Agenda: Information, Probability, Statistical Entropy

- Information and probability
  - simple combinatorics, stochastic variables.
  - Probability distributions, joint probabilities, correlations
  - Statistical entropy
    - Statistical entropy for bi- & multi-partitions
    - Microstates,
    - Stationary states defined by extreme statistical entropy, asymptotic stationary states
    - Constraints: in particle number, total energy,…
    - The Boltzmann factor, probability distribution
- Partition of probability, thermodynamic connection
- Gibbs stability criteria, equilibrium
  - Canonical Observables, Free Energy *A*
  - Grand Canonical Observables, Free Energy *G*
  - Application to chemical reactions
- Partition functions for other degrees of freedom
- Phase space evolution (Eta Theorem)

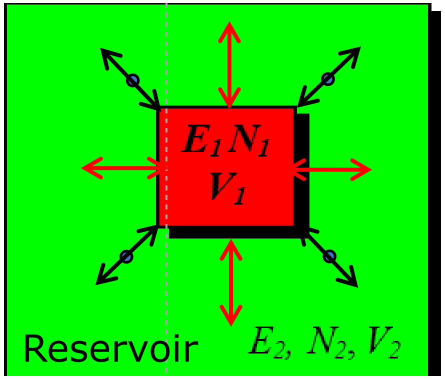
Reading Assignments
Weeks 6 & 7
LN III.1- III.6:

Kondepudi Ch. 20
Additional Material

McQuarrie & Simon
Ch. 3 & 4

Math Chapters
MC B, E

Open Systems: Grand-Canonical Ensembles



Open system: Exchanges of energy and particles occur with surrounding "Particle Reservoir" and "Heat Bath."

→ Combined, (system + reservoirs) = isolated system

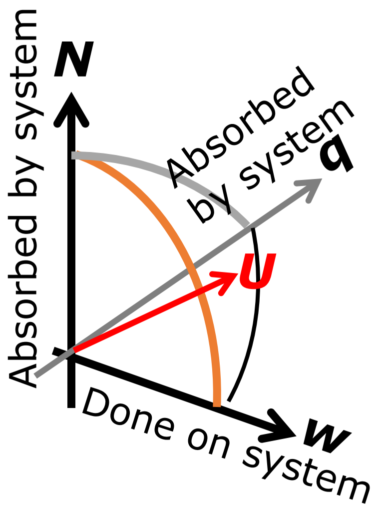
→ Conservation laws in mass and energy

Stationary macro-state is characterized by

N : constituent (particle) number, $0 \le N < \infty$

T: temperature ~ mean internal energy per particle,

V : containment volume.



$$\textit{Differential energy change:}$$

$$dE = \left(\frac{dE}{dT}\right)_{V,N} \cdot dT + \left(\frac{dE}{dV}\right)_{T,N} \cdot dV + \left(\frac{dE}{dN}\right)_{V,T} \cdot dN$$

μ : "chemical potential" energy gain per particle

Grand Canonical Ensemble

Grand canonical ensembles: μ states (***N, i***) have different energies $E_{Ni}(V)$ and different numbers ***N*** of particles → occupation probabilities $\{p_{Ni}\}$

Maximize entropy $dS(\{p_{N1}\}) = 0,$ *boundary conditions (constraints)*

$$\sum_{N,i} p_{Ni} = 1 \qquad \sum_{N,i} E_{Ni} \cdot p_{Ni} = \langle E \rangle, \qquad \text{and} \qquad \sum_{N,i} N \cdot p_{Ni} = \langle N \rangle$$

Sum over # of particles: $N=1,2,...$

μstate #

# of particles

$$\frac{\partial}{\partial p_{Nn}} \left\{ -k_B \sum_{M,m=1}^{\Omega_M} p_{Mm}\, Ln(p_{Mm}) - \lambda_1 \left(\sum_{M,i=1}^{\Omega_M} p_{Mi} \right) - \lambda_2 \left(\sum_{M,j=1}^{\Omega_M} E_{Mj} p_{Mj} \right) - \lambda_3 \left(\sum_{M,k=1}^{\Omega_M} M p_{Mk} \right) \right\} = 0$$

Independent variation rel # of particles: $0 \le N < \infty$; *μstate #* $1 \le i \le \Omega_N$

$$-k_B \left(Ln(\bar{p}_{Nn}) + 1 \right) - \lambda_1 - \lambda_2 E_n - \lambda_3 N = 0 \quad \text{for all} \quad \{\bar{p}_{Nn}\}_{S=S_{max}}$$

$$Ln(\bar{p}_{Nn}) = \frac{1}{k_B}\left(-\lambda_1 - k_B - \lambda_2 E_n - \lambda_3 N \right) \rightarrow p_{Nn} = exp\left\{ -\underbrace{\left(\frac{\lambda_1}{k_B} + 1 \right)}_{-\alpha} - \underbrace{\frac{\lambda_2}{k_B}}_{-\beta} E_{Nn} - \underbrace{\frac{\lambda_3}{k_B}}_{-\gamma} N \right\}$$

