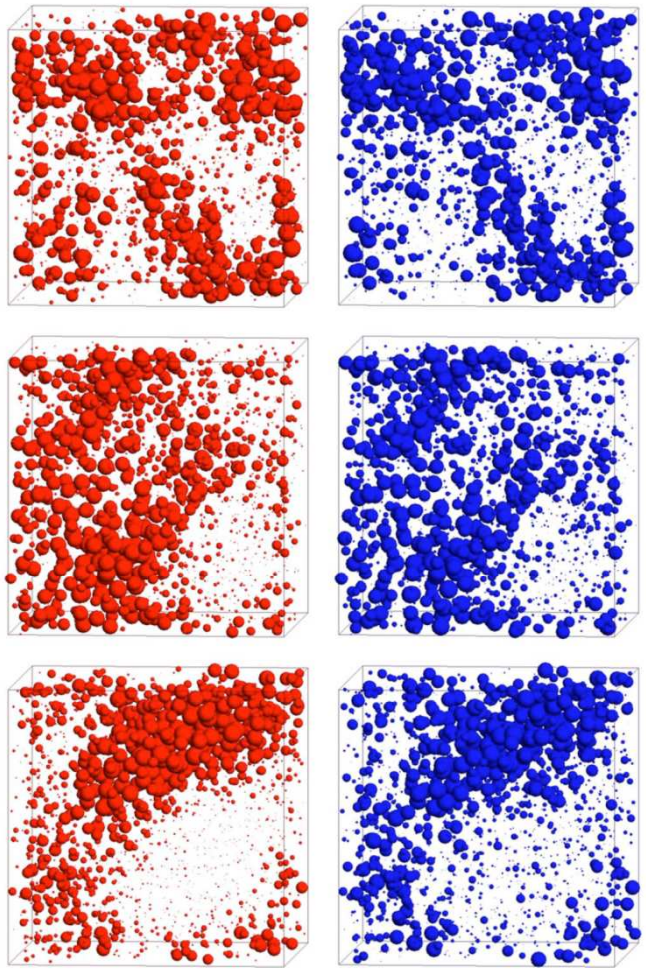
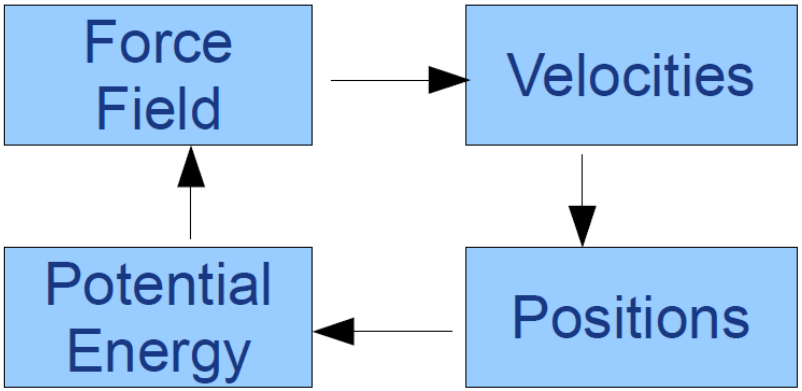
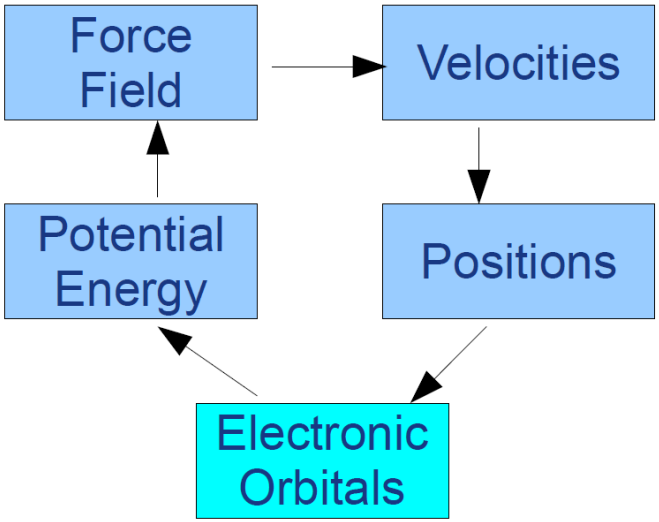


FIG. 3. (Color online) Dynamical heterogeneity (left panels) and structural heterogeneity (right panels) in the initial configuration at $T=350$ K (top panels), 290 K (middle panels), and 270 K (bottom panels). To make each panel, the values of $\langle r_i^2 \rangle_{\mathrm{ic}}$ (or $\langle u_i \rangle_{\mathrm{ic}}$), evaluated at the time of the maximum of S_u, are assigned to each molecule in the initial configuration. These values are sorted

Classical MD



Ab initio MD



Ab initio: Solve the Schroedinger equation for a system of N atoms
Simplified with the DFT scheme (one electron density)

- ❑ No force field necessary. Heavy computational cost
- ❑ Small systems (100s of atoms, 10^6 in Classical MD)
- ❑ Small simulation time (100ps, 100 ns for classical MD)

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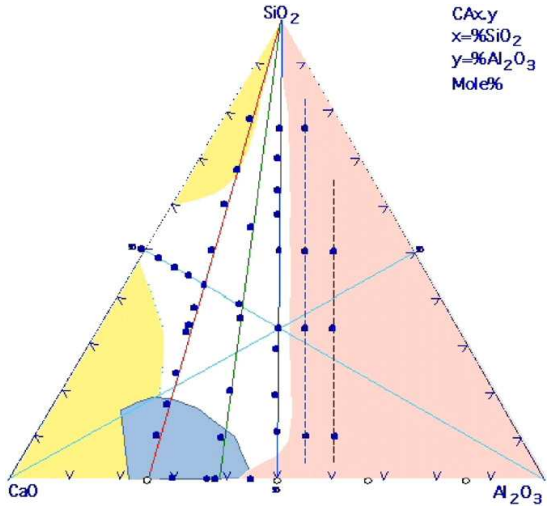
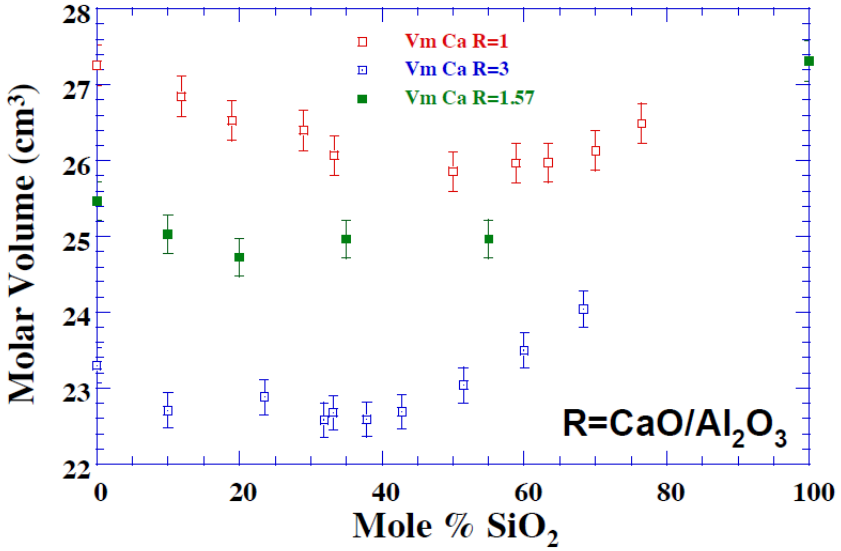


D.R. Neuville et al. , JNCS 353 (2007) 180



• **<u>Motivation</u> : understanding glass transition and compositonal trends**
« Materials science problem »

• Cumbersome study along comp. joins

• Small compositional changes can dramatically alter system properties.

