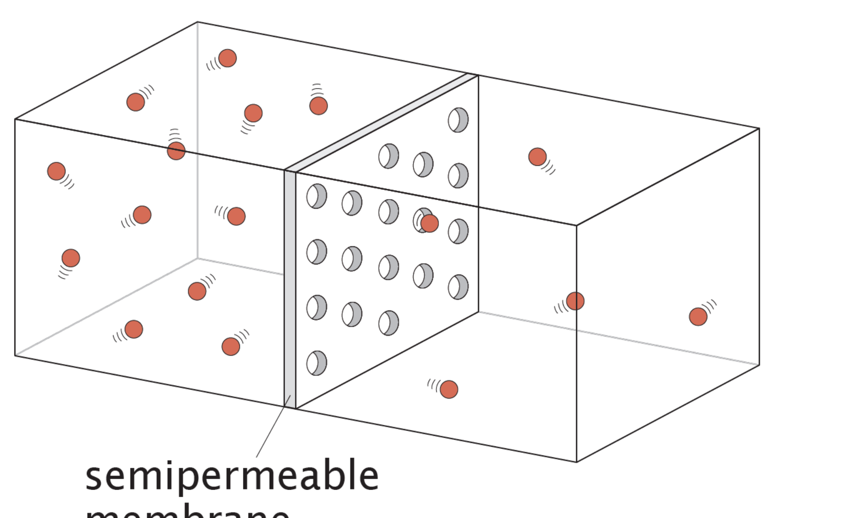
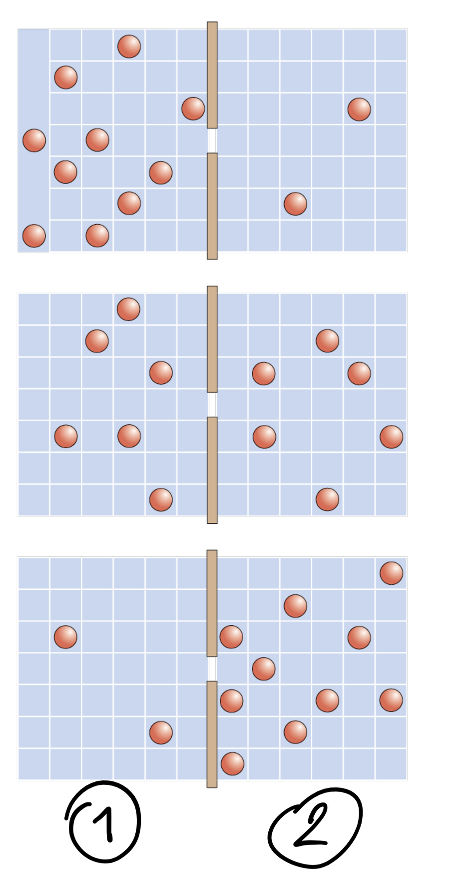
consider a system divided in two partitions



semipermeable membrane

which configuration has the maximum total entropy?



① ②

conservation of mass constraint

S_1 S_2

$N_{tot} = N_1 + N_2 \leftarrow N_1$ N_2 ligands

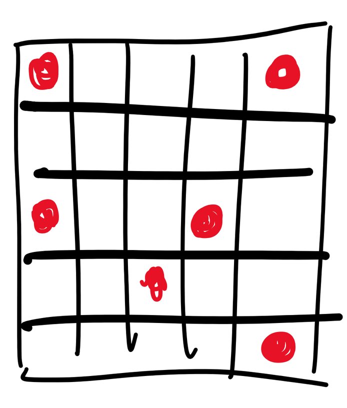
$S_{tot} = S_1 + S_2$

maximum corresponds to the equilibrium state

Let's calculate $S_1(N_1)$ using $S = k_B \ln(W)$

\# of microstates

Partition ① lattice model



Ω boxes of volume v

N_1 molecules

$$W(N_1, \Omega) = \frac{\Omega^{N_1}}{N_1!}$$

$$\Rightarrow S_1 = k_B \ln\left(\frac{\Omega^{N_1}}{N_1!}\right) = k_B\left[\ln \Omega^{N_1} - \ln N_1!\right]$$

$$= k_B\left[N_1 \ln \Omega - \ln N_1!\right]$$

$$S_1 \approx k_B\left[N_1 \ln \Omega - N_1 \ln N_1 - N_1\right]$$

stirling approximation

$\ln N! = N \ln N - N$

$$S_2(N_2) = k_B\left[N_2 \ln \Omega - N_2 \ln N_2 - N_2\right]$$

$$= k_B\left[(N_{tot} - N_1)\ln \Omega - (N_{tot} - N_1)\ln(N_{tot} - N_1) - (N_{tot} - N_1)\right]$$

$N_{tot} - N_1 = N_2$

Now we're ready to calculate the entropy of the whole system.

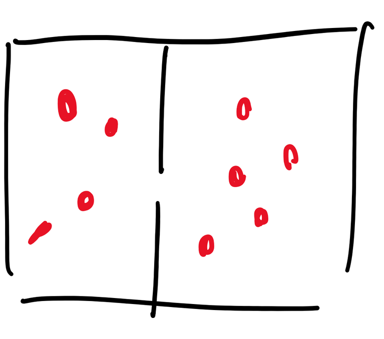
$$S_1 + S_2 = S_{tot}$$

$$= k_B\left[\cancel{N_1 \ln \Omega} - N_1 \ln N_1 \cancel{- N_1}\right] +$$

$$+ k_B\left[(N_{tot} \cancel{- N_1})\ln \Omega - (N_{tot} - N_1)\ln(N_{tot} - N_1) - (N_{tot} \cancel{- N_1})\right]$$

$$= k_B\left[-N_1 \ln N_1 + N_{tot} \ln \Omega - (N_{tot} - N_1)\ln(N_{tot} - N_1) - N_{tot}\right]$$

Let's now think of this problem in the language of the chemical potential



S_1 S_2

$S_{tot} = S_1 + S_2$

2nd law of thermodynamics:

$$0 \leq dS_{tot} = dS_1 + dS_2$$

in equilibrium

$$= \left(\frac{\partial S_1}{\partial N_1}\right) dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right) dN_2$$

worked with differentials as if they were common variables

Now, implement the constraint that

$$N_{tot} = N_1 + N_2$$

$$0 = dN_{tot} = dN_1 + dN_2 \Rightarrow dN_1 = -dN_2$$

total # of molecules doesn't change

$$0 \leq \left(\frac{\partial S_1}{\partial N_1}\right) dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right) dN_2$$

$$0 \leq \left(\frac{\partial S_1}{\partial N_1}\right) dN_1 - \left(\frac{\partial S_2}{\partial N_2}\right) dN_1 = \left[\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right] dN_1$$

We define the chemical potential as

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N}$$

$$0 \leq \left[-\frac{\mu_1}{T} + \frac{\mu_2}{T}\right] dN_1 = (\mu_2 - \mu_1)\, dN_1$$

$\Delta\mu$ is the driving force for particle transport (and conversion)

Let's look at some cases: $\mu_2 > \mu_1 \Rightarrow dN_1 > 0$

$\mu_2 < \mu_1 \Rightarrow dN_1 < 0$

$\mu_2 = \mu_1 \Rightarrow dN_1 = 0$

equality of chemical potential $=$ entropy maximization