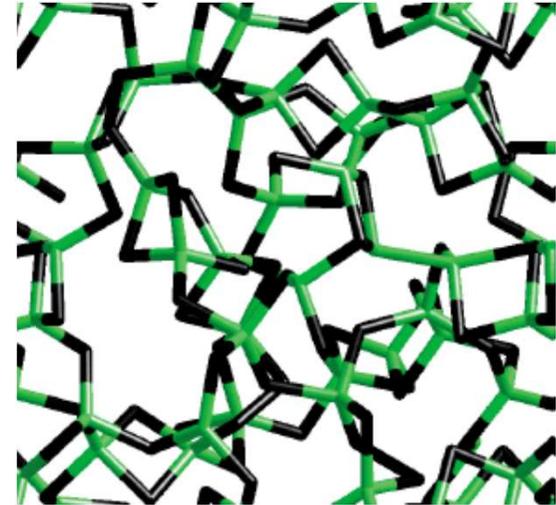


LECTURE 9 : TOPOLOGICAL ENGINEERING

- Constraint theory
- Naumis models
- Temperature-dependent constraints

« *Think topology* »

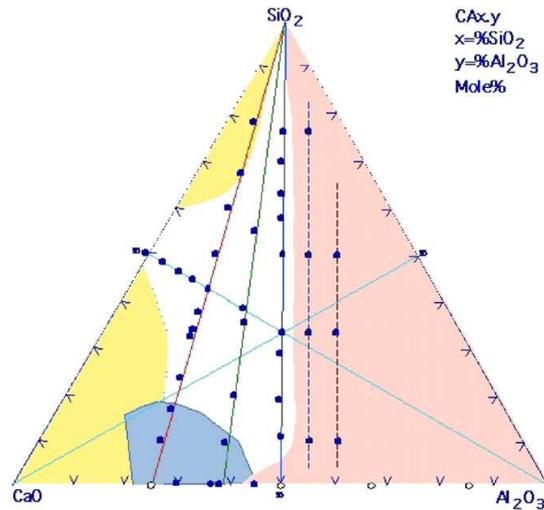
An early advise from J.C. Phillips



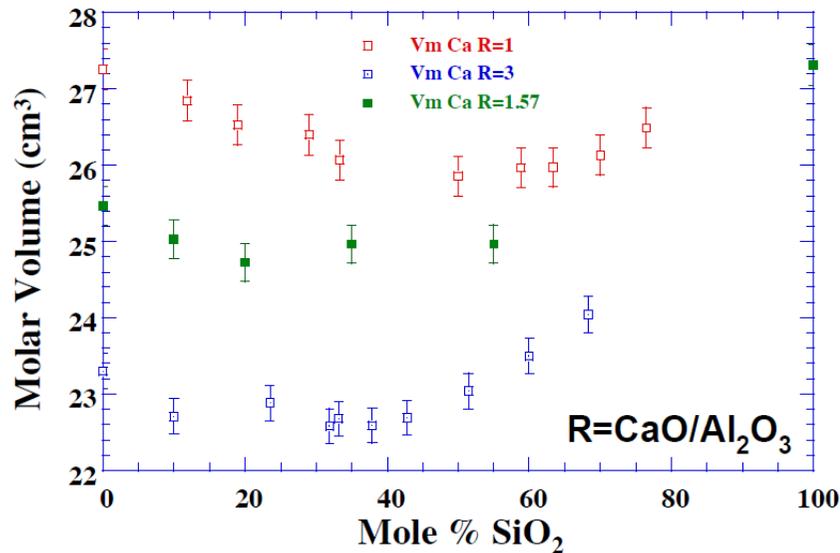
« *If you are not creating controversy, then you're not doing truly good science* »

A recent comment from the same JCP

A) Constraint theory



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



- Motivation :understanding compositional trends in glasses

- 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.

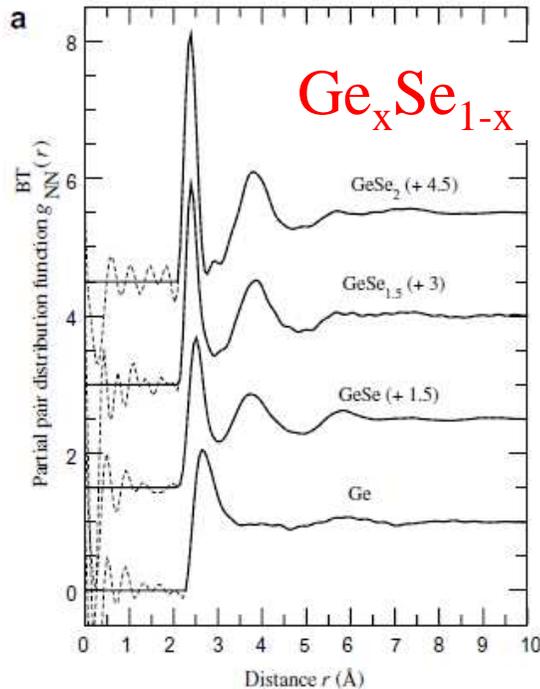
- Can all the unnecessary details be filtered out ? All those which do not influence ultimately the overall properties.

- There is much to learn from structure and from approaches which use as a central tool topology or network connectivity.

A) Constraint theory

Quantifying topology in glasses

Bhatia-Thornton number-number functions $g_{NN}(r)$



Parameters describing the first (r_1) and second (r_2) inter-atomic distances and mean coordination number (\bar{n}) for liquid (*l*-) and glassy (*g*-) Ge-Se compounds as obtained from the $g_{NN}^{BT}(r)$ shown in Figs. 2 and 4. The \bar{n} -values expected from the '8-N' rule are also listed together with the sample temperature and number density

