BINARY ALLOY

(COMMON, for ex. BRASS Cu, Zn

N sites, N_A A atoms
N_B B atoms

$N = N_A + N_B$

$$\frac{S}{k_B} = \ln W = \ln \frac{N!}{N_A!\, N_B!}$$

STIRLING: $\ln N! = N \ln N - N$

$$\frac{S}{k_B} = N \ln N - \cancel{N} - N_A \ln N_A + \cancel{N_A}$$
$$- N_B \ln N_B + \cancel{N_B}$$

$N_A = Nx$
$N_B = N(1-x)$

$$\frac{S}{k_B} = N \ln N - Nx \ln (\underline{Nx})$$
$$- N(1-x) \ln (\underline{N(1-x)})$$

$$\Rightarrow \frac{S}{Nk_B} = \cancel{\ln N} - x \ln x - \underline{x \cancel{\ln N}}$$
$$-(1-x) \ln (1-x - (1-x \ln N$$

$$= \cancel{(-x-1+x)} \ln N$$

$$\Rightarrow S = -N k_B \left(x \ln x + (1-x)\ln(1-x)\right)$$

Review : 2 STATE SYSTEM

E_1 ———

$$\delta_i = E_1 - E_0 \qquad \frac{p_1}{p_0} = e^{-\frac{\delta_i}{kT}}$$

E_0 ———

$$kT \gg \delta_i \qquad \frac{p_1}{p_0} \sim 1$$

→ state 0 and state 1 are equally occupied

$-\delta_i$

$kT << \delta_i \qquad p_0 \approx 1 - e^{\frac{\ }{kT}} \sim 1$

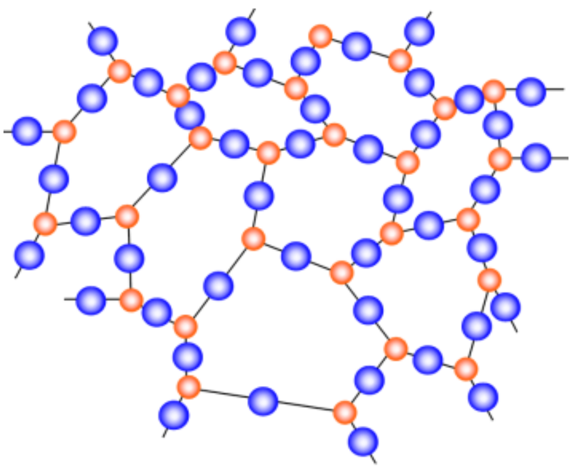
$$p_1 \approx e^{-\frac{\delta_i}{kT}} \sim 0$$

transition (crude, ignore partial occupations)

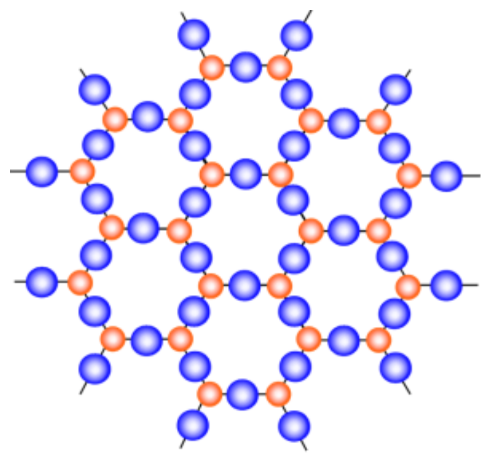
$$kT \approx \delta_i$$

glass:

behaves like liquid on long time scales (1000 yrs) like a solid on shorter time scales



