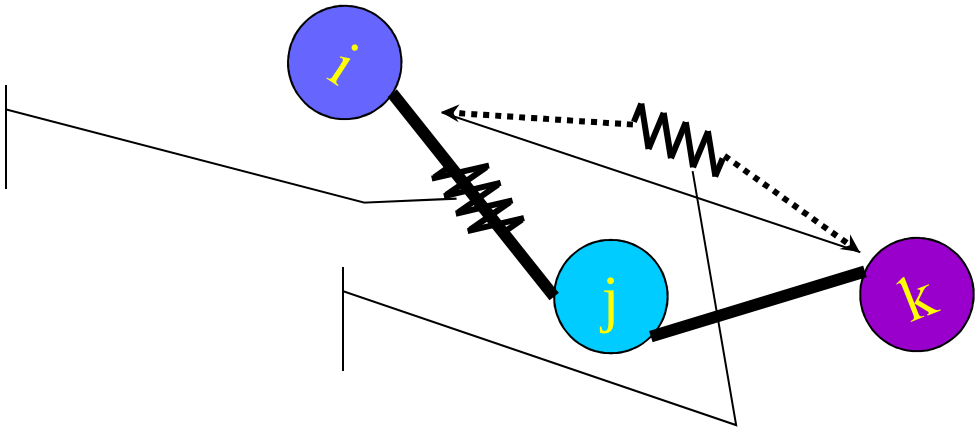
LECTURE 10 : RIGIDTY TRANSITIONS AND INTERMEDIATE PHASES

- Rigidity transitions and compositional trends
- Intermediate phases
- Cluster expansions
- MD based rigidity theory

A) CONSTRAINTS AND RIGIDITY TRANSITIONS

1. Remember (lecture 9) the 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.

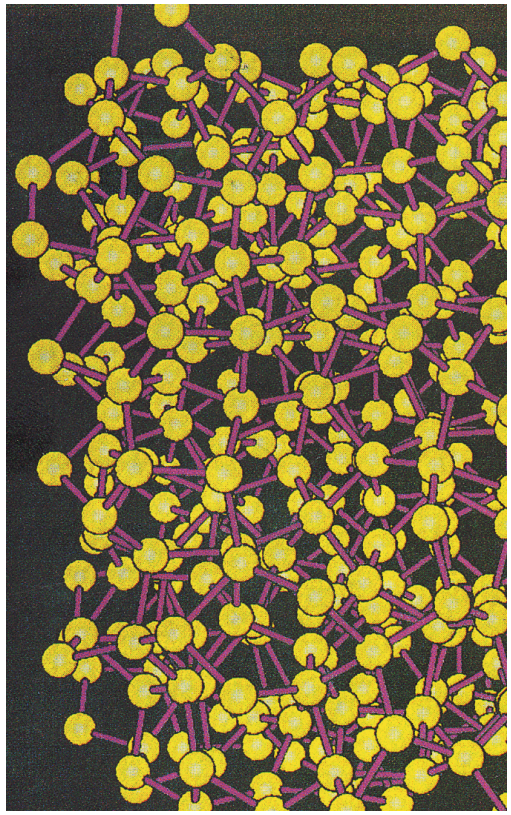
Each time, one adds a bond, one needs to define 2 new angles

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

The number of constraints per atom is :

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

A) CONSTRAINTS AND RIGIDITY TRANSITIONS



2. Rigidity transition:

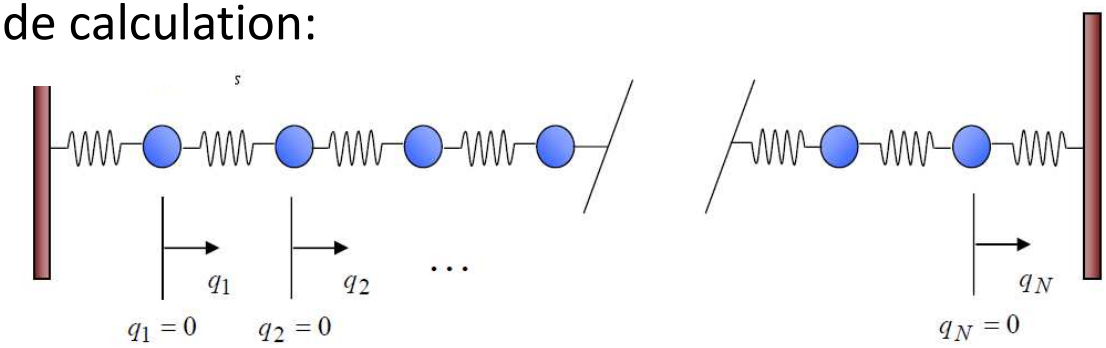
- Amorphous silicon and harmonic potential

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

Stretching Bending

- Bond depletion (<r> decreases).
- 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**:

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

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

A) CONSTRAINTS AND RIGIDITY TRANSITIONS

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 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

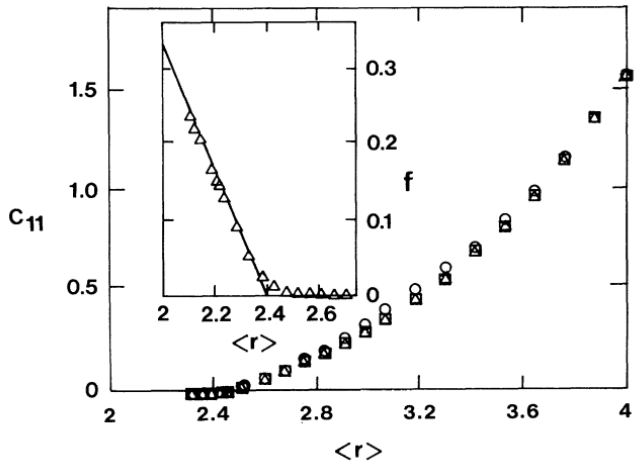


FIG. 1. Elastic modulus C_{11} with $\beta/\alpha = 0.2$ in units where $\alpha = 4a$ and as a function of the mean coordination $\langle r \rangle$. The three symbols are for three different series of random networks. The inset shows the number of zero-frequency modes f (averaged over three networks)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

He and Thorpe, PRL 1985

A) CONSTRAINTS AND RIGIDITY TRANSITIONS

Chalcogenide network glasses

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

Ge_xSe_{1-x}

Ge-Sb-Se, Ge-As-Se, etc…

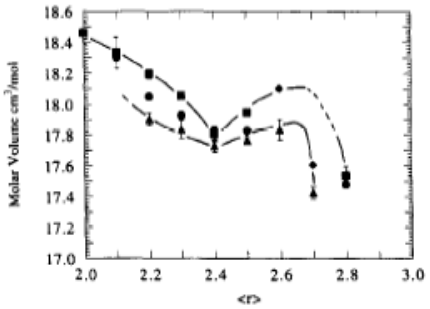


Fig. 6. Dependence of molar volume on $\langle r \rangle$ for binary Ge–Se and ternary Ge–Sb–Se systems. The molar volume at room temperature for the binary and ternary are represented by ■ and ▲, respectively. The molar volume values for the binary glasses given by Ota et al. [11] are represented by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

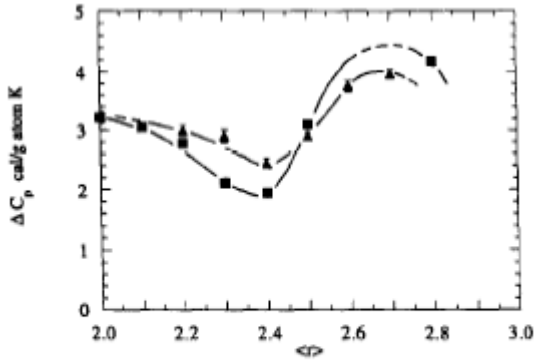


Fig. 10. ΔC_p versus $\langle r \rangle$ for binary Ge–Se and ternary Ge–Sb–Se systems. The ΔC_p values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 1.8%.

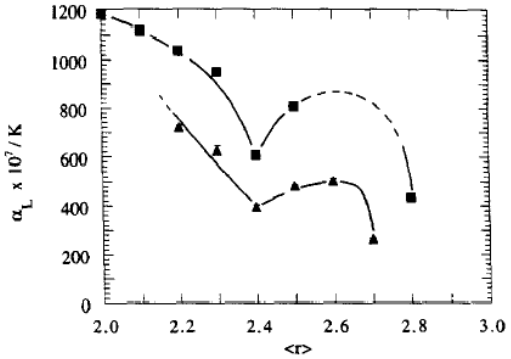
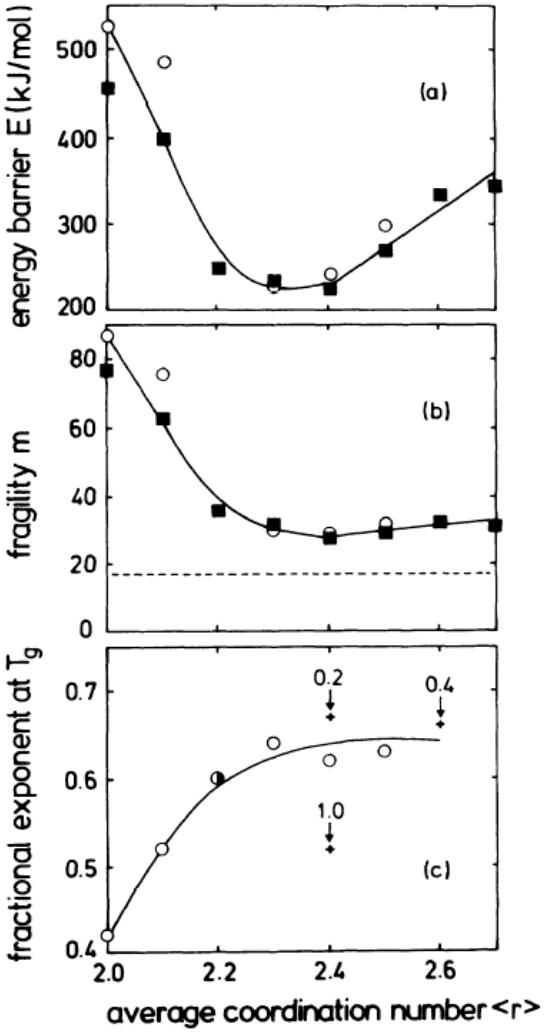


Fig. 4. Liquid state thermal expansion coefficient, α_L, versus $\langle r \rangle$ for the binary Ge–Se and ternary Ge–Sb–Se systems. The α_L values for the binary and the ternary are represented by ■ and ▲, respectively. The curves are drawn as a guide to the eye. The maximum measured error is 3.5%.