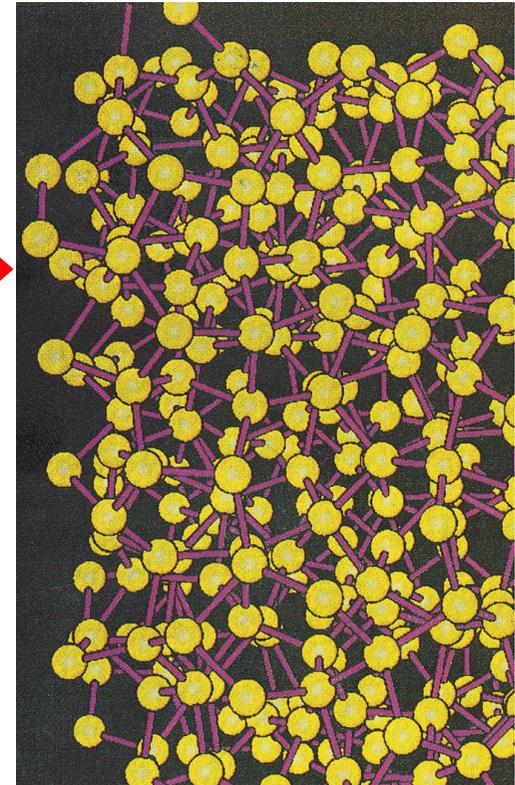
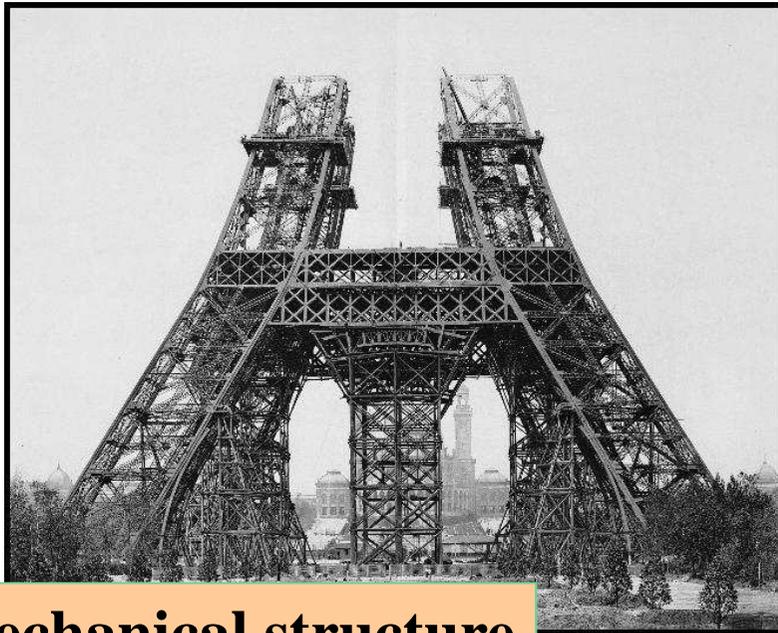
System	r_1 (Å)	r_2/r_1	\bar{n}	\bar{n} ('8-N' rule)	T (°C)	n_0 (Å ⁻³)
<i>l</i> -Ge	2.66(2)	2.237	5.8(4)	4	1000(3)	0.0456(3)
<i>l</i> -GeSe	2.52(2)	1.452	3.5(3)	3	727(2)	0.0387(2)
<i>l</i> -GeSe _{1.5}	2.41(2)	1.618	2.8(2)	2.8	728(3)	0.0336(2)
<i>l</i> -GeSe ₂	2.38(2)	1.609	2.6(1)	2.67	784(3)	0.0311(2)
	2.38(2)	1.605	2.7(1)		800(3)	0.0312(2)
	2.40(2)	1.596	2.7(1)		1000(3)	0.0317(2)
<i>g</i> -GeSe _{1.5}	2.40(2)	1.608	2.6(1)	2.8	1100(3)	0.0322(2)
	2.37(2)	1.616	2.81(5)		26(1)	0.0341(1)
	2.35(2)	1.647	2.69(5)		26(1)	0.0334(1)
<i>g</i> -GeSe ₂	2.35(2)	1.647	2.69(5)	2.67	26(1)	0.0334(1)
<i>g</i> -GeSe ₃	2.35(2)	1.609	2.51(5)	2.5	26(1)	0.0339(1)
<i>g</i> -GeSe ₄	2.35(2)	1.583	2.44(6)	2.4	26(1)	0.0339(1)
<i>g</i> -Se	2.34(2)	1.573	2.03(5)	2	26(1)	0.0327(1)

P.S. Salmon, JNCS 353, 2959 (2007)

$g_{NN}(r)$ -> Measure of the network mean coordination number $\langle r \rangle$
 Ge_xSe_{1-x} glasses follow the 8-N rule, i.e. $\langle r \rangle = 2 + 2x$

A) Constraint theory

Basic idea: An analogy with mechanical structures



Mechanical structure

- Nodes
- Bars
- **Tension**

Molecular network (constraint counting)

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

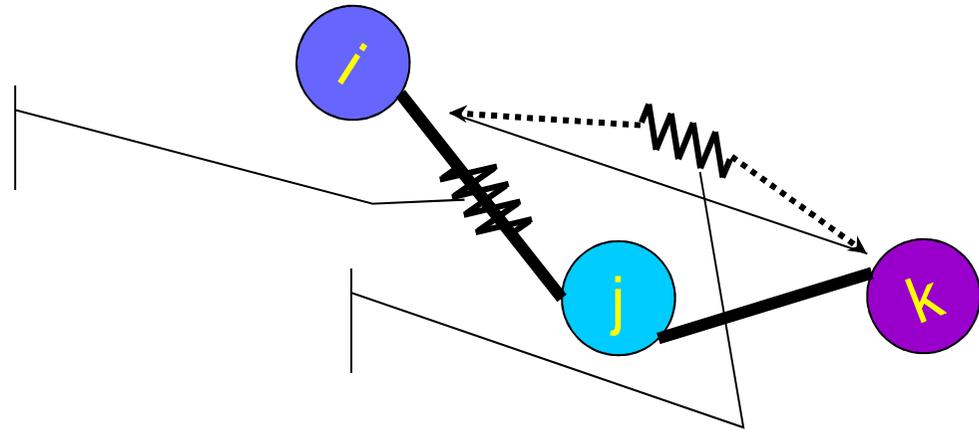
A) Constraint theory

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

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

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

- Then n_c can be simply rewritten as :

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

- Invoking the Maxwell stability criterion for isostatic structures $n_c = D = 3$ we find a stability criterion for:

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

or :

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

Phillips, JNCS 1979

- 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) Constraint theory

Examples of application:

□ $\text{Ge}_x\text{Se}_{1-x}$ glasses:

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

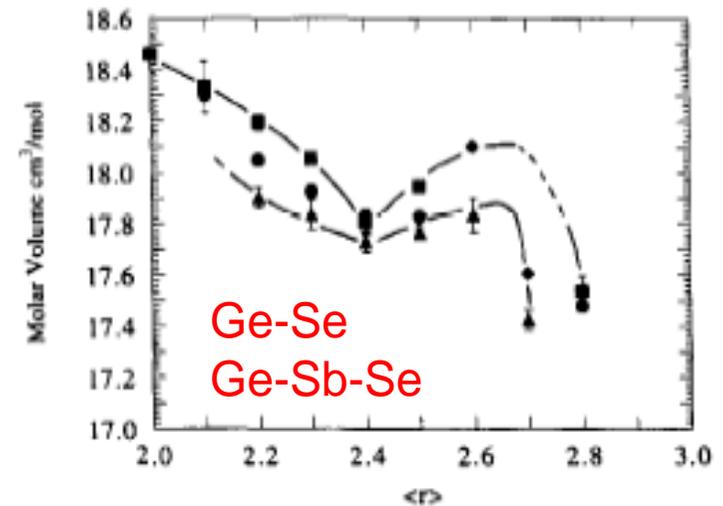
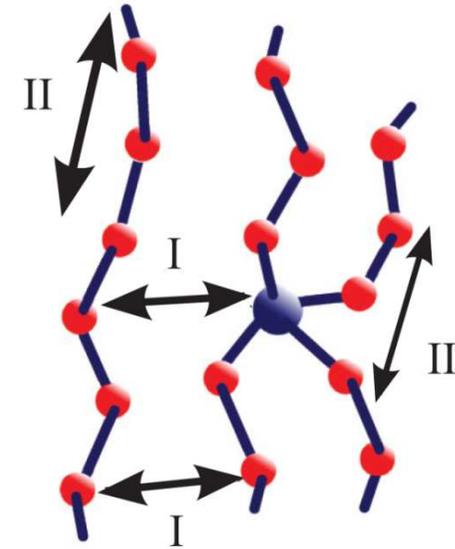
- ❖ Ge has $2r-3=5$ BB and $r/2=2$ BS constraints
- ❖ Se has 1 BB and 1 BS constraint