Amorphous



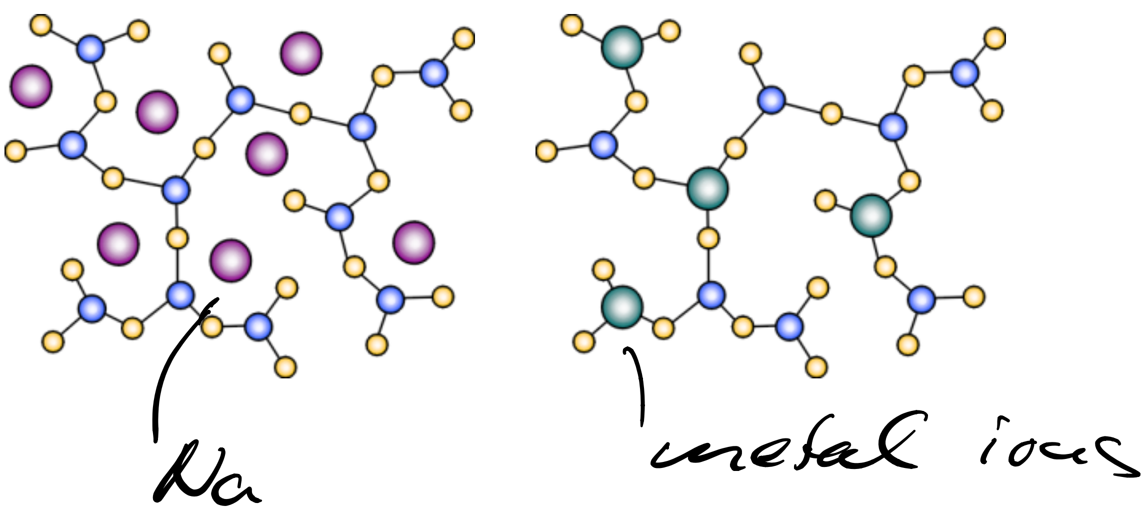
Crystalline

SiO_2

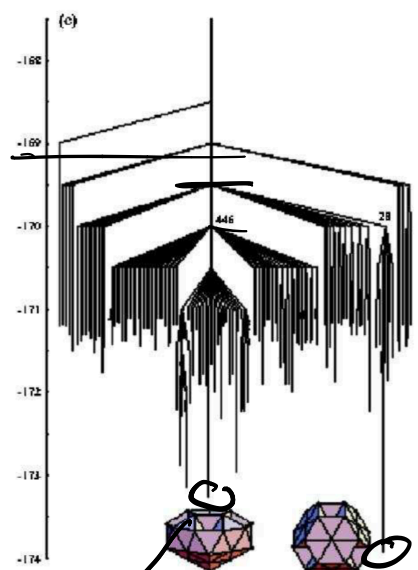
quartz

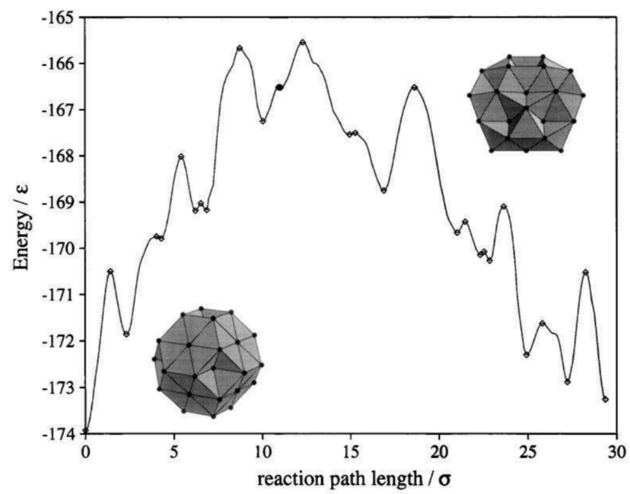
Glasses begin as mixtures of **oxides**. Their compositions can be represented by listing the weight percentages of their components. Compare the percentages for **1**, a typical, modern soda-lime-silica glass (used to make bottles and windows); **2**, laboratory and some baking ware; **3**, optical, high lead crystal; **4**, 96% silica glass (can withstand very high temperatures); **5**, a typical, ancient Roman soda-lime-silica glass.

		1	**2**	**3**	**4**	**5**
Silica	SiO_2	73.6%	80.0%	35.0%	96.5%	67.0%
Soda	Na_2O	16.0	4.	--	--	18.0
Lime	CaO	5.2	--	--	--	8.0
Potash	K_2O	0.6	0.4	7.2	--	1.0
Magnesia	MgO	3.6	--	--	--	1.0
Alumina	Al_2O_3	1.0	2.0	--	0.5	2.5
Iron Oxide	Fe_2O_3	--	--	--	--	0.5
Boric Oxide	B_2O_3	--	13.0	--	3.0	--
Lead Oxide	PbO	--	--	58.0	--	0.01


Na
metal ions

Lennard-Jones cluster LJ_{38}: Extreme case of structural competition





Doye & Wales

E_1 E_0 P_{38}, $Q_{38.3}$

GLASS:

MEASURE RESIDUAL ENTROPY

1) ESTIMATE S_{LIQUID}

2) COOL LIQUID:
MEASURE $t \to Q, T$

$$S_{residual} = S_{liquid}(T_e) - \int_0^{T_e} \frac{dQ}{T} dT$$

$$\Rightarrow S_{residual} \approx N_{MU} \cdot k_B$$

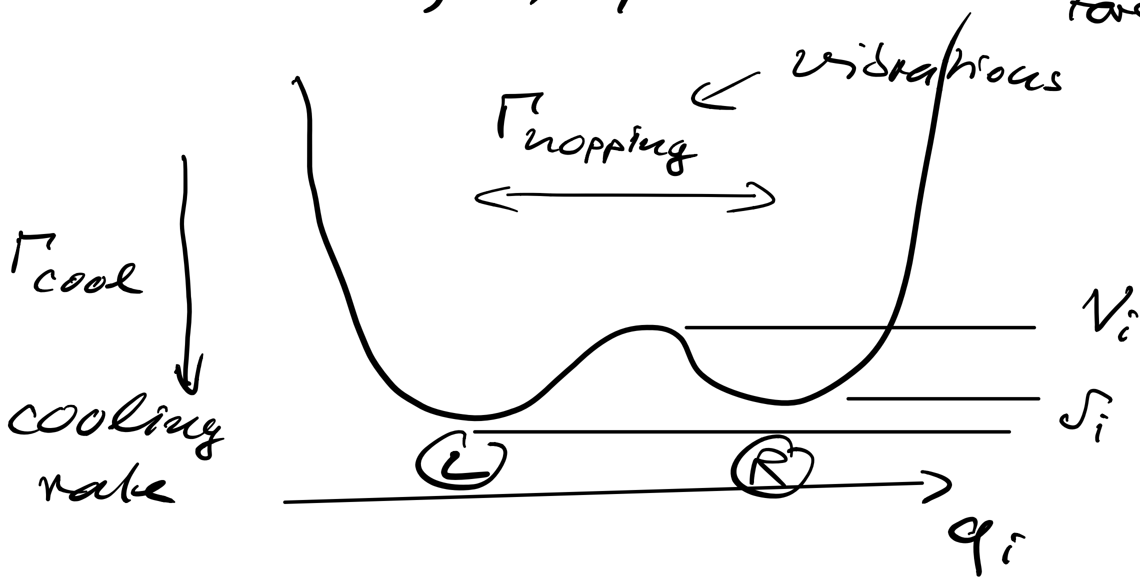
MU =: molecular unit: (SiO_2 for window glass)

SIMPLE MODEL TO RELATE

$S_{THERMO} = \frac{Q}{T}$ TO $S_{STAT} = k \ln \Omega$

- TREAT EACH MU INDEPENDENTLY
- ONE DEGREE OF FREEDOM PER

MU : q_i , $\dot{q}_i$ → angle (bond torsion)



in general $\Gamma_{cool} \gg \Gamma_{hopping}$

Q: "FREEZE IN" ≡ CHOOSE ONE STATE (L OR R)

AT A TEMPERATURE T_i in equil.

$$\frac{p_R}{p_L} = e^{-\frac{\delta_i}{kT_i}}$$

↳ related to V_i

$\delta_i \gg kT_i$ ⇒ MU will be in L $p_L \sim 1$

$\delta_i \ll kT_i$ $p_L \sim p_R$

$\Delta S_{exp} = k_B \ln 2 \sim k_B$

=1 HT

$\overline{}$
0.69

THERMO :

$\delta_i \ll k T_i$

~ HALF THE TIMES ENERGY δ_i
IS NOT RELEASED

$$\frac{\Delta Q}{T_i} \sim \frac{\delta_i}{\delta_i / k_B} \sim k_B$$

NON-EQUILIBRIUM ENTROPY

$S = k_B \ln W$ $\quad W =:$ NUMBER OF MICROSTATES

$= -k_B \ln \frac{1}{W}$ $\quad p_i = p = \frac{1}{W}$

$= -k_B \ln p$ $\quad \sum_i p = 1$

$= -k_B \left(\sum_i p \right) \ln p$

$= -k_B \sum_i \left(p \ln p \right)$

$\Rightarrow$ generalize $p \to p_i$

$$S_{\text{non-equil.}} = -k_B \sum_i (p_i \ln p_i)$$
$$= -k_B \langle \ln p_i \rangle$$

"MOTIVATION"

INFORMATION ENTROPY

SHANNON ENTROPY:

$$S_s = -\sum_i p_i \log_2 p_i$$

S_s is measured in bits

MINIMUM NUMBER OF BITS TO REPRESENT THE INFORMATION CONTAINED IN A "STATE", MESSAGE, IMAGE etc.

e.g. PLACE A BALL IN ONE OF TWO BINS (L or R)

$$\left.\begin{array}{l} L = 0 \\ R = 1 \end{array}\right\} \text{1 bit of information}$$

CONVERT TO NATURAL LOG.

$$S_I = -k_s \sum_i p_i \ln p_i$$

$$x = 2^y \quad | \ln$$

$$\ln x = y \ln 2$$

$$y = \frac{\ln x}{\ln 2}$$

$$k_S = \frac{1}{\ln 2}$$

in TD units $k_S \to \dfrac{k_B}{\ln 2}$

AXIOMATIC DEFINITION OF S_I (MEASURES IGNORANCE OR UNCERTAINTY)

1) ENTROPY IS MAXIMAL FOR EQUAL PROBABILITIES

2) ENTROPY IS UNAFFECTED BY EXRTA STATES WITH ZERO PROBABILITY

$$S(p_1, p_2, \ldots, p_{W-1}, 0)$$
$$= S(p_1, p_2, \ldots, p_{W-1})$$

3)

Quiz

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

$$\frac{\partial^2 \ln Z}{\partial \beta^2} = \dots = \langle E^2 \rangle - \langle E \rangle^2$$