Boehmer and Angell, PRB 1994

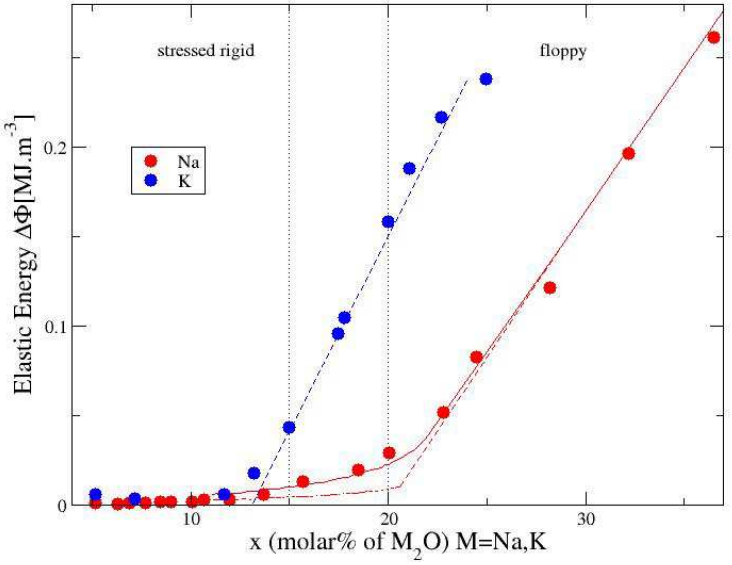
Varshneya et al., JNCS 1991

A) CONSTRAINTS AND RIGIDITY TRANSITIONS

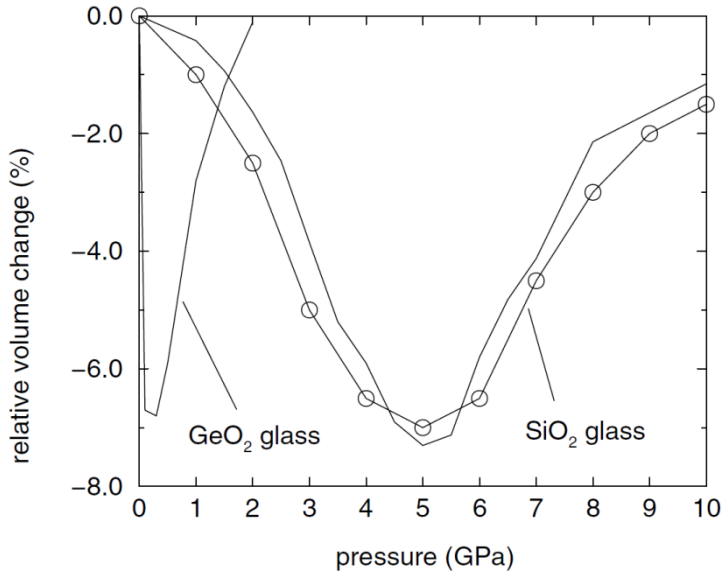
Binary oxides : $(1-x)SiO_2$-xNa_2O

- 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



Trachenko et al., PRL 2005

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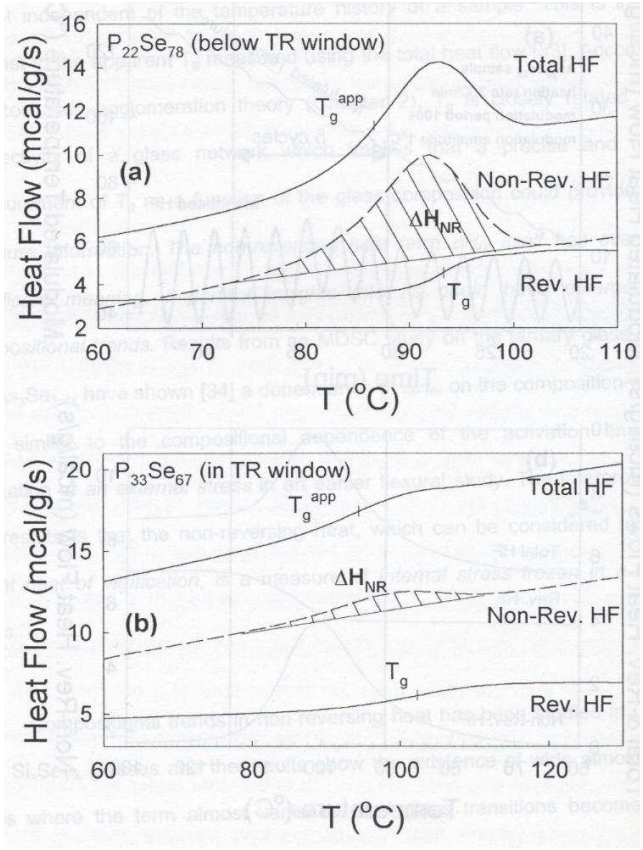
We review Raman scattering, Mössbauer spectroscopy and T-modulated Differential Scanning Calorimetry experiments on several families of chalcogenide glasses. Mean-field constraint theory, and numerical simulations of the vibrational density of state (floppy modes) in random

B. INTERMEDIATE PHASE

Modulated DSC and reversibility windows



Georgiev et al. PRB (2003)

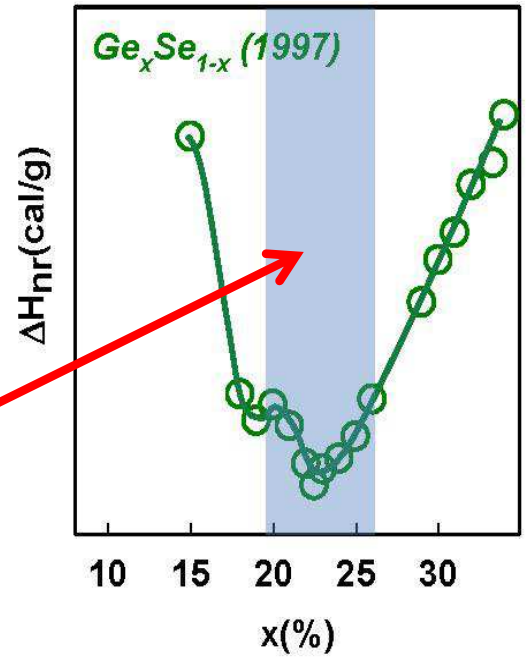
- Use of modulated differential scanning calorimetry (MDSC) across the glass transition

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

- Allows for the definition of 2 heat flows

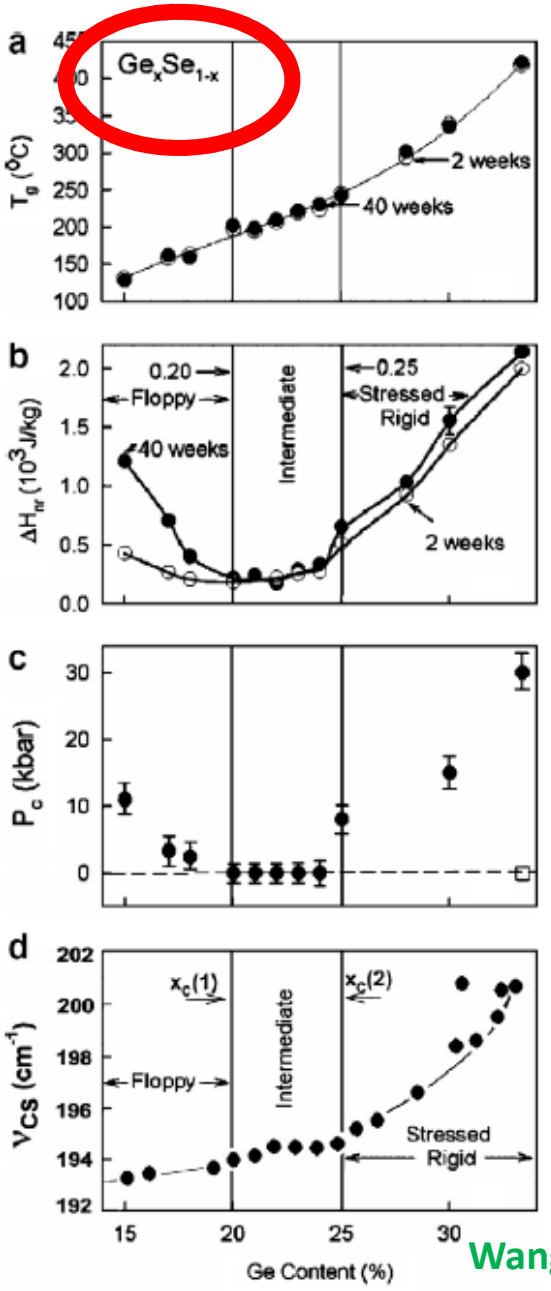
- Reversible (ΔC_p)
- Non-reversible

Non-reversing enthalpy (ΔH_{nr})



Reversibility window

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**
- Nearly vanishing of ΔH_{nr} at Tg
- Stress free character (P_c minimum, Raman)
- Vibrational thresholds (Raman, IR)
- **Generic (chalcogenides, oxides)**

Wang et al., PRB 2005

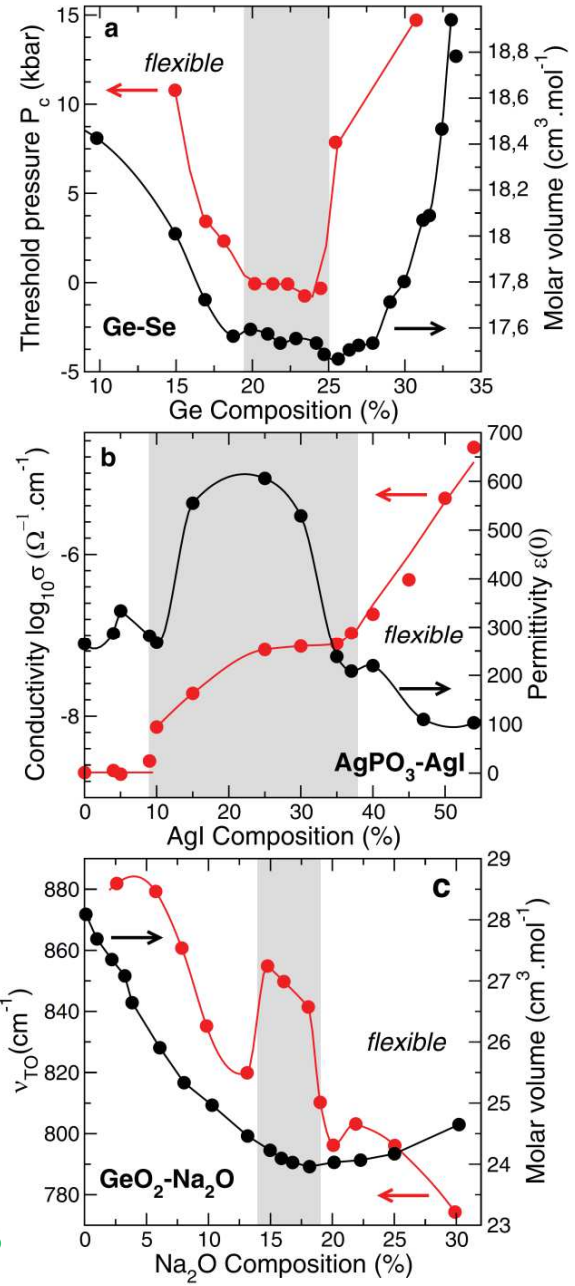
B. INTERMEDIATE PHASE

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

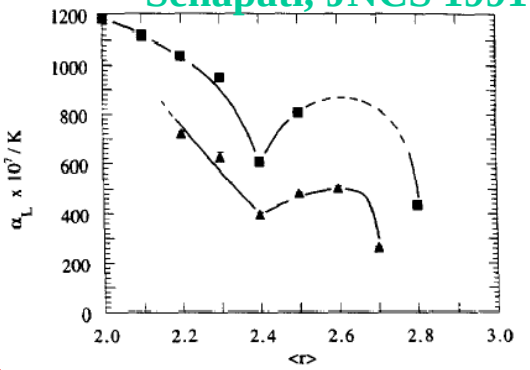
B. INTERMEDIATE PHASE

Why has the RW been missed before ?