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

- ❖ Mean coordination number at 20% Ge

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

$\text{Ge}_{20}\text{Se}_{80}=\text{GeSe}_4$ glasses are isostatic



Varshneya et al. JNCS 1991

B) Naumis models

Constraints and dynamics:

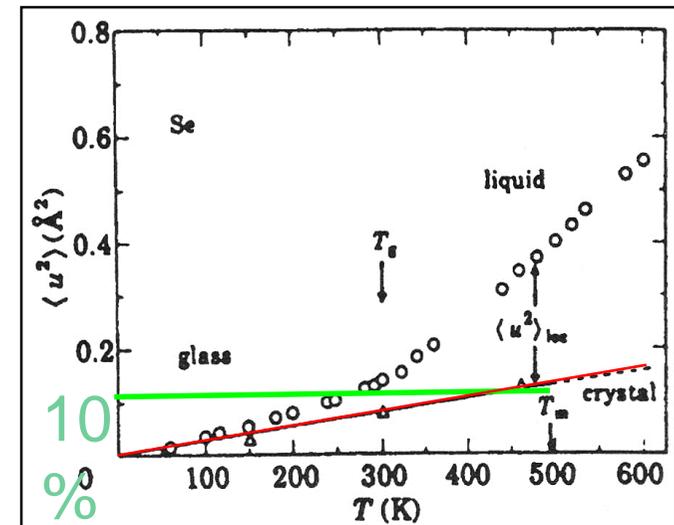
- Starting point is the classical equation relating the msd to the vibrational density of states

$$\langle u^2(T) \rangle = \frac{3k_B T}{m} \int_0^\infty \frac{g(\omega)}{\omega^2} d\omega,$$

- Below T_g , $\langle u^2(T) \rangle$ is linear in T .
- At T_g , the Lindemann criteria applied to glasses establish that

$$\langle u^2(T_g) \rangle = \langle u^2(T_m) \rangle = 0.01 a^2$$

where T_m is the melting temperature and a the crystalline cell length



U. Buchenau, Zorn, EPL (1992).

B) Naumis models

Constraints and dynamics:

- Assume that for a given fraction of floppy modes, the vibrational density of states is given by

$$g(\omega) = (1 - f)g_R(\omega) + f\delta(\omega - \omega_f),$$

with g_R the density of states for $f=0$ and ω_f the frequency of a floppy mode (4meV).

- Remembering that one has :
- $$\langle u^2(T) \rangle = \frac{3k_B T}{m} \int_0^\infty \frac{g(\omega)}{\omega^2} d\omega,$$

one can compute the

$$\langle u^2(T) \rangle = \frac{3k_B T}{m} \left[\left\langle \frac{1}{\omega^2} \right\rangle_R + f \left(\frac{1}{\omega_f^2} - \left\langle \frac{1}{\omega^2} \right\rangle_R \right) \right]$$

where:

$$\left\langle \frac{1}{\omega^2} \right\rangle_R \equiv \int_0^\infty \frac{g_R(\omega)}{\omega^2} d\omega.$$

B) Naumis models

Constraints and dynamics:

- We apply the Lindemann criterion for an overconstrained glass ($f=0$). It follows from :

$$\langle u^2(T) \rangle = \frac{3k_B T}{m} \left[\left\langle \frac{1}{\omega^2} \right\rangle_R + f \left(\frac{1}{\omega_f^2} - \left\langle \frac{1}{\omega^2} \right\rangle_R \right) \right]$$

that:

$$T_g(f=0) \approx \frac{0.01 m a^2}{3k_B \left\langle \frac{1}{\omega^2} \right\rangle_R}$$

and for f non-zero:

$$T_g(f) = \frac{T_g(f=0)}{1 + \alpha f}$$

with:

$$\alpha \equiv \frac{1}{\omega_f^2 \left\langle \frac{1}{\omega^2} \right\rangle_R} - 1 \equiv \left(\frac{\Theta_R}{\Theta_f} \right)^2 - 1$$

B) Naumis models

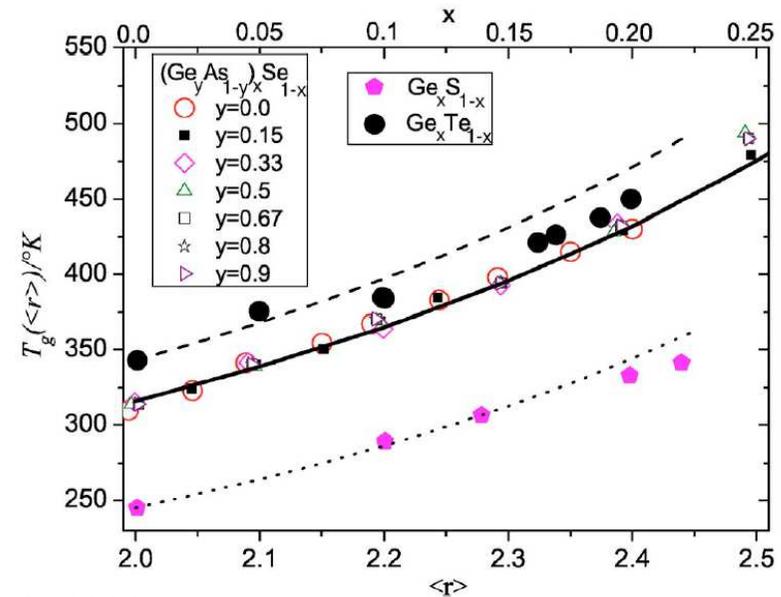
Constraints and dynamics:

□ Since we have the number of floppy modes f :
$$f = \frac{3N - N_c}{3N} = 2 - \frac{5}{6}\langle r \rangle$$

We finally have:
$$T_g(\langle r \rangle) = \frac{T_g(\langle r \rangle = \langle r_c \rangle)}{1 + \alpha\left(2 - \frac{5}{6}\langle r \rangle\right)} \equiv \frac{T_g(\langle r \rangle = 2.0)}{1 - \beta(\langle r \rangle - 2.0)}$$

with
$$\beta = \frac{5\alpha}{2\alpha + 6}$$

- The glass transition is a function of the mean coordination number $\langle r \rangle$ of the glass network.
- Excellent agreement in chalcogenides



G.G. Naumis, PRB 73 (2006)

B) Naumis models

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:

$$\begin{aligned} Z &= \int \cdots \int \prod_{j=1}^N dP_j dQ_j e^{-H/kT} \\ &= \left(\frac{2\pi m k T}{h^2} \right)^{3N/2} \prod_{j=1}^{3N(1-f)} \left(\frac{2\pi k T}{m \omega_j^2} \right)^{1/2} \end{aligned}$$