• Such small compositional changes cannot be described with brute-force methods such as Molecular Dynamics (MD) simulations.

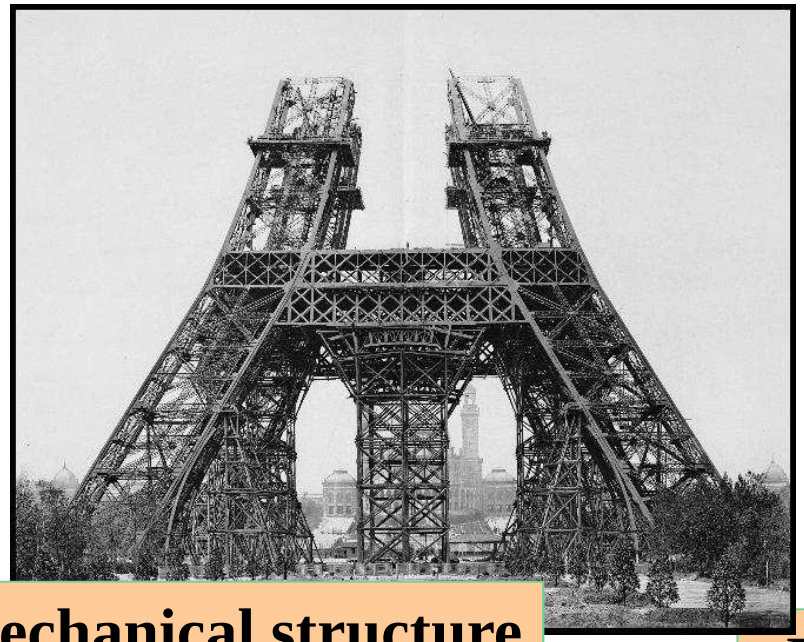
• Can all the unnecessary details be filtered out ? All those which do not influence ultimately the overall properties.

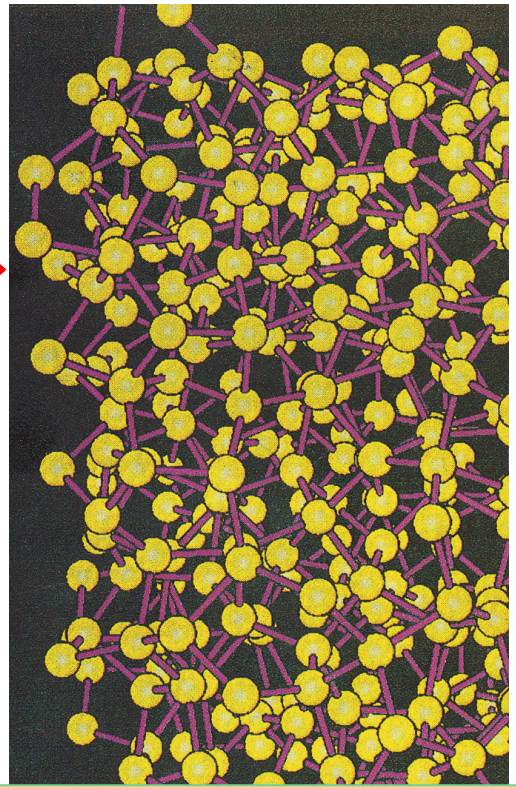
• **There is much to learn from structure and from approaches which use as a central tool topology or network rigidity.**

OUTLINE

- Rigidity theory (Phillips-Thorpe and beyond)
- Mauro-Gupta model of glass transition (mini-review)
- Rigidity and molecular dynamics (our results)

Basic idea: An analogy with mechanical structures





Mechanical structure

- Nodes
- Bars
- **Tension**

Molecular network (contraint counting)

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

Maxwell stability criterion = isostatic truss

Enumeration of mechanical constraints

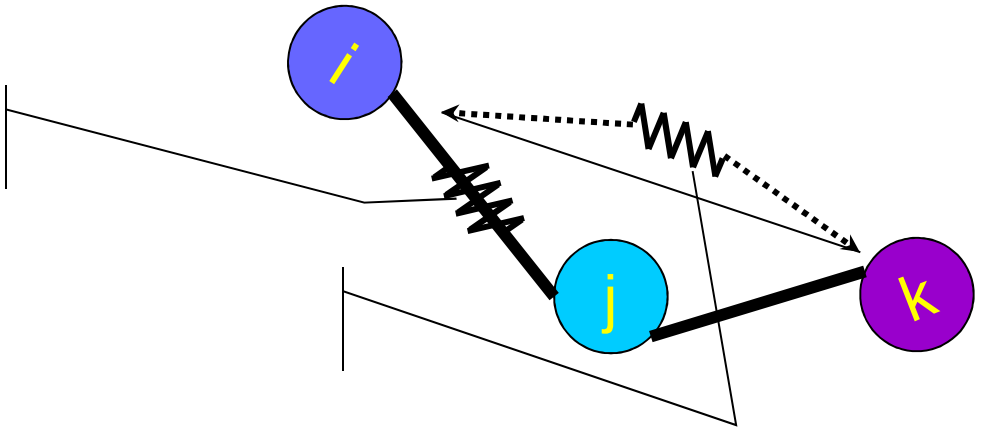
Consider a r-coordinated atom

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 :

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

- We introduce the network mean coordination number

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

- 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:

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

Phillips, JNCS 1979

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

- 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

ALTERNATIVE VIEWPOINT: 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 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

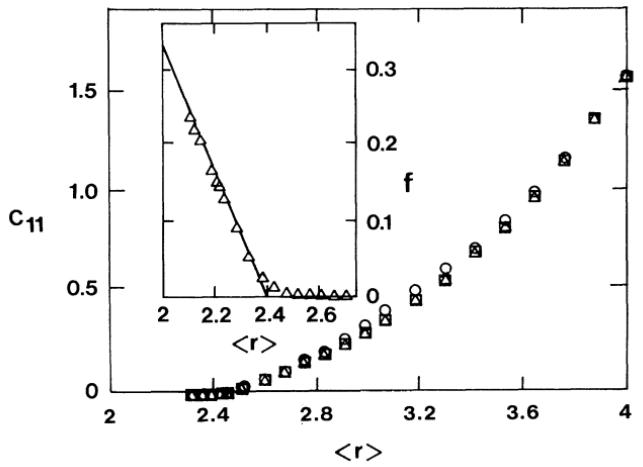
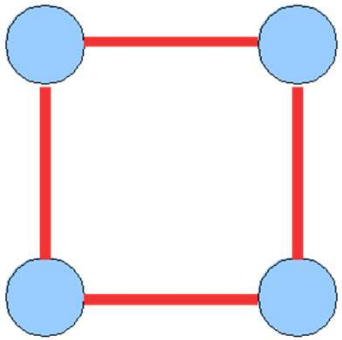


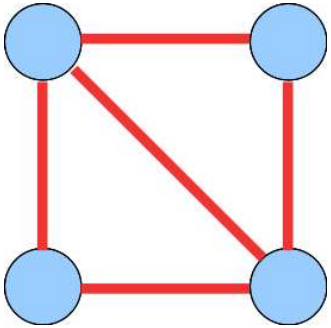
FIG. 1. Elastic modulus C_{11} with $\beta/\alpha = 0.2$ in units where $\alpha = 4a$ and as a function of the mean coordination $\langle r \rangle$. The three symbols are for three different series of random networks. The inset shows the number of zero-frequency modes f (averaged over three networks)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

He and Thorpe, PRL 1985

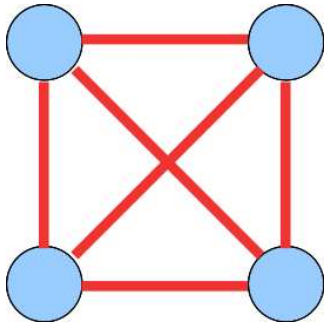
DECRIRE LA TRANSITION VITREUSE – Théorie de la rigidité



Flexible



Isostatic



Stressed

Examples of application:

❑ **Ge_xSe_{1-x} glasses:**

Ge is 4-fold and Se is 2-fold.