Maximizing entropy ➡

$$\bar{p}_{Nn} = e^{-\alpha} \cdot e^{-\beta \cdot E_{Nn}} \cdot e^{-\gamma \cdot N}$$

Grand Canonical Partition Sum

Occupation probabilities $\bar{p}_{Nn} = e^{-\alpha} \cdot e^{-\beta \cdot E_{Nn}} \cdot e^{-\gamma \cdot N}$

Normalization (boundary): $1 = \sum_{Nn} \bar{p}_{Nn} = exp\{-\alpha\} \cdot \sum_{Nn} exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\}$

Define gc partition sum $\Xi(V, \beta, \gamma) = exp\{\alpha\}$

Grand canonical partition sum

$$\Xi(V, \beta, \gamma) = \sum_{Nn} exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\}$$

Grand canonical partition sum over all energies and particle numbers
Parameter $\beta = 1/k_B T$ was determined, g remains to be determined

Grand canonical probabilities

$$p_{Nn} = \frac{1}{\Xi(\beta, \gamma)} exp\{-\beta \cdot E_{Nn} - \gamma \cdot N\} = -\frac{1}{\beta} \frac{d}{dE_{Nn}} Ln\,\Xi(\beta, \gamma)$$

Partition sum is generating function for microstate probabilities

Average Properties of Grand Canonical Ensembles

Grand canonical ensembles: μ states (***N, i***) have different energies $\boldsymbol{E}_{ni}(V)$ and different numbers ***N*** of particles → occupation probabilities $\{p_{Ni}\}$

Grand canonical partition sum

$$\Xi(V,\beta,\gamma) = \sum_{Nn} exp\{-\beta\cdot E_{Nn} - \gamma\cdot N\}$$

$$\langle E(V,\beta,\gamma)\rangle = \frac{1}{\Xi}\sum_{Nn} E_{Nn}\cdot exp\{-\beta\cdot E_{Nn} - \gamma\cdot N\} = -\left(\frac{\partial}{\partial\beta} Ln\,\Xi\right)_{V,\gamma}$$

$$\langle p(N,V,T)\rangle = \frac{-1}{\Xi}\sum_{Nn}\left(\frac{\partial E_{Nn}(V)}{\partial V}\right)\cdot exp\{-\beta\cdot E_{Nn} - \gamma\cdot N\} = \frac{1}{\beta}\left(\frac{\partial}{\partial V} Ln\,\Xi\right)_{\beta,\gamma}$$

$$\langle N(V,\beta,\gamma)\rangle = \frac{1}{\Xi}\sum_{Nn} N\cdot exp\{-\beta\cdot E_{Nn} - \gamma\cdot N\} = -\left(\frac{\partial}{\partial\gamma} Ln\,\Xi\right)_{V,\beta}$$

Entropy and Heat in Grand Canonical Ensemble

Grand canonical partition sum $\Xi\left(V,\beta,\gamma\right)=\sum_{Nn} exp\left\{-\beta\cdot E_{Nn}-\gamma\cdot N\right\}$

$$Internal\ energy\ @S=S_{\max}:$$

$$=Energy\ in\ its\ most\ randomized\ distribution\ over\ many\ states,\ all\ d.o.f.$$

$$=\text{"}Heat\text{"}\ energy\quad T\cdot S=k_B\cdot T\cdot Ln\,\Xi+\langle E\rangle+\left(k_BT\right)\cdot\gamma\cdot\langle N\rangle$$

$$Internal\ energy\ gain\ per\ particle\ @const\ T,V$$

$$Chemical\ potential:\ -\mu:=\frac{\partial}{\partial\langle N\rangle}\left(T\cdot S\right)=\left(k_BT\right)\cdot\gamma\quad\Rightarrow\quad\gamma=\frac{-\mu}{k_BT}$$

$$Statistical\ entropy\ (S_{\max}):\ S=k_BLn\,\Xi+\frac{\langle E\rangle}{T}-\frac{\mu}{T}\langle N\rangle$$

Grand Canonical PF

Grand canonical partition sum $\Xi\left(V,\beta,\gamma\right)=\sum_{Nn} exp\left\{-\beta\cdot E_{Nn}-\gamma\cdot N\right\}$

$$\Xi(V,N,T)=\sum_{E,N}\omega(E,N)\cdot e^{-\frac{E}{k_BT}}\cdot e^{+\frac{N\mu}{k_BT}}=\sum_{E,N}\omega(E,N)\cdot e^{-\frac{E}{k_BT}}\cdot z^N; \quad fugacity\ z=e^{+\frac{\mu}{k_BT}}$$

$$Statistical\ entropy:\ S=S_{\max}=k_B Ln\,\Xi+\frac{\langle E\rangle}{T}-\frac{\mu}{T}\langle N\rangle$$

$$Internal\ energy\ @\,S=S_{\max}:\quad T\cdot S=k_B\cdot T\cdot Ln\,\Xi+\langle E\rangle-\mu\cdot\langle N\rangle$$

$$Additional\ d\langle E\rangle=d\left(p\cdot V\right)\ per\ particle\ @\,const\ T,\not{V}\ (varied\ by\ pressure\ p)$$