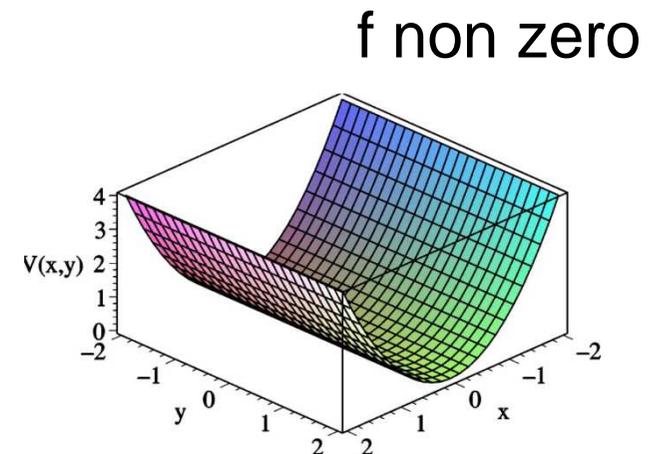
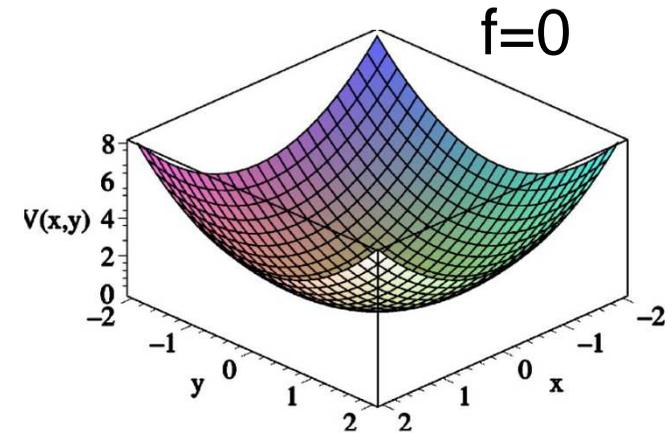
- Floppy modes are cyclic variables of H
- Provides a **channel in the potential energy** landscape (PES) since the energy does not depend upon a change in a floppy mode coordinate

B) Naumis models

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 .
 $S = k_B \ln \Omega$

$$S \approx f 3Nk_B \ln(V / V_0)$$



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

C) Temperature dependent constraints

Basics

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

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

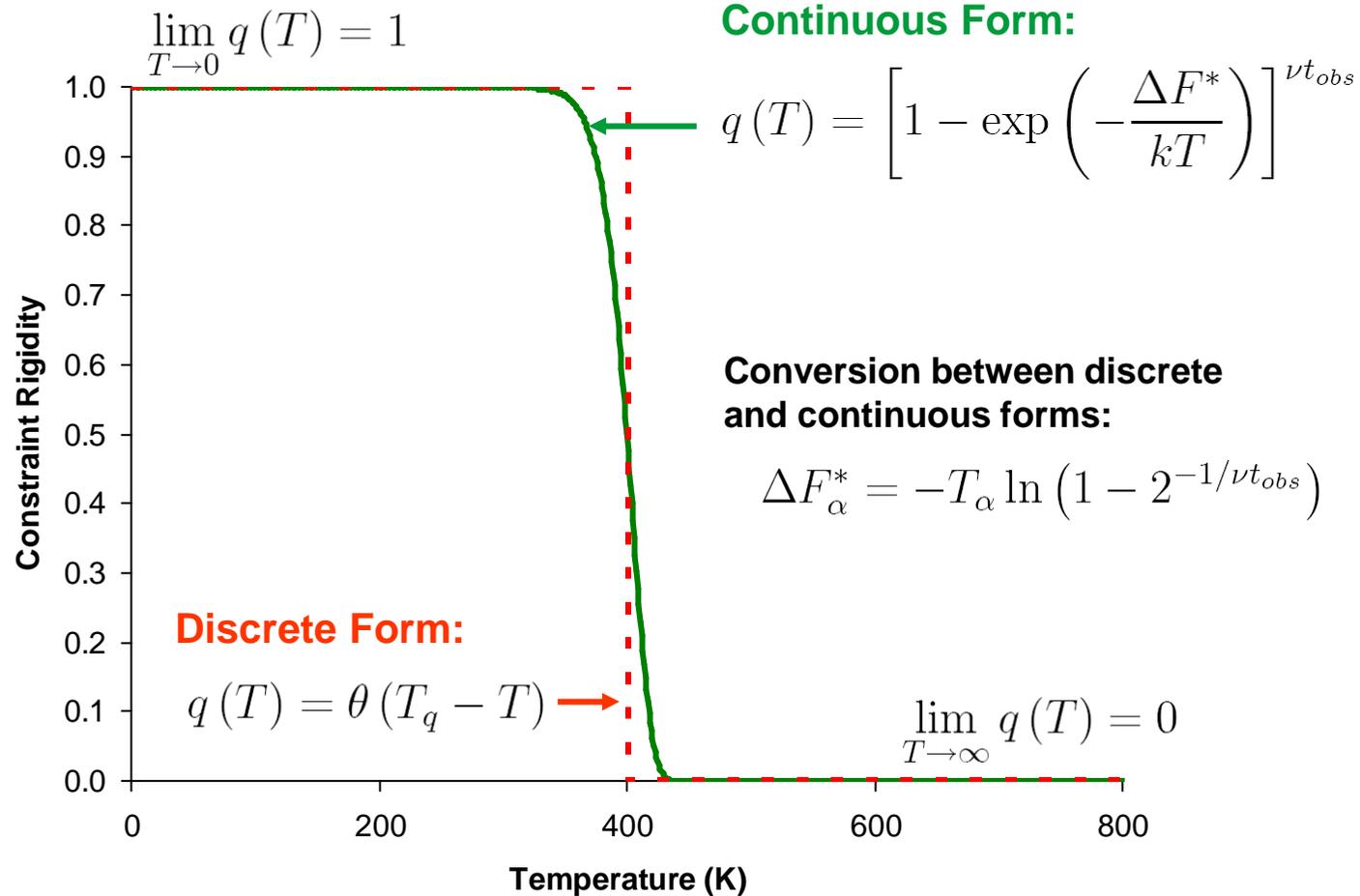
- Required parameters:
 - $N_i(x)$: mole fraction of each network-forming species i
 - $w_{i,\alpha}$: number of α -type constraints for each species i
 - $q_{\alpha}(T)$: temperature-dependent rigidity of constraint α

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

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

C) Temperature dependent constraints

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



C) Temperature dependent constraints

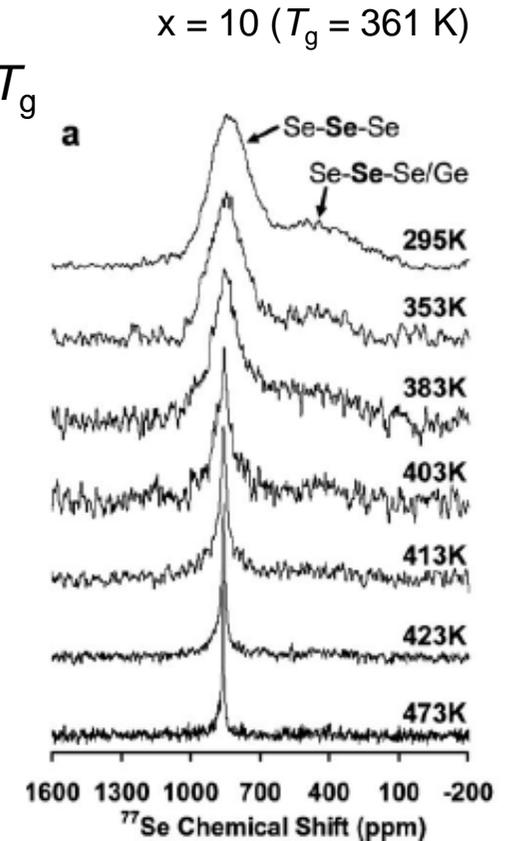
Experimental evidence for temperature-dependent constraints