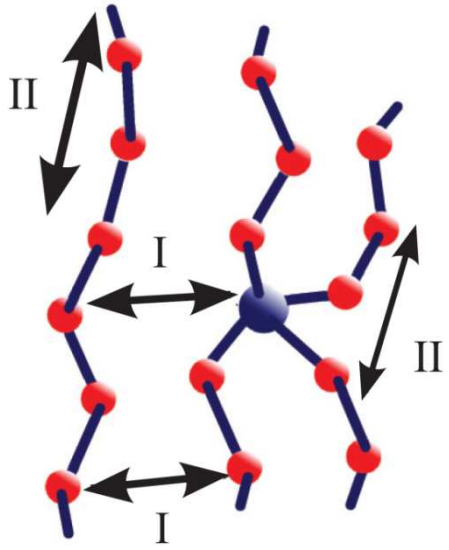
- ❖ Ge has 2r-3=5 BB and r/2=2 BS constraints
- ❖ Se has 1 BB and 1 BS constraint

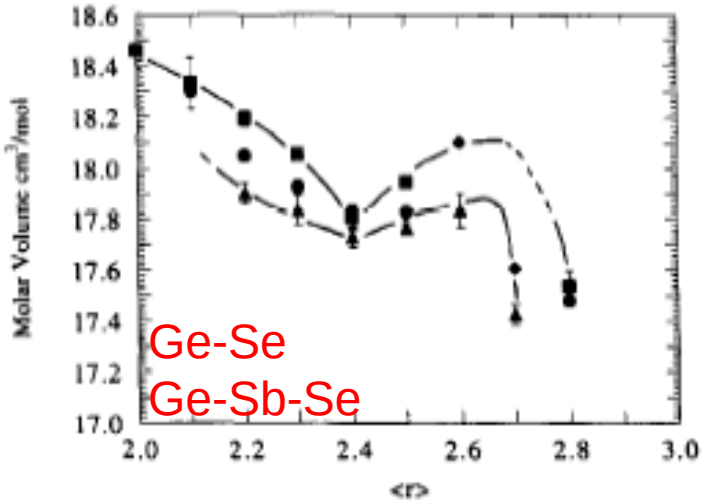
- ❖ nc=2(1-x)+7x=2+5x
- ❖ Stability criterion for n_c=3 i.e. for x=0.2

- ❖ 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





Drawback: ideal network, T=0

Varshneya et al. JNCS 1991

Temperature dependent constraints

Basics

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

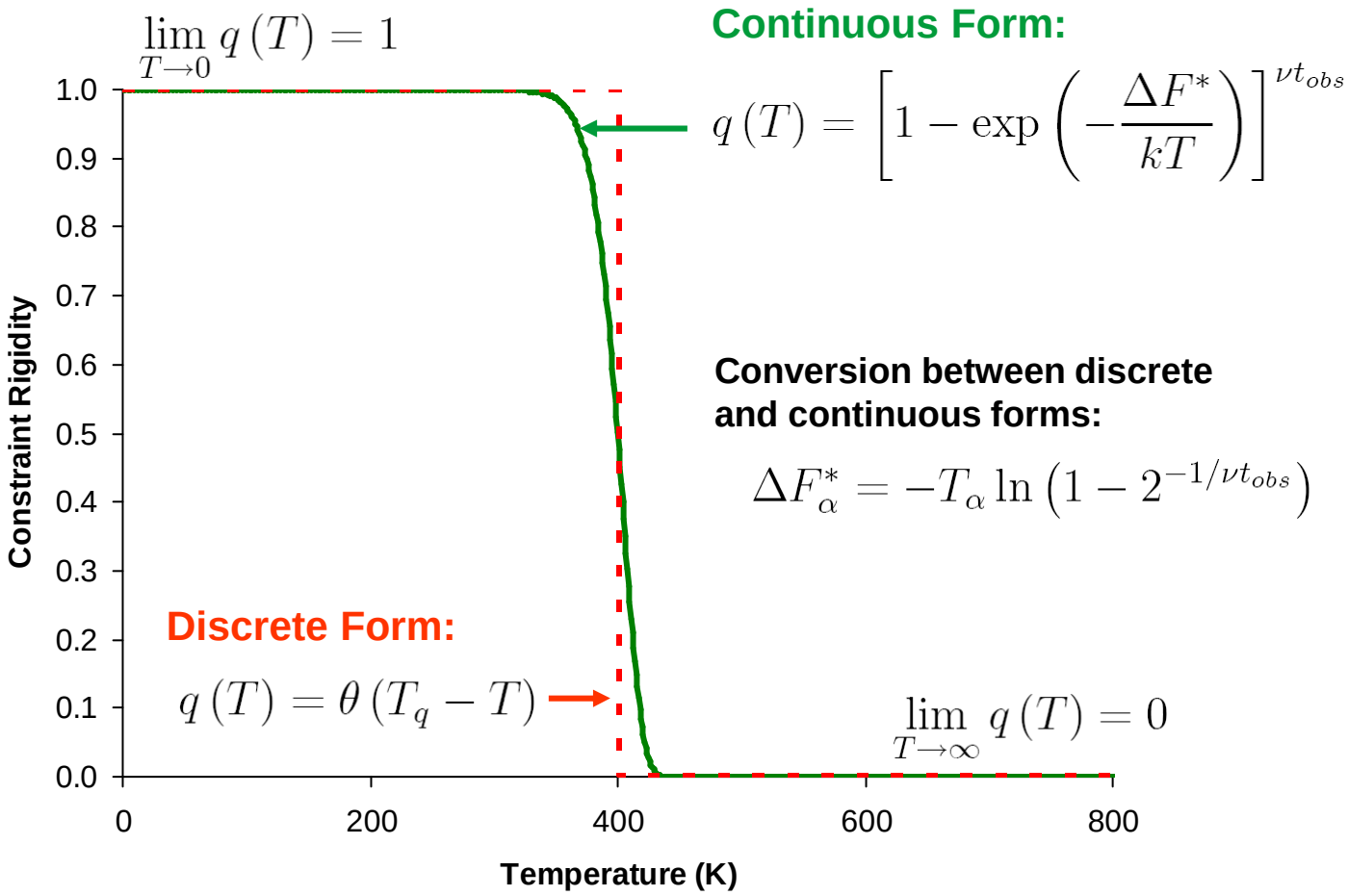
$$n\left(T,x\right)=\sum_{i}N_{i}\left(x\right)\sum_{\alpha}w_{i,\alpha}q_{\alpha}\left(T\right)$$

- 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)

