Agenda: Probability and Partition Function

- Probability distributions, & generating functions,
- Phase space probability, canonical gas
    - Maxwell-Boltzmann distribution
    - Probability and partition function
    - Quantal modifications
    - Mean values and fluctuations,
- Microscopic structure and macroscopic effects,
    - Quantal d.o.f & energy microstates
    - Constrained statistical entropy,
    - Free energies, chem potentials, heat capacities,
    - Gibbs stability criteria, equilibrium
- Canonical and grand canonical partition functions
    - Partition functions for different degrees of freedom
    - Rotational, vibrational d.o.f.
    - Applications, illustrations

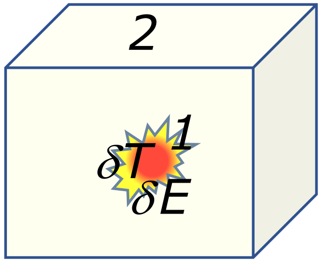
Reading Assignments
Weeks 9 & 16
LN V.3- V.5:

Kondepudi Ch. 17, 15
Additional Material

McQuarrie & Simon
Ch. 4

Math Chapters
MC B, E

Thermal Stability of Canonical System

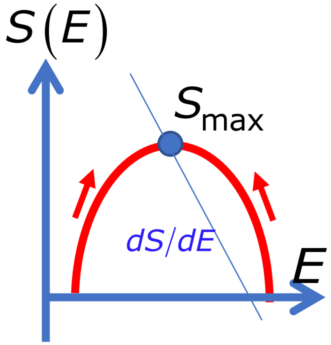


Is stationary system with max entropy stable ? Consider thermal fluctuations $\boldsymbol{\delta T}$ about extremum $\boldsymbol{S \approx S_{max}}$ small disturbance #1 inside large system #2

$$S/k_B = Ln\,Q + \beta \cdot E \quad \rightarrow \quad \left(\frac{\partial S/k_B}{\partial E}\right)_{N,V,\beta} = \beta = \frac{1}{k_B \cdot T}$$

$$Stationary\ \ state\ \ at\ \ S = S_{\max} = S_{\max,1} + S_{\max,2}$$

$$Constant\ \ E \rightarrow \delta E_1 = -\delta E_2,\ \ \beta_1 = \beta_2 \rightarrow T_1 \approx T_2 = T$$



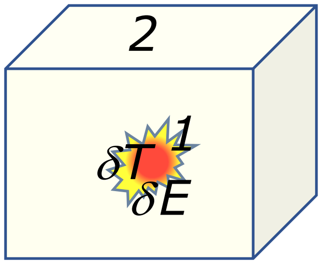
Q: Do small thermal $\boldsymbol{\delta T}$ fluctuations make the total system more stable or less stable? Driving force expected toward more stable configurations *($S \approx S_{max}$)*

$$Taylor\ \ expansion\ \ of\ \Delta S = S - S_{\max}$$

$$\Delta S = \sum_{i=1}^{2}\left(\frac{\partial S}{\partial E_i}\right)\cdot \delta E_i + \frac{1}{2}\sum_{i=1}^{2}\left(\frac{\partial^2 S}{\partial E_i^2}\right)\cdot \left(\delta E_i\right)^2 + \ldots mixed\ \ etc$$

Thermal Stability of Canonical System

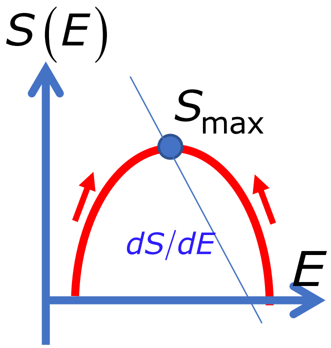
Is stationary system with max entropy stable ?
Consider thermal fluctuations **δT** about extremum **$S \approx S_{max}$** small disturbance #1 inside large system #2



Internal energy E=U

$$S/k_B = Ln\,Q + \beta\cdot E \;\rightarrow\; \left(\frac{\partial S/k_B}{\partial E}\right)_{N,V,\beta} = \beta = \frac{1}{k_B\cdot T}$$

$$\Delta S \approx 0 + \frac{1}{2}\sum_{i=1}^{2}\left(\frac{\partial^2 S}{\partial E_i^2}\right)\cdot(\delta E_i)^2 = \frac{1}{2}\sum_{i=1}^{2}\left(\frac{\partial}{\partial E_i}\frac{1}{T_i}\right)\cdot(\delta E_i)^2 = \frac{1}{2}\delta^2 S$$



$$\frac{\partial}{\partial E_i}\frac{1}{T_i} = -\frac{1}{T_i^2}\overset{1/C_{V_i}}{\boxed{\frac{\partial T_i}{\partial E_i}}}$$