And why are challengers missing it…and getting so annoyed ?

Three experimental conditions have to be met

Senapati, JNCS 1991



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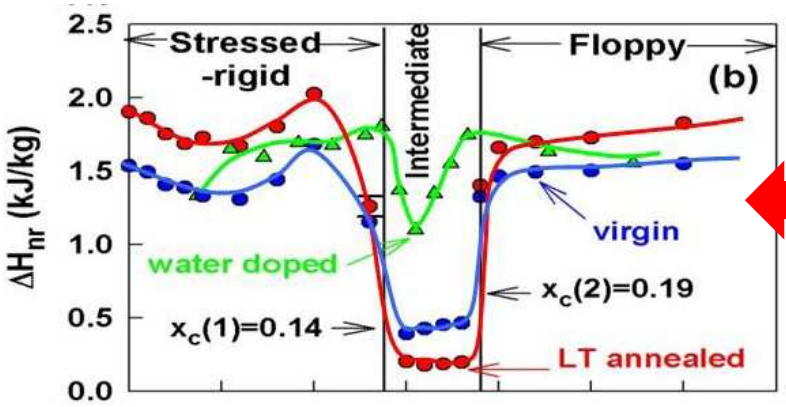
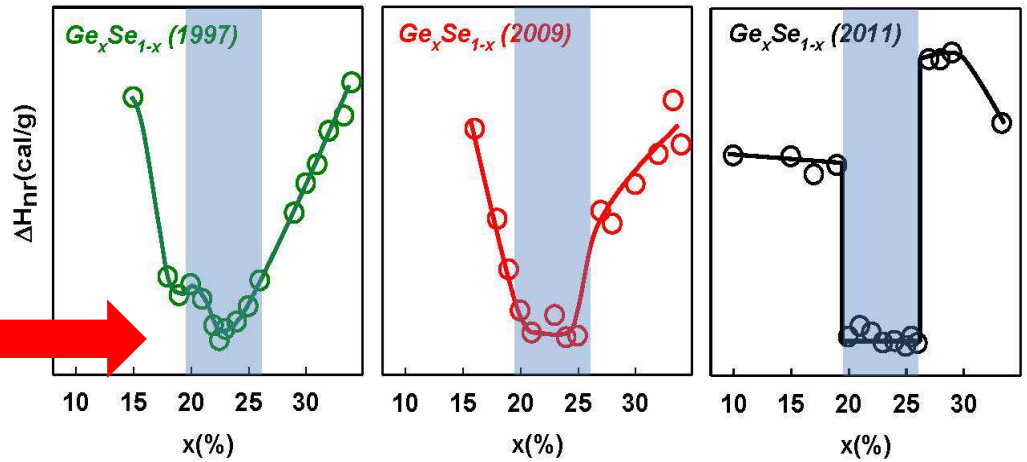
Tiny compositional changes



Sample purity (dryness)

Bhosle et al., IJAGS 2012



Homogeneity

Alloying time+

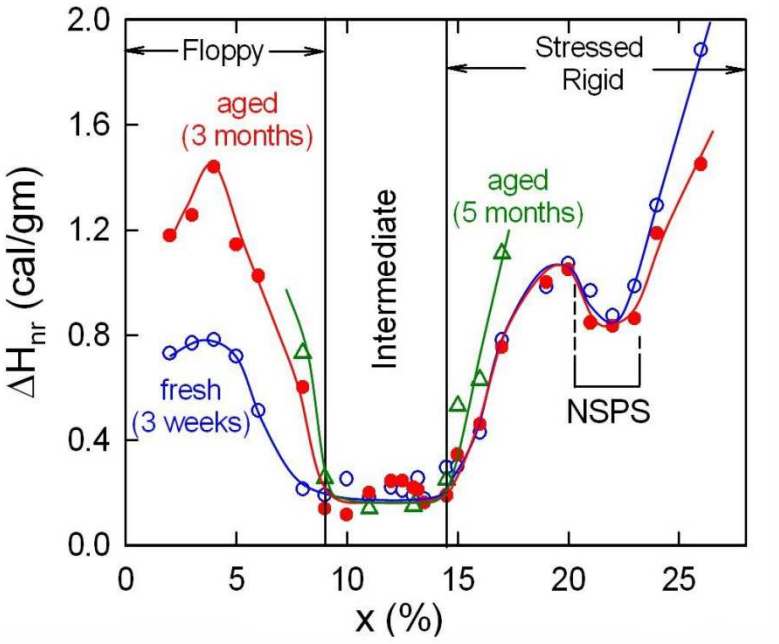
Raman profiling

B. INTERMEDIATE PHASE

Ageing

Not « no ageing » but « weak ageing »

$P_xGe_xSe_{1-2x}$



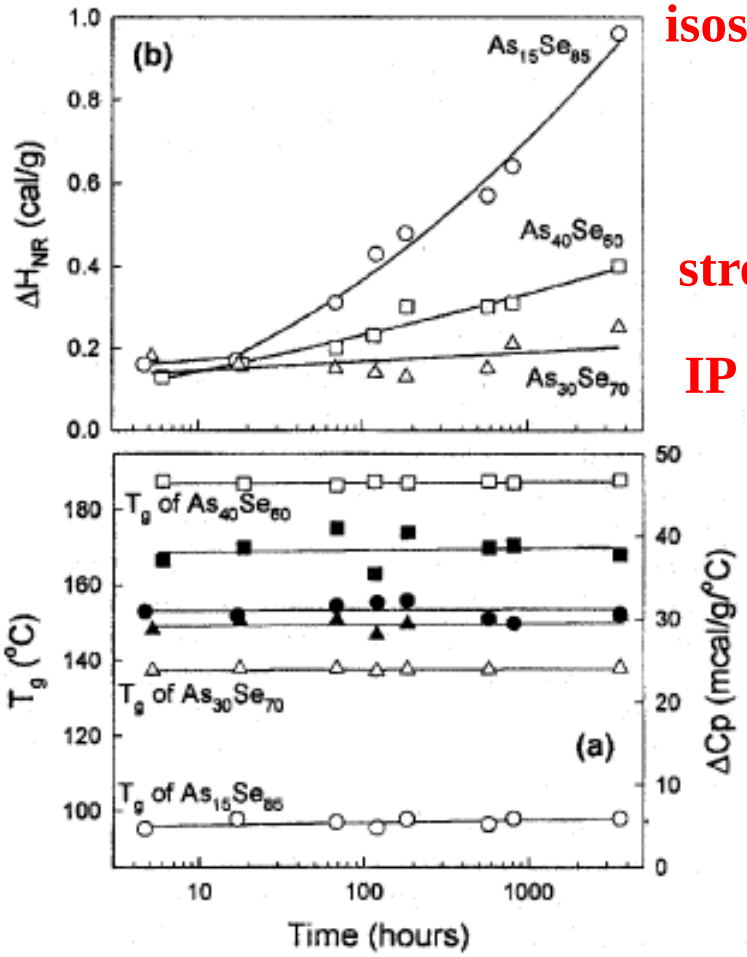
Chakravarthy et al. JPCM (2005)

As_xSe_{1-x}

isostatic

stressed

IP

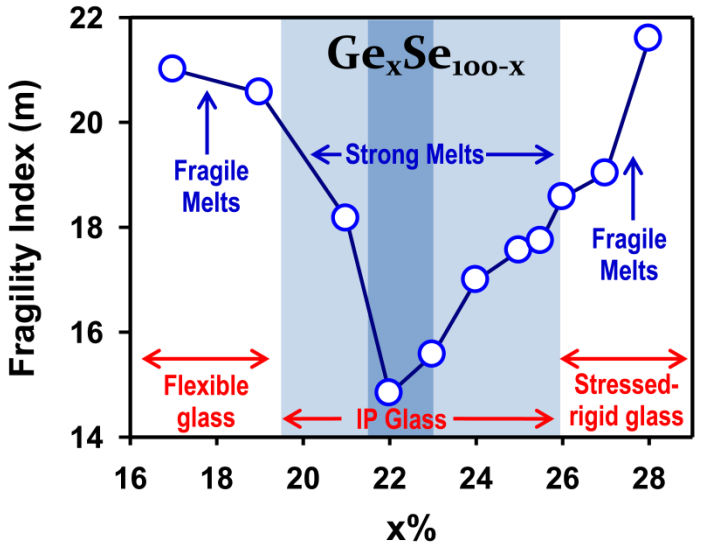


Georgiev et al. JOAM (2003)

B. INTERMEDIATE PHASE

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 electolytes



Gunasekera et al. JCP 2013

Micoulaut et al. PRB 2009

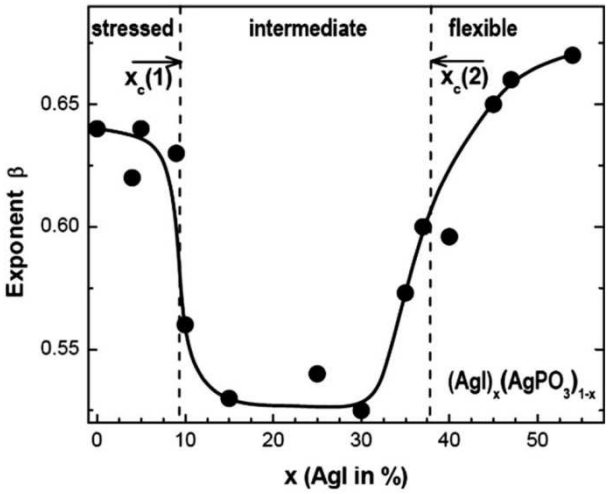
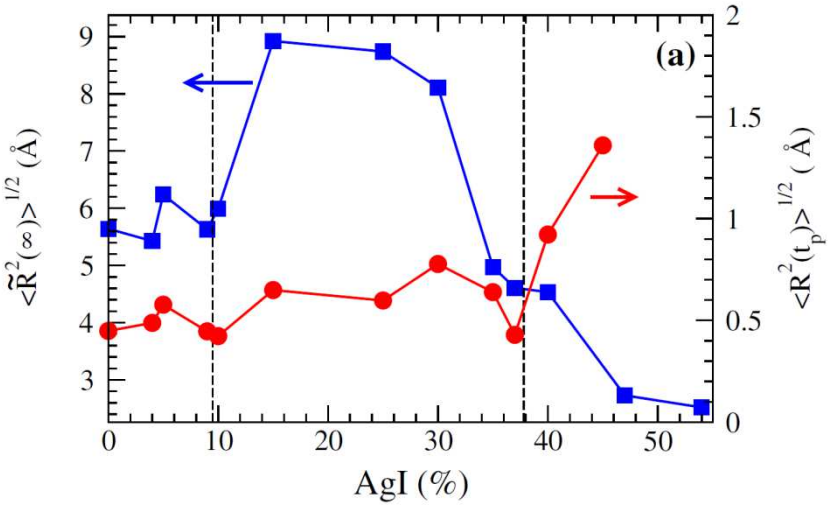


FIG. 6. Variations in the Kohlrausch stretched exponent $\beta(x)$ as a function of the AgI concentration x in $(AgPO_3)_{1-x}$-$(AgI)_x$ glasses.



