

I. LOCAL STABILITY CONDITION: STABILITY INDEX

We shall now set up the local stability condition by looking at the relative population of a chain with tetrahedra length m respect to its neighbors. Basically, the idea is that the chains with length m would be more stable when the transition rates to m are larger than the ones from m .

Looking at the pathways in Fig 2, we write the local stability condition as

$$\begin{aligned}
& T[m_{-1}Si^0 \rightarrow_m Si^0] \times T[m_{+1}Si^0 \rightarrow_m Si^0] \times \\
& T[m_{+1}Si^- \rightarrow_m Si^0] \times T[m_{-1}Si^0 \rightarrow_m Si^-] \times \\
& T[m_{-1}Si^- \rightarrow_m Si^-] \times T[m_{+1}Si^- \rightarrow_m Si^-] \times \\
& T[m_{-1}Si^0 \rightarrow_m Al^-] \times T[m_{+1}Al^- \rightarrow_m Si^0] \times \\
& T[m_{-1}Al^- \rightarrow_m Al^-] \times T[m_{+1}Al^- \rightarrow_m Al^-] > \\
& T[mSi^0 \rightarrow_{m-1} Si^0] \times T[mSi^0 \rightarrow_{m+1} Si^0] \times \\
& T[mSi^0 \rightarrow_{m+1} Si^-] \times T[mSi^- \rightarrow_{m-1} Si^0] \times \\
& T[mSi^- \rightarrow_{m-1} Si^-] \times T[mSi^- \rightarrow_{m+1} Si^-] \times \\
& T[mAl^- \rightarrow_{m-1} Si^0] \times T[mSi^0 \rightarrow_{m+1} Al^-] \times \\
& T[mAl^- \rightarrow_{m-1} Al^-] \times T[mAl^- \rightarrow_{m+1} Al^-]
\end{aligned} \tag{1}$$

where T is the transition rate per chain and per unit time. On the left side of Eqn 1 we give the transitions for all pathways that drive to the chains with length m , neutral or negative; while on the right side, for the pathways from m . Let us now write the expression as a product of fractions

$$\begin{aligned}
& \frac{T[m_{-1}Si^0 \rightarrow_m Si^0]}{T[mSi^0 \rightarrow_{m-1} Si^0]} \times \frac{T[m_{+1}Si^0 \rightarrow_m Si^0]}{T[mSi^0 \rightarrow_{m+1} Si^0]} \times \\
& \frac{T[m_{+1}Si^- \rightarrow_m Si^0]}{T[mSi^0 \rightarrow_{m+1} Si^-]} \times \frac{T[m_{-1}Si^0 \rightarrow_m Si^-]}{T[mSi^- \rightarrow_{m-1} Si^0]} \times \\
& \frac{T[m_{-1}Si^- \rightarrow_m Si^-]}{T[mSi^- \rightarrow_{m-1} Si^-]} \times \frac{T[m_{+1}Si^- \rightarrow_m Si^-]}{T[mSi^- \rightarrow_{m+1} Si^-]} \times \\
& \frac{T[m_{-1}Si^0 \rightarrow_m Al^-]}{T[mAl^- \rightarrow_{m-1} Si^0]} \times \frac{T[m_{+1}Al^- \rightarrow_m Si^0]}{T[mSi^0 \rightarrow_{m+1} Al^-]} \times \\
& \frac{T[m_{-1}Al^- \rightarrow_m Al^-]}{T[mAl^- \rightarrow_{m-1} Al^-]} \times \frac{T[m_{+1}Al^- \rightarrow_m Al^-]}{T[mAl^- \rightarrow_{m+1} Al^-]} > 1
\end{aligned} \tag{2}$$

where the pathways to and from m are given in the numerator and denominator respectively.

