LECTURE 3 : SIMPLE BOND MODELS

- Bond models and chemical order
  - chalcogenides network glasses
- Bond models constrained by composition
  - Silicates, Borates
- Agglomeration models

A) BOND MODELS AND CHEMICAL ORDER for 2-3 networks

Bond statistics

Probing what controls chemical order, i.e. an atom of a given type may or may not tend to connect to another atom of same type.

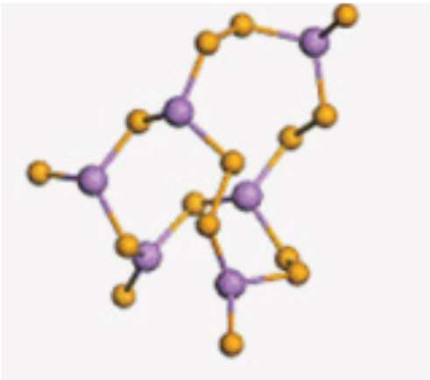
We consider a network of 2 and 3-fold coordinated atoms $\mathbf{3}_x\mathbf{2}_{1-x}$ (As-Se, As-S,…).
The probability of sites is $N_2=(1-x)N$ and $N_3=xN$
There are 3 types of number of bonds N_{ij} connecting atoms of type i and type j

N_{22} N_{23} N_{33}

We can write :

$$2N_{22} + N_{23} = 2N_2,$$

$$2N_{33} + N_{23} = 3N_3.$$



Twice the number of 2-2 bonds plus the number of 2-3 bonds gives the number of bonds stemming from 2 sites (which is twice the number of 2 sites N_2.

A) BOND MODELS AND CHEMICAL ORDER for 2-3 networks

The total number of bonds is $N_B=N_{22}+N_{23}+N_{33}$ so that one can write the bond probabilities y_{ij} as:

$$y_{ij} = \frac{N_{ij}}{N_B}$$

Dividing the sum of the previous equations

$$2N_{22} + N_{23} = 2N_2,$$

$$2N_{33} + N_{23} = 3N_3.$$

by N_B leads to : $N_B = \frac{\langle r \rangle N}{2} = \frac{2+x}{2} N,$

and to:

$$2y_{22} + y_{23} = \frac{4(1-x)}{2+x},$$

$$2y_{33} + y_{23} = \frac{6x}{2+x},$$

i.e. 2 equations and 3 unknowns. We define a chemical bonding parameter $2\theta=y_{23}$.

Then :

$$y_{22} = \frac{2(1-x)}{2+x} - \theta,$$
$$y_{33} = \frac{3x}{2+x} - \theta.$$

where the obvious sum rule : $y_{22} + y_{23} + y_{33} = 1$
is satisfied.
θ characterizes chemical bonding propertiers of the network, i.e. correlations between types of first-neighbor sites.
All the network can be characterized by two parameters (x,θ).

Let us now define $n_j^{(i)}$ as the probability for a bond known to start at a site of coordination i to end at a site of coordination j. Obviously, one has:

$$\sum_j n_j^{(i)} = 1 \quad \text{for all } i.$$

The total number of bonds stemming out of i-sites is : $(2y_{ii} + \sum_{j \neq i} y_{ij}) N_B$

so that we can write:

$$n_i^{(i)} = \frac{2y_{ii}}{2y_{ii} + \sum_{k\neq i} y_{ik}},$$
$$n_j^{(i)} = \frac{y_{ij}}{2y_{ii} + \sum_{k\neq i} y_{ik}}, \; j \neq i.$$

and applied to the 2-3 network, one has :

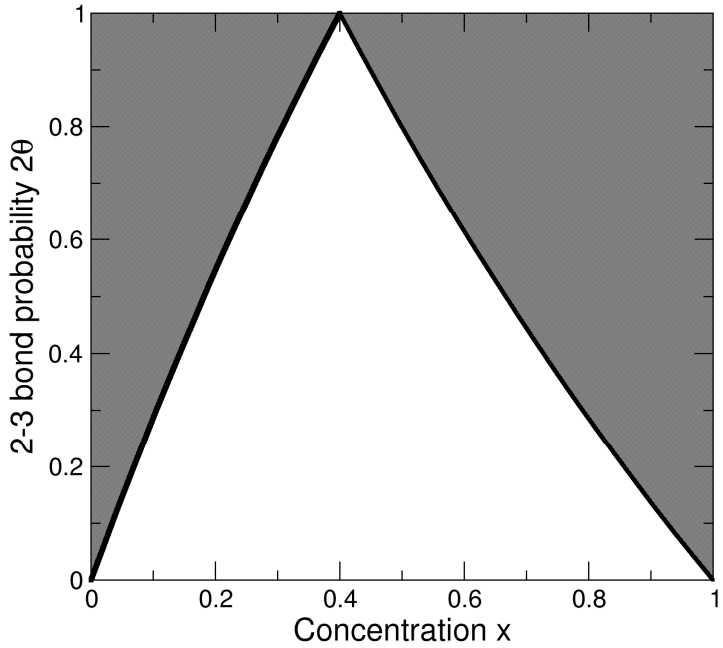
$$n_3^{(2)} = \frac{y_{23}}{2y_{22} + y_{23}} = \frac{\theta(2+x)}{2(1-x)},$$
$$n_2^{(2)} = 1 - n_3^{(2)},$$
$$n_2^{(3)} = \frac{y_{23}}{2y_{33} + y_{23}} = \frac{\theta(2+x)}{3x},$$
$$n_3^{(3)} = 1 - n_2^{(3)}.$$

Obviously, one has for all i and j: $0 \leq n_j^{(i)} \leq 1$
And this leads to the condition for the parameters *x* and θ :

From $n_3^{(3)} \geq 0,$ one has : $\theta \leq \frac{3x}{2+x};$

and from : $n_2^{(2)} \geq 0,$ $\theta \leq \frac{2(1-x)}{2+x}.$

These 2 inequations (plus the θ=0 line) define the allowed space of the x-θ plane:



$$\theta \leq \frac{3x}{2+x};$$ left (low x) boundary

$$\theta \leq \frac{2(1-x)}{2+x}.$$ right (high x) boundary

- Limiting cases:

  θ=0 ($y_{23}=0$) no 2-3 bonds,
  phase separation: two separate networks (2- and 3-coord)

  max value for θ=0.5 ($y_{23}=1$) only possible at x=0.4 (e.g. As_2Se_3)
  perfect chemical order

Between these two extremes (θ=0, y_{23}=1), many situations can be encountered

A) Random bonding: sites are linked up in a random fashion.

Probabilities for a bond to go to a site of a certain type do not depend on the type of the site where the bond started, i.e. $n_j^{(i)}$ does not depend on i.

Thus:

$$n_2^{(2)} = n_2^{(3)},\ n_3^{(2)} = n_3^{(3)}$$

Recalling:

$$\begin{aligned} n_3^{(2)} &= \frac{y_{23}}{2y_{22}+y_{23}} = \frac{\theta(2+x)}{2(1-x)}, \\ n_2^{(2)} &= 1 - n_3^{(2)}, \\ n_2^{(3)} &= \frac{y_{23}}{2y_{33}+y_{23}} = \frac{\theta(2+x)}{3x}, \\ n_3^{(3)} &= 1 - n_2^{(3)}. \end{aligned}$$

One finally has:

$$\theta = \frac{6x(1-x)}{(2+x)^2}.$$

Rq: This is what one would expect, i.e.

y_{23} # 2.2.3.N_2 N_3 # 6x(1-x)

B) Random dilution : Start from a fully 3-coordinated network (x=1)
Remove 3-3 bonds one by one

- Suppose we remove ΔN_B 3-3 bonds.
- We obtain from $N_B = \frac{\langle r \rangle N}{2} = \frac{2+x}{2} N,$ now $\Delta N_B = \frac{N}{2} \Delta x$

When we remove a 3-3 bond, we convert a 3-3 bond into a 3-2 bond (y_{23} increases)