Micoulaut, Malki, PRL 2010

B. INTERMEDIATE PHASE

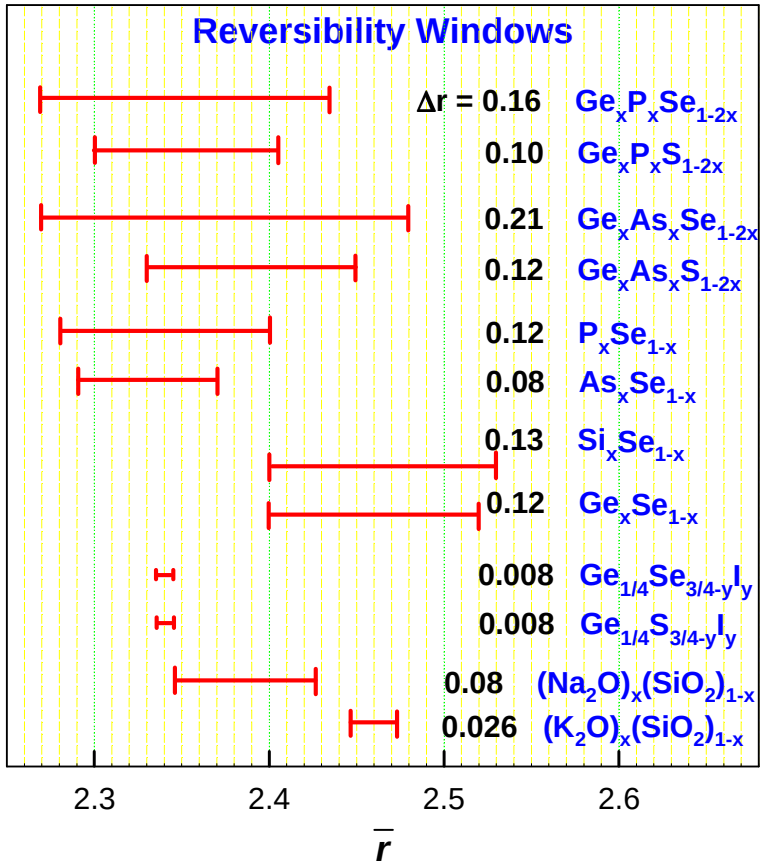
Theory ?

- **Central idea:**
  Self-organization
  Stress avoidance

- Normal mode analysis of self-organized networks.

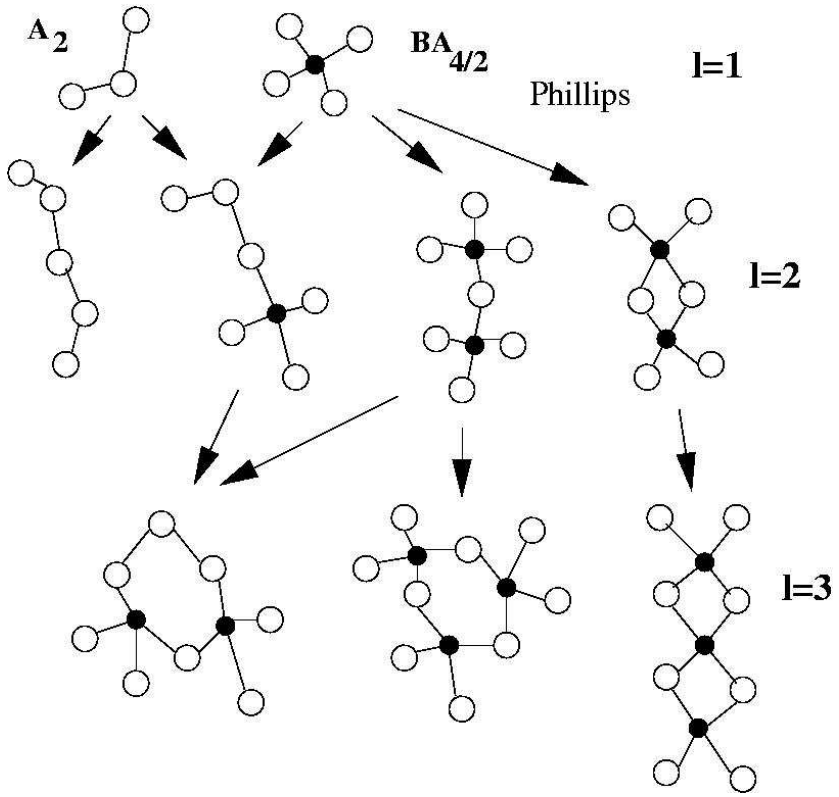
- Constraint counting on selective size increasing clusters

- MD simulations



C. CLUSTER EXPANSIONS

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



Application to $Ge_xSb_xSe_{1-2x}$

Mean-field count gives:

$n_c=7x+4.5x+2(1-2x)=2+7.5x$

$n_c=3$ for $x=13.33\%$

C. CLUSTER EXPANSIONS

Application to $Ge_xSb_xSe_{1-2x}$

- Identify $GeSe_{4/2}$, $SbSe_{3/2}$ and Se_2 local structures
- The local probabilities are given by :

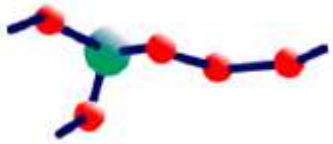
$$P_{Se_2} = \frac{2 - 11x}{2 - 3x} = 1 - P_G - P_{Sb} = P_S$$

$$P_{GeSe_{4/2}} = P_{SbSe_{3/2}} = \frac{4x}{2 - 3x} = P_G = P_{Sb}$$

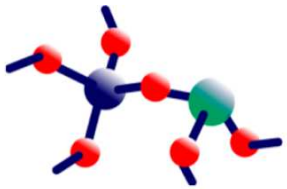
- Consider all possible connections, and compute probabilities: $P_{ij} = \frac{W_{ij}}{Z} P_i P_j e^{-E_{ij}/k_B T}$
- Three energy gains $e_k = \exp[-E_{ij}/kBT]$: E_{flex}, E_{iso}, E_{stress} , E_{ring}
  (rings involve a different constraint count)

$16P_S P_G e_{iso}$

$72{P_G}^2 e_{ring}$



$12P_S P_{Sb} e_{flex}$



$24P_G P_{Sb} e_{stress}$

C. CLUSTER EXPANSIONS

Application to $Ge_xSb_xSe_{1-2x}$

- Three parameters (unknowns). Reduced by concentration equation:

$$P_{GG} + \frac{1}{2}P_{GS} + \frac{1}{2}P_{GSb} = x = P_{SbSb} + \frac{1}{2}P_{SbS} + \frac{1}{2}P_{GSb}$$

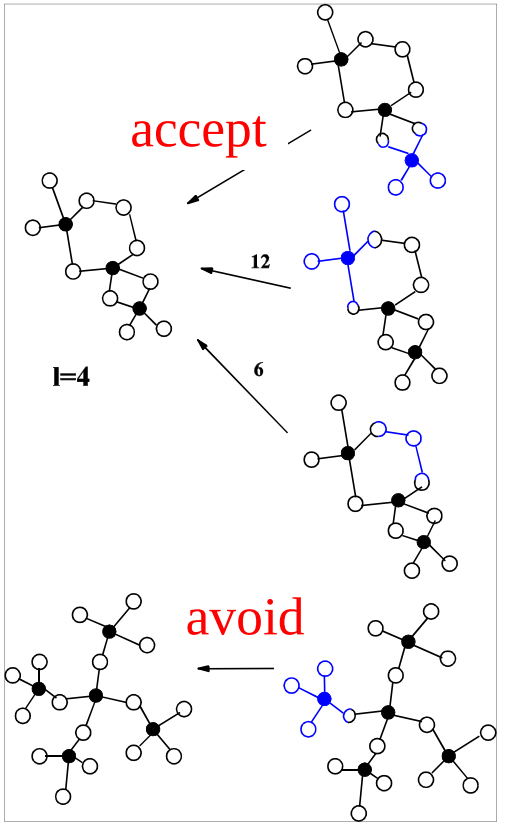
- **Self-organization.** Avoid stressed rigid connections (e_{stress}=0). Solve concentration equation for $e_{flex}=\exp[(E_{iso}-E_{flex})/k_BT]$:

$$e_{flex} = \frac{2(72xe_{ring} + 4 - 31x)}{3(2 - 11x)}$$

- One obvious limit (**stress transition**).

$$x_c = \frac{4}{31 - 72e_{ring}}$$

- For $x < x_c$, weak stress only in small rings (ES). For $x>x_c$, stress is dendritic and percolates (CS connections)



C. CLUSTER EXPANSIONS

Application to $Ge_xSb_xSe_{1-2x}$

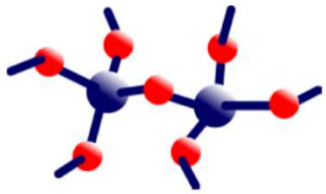
- For a given set N_l of clusters of size l, floppy mode count using ring corrections

$$n_c^{(l)} = \frac{\sum_{i=1}^{\mathcal{N}_l} n_{c(i)} p_i}{\sum_{i=1}^{\mathcal{N}_l} N_i p_i}$$

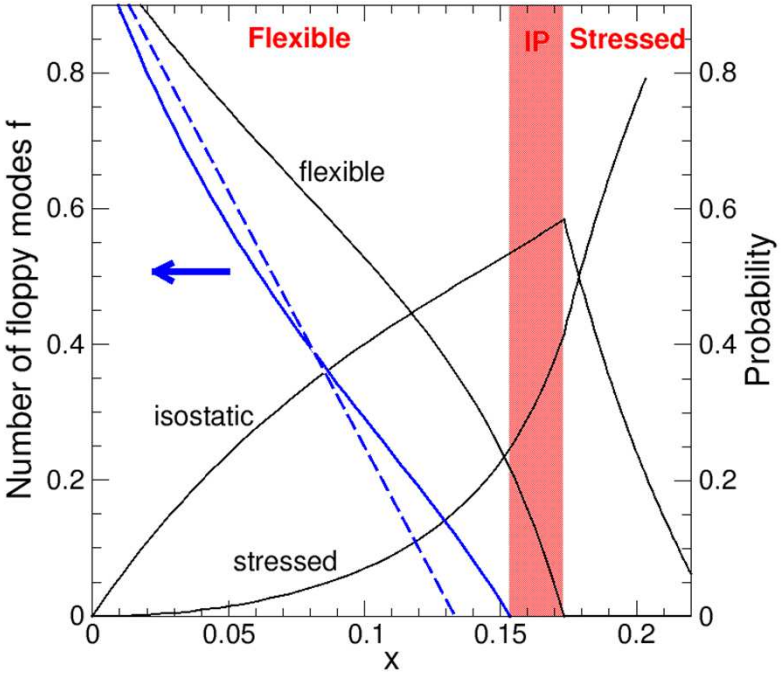
- Require $f^{(l)}=3-n_c^{(l)}=0$ (**rigidity transition** x_r).
- Threshold x_r (rigidity) is different from x_c (stress). Intermediate phase mostly isostatic.
- Rigidity mostly driven by the ES/CS ratio.

