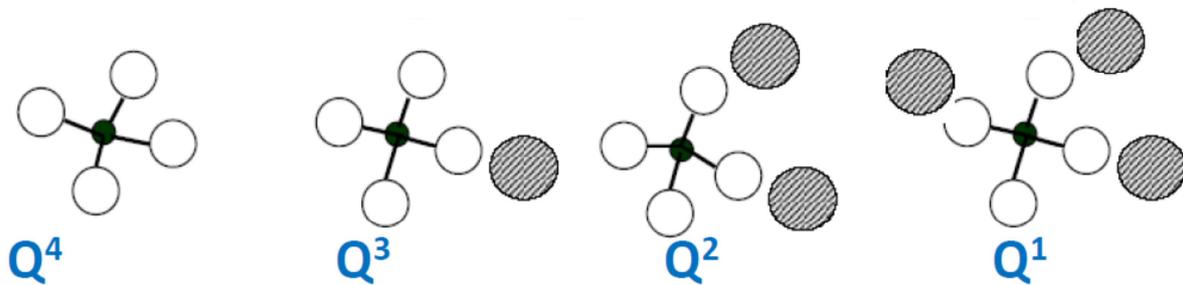


## IMI Course on Atomistic Modeling of Glass Structure

### Bond models and cluster expansion in silicates

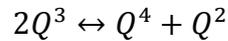
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The short range order in modified alkali silicates  $(1-x)\text{SiO}_2-x\text{M}_2\text{O}$  ( $\text{M}=\text{Li},\text{Na},\text{K}$ ) can be described from  $Q^n$  populations (Figure) representing a Si tetrahedron with  $(4-n)$  non-bridging oxygens. For instance,  $Q^4$  is the local structure of the base network former  $\text{SiO}_2$  (silica) when  $x=0$ . We assign to each of these  $Q^n$  functions a probability  $p_4(x)$ ,  $p_3(x)$ ,  $p_2(x)$ ,  $p_1(x)$  and a corresponding coordination number  $r_n=n$  connecting to the rest of the network, i.e.  $r_4=4$  for silica.



1. The chemical formula of a 100%  $Q^3$  network is  $\text{M}_2\text{Si}_2\text{O}_5$ . What is the corresponding composition  $x$ ? Can you provide both chemical formula and composition for networks made of 100%  $Q^4$ ? 100%  $Q^2$ ? 100%  $Q^1$ ? 100%  $Q^0$ ?
2. **Reproducing the results of the lecture 3.** We first focus on the low modified alkali content ( $x < 33\%$ ) when one can safely set  $p_1$  and  $p_2$  to zero.
  - a. Write down the normalization condition and the charge conservation law. Provide an estimate of  $p_4(x)$  and  $p_3(x)$ .
  - b. We now assume that in the region  $x < 50\%$ , one has  $p_4=A(1-2x)$  and  $p_3=A(3-5x)$ . How can one justify such assumptions? Using the charge conservation law+normalization, estimate  $A$ , and calculate the population  $p_4(x)$ ,  $p_3(x)$  and  $p_2(x)$ . Check that the statistics is valid only for  $28.2\% < x < 50\%$  alkali.
3. We now **investigate the region at higher composition** ( $x > 50\%$ ) where  $p_4$  can be set to zero. As before, one assumes that  $p_3=B(3-5x)$ , but also that  $p_2=B(3-4x)$ . Justify again, this choice.
  - a. Do the same job as before. Extract a statistics of  $p_3(x)$ ,  $p_2(x)$  and  $p_1(x)$ . Check that these results are valid only for  $44.6\% < x < 60\%$ .
  - b. How do these results connect to the previous ones found in 2? Comments?

4. One of the major flaws of such simple (but nice) methods is that one does not distinguish between the effect of different alkalis (see the experimental  $Q^n$  distribution of Maekawa et al. on slide 20 of lecture 3 for Li, Na and K silicates). An interesting way to circumvent this problem is to **introduce an equilibrium constant**  $K_e$  associated with a disproportionation reaction involving  $Q^4$ ,  $Q^3$  and  $Q^2$  species:



Equation above can be considered as an equilibrium reaction with an equilibrium constant defined from the probabilities of finding the different species:

$$K_e = \frac{p_4 p_3}{p_3^2}$$

- Using the normalization condition and the charge conservation law, write now the probability distribution  $p_4(x)$ ,  $p_3(x)$  and  $p_2(x)$  for  $x < 50\%$  as a function of the parameter  $K_e$ .
  - Represent these distributions for some cases in  $K_e$ . Comments ?
  - If you have a great software, you may even try to fit your distribution ( $p_3, p_2, p_4$ ) with the data of Maekawa.
5. Coming back to the statistics of  $Q^n$  of question 1 and 2, **build up all possible doublet clusters**  $Q^i-Q^j$  ( $i, j=4, 3, 2$ ) and their corresponding probabilities. Try to extract a probability of finding  $Q^4$ ,  $Q^3$  and  $Q^2$  structures from the obtained statistics. Would you mind doing it for triplet clusters  $Q^i-Q^j-Q^k$  ?