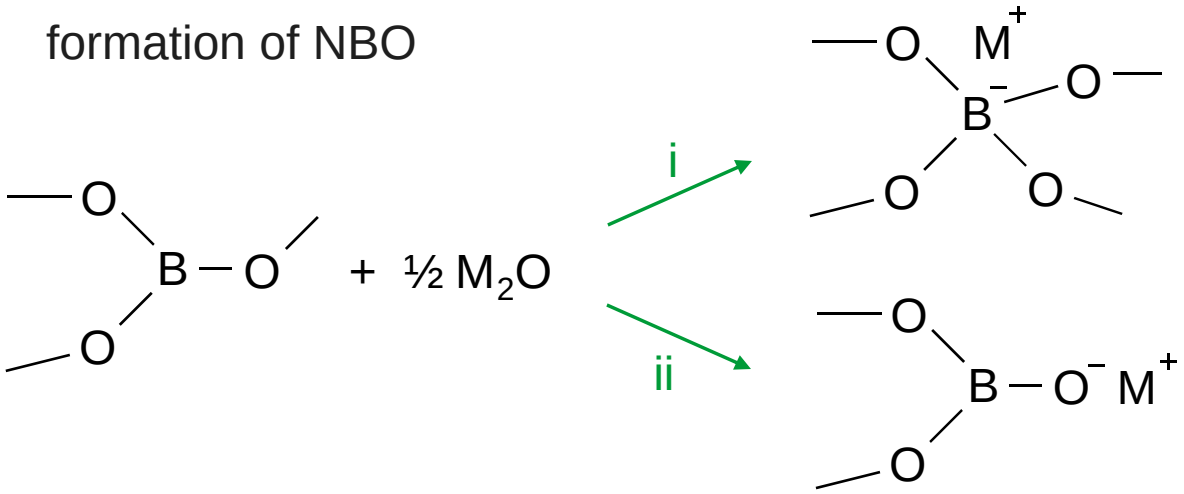
$q_\alpha(T)$: temperature-dependent rigidity of constraint α



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

- Applied to borate glasses Na2O-B2O3

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



- Simple bond models for alkali borates for

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

x<0.33 $N_4(x) = R = \frac{x}{1-x}$

Step 2: Count constraints (topological degrees of freedom)

- 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.

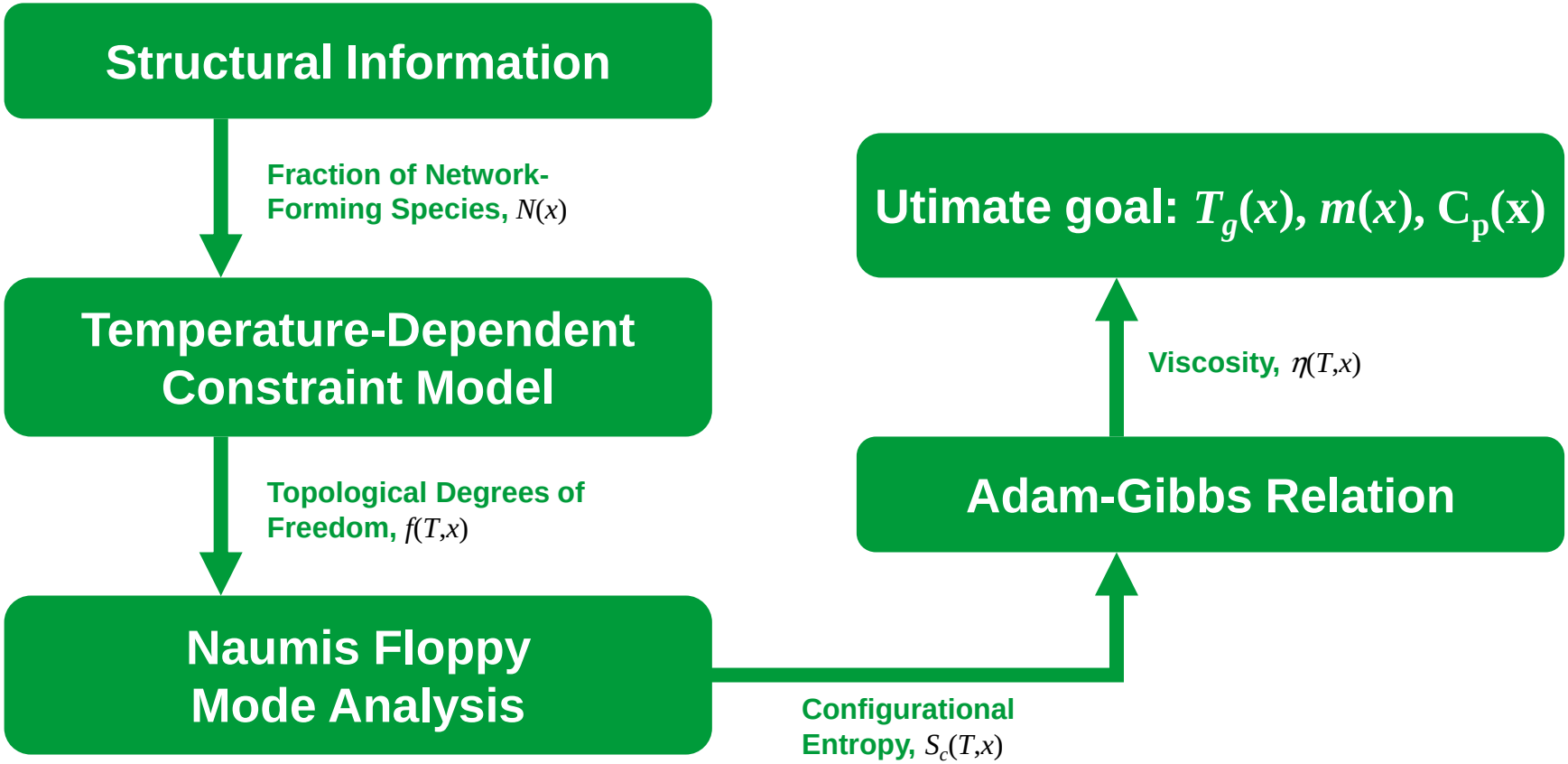
- γ: B-O-B and B-O-$M^{(NB)}$ angular constraints
  - One γ constraint at each bridging oxygen

- 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

Similar procedure for borosilicates.

Step 3: Calculating properties…the roadmap



Step 3: 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. Naumis' model S_c # f (floppy modes) **Naumis, Phys. Rev. E71, 026114 (2005).**

D. This allows writing:

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

Step 3: 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, we obtain:

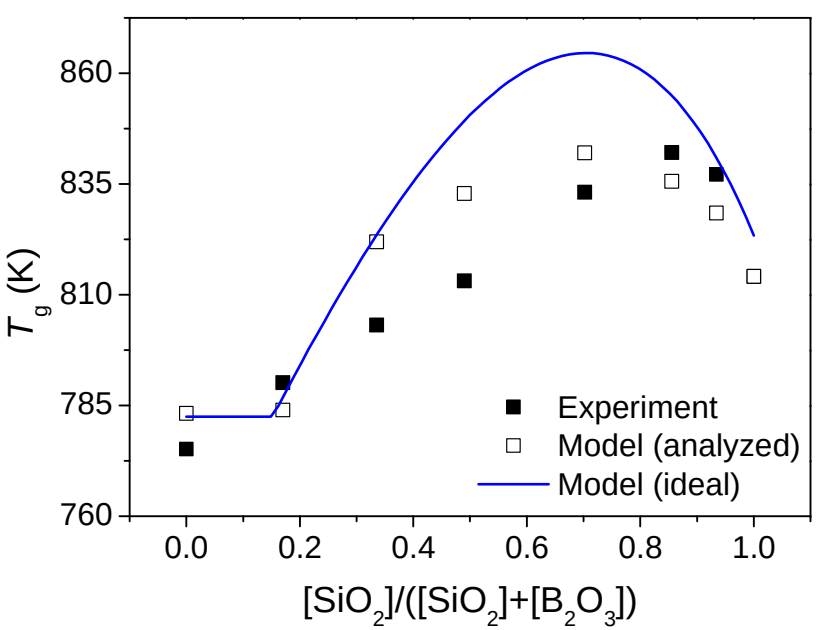
$$m(x) = m_0 \left(1 + \left. \frac{\partial \ln f(T,x)}{\partial \ln T} \right|_{T=T_g(x)} \right)$$