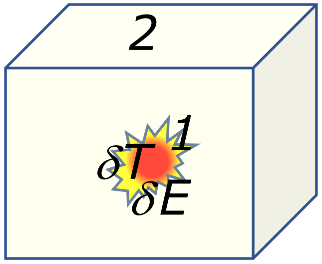
"*heat capacity*" C_V

$$C_{Vi} = \frac{\partial E_i}{\partial T_i} \rightarrow \delta E_i = C_{Vi}\cdot\delta T_i$$

$$\boxed{\delta^2 S \approx -\frac{(C_{V1}+C_{V2})}{T^2}(\delta T)^2 < 0}$$

Also: mechanical stability if $\kappa > 0$. → **$S=S_{max}$ → stable, "equilibrium" state**

Canonical Stability and Free Energy



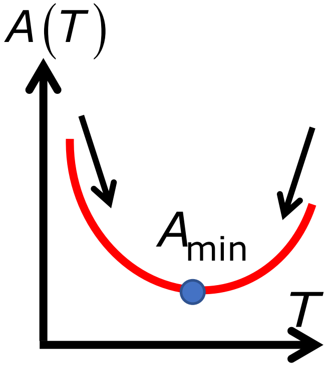
Internal energy E=U

Is stationary system with max entropy stable ?
Consider thermal fluctuations δT about extremum $S \approx S_{max}$ small disturbance #1 inside large system #2

$$S = k_B \cdot Ln\,Q + \beta \cdot E = k_B \cdot Ln\,Q + \frac{E}{T}$$

$$T \cdot S = k_B \cdot T \cdot Ln\,Q + E \quad \rightarrow \quad -k_B T \cdot Ln\,Q = \left(E - T \cdot S\right)$$

$$\text{"}\mathit{Helmholtz\ Free\ Energy}\text{"} \quad \boxed{A = \left(E - T \cdot S\right)}$$



$$Ln\,Q = -\frac{A}{k_B T} \quad \rightarrow \quad \boxed{Q = e^{-A/k_B T}}$$

Helmholtz free energy *A(N,V,T)* represents a driving potential, driving system to maximum stability →
→ $S = S_{max}$ → stable, "equilibrium" state

Extremum-Maximum Entropy ← → Minimum of Free Energy

Summary Canonical/μCanonical PF

Canonical PF

$$Q = Q(N, V, T)$$

Free energy

$$A = -k_B T \cdot Ln Q$$

Entropy

$$S = k_B \cdot Ln\, Q + \frac{E}{T}$$

$$S = -\left(\frac{\partial\, LnA}{\partial T}\right)_V$$

Pressure

$$p = -\left(\frac{\partial\, LnA}{\partial V}\right)_T$$

Internal (heat) energy

$$E = k_B T^2 \left(\frac{\partial LnQ}{\partial T}\right)_V$$

Partition function = generating function for the probability distribution of all macroscopic thermodynamic observables in equilibrium.

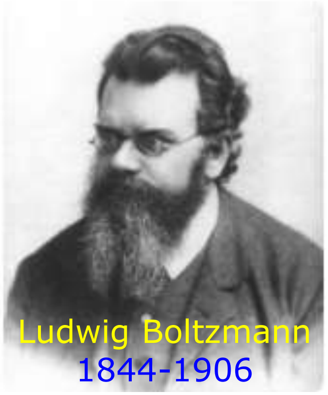
Expectation values for the internal energy (E or U), pressure, entropy, and free energy can be derived from ***Q*** with differential operators.

Closed-form expression derived for Q in terms of a macroscopic Free Energy A and temperature T.

$$\boxed{Q = \sum_E \varpi(E) \exp\{-E/T\} \to \varpi(E)}$$

For a microcanonical ensemble, degeneracy $\omega(E)$ directly determines expectation values for all observables.

Statistical = Thermodynamic Entropy


Ludwig Boltzmann
1844-1906

Thermodynamic Entropy : $S = k \cdot Ln\,\Omega$

Boltzmann 1877

$\Omega =$ *number of accessible states*

Shown here that Ω *and hence* $Ln\Omega$ *are maximum at equal partitions* $\rightarrow\rightarrow$ *corresponds to constant* p_n, *i.e. flat probability distributions*

$0 \le S \le S_{\max}$

$$\boxed{\Omega = e^{S/k}}$$

$$\Omega = e^{S/k} \propto 2^{S/k}$$

Information, entropy and number of states are essentially given by the number of bits $Log_2\Omega$ or the number of nats $Ln\,\Omega$

States with maximum entropy are stationary (dyn. equilibrium), no driving force exists toward different $\{p_n\}$