But not all glasses have ES structures…

n_c=3.25



n_c=3.67



D. MD BASED RIGIDITY THEORY

1. We start from the estimation of constraints:

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

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)

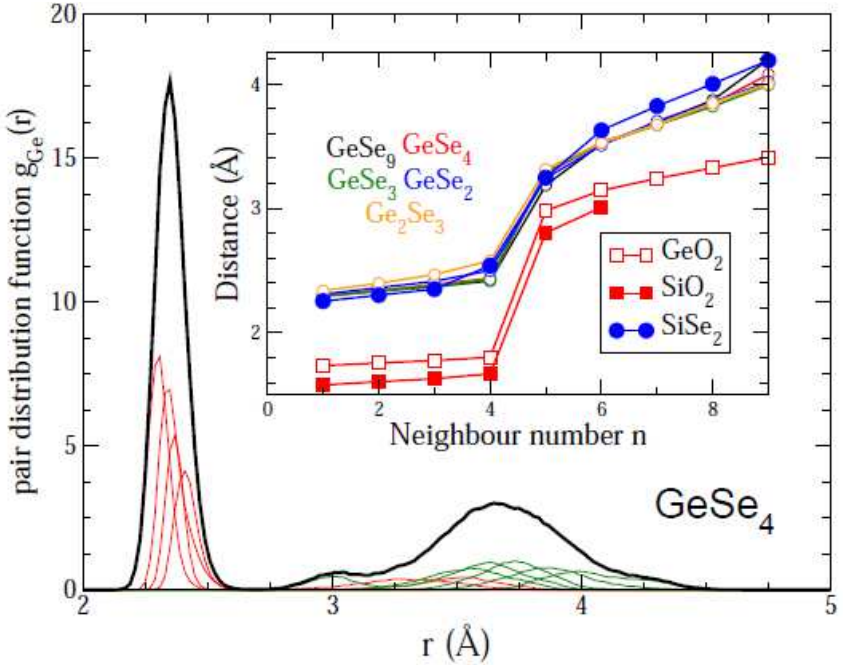
- **n_c at all thermodynamic conditions (T,P,x)**

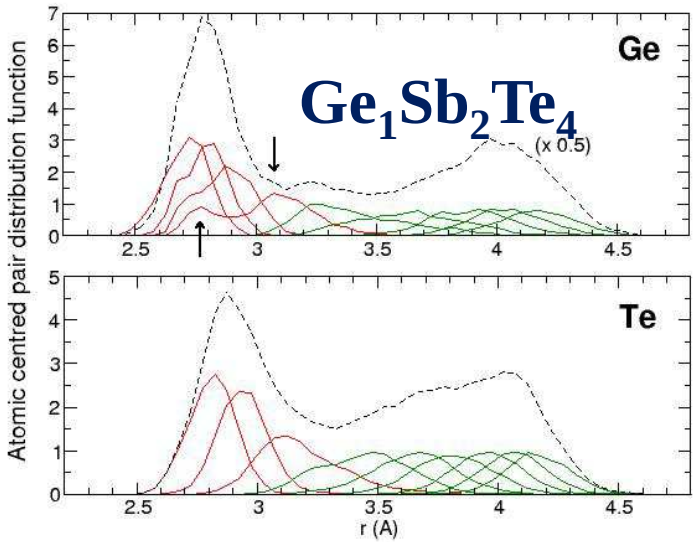
2. General idea:

- ❑ 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)





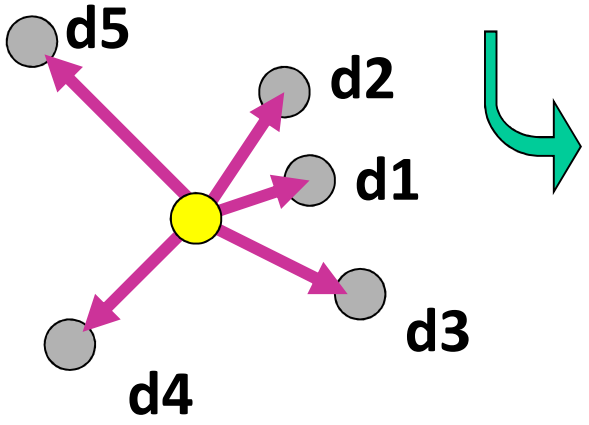
Straightforward in oxydes and
4 neighbours around Ge,Si

- ❖ two local environments for Ge
- ❖ CN(Te) >2

Micoulaut et al. PRB 2010

❑ Compute from these trajectories

1. bond-bending (work on angles)

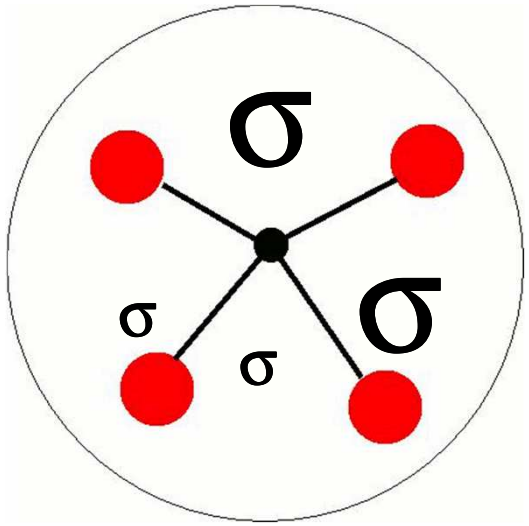


N first neighbor distance distrib.

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

Peugeot labelling

- Not all are independent !



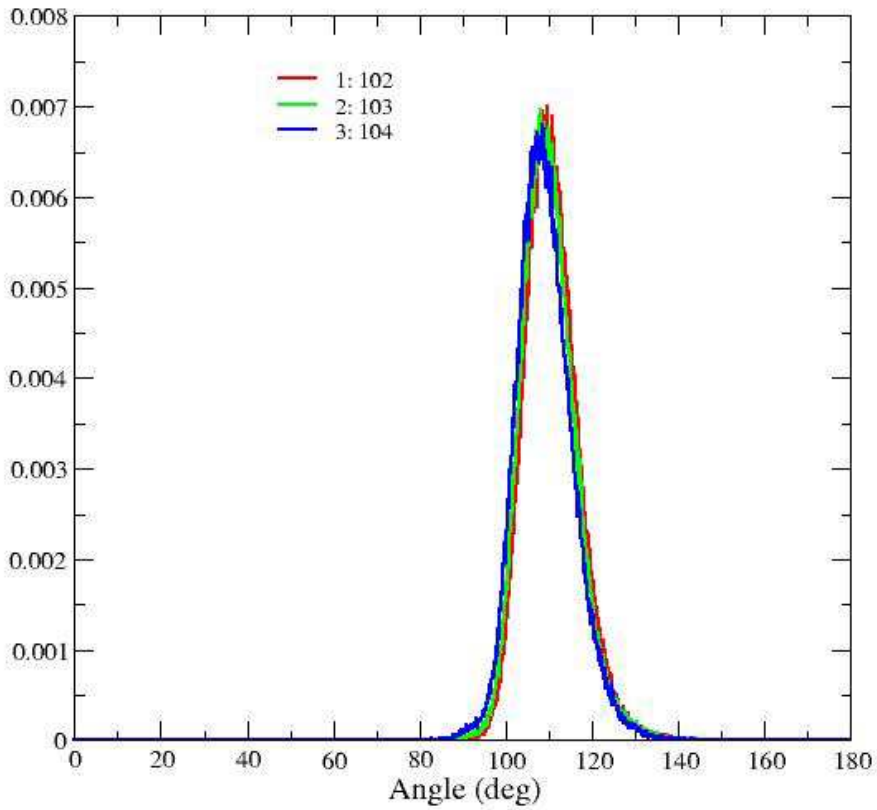
Estimate of bond-bending from partial bond angle distribution (PBAD) $P_i(\theta)$

with i<N(N-1)/2 arbitrary for a given atomic j0k triplet

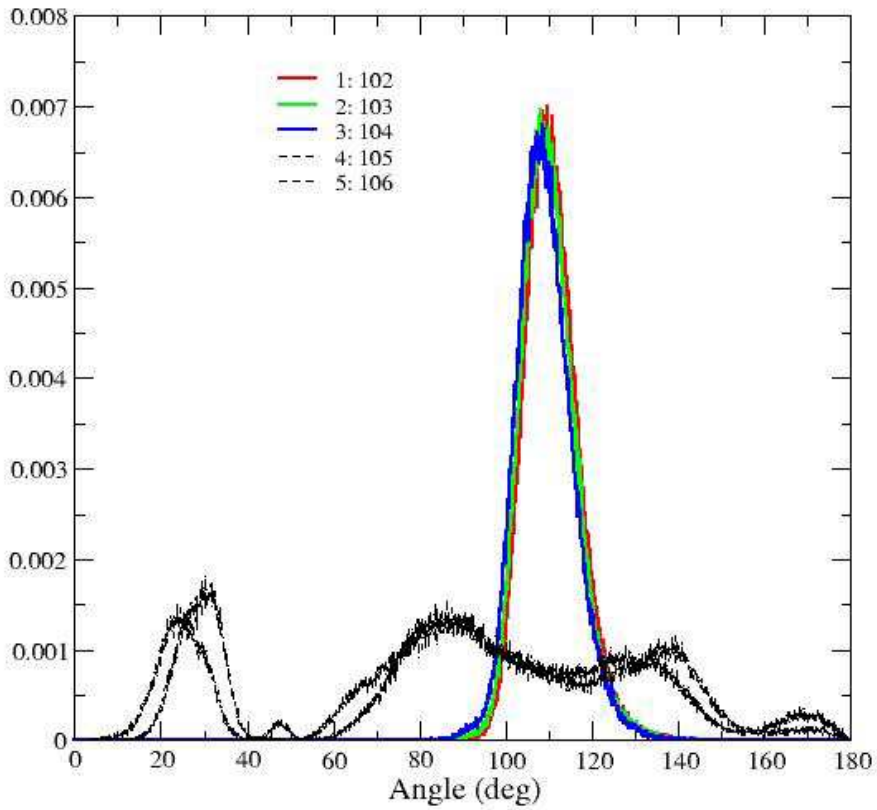
- Splitting the BAD into contributions from neighbours.
- Compute the second moment (σ_ι , sometimes fwhm) of each PBA Distribution.