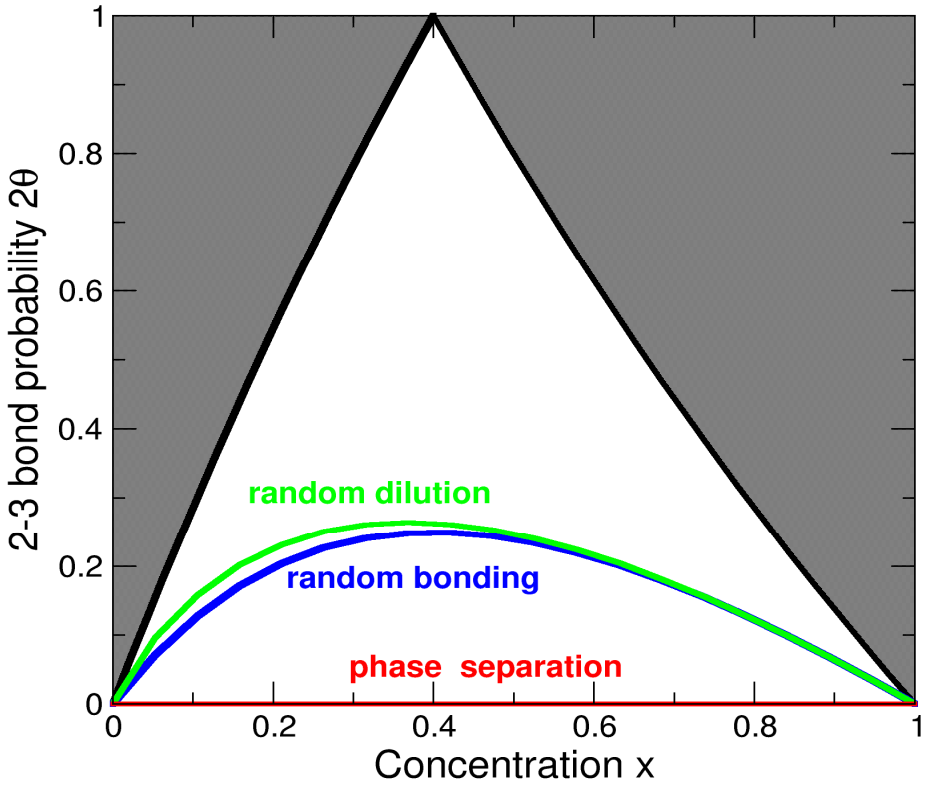
But if the 3-site is also connected to 2-site, we convert into 2-2 from 2-3 (y_{23} decreases).

The change in the number of 2-3 bonds is given by :

$$\Delta N_{23} = 4(n_3^{(3)} - n_2^{(3)}) \Delta N_B = 4 \left(1 - \frac{2\theta(2+x)}{3x} \right) \Delta N_B,$$

Using $N_{23} = 2\theta N_B = \theta(2+x)N$ we finally obtain :

$$(2+x)\frac{d\theta}{dx} = -2 + \frac{8+x}{3x}\theta. \qquad \text{and} \qquad \boxed{\theta = \frac{6x(1-x^{1/3})}{2+x}.}$$



Random dilution result is different from random bonding
(randomly diluted networks are not perfectly randomly bonded)

Restriction: Dilution is not truly random. Otherwise, 1-coordinated sites would appear.

Energy considerations :

We can setup an associated thermodynamic framework.

Bragg-Williams approach separating the free energy F=E-TS into two parts that can establishes separately.

If the energy associated with 3 kinds of bonds, E_{22}, E_{23}, and E_{33}, then we may write:

$$E = N_{22}E_{22} + N_{23}E_{23} + N_{33}E_{33}$$

and the statistical entropy is given by :

$$S = k_B ln \frac{N_B!}{N_{AA}!\,\frac{1}{2}N_{AB}!\frac{1}{2}N_{AB}!\,N_{BB}!}$$

Using Stirling approximation (*ln N! ~N ln N – N*), we obtain:

$$S = k_B N_B \left[\frac{N_{AA}}{N_B} ln \frac{N_{AA}}{N_B} + \frac{N_{AB}}{N_B} ln \frac{N_{AB}}{2N_B} + \frac{N_{BB}}{N_B} ln \frac{N_{BB}}{N_B}\right]$$

or :

$$S = k_B N_B \left[y_{AA} \ln y_{AA} + y_{AB} \ln \frac{y_{AB}}{2} + y_{BB} \ln y_{BB}\right]$$

Using the expressions from above :

$$y_{22} = \frac{2(1-x)}{2+x} - \theta,$$
$$y_{33} = \frac{3x}{2+x} - \theta.$$

one obtains the free energy F/N_B per bond number:

$$\frac{F}{N_B} = \left(\frac{2(1-x)}{2+x} - \theta\right) E_{22} + 2\theta E_{23} + \left(\frac{3x}{2+x} - \theta\right) E_{33}$$
$$-k_B T \left[\left(\frac{2(1-x)}{2+x} - \theta\right) \ln\left(\frac{2(1-x)}{2+x} - \theta\right) + 2\theta ln\theta + \left(\frac{3x}{2+x} - \theta\right) ln\left(\frac{3x}{2+x} - \theta\right)\right]$$

as F is only a function of the single parameter θ, we can minimize the free energy with respect to θ, by setting dF/dθ=0 , to give:

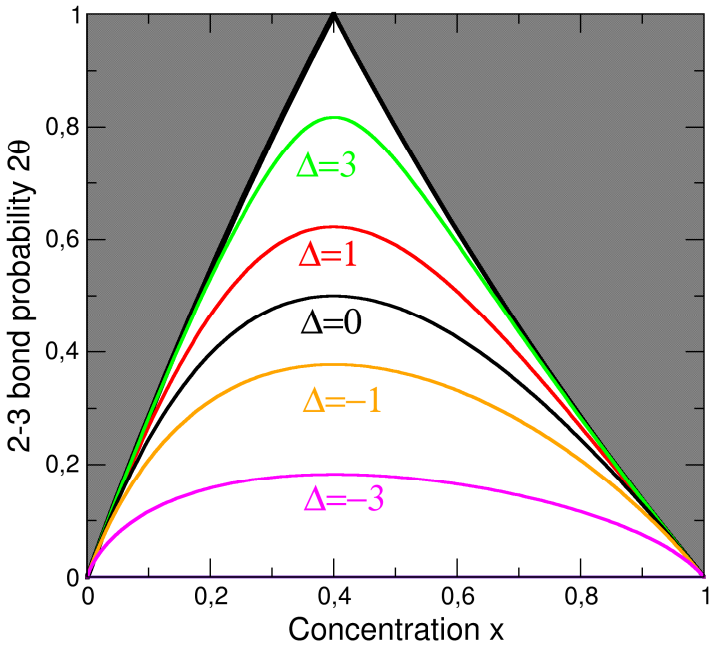
$$E_{22} - 2E_{23} + E_{33} = k_B T - k_B T \left[\ln\left(\frac{2(1-x)}{2+x} - \theta\right) + 2ln\theta + ln\left(\frac{3x}{2+x} - \theta\right)\right]$$

which gives the relationship between θ, x and T for a given system (here the 3-2)

which is equal to :

$$\theta = \frac{1 - \sqrt{1 - \frac{24x(1-x)(1-e^{-\frac{\Delta}{k_B T}})}{(2+x)^2}}}{2(1-e^{-\frac{\Delta}{k_B T}})} \qquad (1)$$

with : $\Delta = E_{22} - 2E_{23} + E_{33}$



Various limits are interesting:

- **Random bonding**: which means that one sets Δ=0, and from equ. (1), one recovers the random bond distribution:

$$\theta = \frac{6x(1-x)}{(2+x)^2}.$$

Phase separation : $E_{23} >> E_{22}+E_{33}$ or $\Delta << 0$ then θ goes to 0

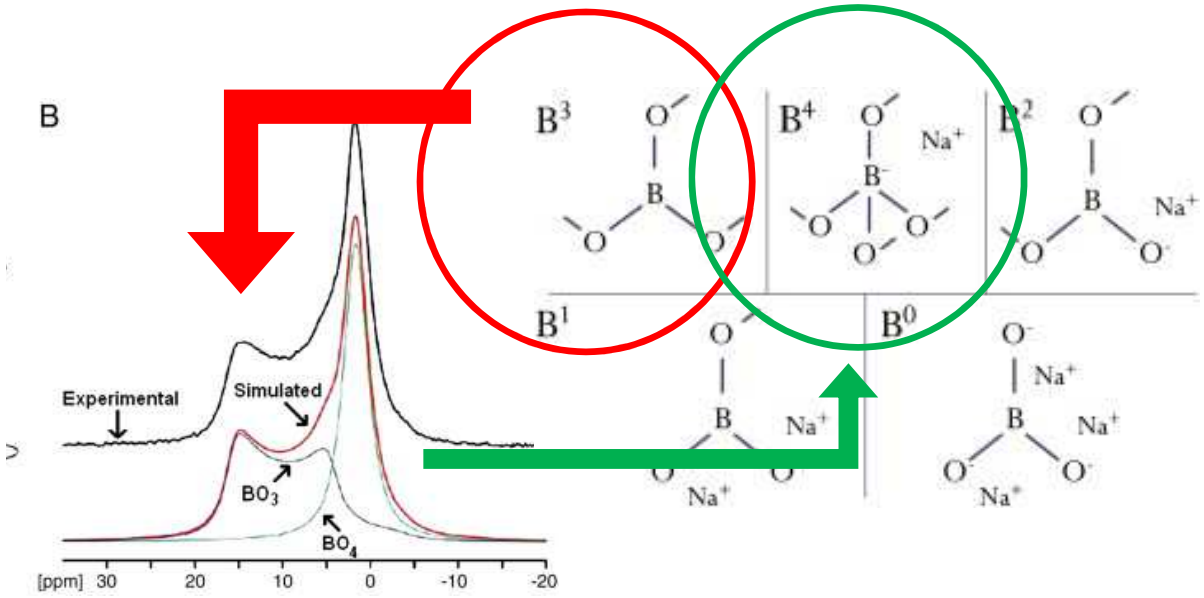
Other limit : $\Delta >> 1$
we have from (1) : θ=1/2 at x=0.4
Full heterpolar bond network at the stoichiometric composition.