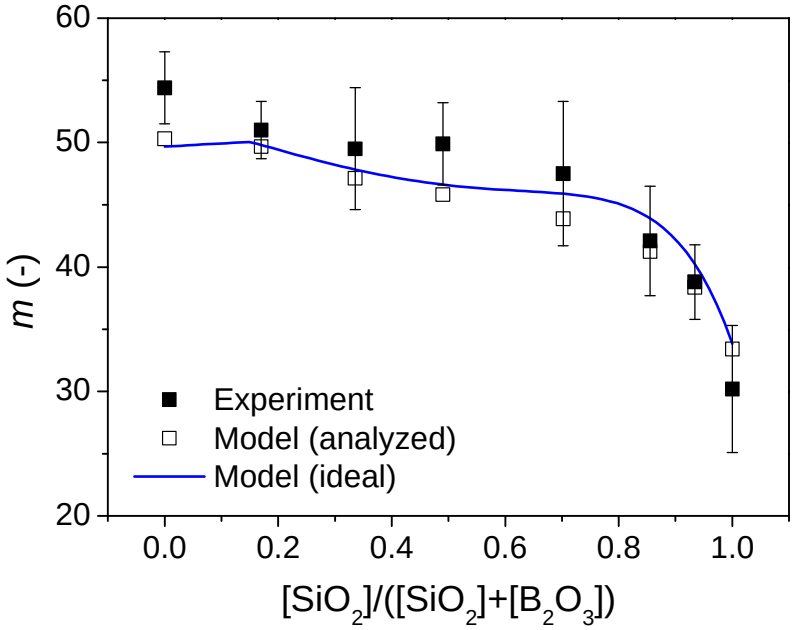
F. Application to sodium borates

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

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

Results: Fragility and Tg variation of sodium borosilicate glass

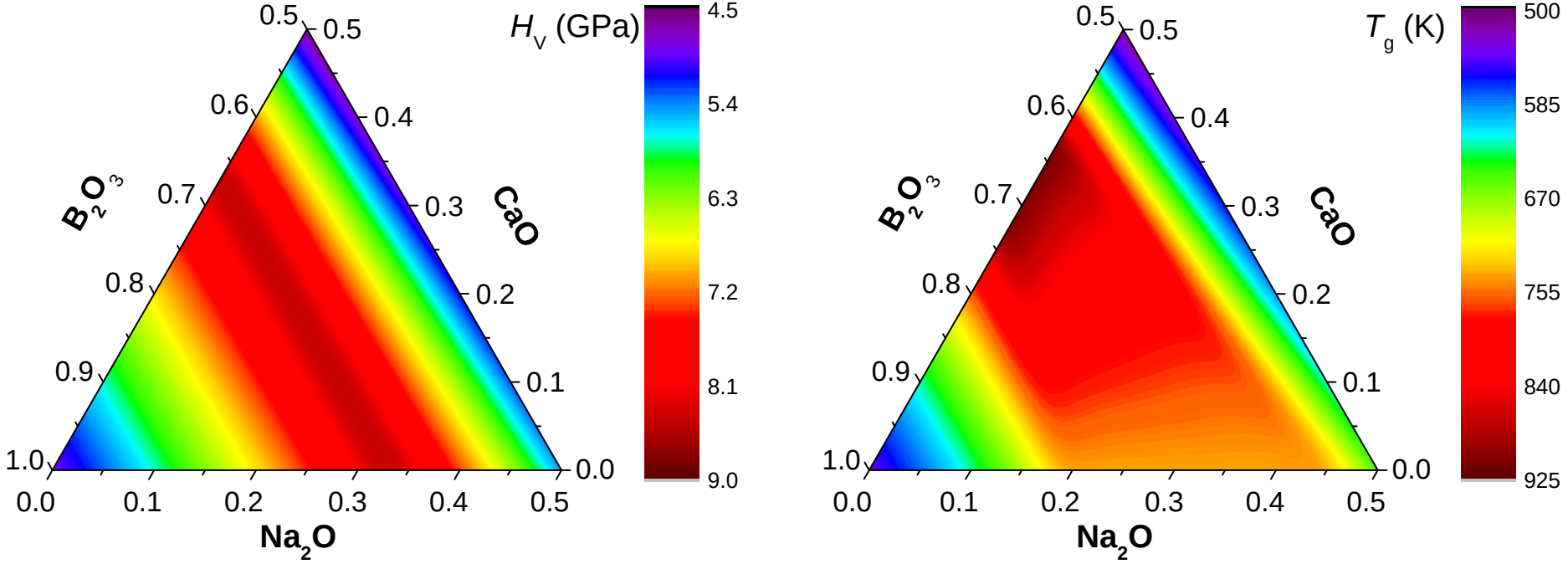




- T_g of a borate glass can be predicted from that of a silicate glass with $f(x,y,z,T)$ as the only scaling parameter
- Fragility: onset temperatures $T_{\beta,Si}$ and T_μ are treated as fitting parameters (1425 K)

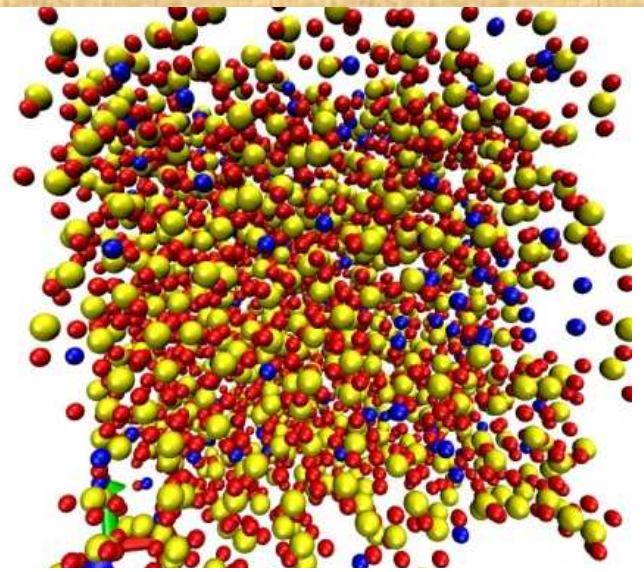
Smedskjaer et al., *J. Phys. Chem. B* 115, 12930 (2011)

Results: Quantitative designe of glasses (borates)