We define $n({}_mX^q)$ as the average population of chains ${}_mX^q$ with tetrahedra length m , where $X=Si$ or Al and $q=+,0$, or $-$. At thermal equilibrium, we have: $n({}_mX^q)T[{}_mX^q \rightarrow {}_{m-1}Y^p] = n({}_{m-1}Y^p)T[{}_{m-1}Y^p \rightarrow {}_mX^q]$. Given the Boltzmann distribution function, we can write $n({}_mX^q) = (N/Z)e^{-(E({}_mX^q)/k_B T)}$, where N is the total number of chains, Z is the partition function, $E({}_mX^q)$ is the energy of chain size m , k_B is the Boltzmann constant and T the temperature. Then, combining these two equations we have

$$\frac{T[{}_{m-1}Y^p \rightarrow {}_mX^q]}{T[{}_mX^q \rightarrow {}_{m-1}Y^p]} = e^{-((E({}_mX^q)-E({}_{m-1}Y^p))/k_B T)} \quad (3)$$

Inserting these fractions of transition ratios in Eq. 1 and after little algebra, we find that the local stability condition for length m is

$$\begin{aligned} & 2E({}_{m-1}Si^0) + E({}_{m-1}Si^-) + E({}_{m+1}Si^0) + 2E({}_{m+1}Si^-) \\ & \quad - 3E({}_mSi^-) - 3E({}_mSi^0) \\ & E({}_{m-1}Si^0) + E({}_{m-1}Al^-) + 2E({}_{m+1}Al^-) \\ & \quad - E({}_mSi^0) - 3E({}_mAl^-) > 0. \end{aligned} \quad (4)$$

One sees that the right hand term in the previous expression may be defined as the local stability index $\Sigma(m)$. It gives an idea of the chain stability with length m respect to its neighbors, when removing or adding monomers following the pathways of Fig. 2. In fact, it is a sort of chemical potential for the involved pathways. Maxima in $\Sigma(m)$ determine that the chains with length m are specially stable.

We wish to discuss the role of the Al pathways, given with full lines in Fig. 2. Thus, we divide the stability index in two contributions

$$\Sigma(m) = \Sigma_{Si}(m) + \Sigma_{Al}(m) \quad (5)$$

where $\Sigma_{Si}(m)$ comes from the pure Si -based pathways,

$$\begin{aligned} \Sigma_{Si}(m) = & 2E({}_{m-1}Si^0) + E({}_{m-1}Si^-) + E({}_{m+1}Si^0) + 2E({}_{m+1}Si^-) \\ & - 3E({}_mSi^-) - 3E({}_mSi^0) \end{aligned} \quad (6)$$

and $\Sigma_{Al}(m)$ denotes the contributions due to the new pathways of aluminosilicate chains,

$$\begin{aligned} \Sigma_{Al}(m) = & E({}_{m-1}Si^0) + E({}_{m-1}Al^-) + 2E({}_{m+1}Al^-) \\ & - E({}_mSi^0) - 3E({}_mAl^-). \end{aligned} \quad (7)$$

TABLE I: Condensation energy of a neutral silicate chain of length m-1 ($_mSi^0$) with an aluminum monomer ($_1Al^-$), with a neutral silicon monomer ($_1Si^0$) and with a charged silicon monomer ($_1Si^-$). Following the same order the end chains are $_mAl^-$, $_mSi^0$ and $_mSi^-$. Remember that the chains are denoted as $_mX^q$, where m is the tetrahedra length, q is the charge, and X is Si or Al. X=Si indicate that silicon atoms site in the tetrahedra center; and X=Al, an Al atom is at the end tetrahedra of the chain. Water molecules compensate the missing OHs and the protons in the reactions (see Eqns. 1 and 2 in text for some examples), but to simplify they are not written. Chain growth occurs because these energy differences are exothermic.

m	$_mAl^-$	$_mSi^0$	$_mSi^-$
2	1.46	0.82	1.19
3	0.52	0.17	0.18
4	0.73	0.44	0.39
5	1.08	0.33	1.39
6	0.86	0.6	0.62
7	0.8	0.45	0.36
8	1.77	0.32	1.46
9	0.73	0.5	0.34