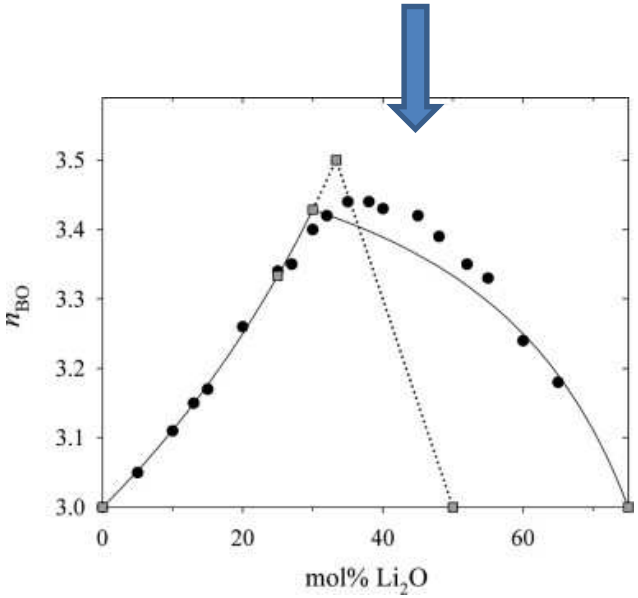
B) BOND MODELS AND CONSTRAINTS FROM COMPOSITION

We have seen that in most glass-formers, the local or intermediate range order is controlled by the composition.

❑ Alkali borates (1-x) B_2O_3 – xNa_2O

Addition of soda creates different local species in alkali borates , and their probability of occurrence depends on the composition.
Can be directly compared to experiments (NMR, Raman,…) . Statistics of 4-fold boron





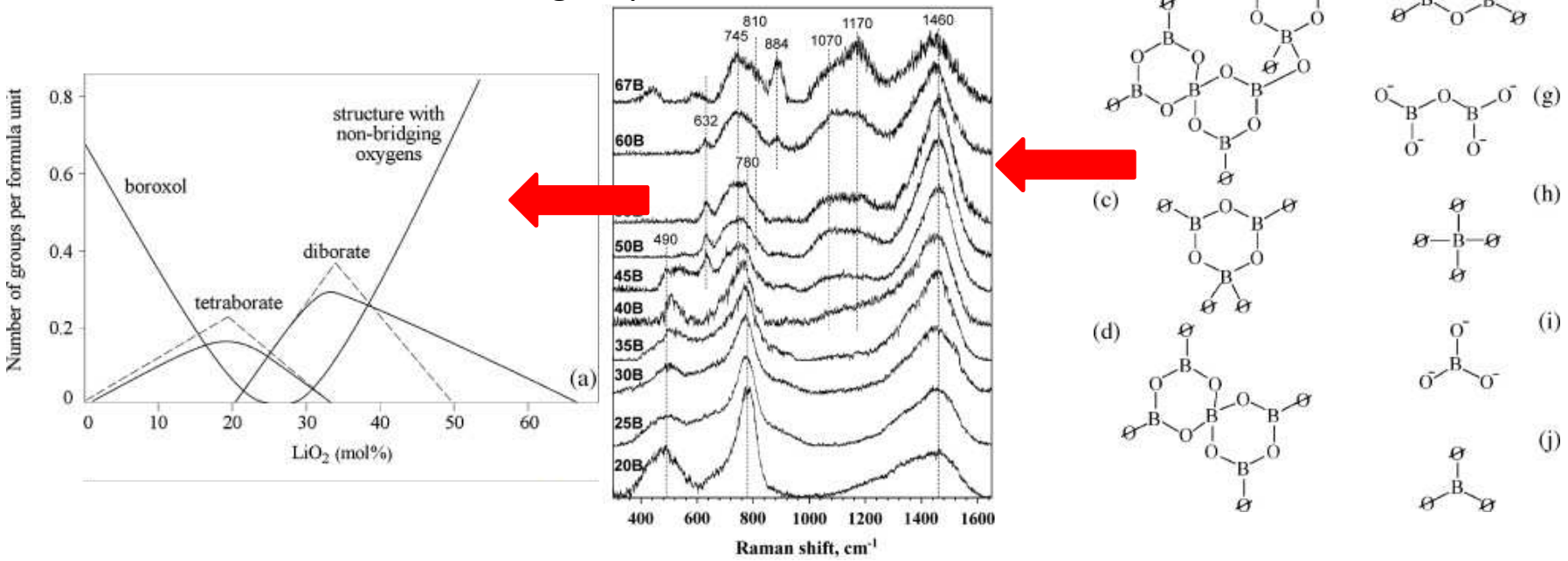
A. Hannon et al. JNCS 353, 1688 (2007).

A) BOND MODELS AND CHEMICAL ORDER for 2-3 networks

Signatures of intermediate range order in **(1-x) B_2O_3 – xNa_2O**

Boroxol rings in pure B_2O_3. Addition of soda leads to the occurrence of new super structural units

Again, can be directly compared to experiments (Raman,…). Statistics of of such structural groups.



Osipov et al., JPCS, 74, 971 (2013)

❑ Alkali (thio)silicates

(1-x) SiO_2- x Na_2O, (1-x) SiS_2- x K_2S, (1-x-y) Al_2O_3-x SiO_2-y CaO, GeO_2-Li_2O

The local structure of silicate glasses can be characterized by Q^n speciation (NMR, Raman)

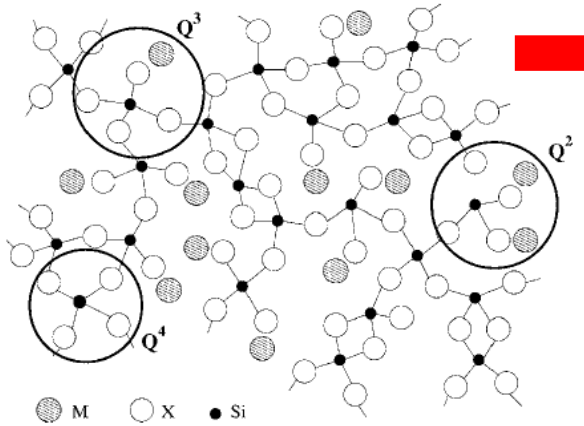
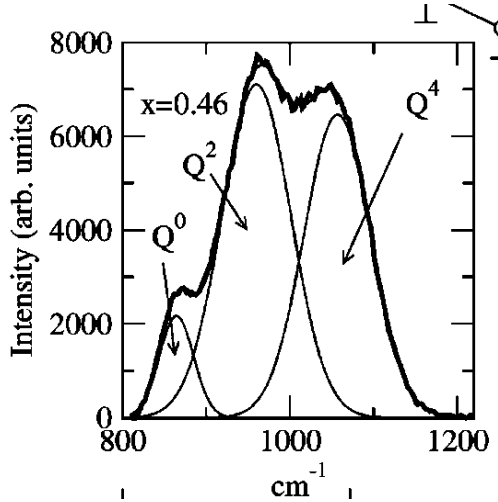
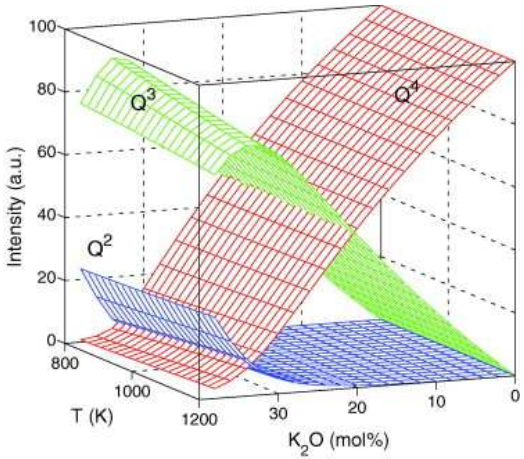


FIG. 1. Example of a network of $(1-x)SiX_2-xM_2X$ with three kinds of species (Q^2, Q^3, and Q^4, defined in the marked circles).