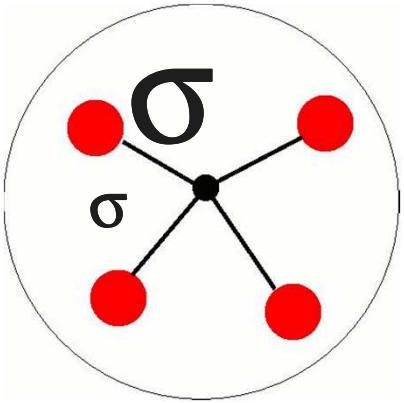
- Topological modeling: exploring new composition spaces where glasses have not yet been melted
- Difference in scaling is due to *T*-dependence of constraints

- Molecular Dynamics of 2 SiO_2-Na_2O (NS2).
- 3000 atoms, Teter potential (**Du and Cormack, JNCS 349, 66 (2004)**)

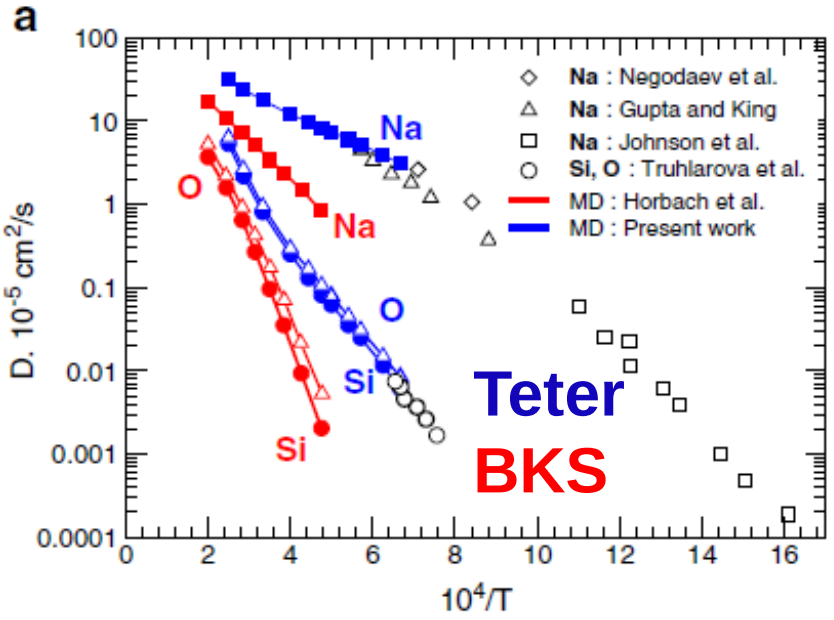


Allows for a neat determination of the Mauro-Gupta functions q(T,P).

1. **bond-stretching (# nb of neighbours or neighbor distribution + radial excursion).**
2. **Bond bending (angular excursion)**



Distribution of σ's

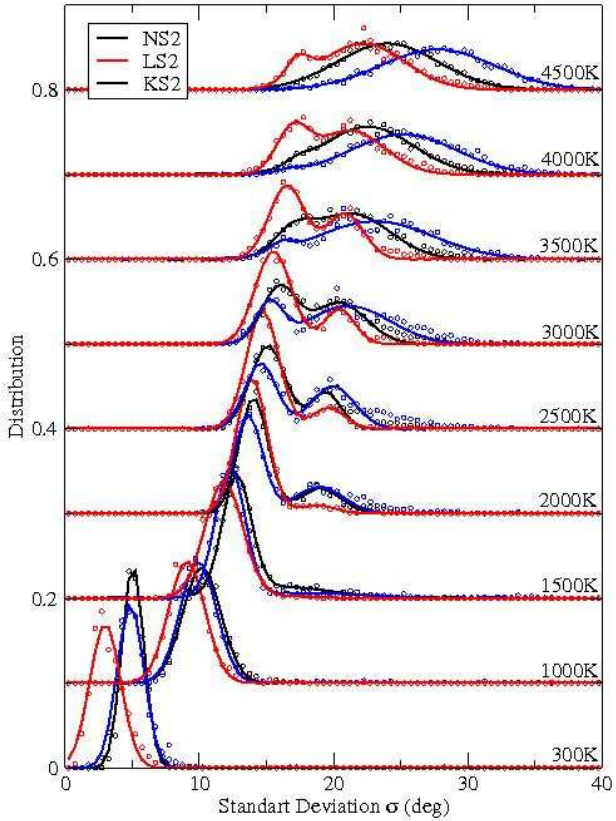


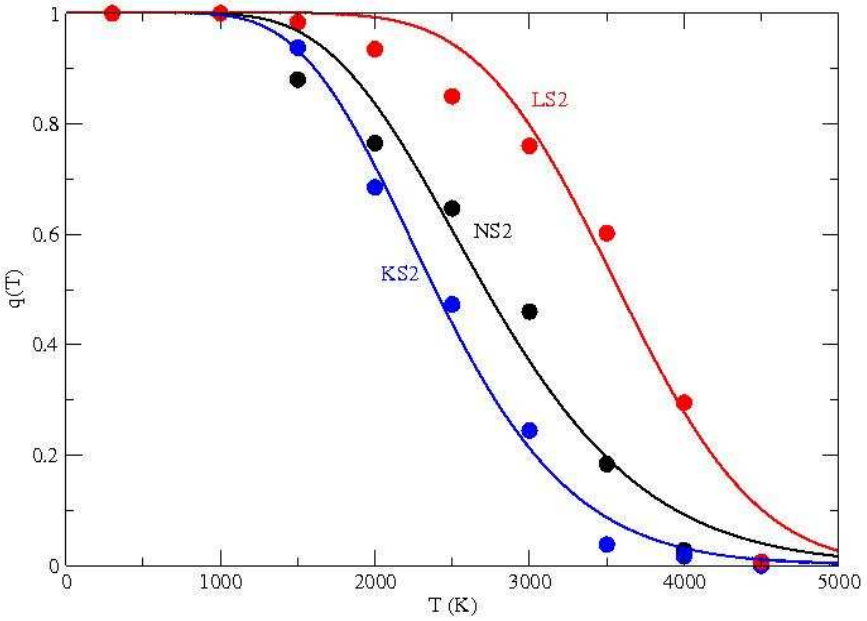
M. Bauchy et al., Chem. Geol. 346, 47 (2013)

Atomic scale basis for the Mauro- Gupta approach

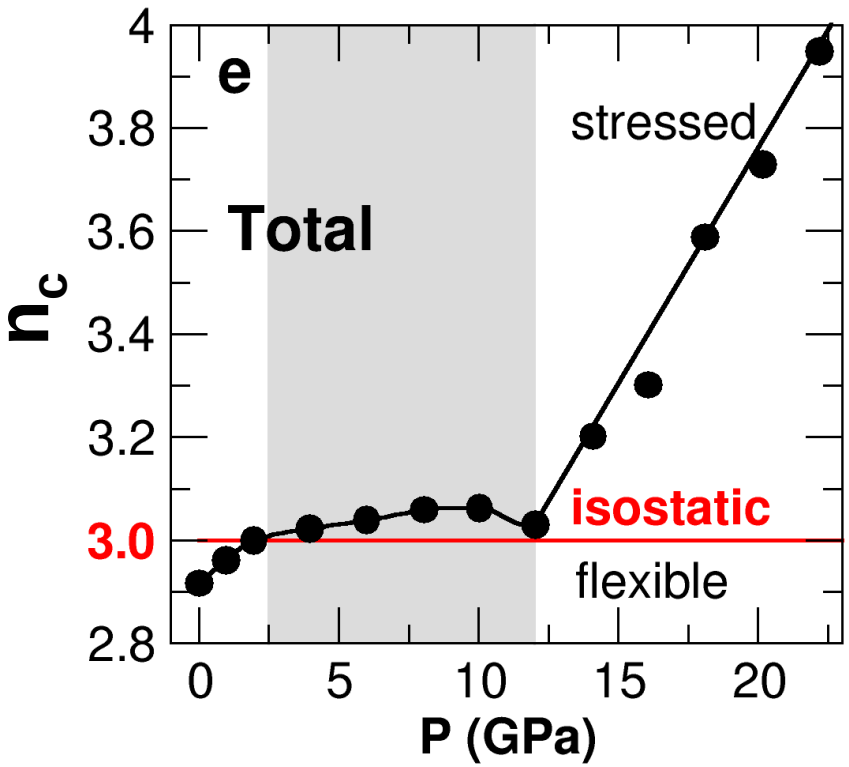
- MD-counting approach allows to compute the number of BS and BB constraints in silicate glasses.