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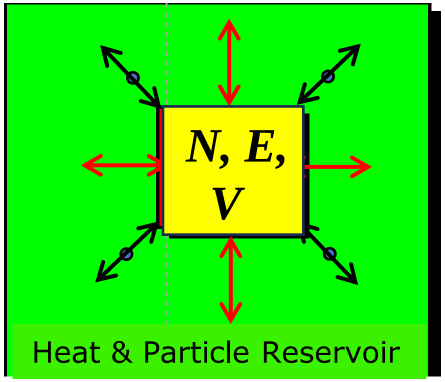
Open Systems: Grand-Canonical Ensembles



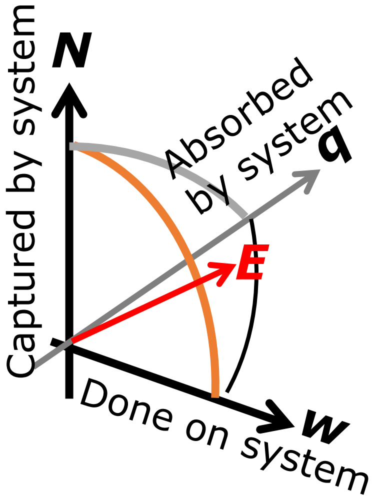
Open system: Exchanges of energy and particles occur with surrounding "Particle Reservoir" and "Heat Bath."
→ Combined, (system + reservoirs) = isolated system
Stationary macro-state characterized by $\langle N\rangle,\langle E\rangle \propto T,V$

→ Conservation laws in mass and energy + constraints

Maximize entropy $dS(\{p_{N,i}\}) = 0$ *under Constraints*

$$\sum_{M=1,i=1}^{\Omega_N} p_{M,i} = 1; \quad \sum_{M,i}^{\Omega_N} E_{M,i}\cdot p_{M,i} = \langle E\rangle; \quad \sum_{M,i}^{\Omega_N} M\cdot p_{M,i} = \langle N\rangle$$

$$\Omega_N = \text{Number of intrinsic states for } N-\text{particle system (arbitrary)}$$



Differential internal energy change:

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

C_V: heat capacity at $V=const.$, p : internal pressure
μ =chemical potential = energy gained per captured particle

State Probability: Grand Canonical Ensemble

Grand canonical ensembles: μstates (***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 over # of particles: *N=1,2,...*

$$\sum_{N,i} p_{Ni} - 1 = 0; \qquad \sum_{N,i} E_{Ni}\cdot p_{Ni} - \langle E\rangle = 0, \qquad \sum_{N,i} N\cdot p_{Ni} - \langle N\rangle = 0$$

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

i,j,k,m μstate #

N, M # of particles

Independent variation rel # of particles: $0 \le N \to \infty$; $\mu state_N$ # $1 \le i \le \Omega_N$

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

State Probability: Grand Canonical Ensemble

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

Constraints : $\sum_{N,i} p_{Ni} = 1;\ \sum_{N,i} E_{Ni}\cdot p_{Ni} = \langle E\rangle;\ \sum_{N,i} N\cdot p_{Ni} = \langle N\rangle$

Sum over # particles ($N=1,2,\ldots$), μstates i

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

Use this to calculate ***S !***

$$\bar{p}_{Nn} = \left(e^{-\alpha}\right)\cdot e^{-\beta\cdot E_{Nn}}\cdot e^{-\gamma\cdot N} = \left[\Xi(V,\beta,\gamma)\right]^{-1}\cdot e^{-\beta\cdot E_{Nn}}\cdot e^{-\gamma\cdot N}$$

Grand canonical partition sum

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

Grand Canonical Ensemble: Entropy, Heat, and Work

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

Internal energy @ $S=S_{max}$:= *Energy in its most randomized distribution over many states & all d.o.f. is changed by "heat supply", particle addition + work done by or on system: PF must contain all information!*

$$\boxed{T\cdot S = k_B\cdot T\cdot Ln\,\Xi + \langle E\rangle + \left(k_BT\right)\cdot\gamma\cdot\langle N\rangle}$$

Internal energy gain (bonding) per particle @ const T,V

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

$$\boxed{\gamma = \frac{-\mu}{k_BT}}$$

Grand Canonical Ensemble: Entropy, Heat, and Work

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

$Internal\ energy\ @S = S_{\max} := Energy\ in\ its\ most\ randomized\ distribution$ $over\ many\ states\ \&\ all\ d.o.f.\ is\ changed\ by$ "*heat supply*", *particle addition* + *work done by or on system* : *PF must contain all information*!

$$\boxed{T \cdot S = k_B \cdot T \cdot Ln\,\Xi + \langle E \rangle + (k_B T) \cdot \gamma \cdot \langle N \rangle}$$

$T \cdot S = Energy(N,T,V)$ *must also depend on work done by or on system, e.g.,*

on $V \to p \cdot V = energy \to Additional\ d\langle Energy \rangle = \ldots + d(p \cdot V)\ \ @const\ T, p$

Identify terms

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

GC PF Closed Form

Verify consistency by deriving expressions for TD variables from this PF.