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

Ge-centred PBAD in GeO_2 for arbitrary N=6

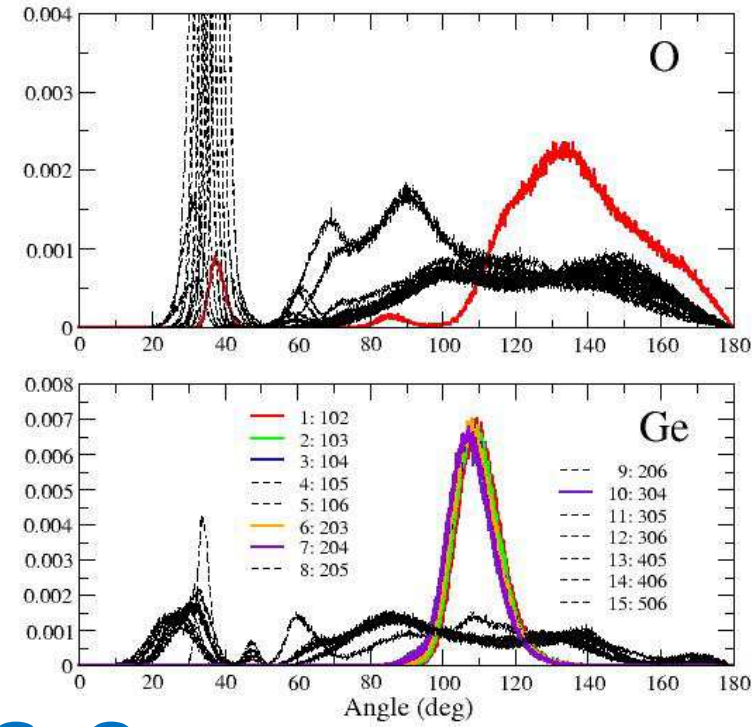


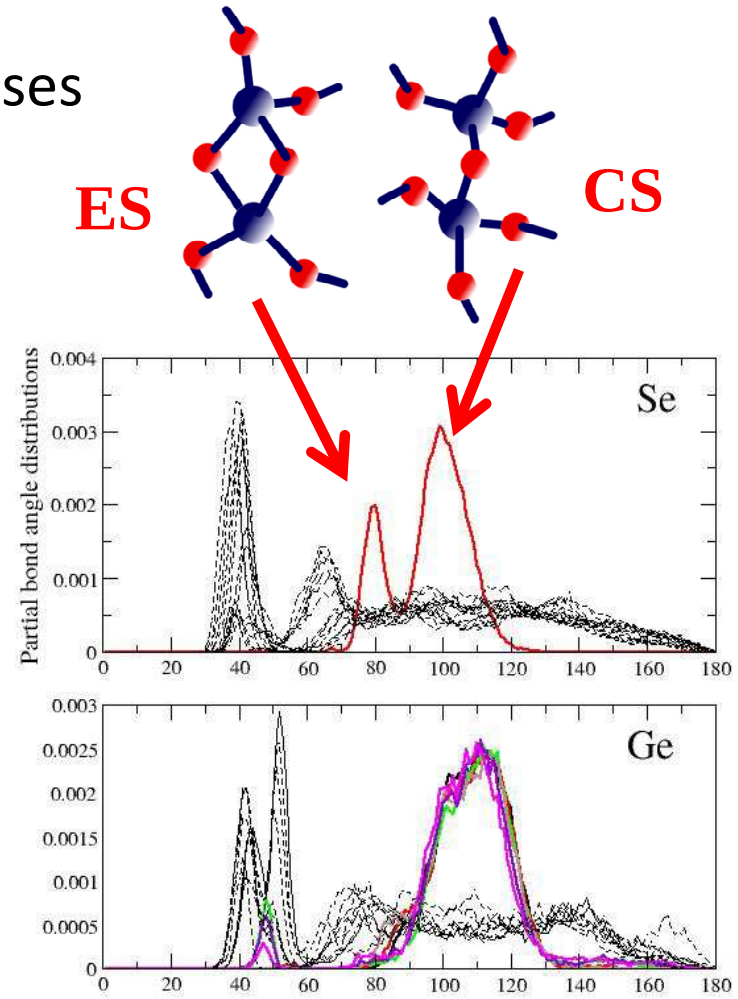
Ge-centred PBAD in GeO_2 for arbitrary N=6



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

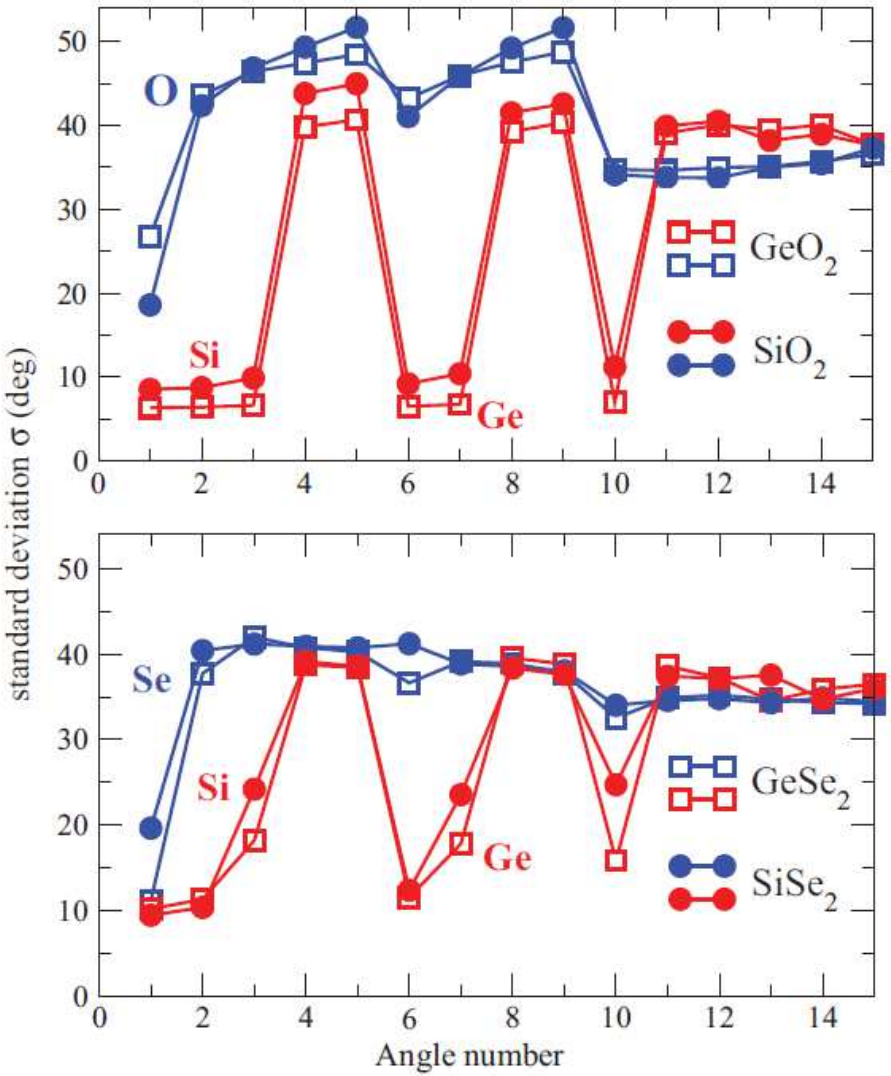
Tetrahedral angle (109°) well defined

$GeSe_2$

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**

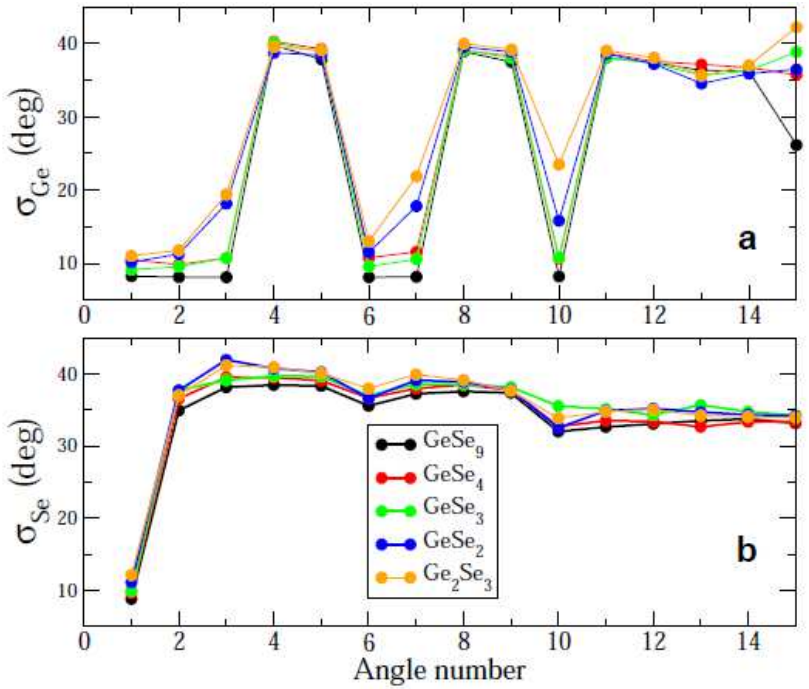
- 6 Ge,Si angles have a low standard deviation (but only 5 independent)

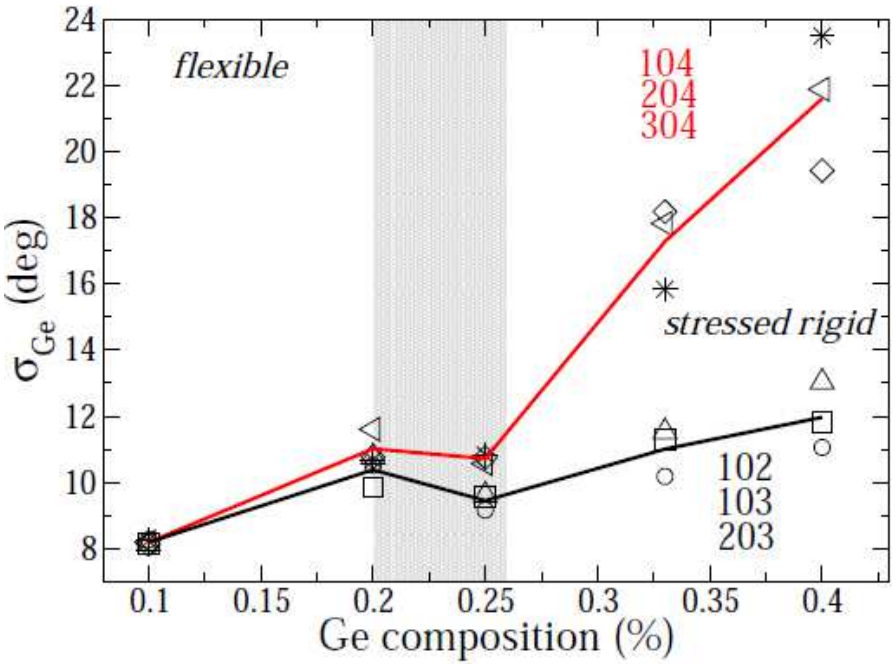
- Equivalent tetrahedral anglular excursion in oxides (rigid tetrahedron).