- This method allows to study thermally-activated broken constraints and to evaluate the Mauro-Gupta q(T) function.



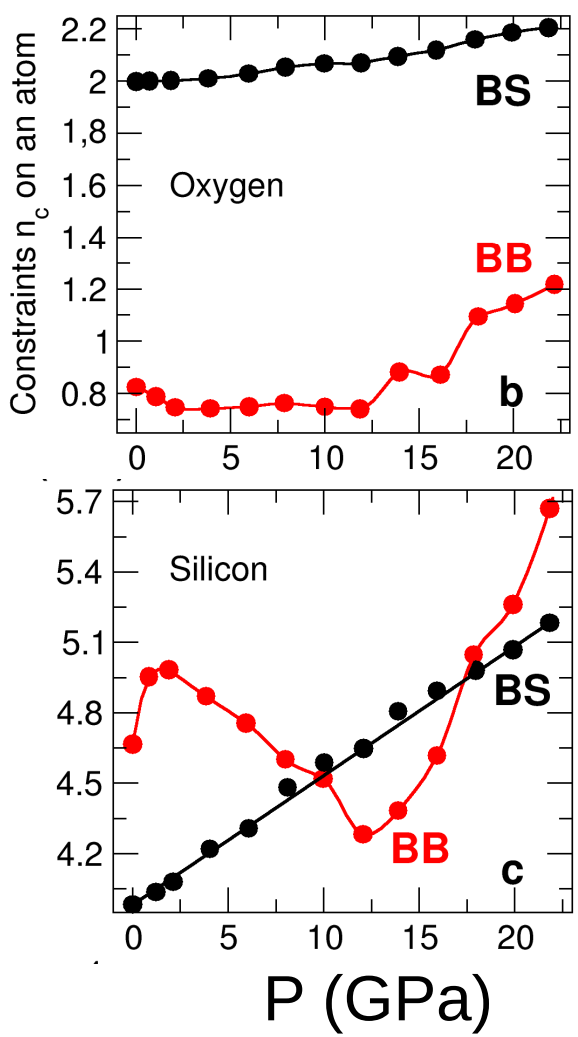


Effect of rigidity under pressure

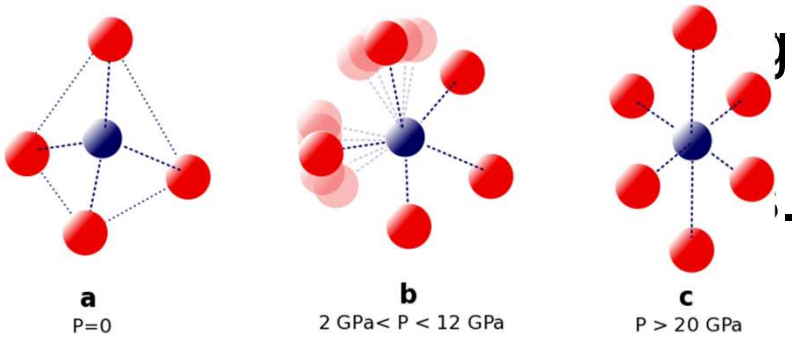


- At P=0, the NS2 silicate glass is flexible (Rigid to Flexible transition for 20% Na_2O)
- In the Pressure window, saturation of nc to a limiting value nc ~3.
- Isostatic character of the network
- Evidence for an isostatic window

Effect of rigidity



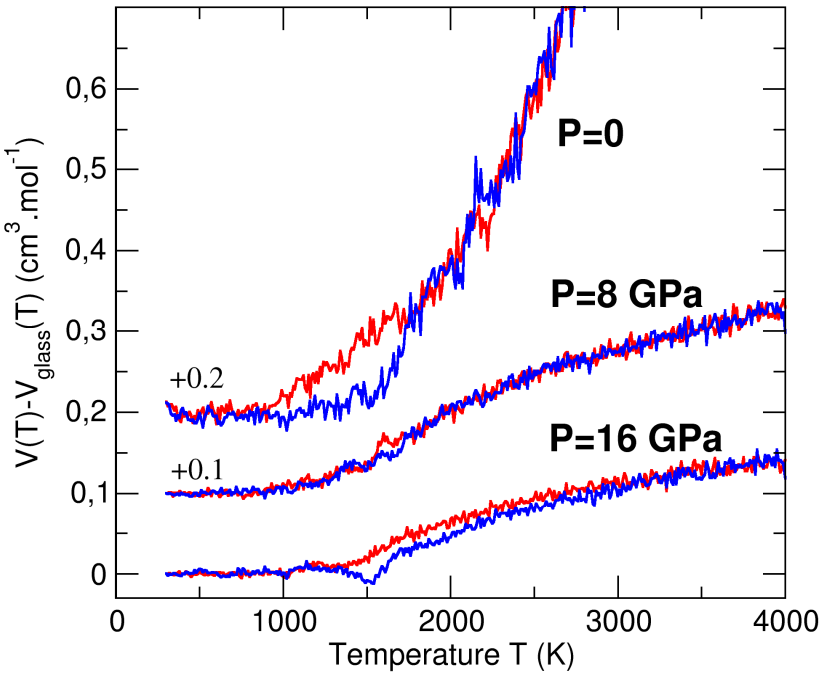
- **Detail:** With increase of pressure, stretching constraints (BS) and stress increase.
- Linked with increase of Si and O coordination.



Consequences

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

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



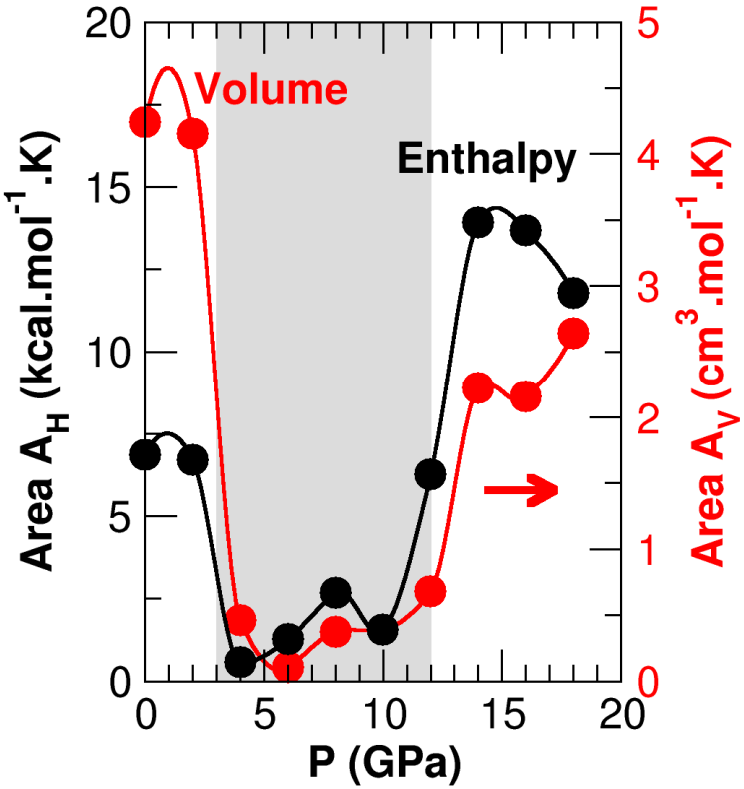
- Thermal anomalies are linked with anomalies in transport in the liquid and with structural anomalies in the glass.