□ High-temperature ^{77}Se NMR study of $\text{Ge}_x\text{Se}_{100-x}$ system
Temperature-dependent dynamics of Se atoms around T_g

□ Narrowing of the Se-**Se**-Se resonance with increasing T implies rapid rotation of the selenium chain segments

□ However, the Ge-**Se**-Se/Ge selenium environments remain relatively rigid in the temperature range around T_g

Theoretical evidence for temperature-dependent constraints (**lecture 10**)



Gjersing, Sen, Youngman, *Phys. Rev. B* (2010)

C) Temperature dependent constraints

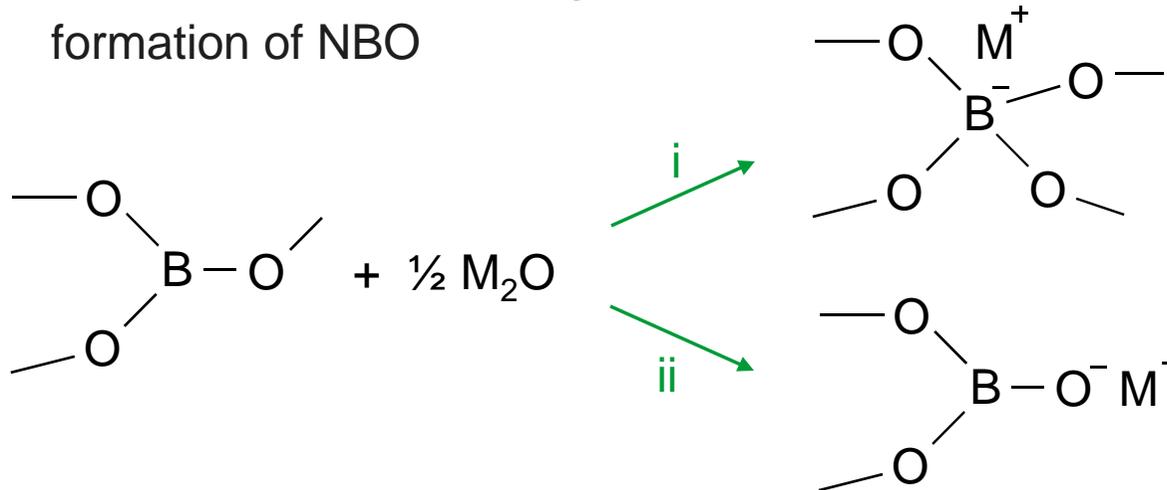
Steps

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

C) Temperature dependent constraints

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

- ❑ Applied to borate glasses Na₂O-B₂O₃
- ❑ Addition of modifier oxide to B₂O₃ can cause
 - boron coordination change
 - formation of NBO



- ❑ Remember of simple bond models for alkali borates (**lecture 3**) for $x > 0.33$

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

C) Temperature dependent constraints

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

□ Complete statistics

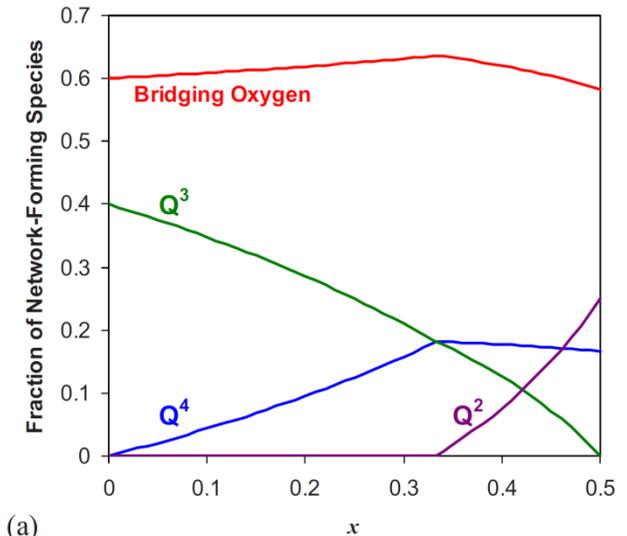
$$x > 0.33 \quad N_2(x) = \frac{3(3x-1)}{5(1-x)} \quad N_3(x) = \frac{1-2x}{1-x} \quad N_4(x) = \frac{3-4x}{5(1-x)}$$

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

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

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

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



Mauro et al. JCP 2009

C) 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 Q⁴ unit.
 - Three at each Q³ 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

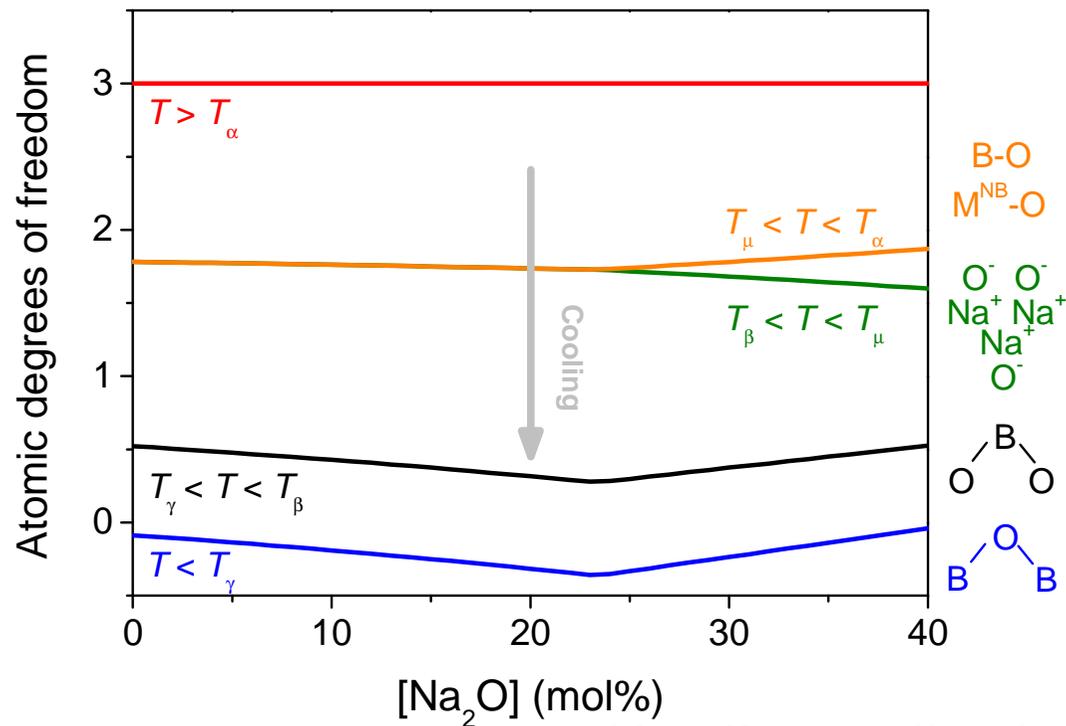
Each involves an onset temperature at which $q(T)$ becomes active
Similar procedure for borosilicates