M. Malki et al., EPL 64, 661 (2003)

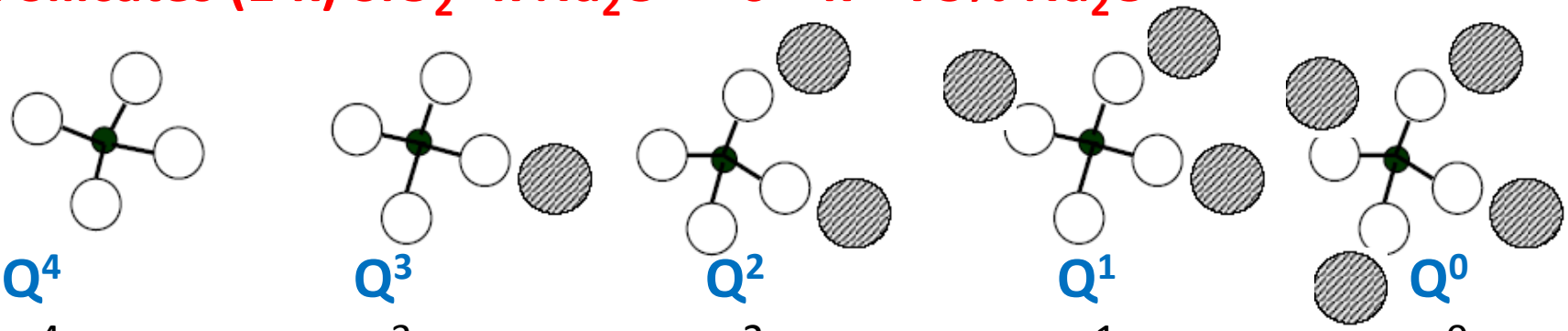


Experimentally, the Q^n statistics can be followed with composition, temperature, pressure

W.J. Malfait et al., JNCS 353, 4029 (2007).

B) BOND MODELS AND CONSTRAINTS FROM COMPOSITION

1. Silicates (1-x) SiO_2 - x Na_2O $0 < x < 75\%$ Na_2O



Q^4
r=4
$N_4(x)$

Q^3
r=3
$N_3(x)$

Q^2
r=2
$N_2(x)$

Q^1
r=1
$N_1(x)$

Q^0
r=0
$N_0(x)$

We can write

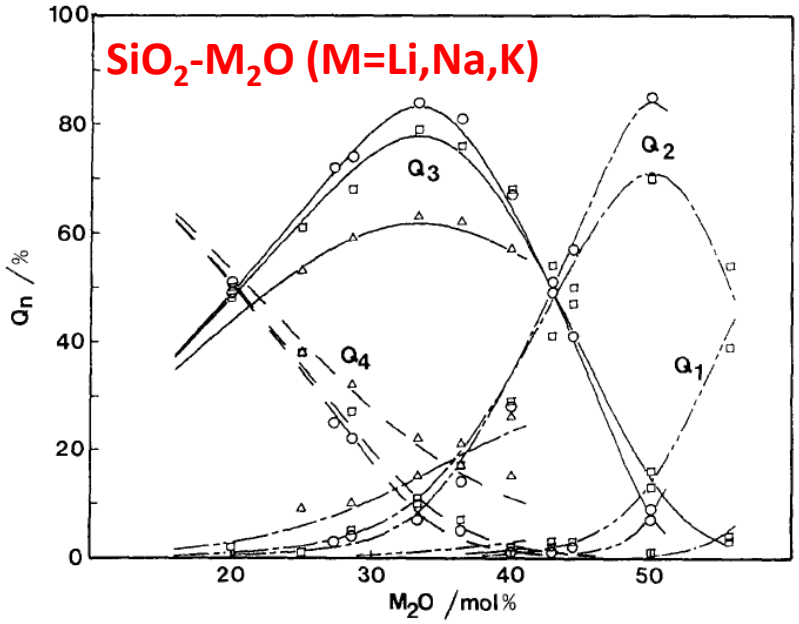
- Normalization condition : $\sum_i N_i(x) = 1$

- Charge conservation law : $(1-x)\sum_i (4-i)N_i(x) = 2x$

Describing the whole compositional space : **2 equations, 5 unknowns**

The same problem holds for most of the glass systems where several local species can be found

Reducing the unknowns …



H. Maekawa et al. JNCS 127, 53 (1991)

1) A certain number of species (here Q^n) are zero over wide compositonal zones.

Set the probability $N_i(x)=0$
E.g. $N_1(x)=0$ for $x<0.40$

Reduces the number of unknowns.
Split the compositional domain into parts

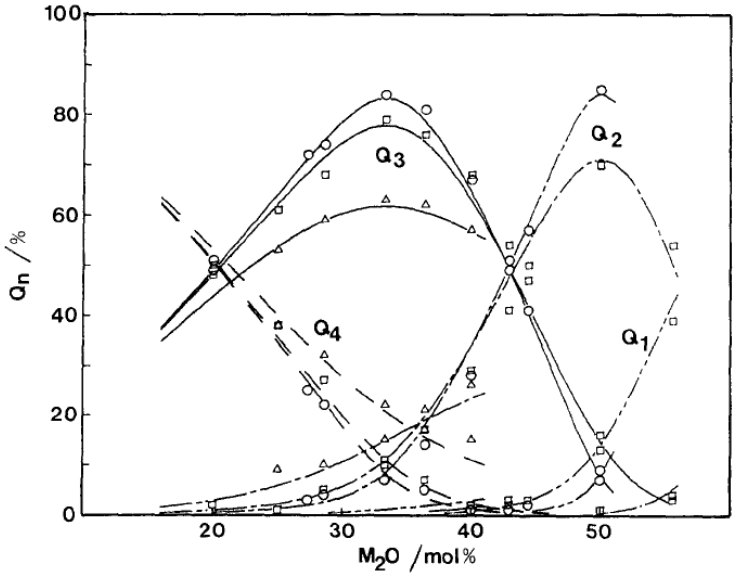
2) Some species go to zero at some concentration

- e.g. $N_3(x)=0$ at $x=0.50$ for Na and K silicates
- i.e. $N_3(x) = A(1-2x)$ for $x<0.50$, zero otherwise
- Defines **piecewise functions** for the species probabilities

3) Disproportionation reaction or other clever constraints $2Q^3 \rightleftharpoons Q^4 + Q^2$ $K_e = \frac{p_4^{(1)} p_2^{(1)}}{p_3^{(1)} p_3^{(1)}}$

permits to increase the number of equations for a given set of unknowns

1) Application : Constraints from composition



H. Maekawa et al. JNCS 127, 53 (1991)

There are compositional regions where some $N_i(x)=0$
Splitting the compositional regions:

a) assume only Q^4 and Q^3 (x low)

$$N_4(x) + N_3(x) = 1$$

$$N_4(x) = \frac{1-3x}{1-x}$$

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

b) Assume that $N_3(x)=0$ at x=60%, i.e. $N_3(x)=A(3-5x)$ and $N_4(x)=A(1-2x)$
One then also has :

$$N_4(x) + N_3(x) + N_2(x) = 1$$

$$N_3(x) + 2N_2(x) = \frac{2x}{1-x}$$

3 unknowns, 2 equations (1 redundant), 2 constraint
And initial conditions : $N_3(0) = N_2(0) = 0$

We obtain from $$N_3(x) + 2N_2(x) = \frac{2x}{1-x}$$

The population of Q^2 given by: $$N_2(x) = \frac{x}{1-x} - \frac{1}{2}A(3-5x)$$

And the normalization condition $N_4(x) + N_3(x) + N_2(x) = 1$ allows obtaining A:

$$A = -\frac{2(2x-1)}{(1-x)(5-9x)}$$

So that we have the solution:

$$N_4(x) = \begin{cases} \frac{1-3x}{1-x} & 0 \le x \le x_0 \\ \frac{2(1-2x)^2}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

$$N_3(x) = \begin{cases} \frac{2x}{1-x} & 0 \le x \le x_0 \\ \frac{2(1-2x)(3-5x)}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

$$N_2(x) = \begin{cases} 0 & 0 \le x \le x_0 \\ \frac{-19x^2+16x-3}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

$$x_0 = \frac{8-\sqrt{7}}{19}$$

❑ Why is it piecewise ?

$$x_0 = \frac{8-\sqrt{7}}{19}$$

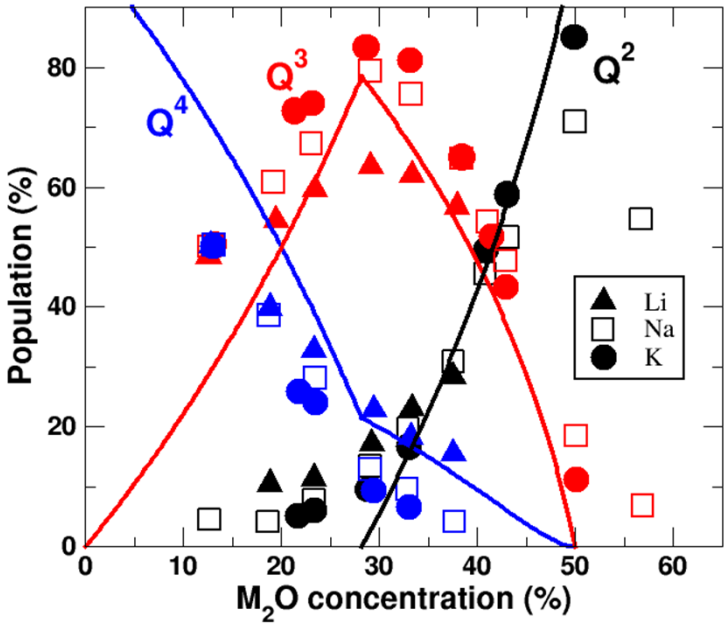
$$N_4(x) = \begin{cases} \frac{1-3x}{1-x} & 0 \le x \le x_0 \\ \frac{2(1-2x)^2}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

$$N_3(x) = \begin{cases} \frac{2x}{1-x} & 0 \le x \le x_0 \\ \frac{2(1-2x)(3-5x)}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

$$N_2(x) = \begin{cases} 0 & 0 \le x \le x_0 \\ \frac{-19x^2+16x-3}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

x_0 =0.282 is given by the continuity condition at low x when $N_2(x)=0$ (previous solution)

- No Cation dependence
- Incorporation of Ke ?