Grand Canonical PF: Gibbs Free Energy

Grand canonical partition sum

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

same *N*

$$\boxed{\Xi = \exp\left\{\frac{p\cdot V}{k_B\cdot T}\right\}}$$

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

$\because$ *q.e.d.*

Max statistical entropy (from before):

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

$$\boxed{S = \frac{\langle p\rangle}{T}\cdot V + \frac{\langle E\rangle}{T} - \frac{\mu}{T}\langle N\rangle}$$

Rearrange terms

Gibbs Free Energy $\boxed{G(p,T,N) := \mu\cdot N = E + p\cdot V - T\cdot S}$

Extensive state variable G ←→ S

Per particle $\mu = dG/dN$

Grand Canonical PF: G*(p,T,N)*

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

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

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

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

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

$$G_i(p) - G_i^0(p_0) = N_i\cdot k_B\cdot T\cdot Ln(p_i/p_0);\ \textit{partial pressure}\ p_i$$

For species ***i*** $\boxed{\mu_i(p,T) - \mu_i^0(T) = k_B\cdot T\cdot Ln\left(\frac{p_i}{p_0}\right)}$

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

Grand Canonical PF: Mixtures and Reactions

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

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

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

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

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

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

$$by\ varying\ relative\ abundances\ N_i\Big/\sum_i N_i$$

Grand Canonical PF: Application to Reactions

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

$$\boxed{\mu_i\left(p,T\right)=\mu_i^0\left(T\right)+k_B\cdot T\cdot Ln\left(p_i/p_0\right);\quad p_0:=101kPa}$$

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

Generic Chem. Reaction $\nu_A\cdot A+\nu_B\cdot B\rightleftharpoons\nu_C\cdot C+\nu_D\cdot D$ ← 1 mole each

$$\boxed{\textit{Extent (progress) of reaction observable} =: \xi}$$

$$\boxed{d\xi_i=-\frac{dA}{\nu_A}=-\frac{dB}{\nu_B}=\frac{dC}{\nu_C}=\frac{dD}{\nu_D}\quad(>0:\text{forward})}$$

Affinity of reaction

weighted average μ *:*

per mol

$$\boxed{A=\left(\nu_A\cdot\mu_A+\nu_B\cdot\mu_B\right)-\left(\nu_C\cdot\mu_C+\nu_D\cdot\mu_D\right)=\sum_{i=A,B,C,D}A_i}$$

$$@G_{min}:\ d\left(G/N\right)=\sum_i A_i\cdot d\xi_i=0\rightarrow$$

$$\text{per mole } dA=\ldots=dD\rightarrow 0=d\left(G/N\right)=\sum_i d\xi_i=$$

$$T\cdot dS\left(\xi\right)=dE+p\cdot dV-\left(\mu_A\cdot A+\mu_B\cdot B\right)d\xi$$

Grand Canonical PF: Application to Reactions

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

$$\mu_i(p,T) = \mu_i^0(T) + k_B \cdot T \cdot Ln(p_i/p_0); \quad p_0 := 101kPa$$

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

Generic Chem. Reaction

$$\nu_A \cdot A + \nu_B \cdot B \rightleftharpoons \nu_C \cdot C + \nu_D \cdot D$$

Total # of particles in system

$$\sum_i N_i = \nu_A \cdot A + \nu_B \cdot B + \nu_C \cdot C + \nu_D \cdot D$$

$$\sum_i N_i \neq const. \rightarrow Changes\ as\ reaction\ proceeds\ \sum_i N_i(\xi) = f(\xi)$$

Extent (progress) of reaction observable $=: \xi$

$$d\xi = \frac{dC}{\nu_C} = \frac{dD}{\nu_D} = -\frac{dA}{\nu_A} = -\frac{dB}{\nu_B} \quad (> 0 : forward)$$

Affinity of reaction weighted average μ :

$$A = (\nu_A \cdot \mu_A + \nu_B \cdot \mu_B) - (\nu_C \cdot \mu_C + \nu_D \cdot \mu_D) = \sum_i A_i$$

$$d(G/N) = \sum_i A_i \cdot d\xi_i = \rightarrow 0$$

$$T \cdot dS(\xi) = dE + p \cdot dV - (\mu_A \cdot A + \mu_B \cdot B)d\xi$$