C) Temperature dependent constraints

Step 3: Ranking of constraints according to temperature

- Constraints become rigid as temperature is lowered

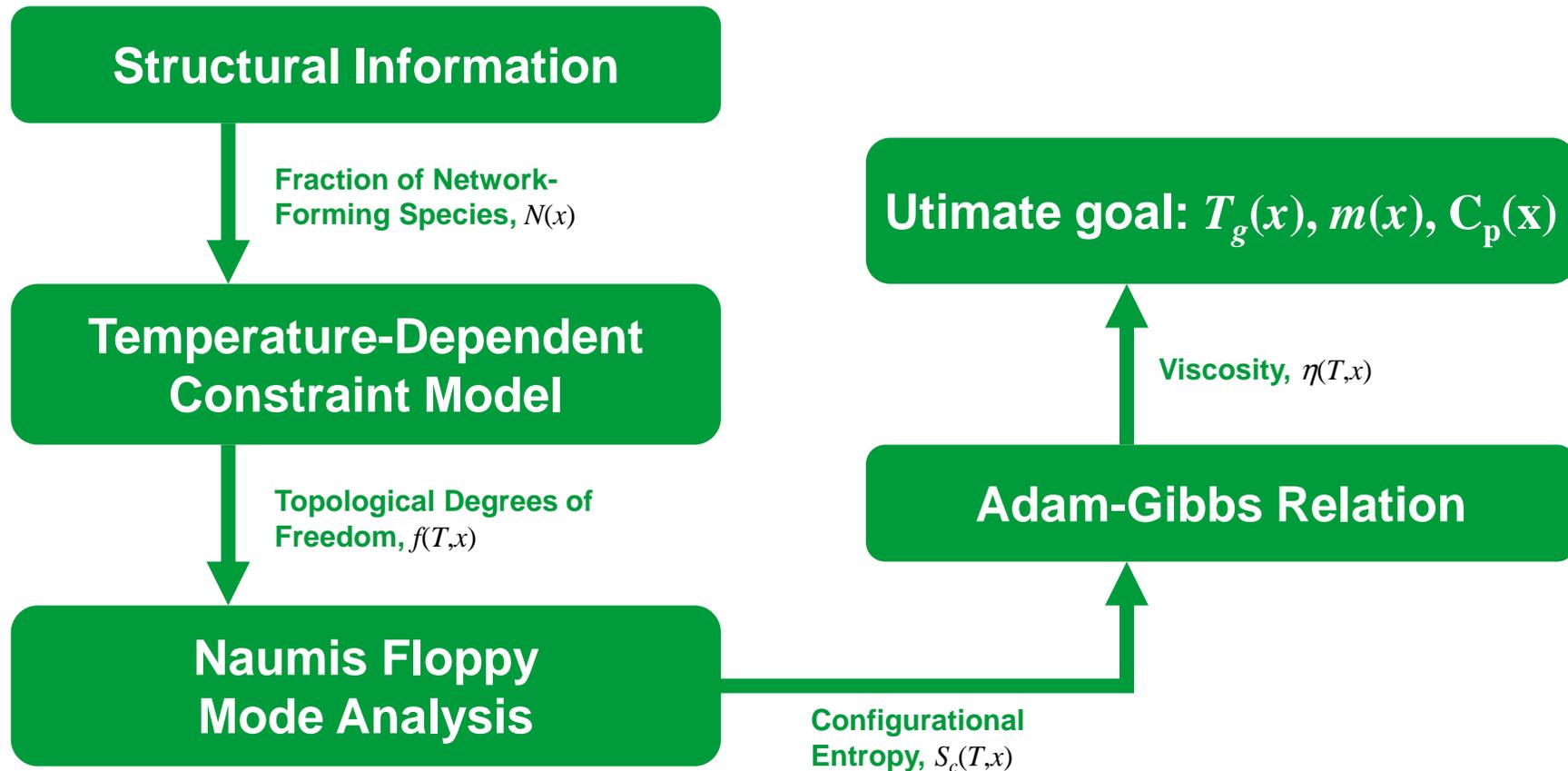
– Onset temperatures: $T_\gamma < T_\beta < T_\mu < T_\alpha$



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

C) Temperature dependent constraints

Step 4: Calculating properties...the roadmap



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

C) 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, we obtain:

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

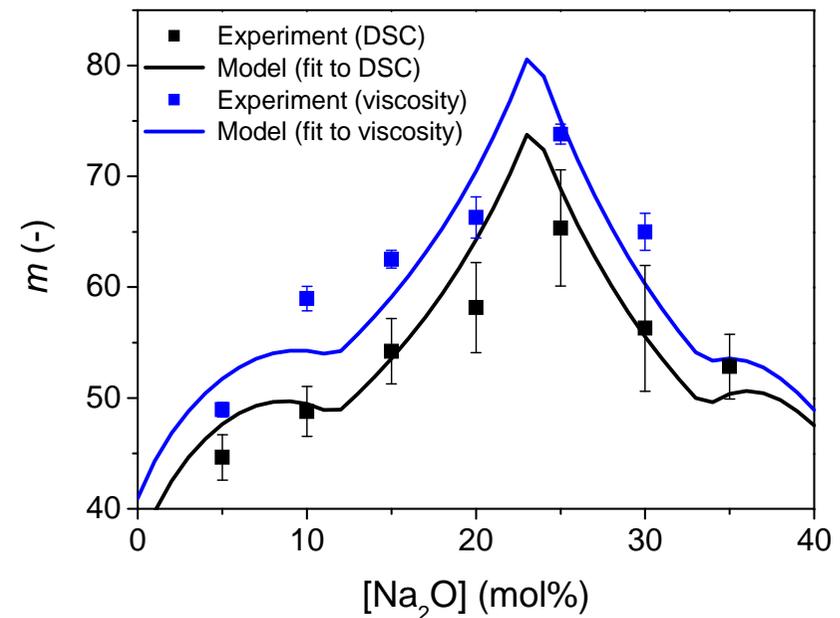
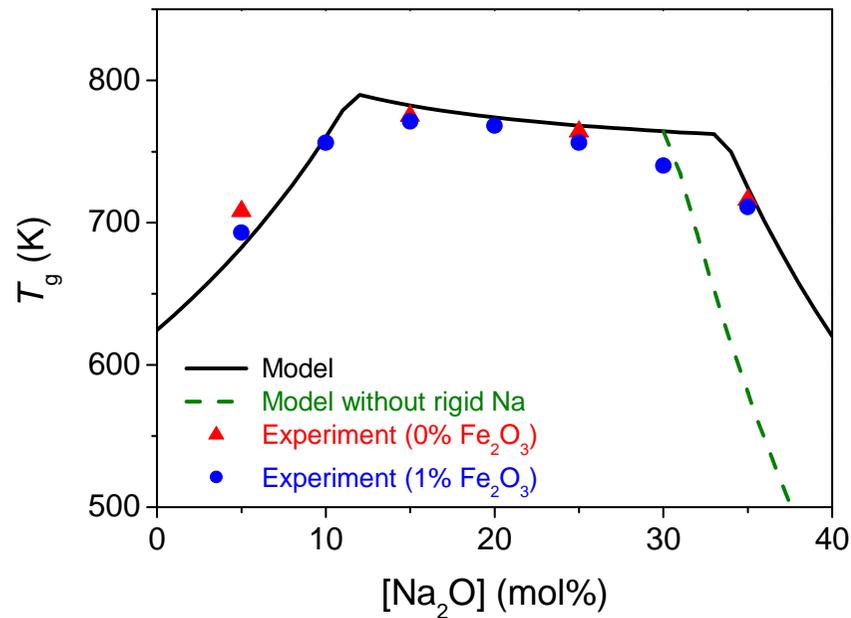
F. Application to sodium borates