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

- 1 Se angle with a low σ in $GeSe_2$

Standard deviations and rigidity transitions



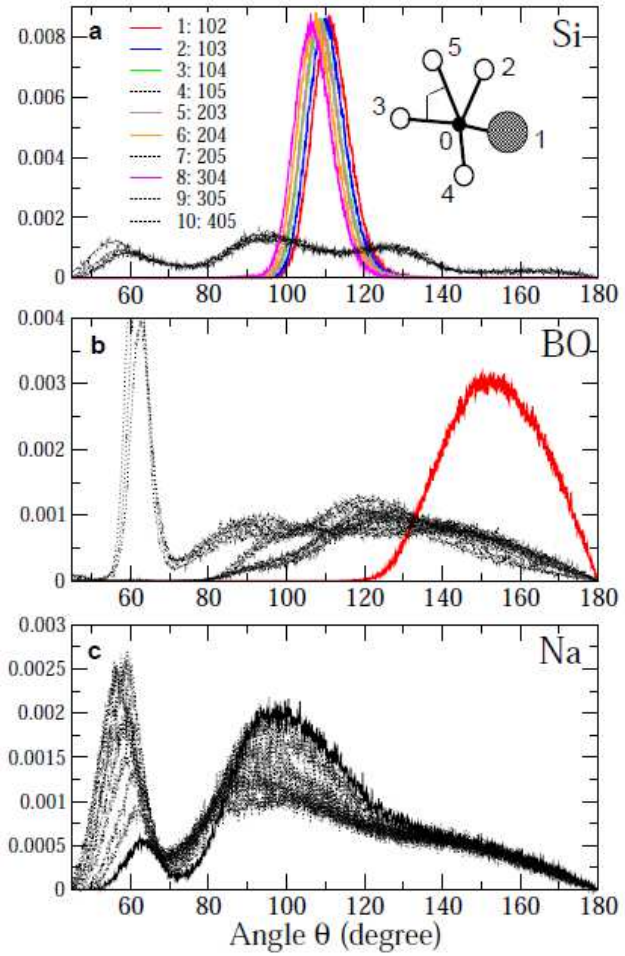


- **Rigidity (increasing Ge) affects mostly the Ge intra-tetrahedral motion.**
  Stress transition leads to an asymetric intra-tetrahedral angular motion involving the neighbour 4. Weak changes in σ_{Se}

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

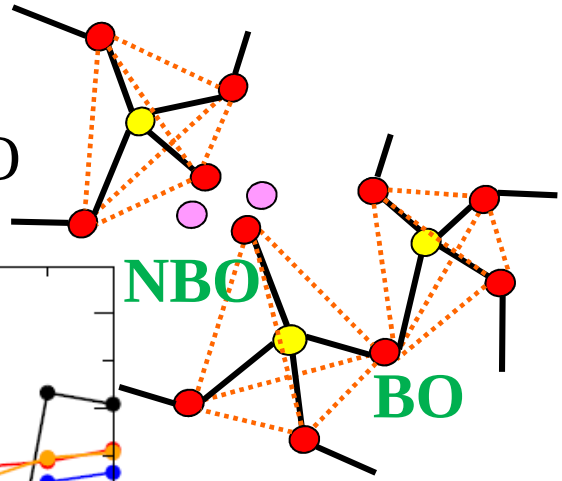
Effect of temperature

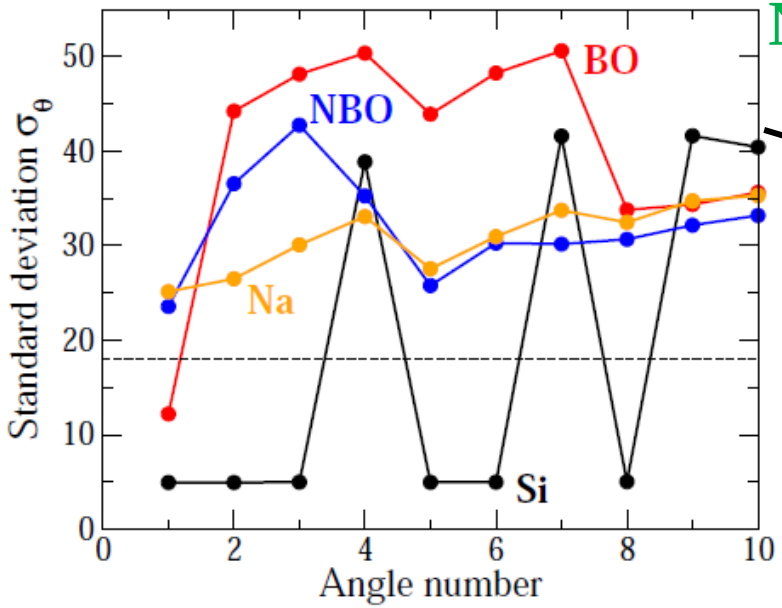
Focus on bond-bending constraints



Bauchy et al, JNCS 2011

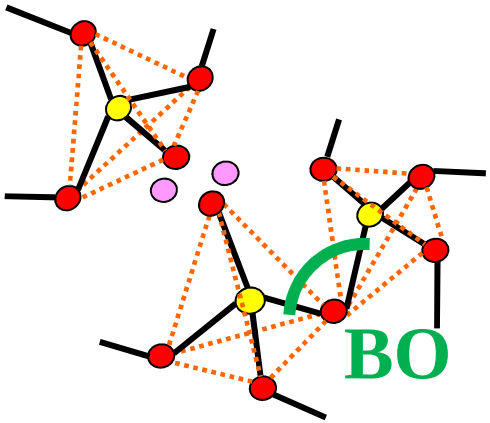
SiO_2-$2Na_2O$





- 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)



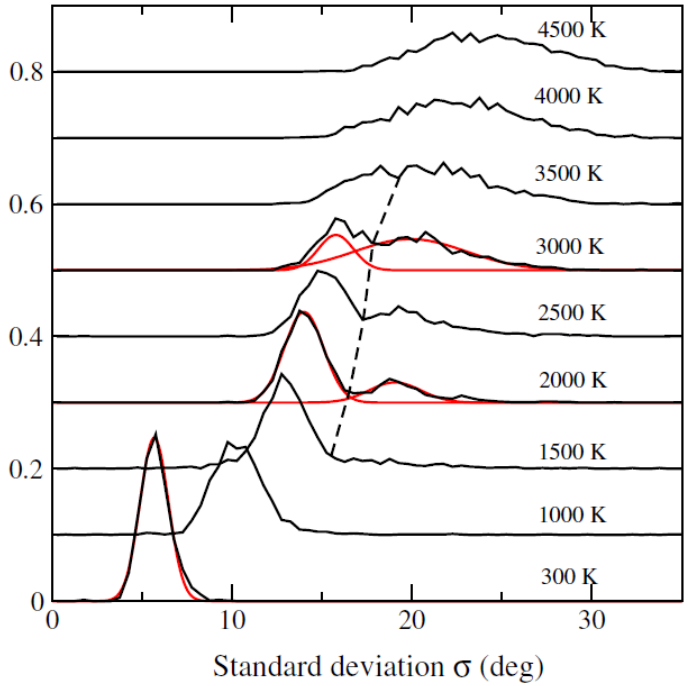
During the time trajectory ,
evaluate for each BO-centred angle a BAD.

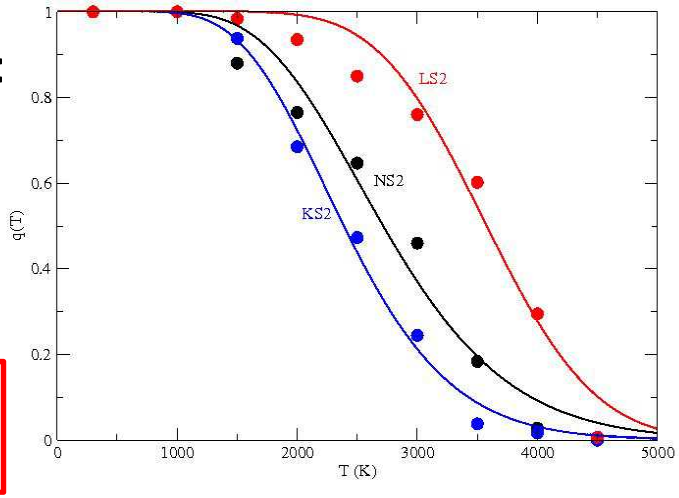
Compute its second moment σ.

-> Distribution of standard deviations f(σ) after Ensemble average the whole system.

- **Low Temperature:** distribution centred at low σ: intact constraints
- **High temperature:** distribution centred at large σ: broken constraints
- Numerical basis for the empirical Mauro-Gupta function (lecture 9):

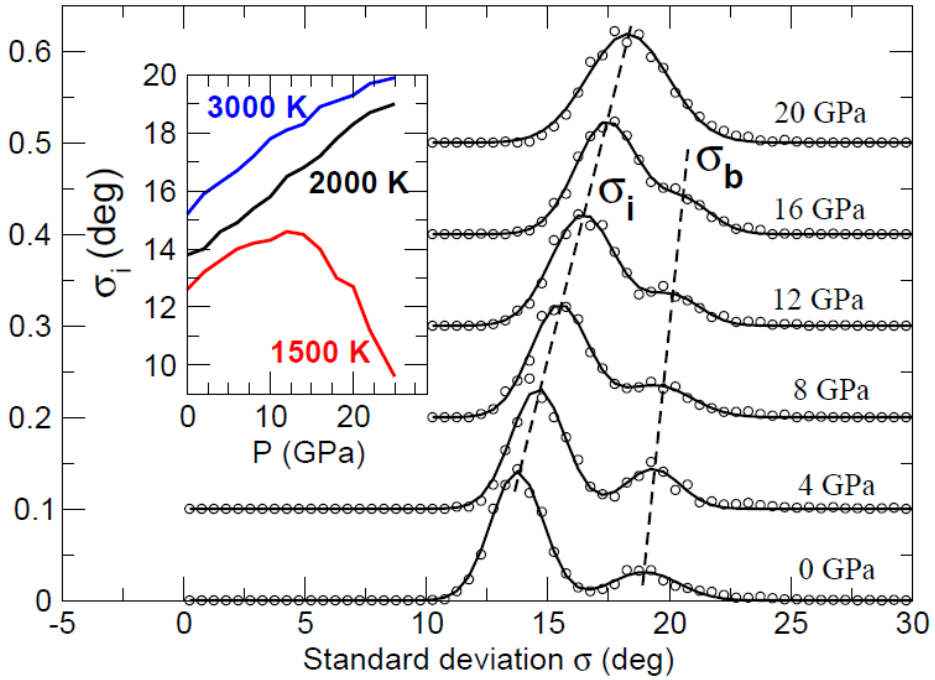
$$q\left(T\right) = \left[1 - \exp\left(-\frac{\Delta F^{*}}{kT}\right)\right]^{\nu t_{obs}}$$





Effect of pressure: evidence for the intermediate phase from MD

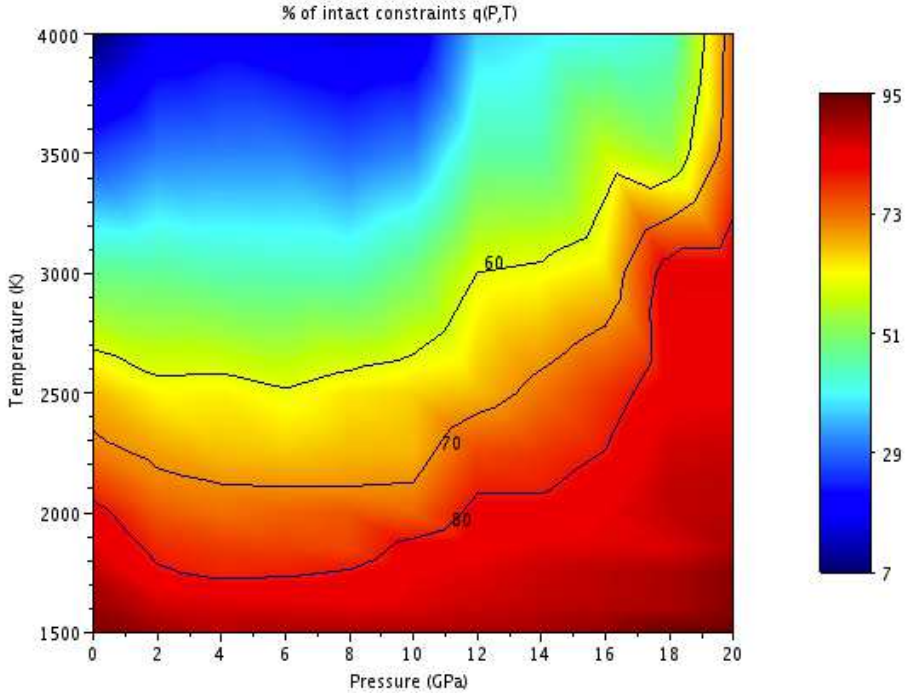
Extending the Mauro-Gupta function from q(T) to q(T,P)