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

Consequences

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

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



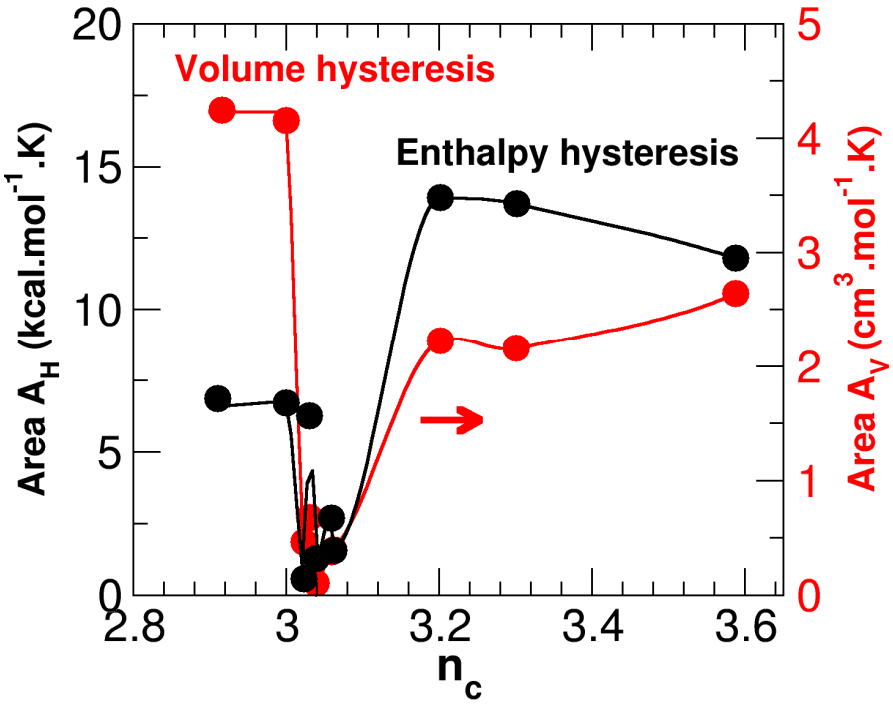
- Thermal anomalies are linked with anomalies in transport in the liquid and with structural anomalies in the glass.

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

Consequences

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

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

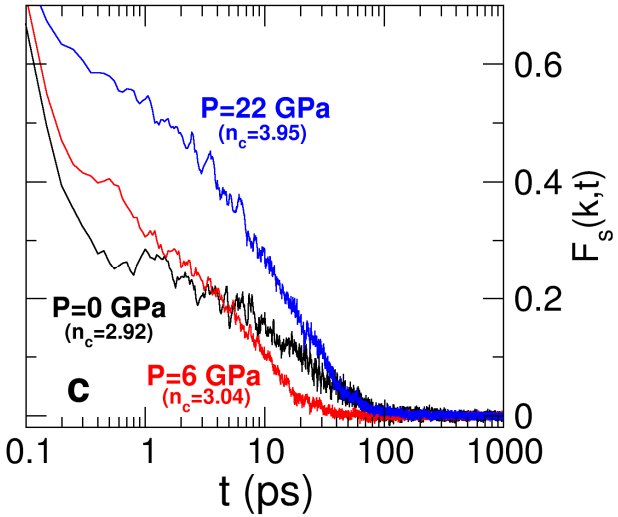


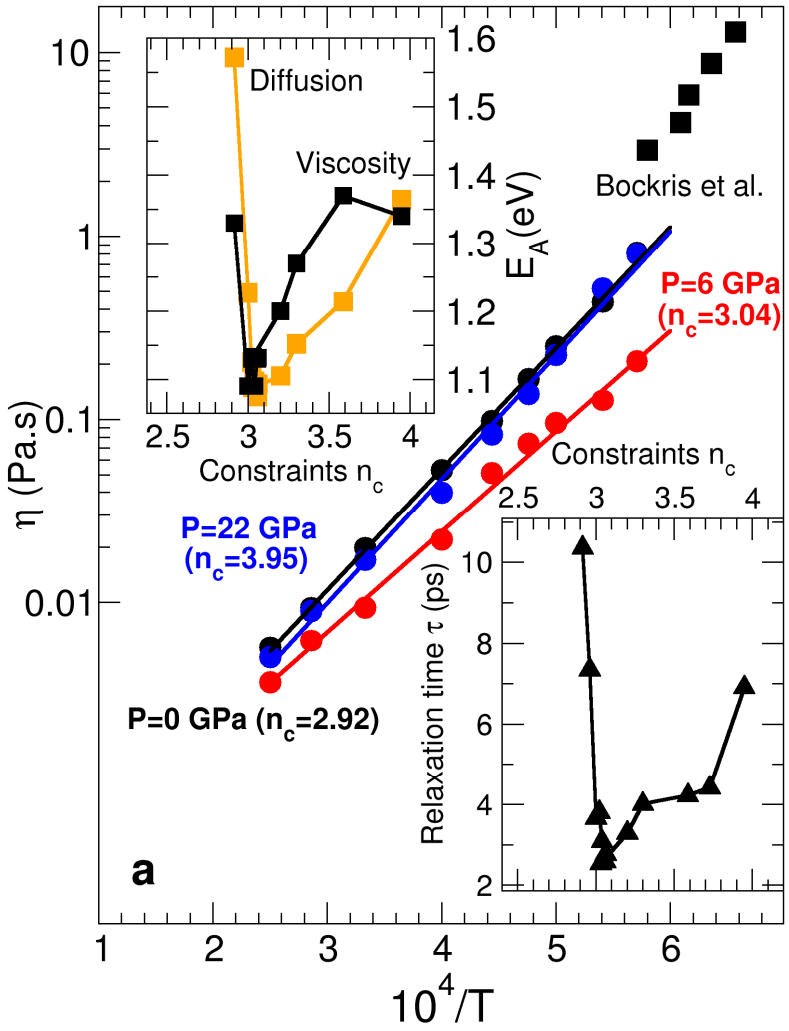
- Thermal anomalies are linked with anomalies in transport in the liquid and with structural anomalies in the glass.

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

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

$$F_s(\boldsymbol{k},t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp[i\boldsymbol{k}.(\boldsymbol{r}_j(t) - \boldsymbol{r}_j(0)] \right\rangle$$





Conclusion

- Topology is a useful tool for the understanding compositional trends in glasses
- The scaling of glass properties with composition can be quantitatively predicted from mechanical constraints
- Account for the temperature dependence of network constraints leads to the prediction of glass properties
- Comparison with other modeling approaches
  - Disadvantages: fewer details; requires *a priori* knowledge of structure and constraints
  - Advantages: simple; isolates key physics; analytical

References

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