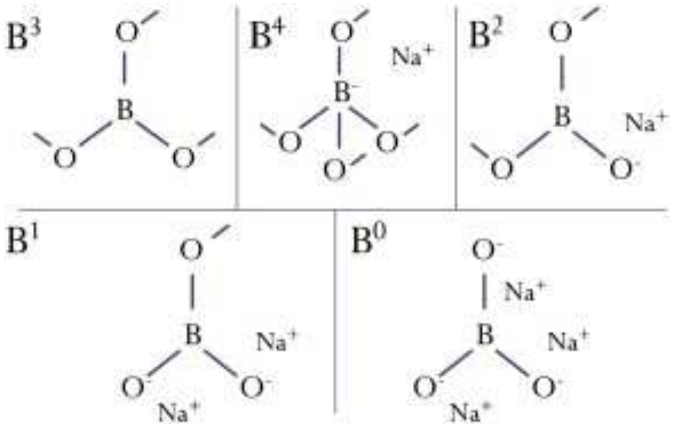


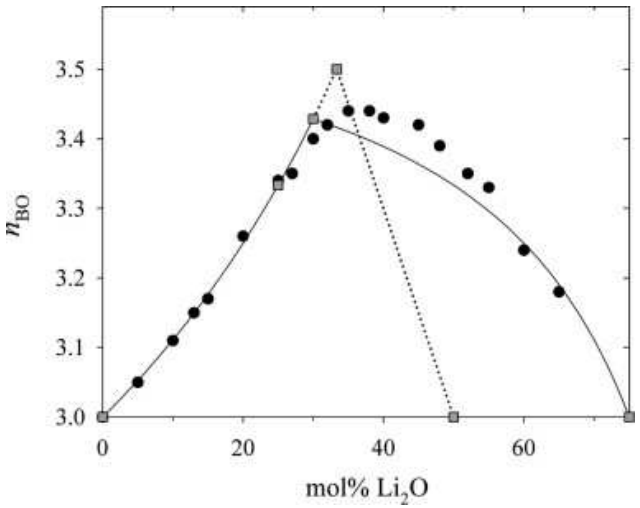
Data: Maekawa et al. 1991

B) BOND MODELS AND CONSTRAINTS FROM COMPOSITION

1. Borates $(1-x)B_2O_3 - x\ Na_2O$ $\quad 0 < x < 75\%\ Na_2O$

- Literature : Random pair model (Gupta, Wright,…)
- **Same strategy** as for the silicates, e.g. identify a composition at which one is sure that one of the species will be zero (or non-zero).
- Consider 3 building blocks:
  - **B3** (base unit of the network former B_2O_3), N_3
  - **B4** (tetrahedral boron created by charge compensation), N_4
  - **B2** (a B3 having one NBO), N_2
- Gupta (1986) assumptions:
  1. BO_4 occur in corner-sharing pairs
  2. Pairs of BO_4 cannot be bound to each other
  3. NBOs occur only in BO_3 groups and not BO_4





A. Hannon et al. JNCS 353, 1688 (2007).

- « *Pairs of BO_4 cannot be bound to each other* ». This means that an alkali-to boron ratio of less than one-half (R=x/(1-x)<1/2 or x<1/3) will lead to all alkali converting BO_3 into BO_4.

- One thus has at low composition: $N_3(x) = 1 - R = 1 - \frac{x}{1-x} = \frac{1-2x}{1-x}$

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

- At larger compositions (R>1/2), alkalis now create NBOs and one has B2 units appearing. At very large composition (pyroborate, R=3, potentially N_0=100%), one assumes that N_4=0. Thus, one has : $N_4(x) = A(3 - R)$

- With the constraint that at R=1/2, one must have :

$$N_4(x) = A(3 - R) = R$$

we obtain: A=1/5

- For R>1/2 , write charge conservation law: $N_4(x) + N_2(x) = R = \frac{x}{1-x}$

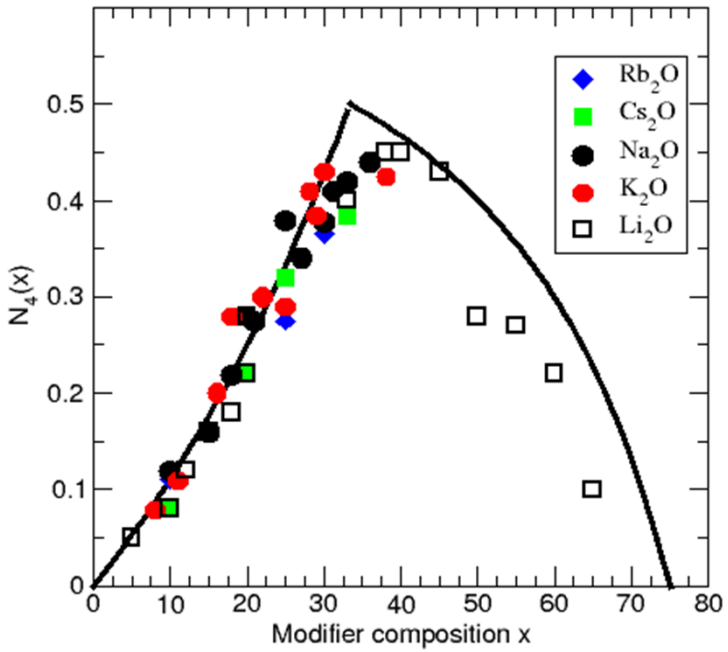
And normalization condition: $N_4(x) + N_2(x) + N_3(x) = 1$

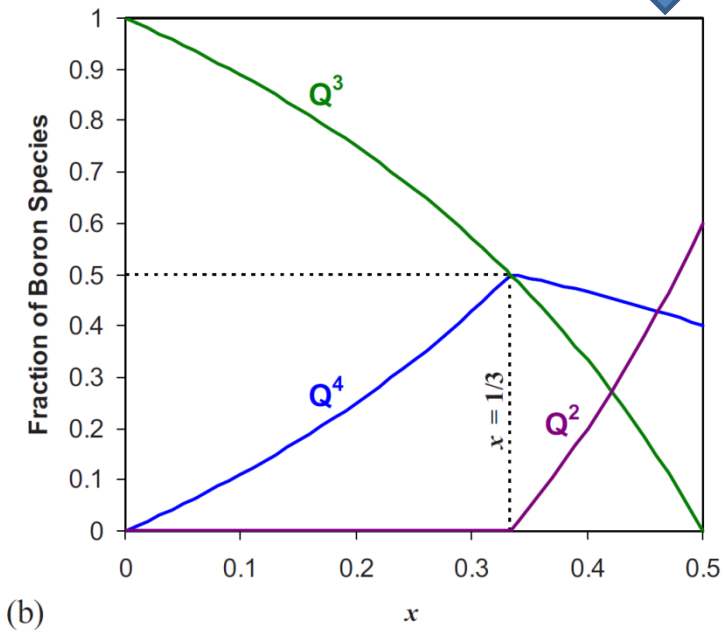
- One obtains for x>1/3:

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

- At x=1/2, all B3 have been converted to B4 and B2

- Excellent reproduction of the fraction of B4





Data: Bray and O'Keefe, PC glasses (1963)

