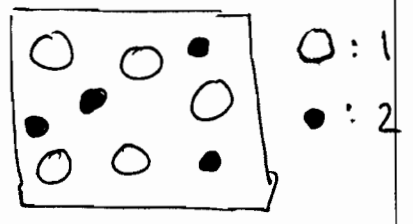


Semi-grand Simulations : f+s §9.1

When only chemical potential differences $\Delta\mu$ (rather than absolute μ 's) are imposed:

E.g. $(N_1 + N_2)$ or μ_2 fixed
 $\mu_1 - \mu_2 = \Delta\mu$ fixed
 V, T fixed



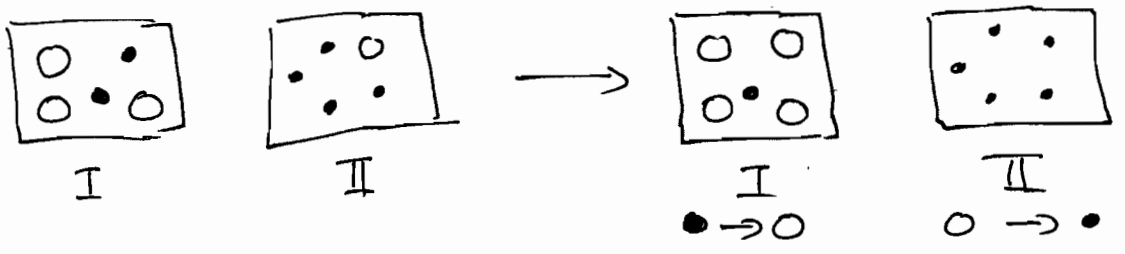
$\text{O} \xrightarrow{\text{soi}} \bullet$ attempt $P_{\text{acc}} = \min \left[1, \frac{N_1}{N_2 + 1} \exp(-\beta\Delta\mu - \beta\Delta u) \right]$

$\bullet \xrightarrow{\text{soi}} \text{O}$ attempt $P_{\text{acc}} = \min \left[1, \frac{N_2}{N_1 + 1} \exp(-\beta\Delta u + \beta\Delta\mu) \right]$

What good is this? (here we have incorporated the N_i 's into μ_i)

→ when one of the two components is easier to insert/remove than the other, it is more efficient to only attempt insertions/removals for the component that is easy to transfer

Also in Gibbs ensemble: $P_{\text{acc}} = \min \left[1, \frac{N_2^{\text{I}}}{N_1^{\text{I}} + 1} \frac{N_1^{\text{II}}}{N_2^{\text{II}} + 1} \exp(-\beta\Delta u) \right]$



Reactive Ensemble

Johnson, AJP, Gubbins, Molec. Phys. 81:717 (1994)

A chemical reaction at equilibrium imposes a constraint on the sum of chemical potentials of the participating components:

$$\sum_{i=1}^C v_i \mu_i = 0$$

v_i : stoichiometric coefficients
+ for products
- for reactants

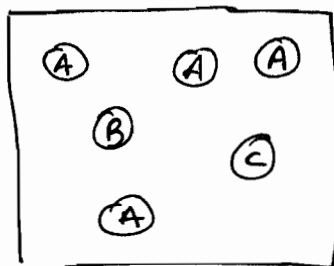
$$\prod_{i=1}^C (f_i / f_i^\circ)^{v_i} = \exp\left(-\frac{\Delta G_{rxn}^\circ}{kT}\right) = K(T)$$

product of fugacities

equilibrium "constant"

In semigrand ensemble, $\Delta\mu$ imposes a fugacity ratio of the two components)

Consider a simple chemical reaction, $A \rightleftharpoons B + C$



Reactive step: (50%) Select random

(A) molecule, replace it w/ (B) and add (C) in random location

$$P_{acc} = \min\left[1, \frac{N_A V}{(N_B + 1)(N_C + 1)} e^{-\beta(\Delta G_B + \Delta G_C - \Delta G_A)}\right]$$

$$\Delta G^\circ = G_B^\circ + G_C^\circ - G_A^\circ$$

(50%) Select random (B) molecule, random (C) molecule
replace (B) w/ (A), delete (C)

$$P_{\text{acc}} = \min \left[1, \frac{N_B N_C}{(N_A+1)V} e^{-\beta \Delta u + \beta \Delta G^{\circ}} \right]$$

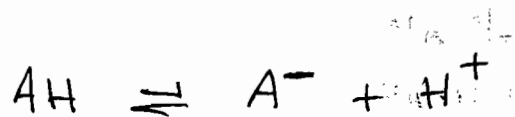
At the limit of no interactions (ideal gases), $\Delta u = 0$ and it is easy to show that the simulation will equilibrate when:

$$\frac{P_C P_B}{P_A} = e^{-\beta \Delta G^{\circ}} = K(\tau)$$

$$P_A = N_A/V$$

$$P_B = N_B/V \quad P_C = N_C/V$$

This approach can be particularly useful for association / dissociation equilibria,



$$K_a = \exp(-\beta \Delta G^{\circ})$$

$$pK_a = -\log_{10}(K_a)$$