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

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

C) Temperature dependent constraints

Results: Fragility and T_g variation of calcium borate glasses

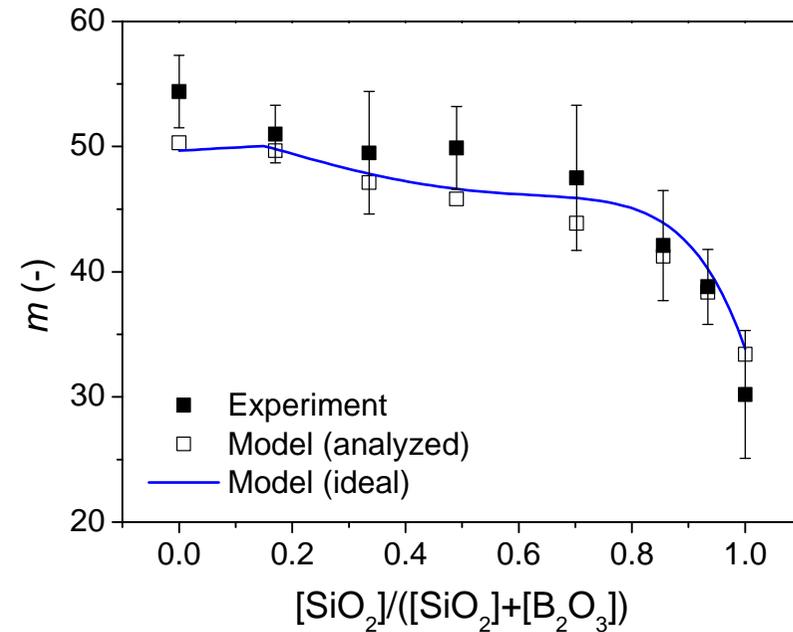
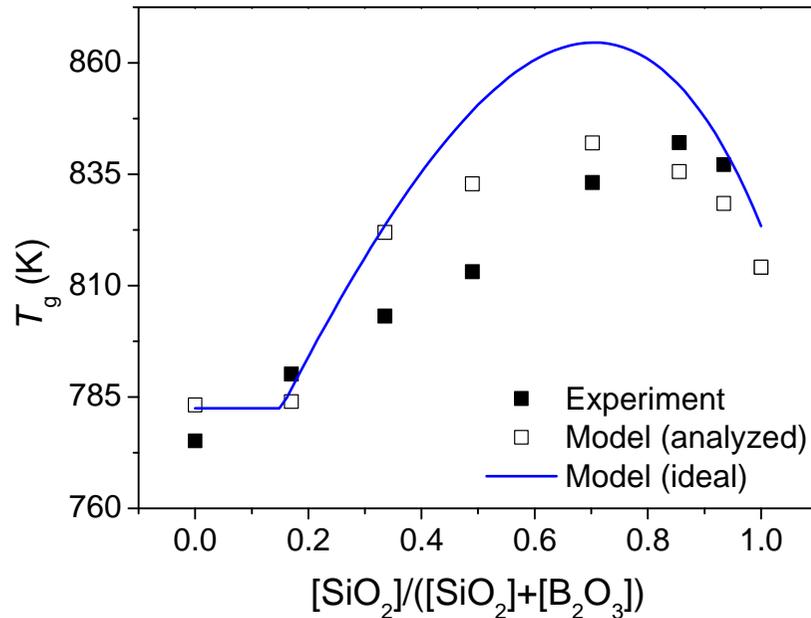


- Na sets up a locally rigid environment, whereas Ca does not
- Prediction of fragility with only one fitting parameter (νt_{obs})

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

C) Temperature dependent constraints

Results: Fragility and T_g 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)

C) 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) $\rightarrow n_{\text{crit}}$

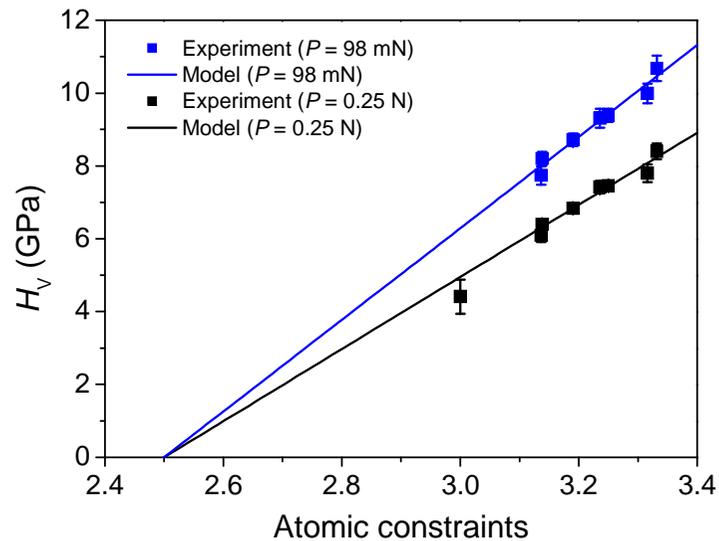
- ❑ Proposal: hardness is proportional to the number of 3D network constraints at room temperature

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

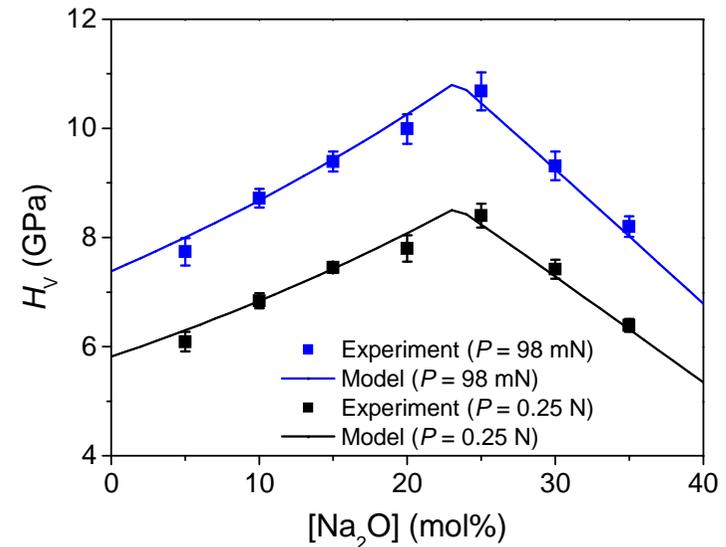
?