Mauro et al. JCP 2009

C) BOND AGGLOMERATION MODELS: APPLICATION TO B_2O_3

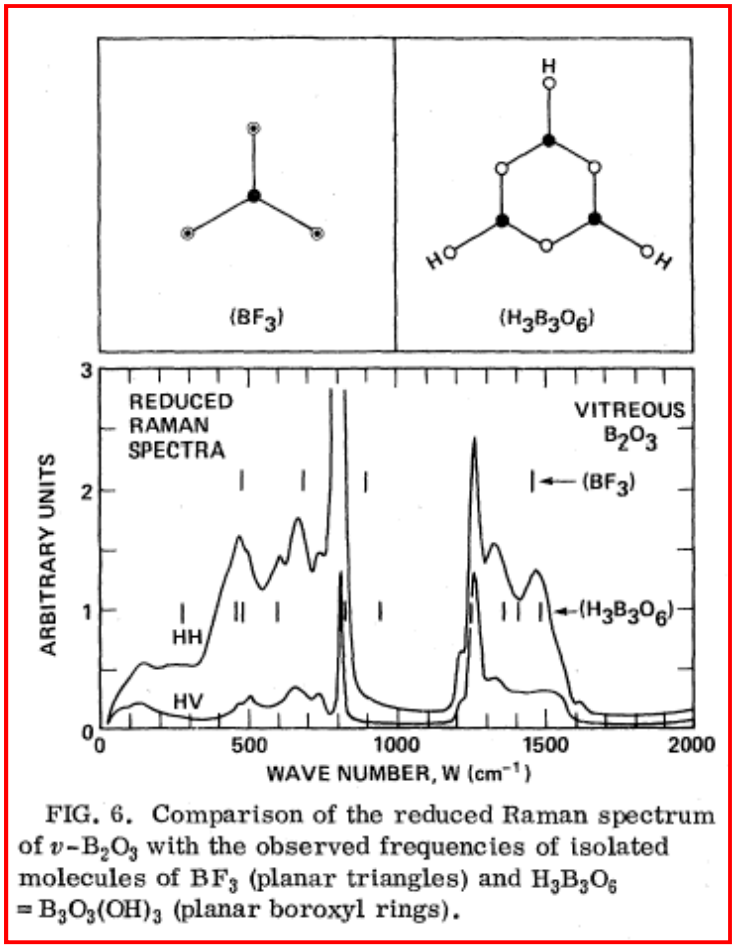
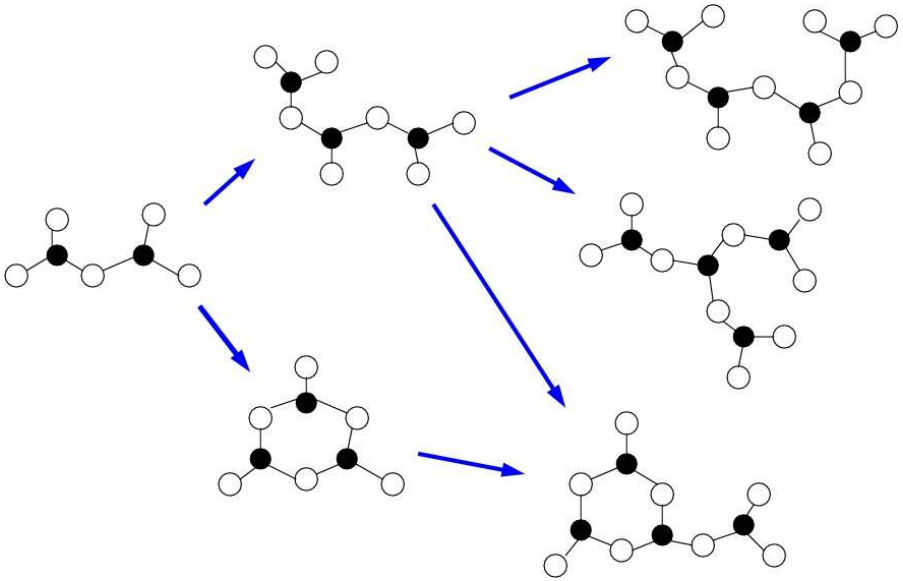


FIG. 6. Comparison of the reduced Raman spectrum of v-B_2O_3 with the observed frequencies of isolated molecules of BF_3 (planar triangles) and $H_3B_3O_6$ = $B_3O_3(OH)_3$ (planar boroxyl rings).

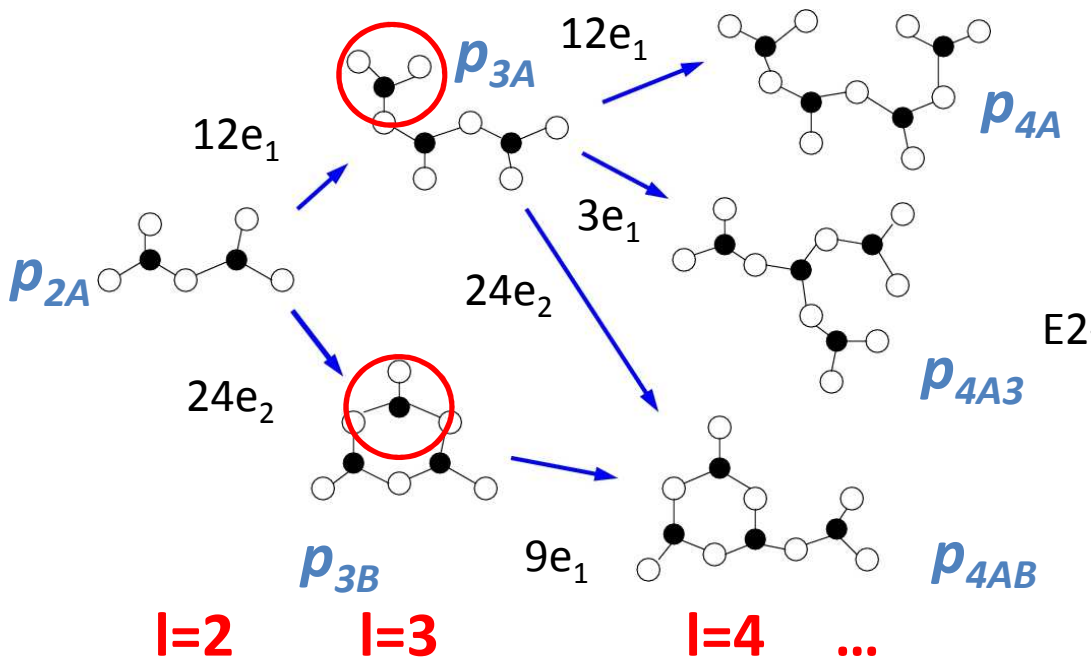
Galeener et al., 1980

General idea :

- ❑ Compute size increasing clusters from known local structures. Combinatorics
- ❑ Probabilities evaluated within Canonical Ensemble (Boltzmann factors with E_i)
- ❑ Fit parameters (E_i) by requesting particular thermal conditions.
- ❑ Fit parameters from convergence criteria



1) Establishing all the clusters (production pathways) **<u>at a given step (or size l)</u>**



e1=exp[-E1/kT]
e2=exp[-E2/kT]

E2-E1: boroxol ring energy

2) Compute cluster probability pi (Wi,Ei)

$$p_{3A} = \frac{12e_1}{12e_1 + 24e_2} p_{2A} = \frac{1}{1 + 2e_2/e_1}$$

$$p_{3B} = \frac{24e_2}{12e_1 + 24e_2} p_{2A} = \frac{2e_2/e_1}{1 + 2e_2/e_1}$$

$$p_{4AA} = \frac{12e_1}{15e_1 + 24e_2} p_{3A} = \frac{4}{5 + 8e_2/e_1} p_{3A}$$

$$p_{4A3} = \frac{3e_1}{15e_1 + 24e_2} p_{3A} = \frac{1}{5 + 8e_2/e_1} p_{3A}$$

$$p_{4AB} = \frac{24e_2}{15e_1 + 24e_2} p_{3A} + \frac{9e_1}{9e_1} p_{3B} = \frac{8e_2/e_1}{5 + 8e_2/e_1} p_{3A} + p_{3B}.$$

3) Compute $C_p(T)$ at any step l from the partition function $Z^{(l)}$ from the number of clusters $N_{(l)}$

$$Z_{(2)} \sim 12\,e^{-E_1/kT} + 24\,e^{-E_2/kT}.$$

$$Z_{(3)} \sim \prod_{\alpha=1}^{2} Q_\alpha^{(3)} = 9e_1(15e_1 + 24e_2).$$

$$Z_{(l)} \sim \left[2\pi M_{(l+1)} k_B T\right]^{3N_{(l+1)}/2} \prod_{\alpha=1}^{N_{(l)}} Q_\alpha^{(l)}$$

Table 1. The number of multiplets at each step of the agglomeration process.

Step l	Number of multiplets	Number of multiplets with: 1 boroxol	2 boroxols	3 boroxols
0	1	—	—	—
1	1	—	—	—
2	2	1	—	—
3	3	1	—	—
4	4	2	—	—
5	9	4	1	—
6	14	6	2	—
7	31	14	6	—
8	62	30	13	1
9	135	60	34	4
10	288	129	74	15

- Compute Cp from $Z^{(l)}$ via the relation

$$U_{(l)} = \frac{3}{2}k_B T + \frac{1}{N_{(l+1)}} k_B T^2 \frac{\partial}{\partial T} \sum_{\alpha=1}^{N_{(l)}} \ln\, Q_\alpha^{(l)}$$

$$C_p^{(l)} = \frac{3}{2}k_B + \frac{1}{N_{(l+1)}}\left(2k_B T \frac{\partial}{\partial T} + k_B T^2 \frac{\partial^2}{\partial T^2}\right) \sum_{\alpha=1}^{N_{(l)}} \ln\, Q_\alpha^{(l)}.$$

Heat capacity

Require $d^2C^{(l)}_p/dT^2=0$ at $T_g=(T_g)_{exp.}$ Determine parameters (E2-E1)