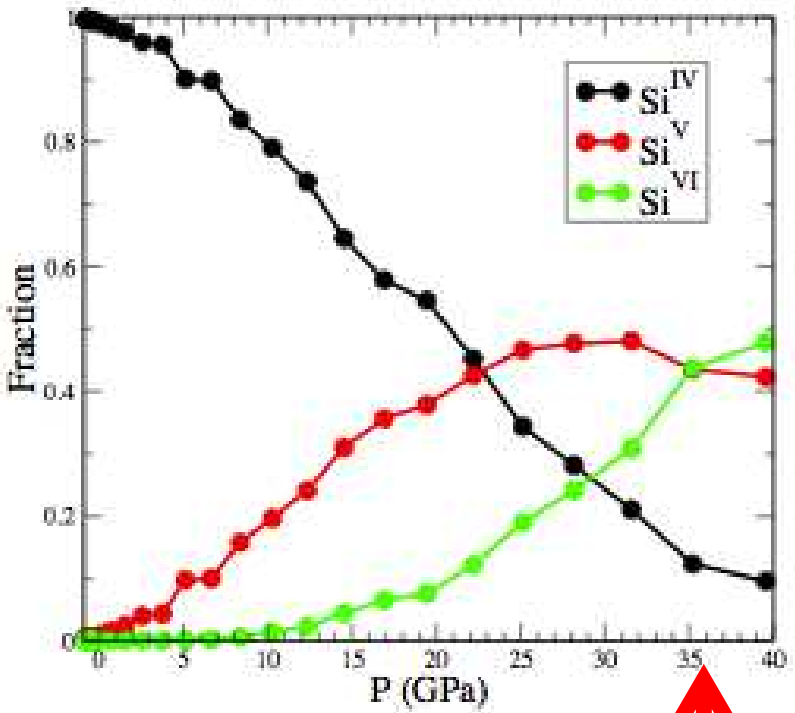


Distributions of the standard deviation of BO angles for increasing pressure

- ❑ Collapse of the broken BB contribution at large σ.
- ❑ Drift of the σi=σ(intact) du to the presence of stress.

Population of intact BB constraints q(P,T)





- Softening of the BB constraint of the BO to avoid pressure-induced stress (increase in Si connectivity Si^{IV}->Si^{V}->Si^{VI}).

- Adaptation only possible up to a certain point in P.
- Pressure analogue of the network self-organization (intermediate phase)

Link with transport properties

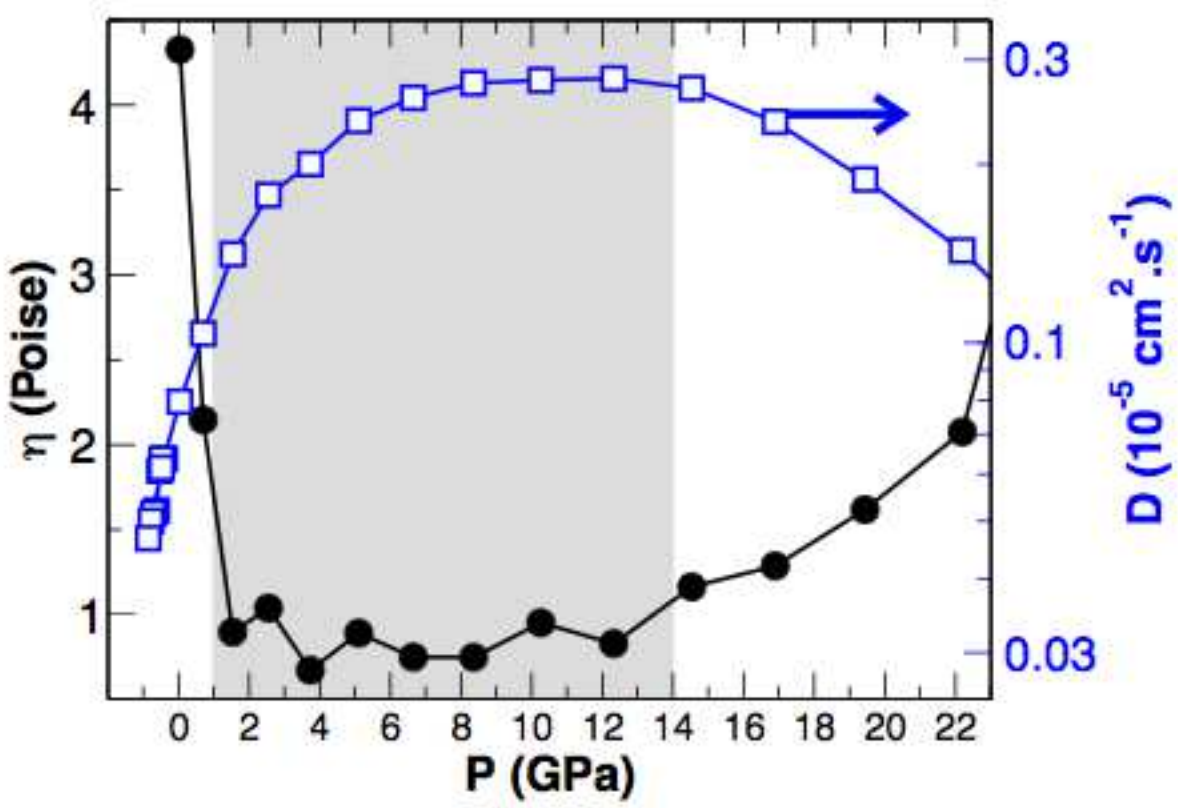
Diffusion (msd) and viscosity (Green-Kubo, Stress auto-correlation)

- In the pressure window:

- minimum of viscosity
- maximum of O diffusion

(similar features as d-SiO_2, H_2O, Debenedetti, 2000)

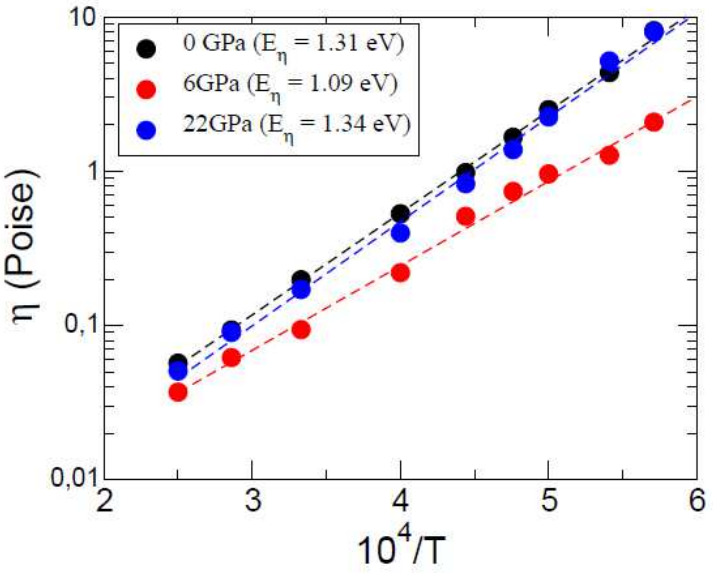
Correlation of the q(P) minimum window with transport properties anomalies

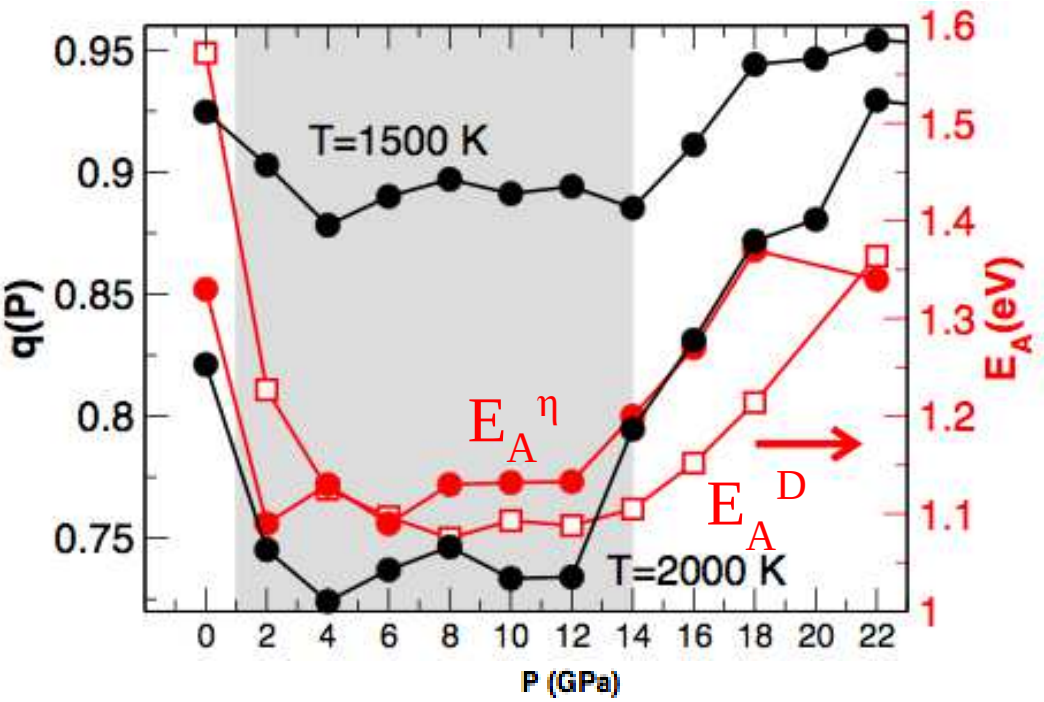


NS2 liquid, T=2000K

Link with transport properties

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





$D = D_0 \exp(- E_A^D / kT)$

$\eta = \eta_0 \exp(E_A^\eta / kT)$

Bauchy et al. PRL 2013

- Minimum of the activation energies (D,η) in the same pressure window 2 < P < 12 Gpa.

Conclusion:

- Rigidity transitions provide an interesting framework for the understanding of compositional trends in glasses
- Adaptative Intermediate phase with surprising properties (ongoing research). Design new applications ?
  - Weak ageing phenomena
  - Space-filling tendencies
  - Fragility anomaly
  - Stress-free character
  - **Experimental challenge (sample preparation)**
- Cluster models capture salient features of the IP
- MD based constraint theory leads to an atomic scale insight and links with properties (viscosity, diffusivity anomalies, etc.)

Next lecture (11): Dynamics and glass transition