Gibbs Free Energy $G:=\mu\cdot\langle N\rangle=\langle E\rangle-T\cdot S+p\cdot V$

Extensive state variable

$$p\cdot V=k_B\cdot T\cdot Ln\,\Xi\rightarrow \Xi=\exp\left\{\frac{p\cdot V}{k_B\cdot T}\right\}$$

Grand Canonical PF: Application to Reactions

$$\text{Gibbs Free Energy } G = \boxed{G(p,T,N) = \mu \cdot \langle N \rangle = \langle E \rangle - T \cdot S + p \cdot V}$$ *extensive*

$$\text{Chemical potential } \mu = \left(\frac{\partial G}{\partial N}\right)_{p,T} ;\text{also } V = \left(\frac{\partial G}{\partial p}\right)_{T} \quad \text{note}: \begin{matrix} N = \langle N \rangle \\ p = \langle p \rangle \end{matrix}$$

System with multiple components $\{N_i\}$:

$$G\left(p,T,\{N_i\}\right)_{p,T} = \sum_i G\left(p,T,N_i\right)_{p,T} = \sum_i \mu_i \cdot N_i$$

$$\text{Stationary state (Equilibrium)}_{\mathbf{p,T}} : S = S_{\max} :$$

$$G \text{ at minimum } \rightarrow \text{solve } dG\left(p,T,\{N_i\}\right)_{p,T} = \sum_i \mu_i \cdot dN_i = 0$$

Grand Canonical PF: Application to Reactions

$$Gibbs\ Free\ Energy\ \boxed{G = G(p,T,N) = \langle E \rangle - T\cdot S + p\cdot V}\ \textit{extensive}$$

$$Chemical\ potential\ \ \mu = \left(\frac{\partial G}{\partial N}\right)_{p,T};\ also\ V = \left(\frac{\partial G}{\partial p}\right)_{T}\ note: \begin{matrix} N = \langle N \rangle \\ p = \langle p \rangle \end{matrix}$$

$$Stationary\ state\ (Equilibrium)_{\mathbf{T}}:\ vary\ pressure\ to\ find\ S = S_{\max}$$

$$G(p) - G^{0}(p_0) = \int_{p_0}^{p} dG(p,..) = \int_{p_0}^{p} V(p)\,dp \rightarrow\ need\ EoS\ V(p) = ?$$

$$Assume\ e.g.\ gas\ EoS\ p\cdot V = N\cdot k_B\cdot T \rightarrow G(p) - G^{0}(p_0) = N\cdot k_B\cdot T\cdot Ln\left(\frac{p}{p_0}\right)$$

$$\boxed{\mu(p,T) - \mu^{0}(\cancel{p_0},T) = k_B\cdot T\cdot Ln\left(\frac{p}{p_0}\right)}$$

For EoS
$p\cdot V = N\cdot k_B\cdot T$

Grand Canonical PF: Application to Reactions

Apply to chemical reaction in gas phase (because of *EoS* used)

$$\mu(p,T) = \mu^0(\cancel{p_0},T) + k_B \cdot T \cdot Ln\left(\frac{p}{p_0}\right)$$

For EoS
$p \cdot V = N \cdot k_B \cdot T$

$$\nu_A \cdot A + \nu_B \cdot B \rightleftharpoons \nu_C \cdot C + \nu_D \cdot D \quad \text{or} \quad \nu_A \cdot A + \nu_B \cdot B - \nu_C \cdot C - \nu_D \cdot D = 0$$

Change in chemical potential $(T = const.)$:

$$\Delta\mu = \nu_C \cdot \mu_C - \nu_D \cdot \mu_D - \nu_A \cdot \mu_A + \nu_B \cdot \mu_B \qquad \text{similar for } \Delta\mu^0(p_A,\ldots,p_D)$$

$$\Delta\mu = \Delta\mu^0 + k_B T \cdot LN\left[\frac{(p_C)^{\nu_C}(p_C)^{\nu_D}}{(p_A)^{\nu_A}(p_B)^{\nu_B}}\right] \quad \text{all relative to } p_0$$

$$S = S_{max} \rightarrow \Delta\mu = 0 \rightarrow \Delta\mu^0 = -k_B \cdot T \cdot Ln\left[\frac{(p_C)^{\nu_C}(p_C)^{\nu_D}}{(p_A)^{\nu_A}(p_B)^{\nu_B}}\right] = -k_B T \cdot Ln\, K_p$$

Equilibrium Constant

$$K_p = exp\left\{-\frac{\Delta\mu^0}{k_B \cdot T}\right\}$$

$$K_p = exp\left\{-\frac{\Delta\mu^0}{R \cdot T}\right\}$$

for ν_i in moles