E.g. evaluate fraction of boroxols

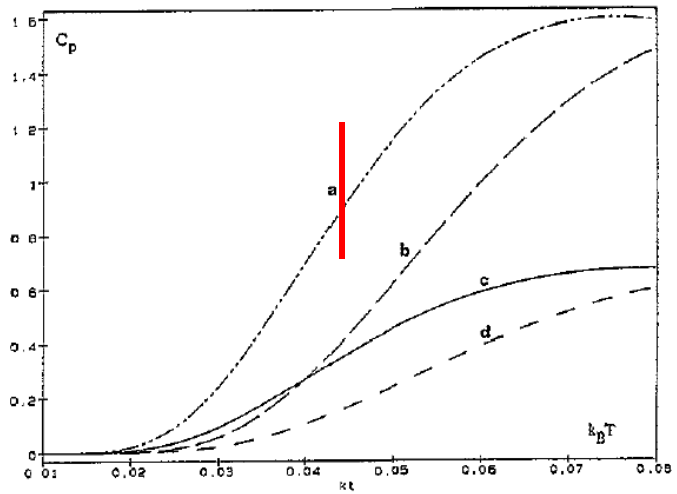
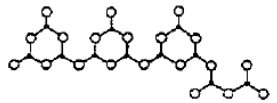
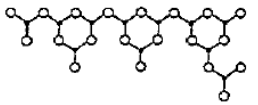
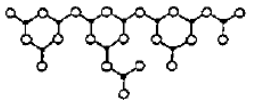
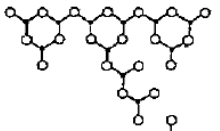
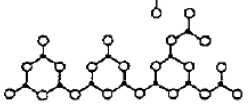
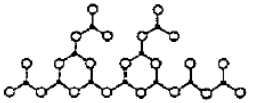
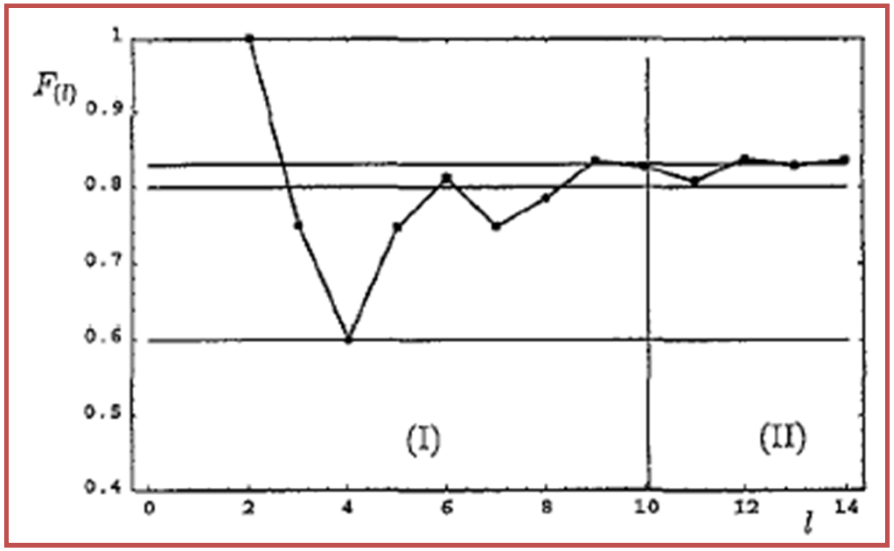


Figure 8. Normalized heat capacity curve (reduced units) for different steps of agglomeration ($l = 8$ (curves a and b) and $l = 9$ (curves c and d)) with $E_1 - E_2 = 0.20$ eV and $E_1 - E_2 = 0.26$ eV. The plot concerns only the second term of equation (11), which is the most significant.

Direct computation $l = 10$	Multiplet approximation $l = 10^*$	
0.1748	0.1740	
0.1743	0.1740	
0.3782	0.3780	
0.0859	0.0852	
0.1472	0.1472	
0.0306	0.0306	

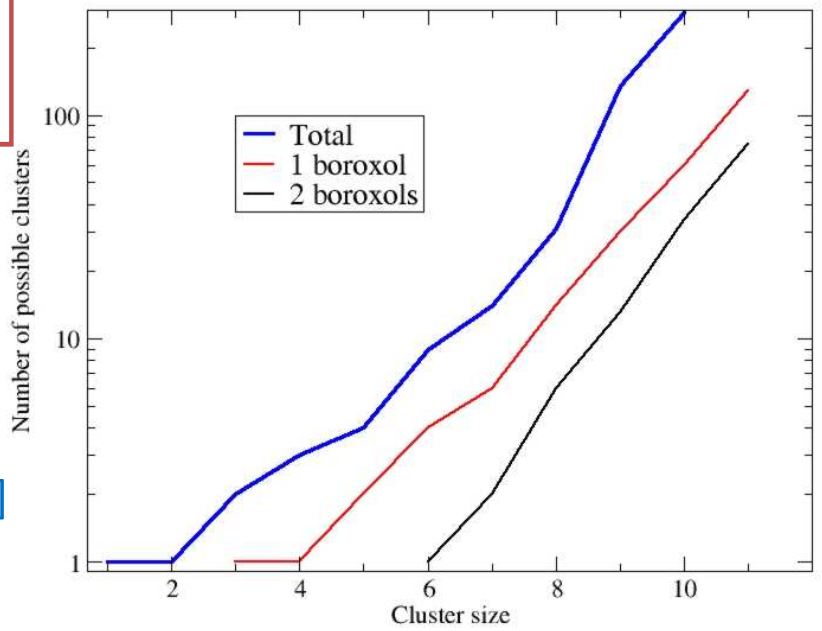
Results



The computed fraction $F_{(l)}$ converges to the experimental value of F_{exp}=0.83

- Fitting parameter
  E2-E1=$E_{boroxol}$-E_1=5.3 kcal/mol

- Expt.: 6 kcal/mol [Quantum Mechanicl]
  5.0 kcal/mol [Raman Intensity with T]



Exponential growth of the number of clusters

D) COMBINING AGGLOMERATION AND PAIR MODELS

- One can combine both approaches to obtain larger structural correlations

  Q^3-Q^4 in a sodium silicate glass,
  Q^2-Q^3 in a phosphate glass

These can be detected from NMR spectroscopy

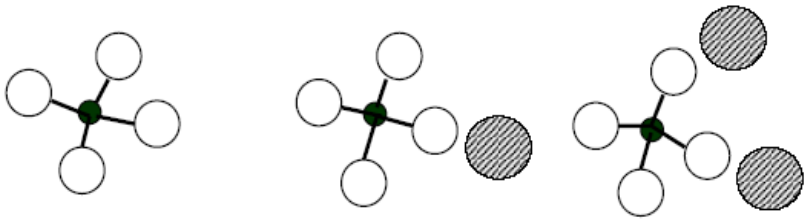
- Start from a local structure statistics
- Build all possible connections by agglomerating the basic species together.
- Compute probabilities

$$N_{ij}(x) \propto W_{ij} N_i(x) N_j(x)$$

$$N_4(x) = \begin{cases} \frac{1-3x}{1-x} & 0 \le x \le x_0 \\ \frac{2(1-2x)^2}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

$$N_3(x) = \begin{cases} \frac{2x}{1-x} & 0 \le x \le x_0 \\ \frac{2(1-2x)(3-5x)}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

$$N_2(x) = \begin{cases} 0 & 0 \le x \le x_0 \\ \frac{-19x^2+16x-3}{(1-x)(5-9x)} & x_0 \le x \le 0.5 \end{cases}$$

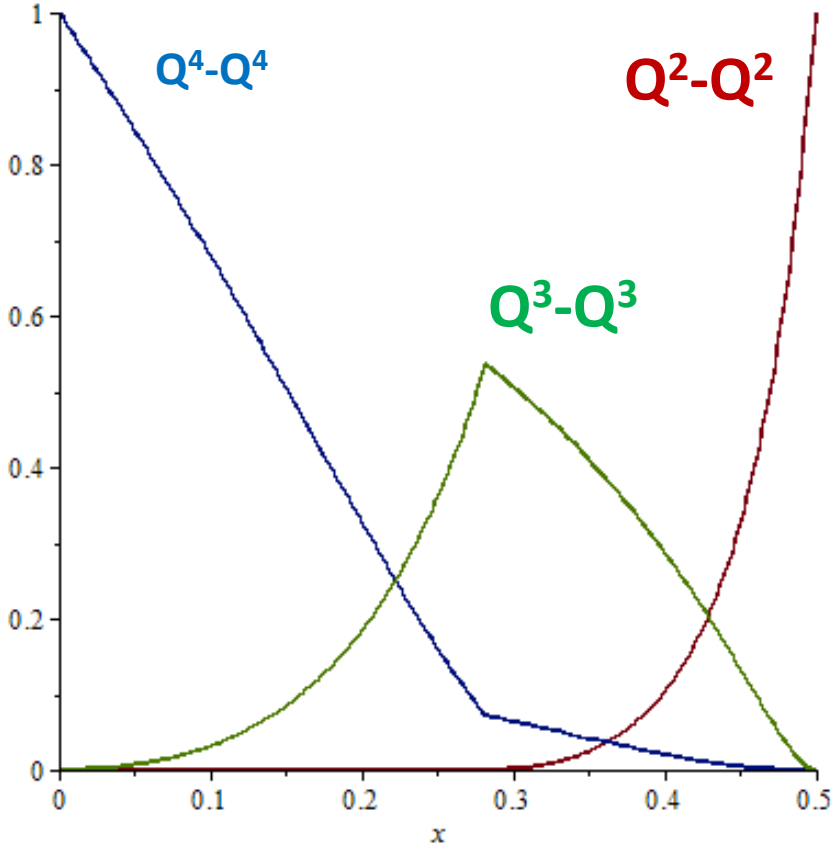


- In the random bonding case, one obtains: e.g.:

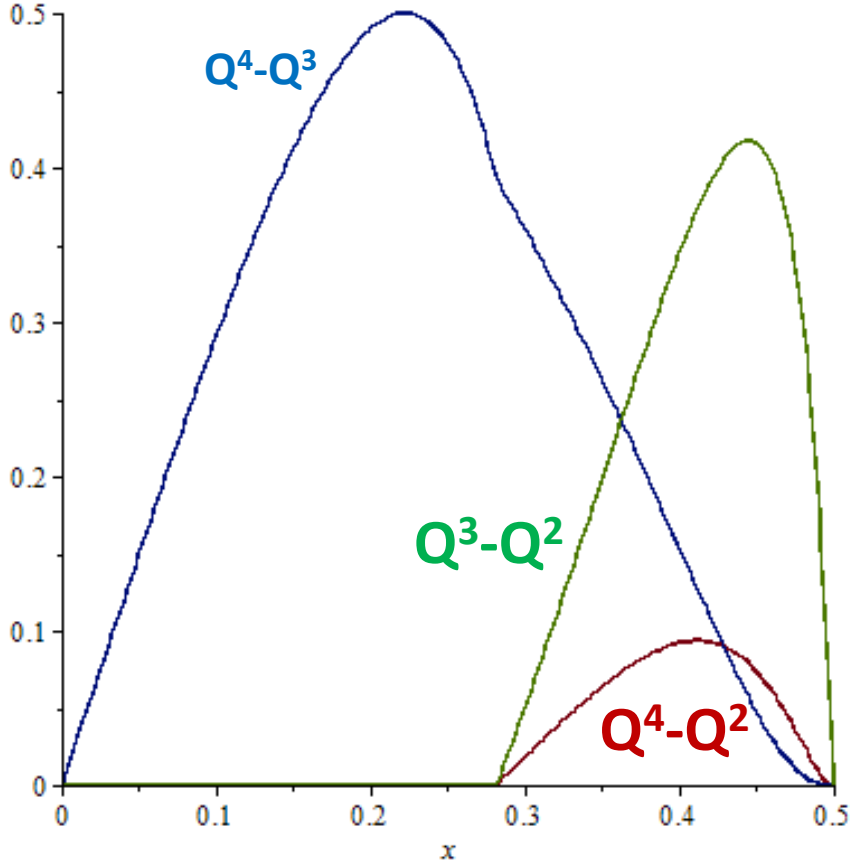
$$p_{44} \propto 16N_4(x)^2 = \begin{cases} \dfrac{4(3x-1)^2}{(2-3x)^2} & if\ x < x_0 \\ \dfrac{11664(1-2x)^2}{(9x-5)^2(3-2x)^2} & if\ x > x_0 \end{cases}$$

$$p_{43} \propto 24N_3(x)N_4(x) = \begin{cases} \dfrac{12x(1-3x)}{(2-3x)^2} & if\ x < x_0 \\ \dfrac{17496(1-2x)^3(3-5x)}{(9x-5)^2(3-2x)^2} & if\ x > x_0 \end{cases}$$

- Allows having some insight into the network structure and bonding pairs
- Comparable to NMR statistics



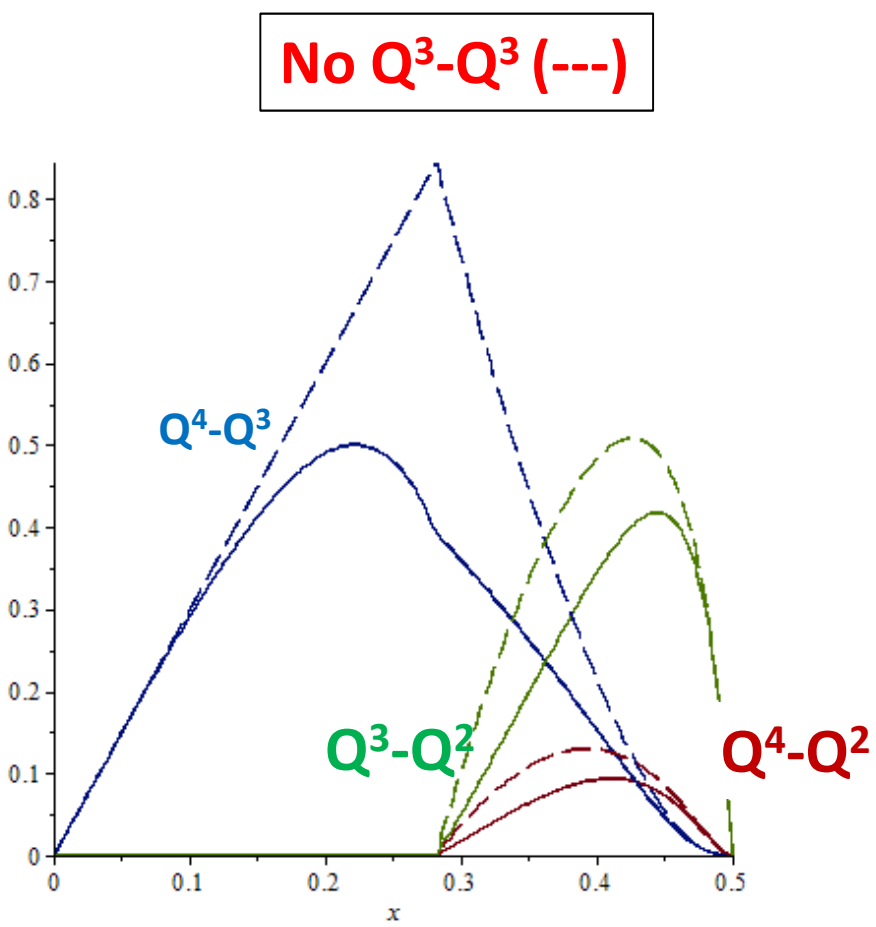
Na_2O concentration

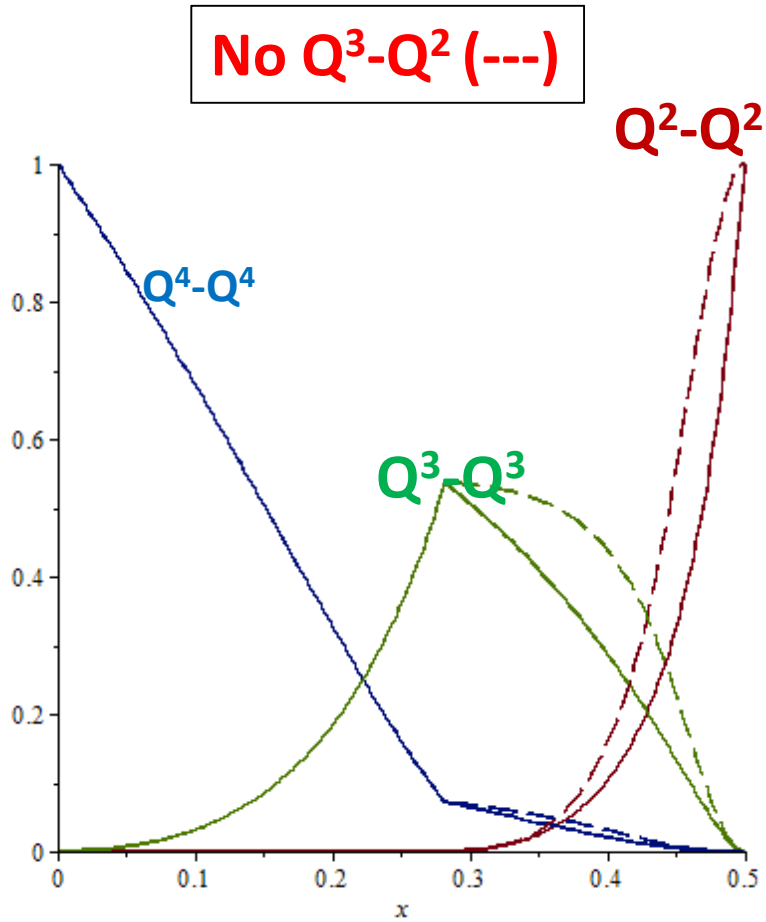


Na_2O concentration

Exploring structural scenarii…

- By selecting or non-selecting appropriate pairs of local structures, one can explore bonding statistics and compare with possible experiments.





Conclusion

- Bond models are useful, they allow a simple insight into the local structure
- Especially relevant for glasses with changing composition
- Can be compared to NMR, Raman
- Starting point (structural model) for other investigation (soon)

- **Next time:** MD simulations: basics
- **Home work assignment:** Speciation of silicate glasses.