C) Temperature dependent constraints

Results: Hardness H_V in borates



dH_V/dn



- 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, *Phys. Rev. Lett.* 105, 115503 (2010)

C) Temperature dependent constraints

Results: Calculating the specific heat from constraints

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

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

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

– Adam-Gibbs model

$$\eta = \eta_\infty \exp\left(\frac{B}{TS_{conf}}\right) \longrightarrow m = m_0 \left(1 + \left. \frac{\partial \ln S_{conf}(T)}{\partial \ln T} \right|_{T=T_g} \right)$$

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

C) Temperature dependent constraints

Results: Calculating the specific heat from constraints

$$\Delta C_p[x, y, z, T_g(x, y, z)] = \frac{1}{T_g(x, y, z)} \left(\frac{\partial H_{\text{conf}}}{\partial \ln S_{\text{conf}}} \right)_{P, T=T_g(x, y, z)} \left(\frac{m(x, y, z)}{m_0} - 1 \right)$$

$$\Delta C_p[x, y, z, T_g(x, y, z)] = \frac{S_{\text{conf}}[x, y, z, T_g(x, y, z)]}{T_g(x, y, z)} \left(\frac{\partial H_{\text{conf}}}{\partial S_{\text{conf}}} \right)_{P, T=T_g(x, y, z)} \left(\frac{m(x, y, z)}{m_0} - 1 \right)$$

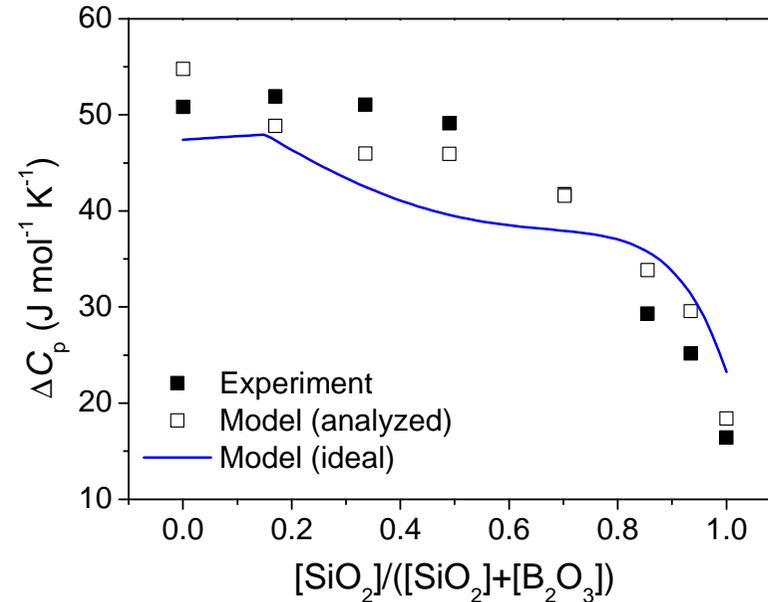
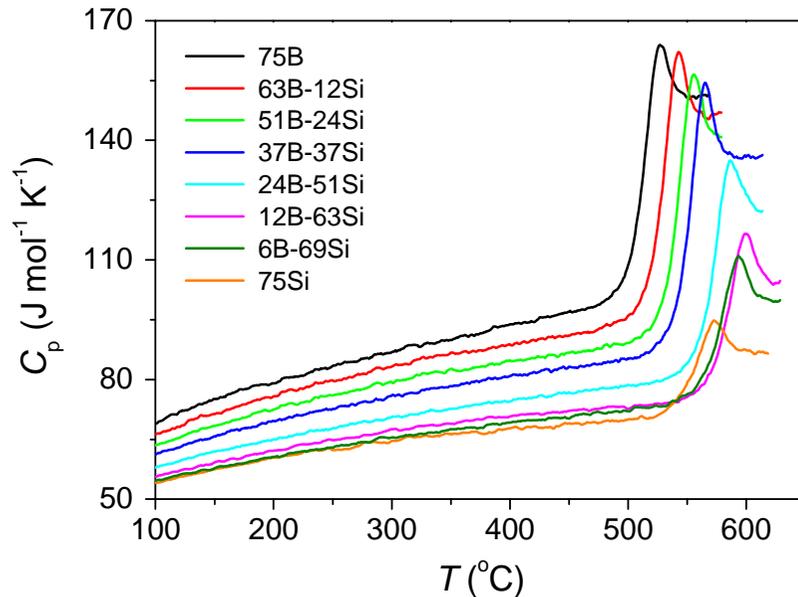
According to temperature-dependent constraint theory, configurational entropy at T_g is inversely proportional to T_g .

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

$$\Delta C_p[x, y, z, T_g(x, y, z)] = \frac{A((x, y, z)_R)}{[T_g(x, y, z)]^2} T_{\text{conf}}(x, y, z) \left(\frac{m(x, y, z)}{m_0} - 1 \right) = \frac{A((x, y, z)_R)}{T_g(x, y, z)} \left(\frac{m(x, y, z)}{m_0} - 1 \right)$$

C) Temperature dependent constraints

Results: Results for the specific heat (borosilicates)

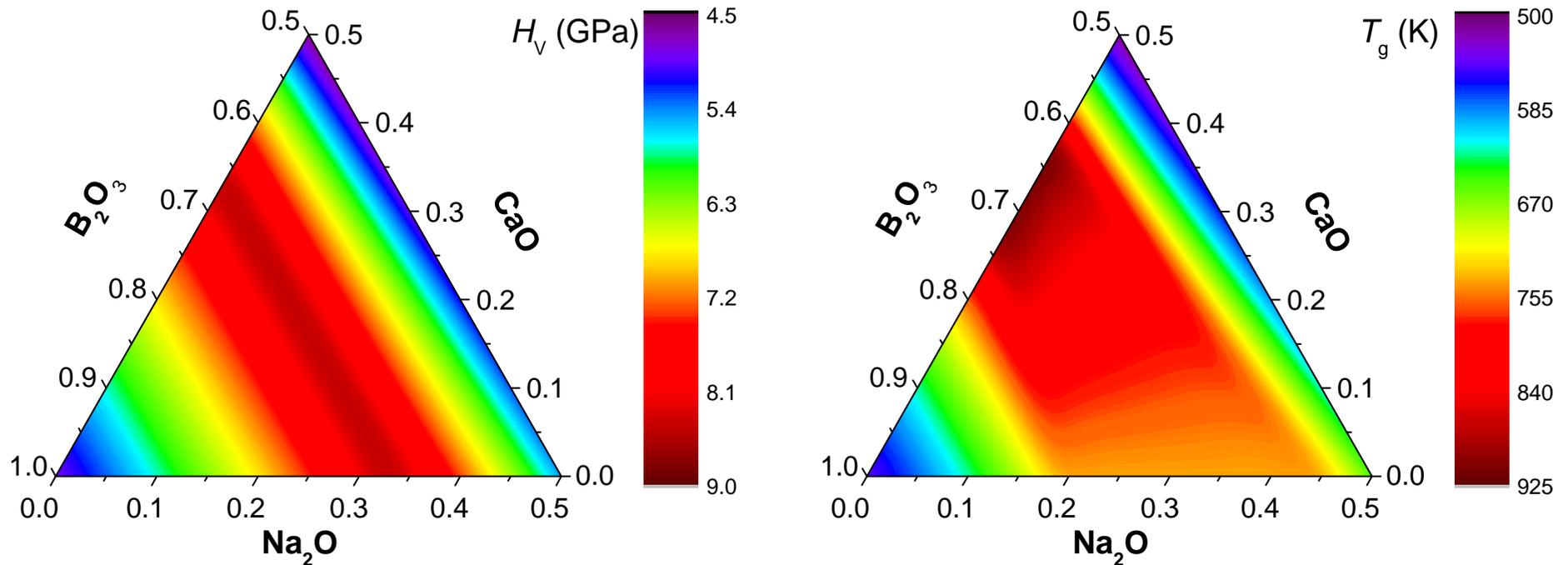


- ❑ $\Delta C_p(x,y,z)$ can be predicted with A is the sole fitting parameter (19 kJ/mol)
- ❑ Thermodynamic property changes during the glass transition are connected to the kinetic fragility index

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

C) Temperature dependent constraints

Results: Quantitative design 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

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

Next lecture: Rigidity transitions and intermediate phases

Home reading: Topological constraint theory of glass, J.C. Mauro, 2012