Equal a priori probabilities

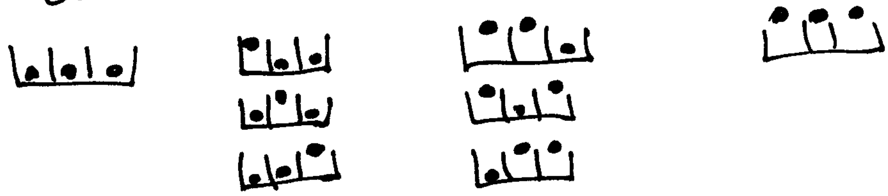
Fundamental Postulate of Statistical Mechanics

> for a system at constant N, V, E, **all** microstates are **equally** probable at equilibrium

Systems that obey this postulate are deemed "ergodic" – others are "non-ergodic" (e.g., glasses)

E.g., two-state system, 3 slots

$E=0$ $\quad$ $E=b$ $\quad$ $E=2b$ $\quad$ $E=3b$



$$\mathcal{P}_m = \frac{1}{\Omega(N,V,E)} \quad \text{for any "allowed" microstate } m$$

For other sets of macroscopic constraints (e.g. const. NVT to be discussed shortly) not all states have the same probability. However, we can always define an "ensemble average" for a property X

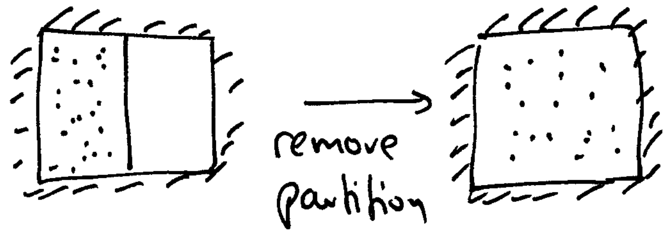
$$\underbrace{\langle X \rangle}_{\text{angle brackets denote ensemble average}} = \sum_{\text{all microstates } m} \mathcal{P}_m X_m$$

For ergodic systems,

$$\underbrace{\langle X \rangle}_{\text{ensemble average}} = \underbrace{\lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} X(t)\,dt}_{\text{time average}}$$

ensemble average = time average

Maximum Entropy Principle



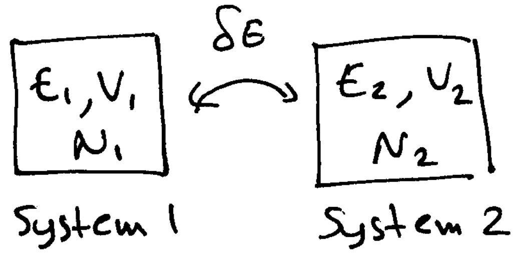
$S(E,V,N \mid \text{internal constraints}) < \underbrace{S(E,V,N)}_{\text{no constraints}}$

more microstates possible when internal barriers are removed

Second Law of Thermodynamics: For any spontaneous process in an isolated system, the entropy goes up

S is maximized at constant N, V, E conditions

Conditions of Equilibrium



what happens if we bring together systems 1 and 2, allowing them, e.g. to exchange energy?

$\Omega_T = \Omega_1 \times \Omega_2$ (each microstate of 1 can be coupled with a microstate of 2)

$E_1 + E_2 = E_T = \text{constant}$ $[\Rightarrow dE_1 = -dE_2]$

The probability of a state of the total system with ~~energy~~ system 1's E_1 is proportional to Ω_T consistent with this energy:

$$\wp(E_1) \propto \Omega_1(E_1) \times \Omega_2(E_T - E_1)$$

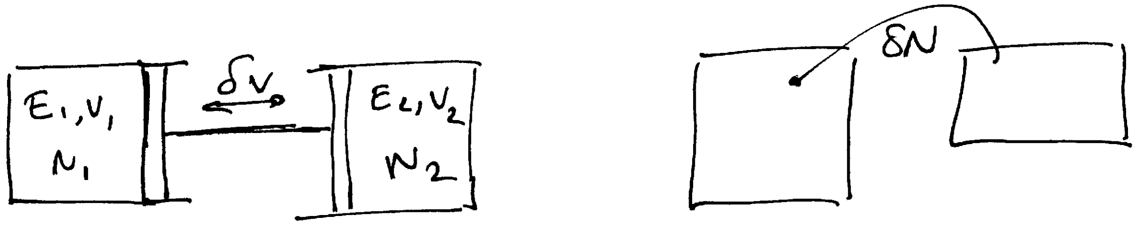
If N_1 and N_2 are large, the probability $\mathcal{P}(E_1)$ becomes very sharply peaked – the highest (maximum) probability occurs when

$$\frac{\partial \mathcal{P}(E_1)}{\partial E_1} = 0 \Rightarrow \Omega_1(E_1)\frac{\partial \Omega_2(E_T - E_1)}{\partial E_1} + \Omega_2(E_T - E_1)\frac{\partial \Omega_1}{\partial E_1} = 0$$

$$\Rightarrow -\frac{\partial \ln \Omega_2}{\partial E_2} + \frac{\partial \ln \Omega_1}{\partial E_1} = 0 \Rightarrow \frac{1}{T_2} = \frac{1}{T_1} \Rightarrow \boxed{T_1 = T_2}$$

∴ when energy transfer is possible, equilibrium occurs when the temperature of the two systems is equal

In a similar fashion, if volume or mass could be exchanged between the two systems



$$\frac{\partial \ln \Omega_1}{\partial V_1} = \frac{\partial \ln \Omega_2}{\partial V_2} \Rightarrow \qquad \frac{\partial \ln \Omega_1}{\partial N_1} = \frac{\partial \ln \Omega_2}{\partial N_2} \Rightarrow$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad -\frac{\mu_1}{T_1} = -\frac{\mu_2}{T_2}$$

$$\Rightarrow P_1 = P_2 \qquad \Rightarrow \mu_1 = \mu_2$$

[assumes $T_1 = T_2$, from energy (thermal) contact]

$$\left.\begin{matrix} T_1 = T_2 \\ P_1 = P_2 \\ \mu_1 = \mu_2 \end{matrix}\right\} \text{Conditions of equilibrium}$$

$\underline{\max S(N,V,E) \implies \min E(S,V,N)}$

$\underline{\text{Maximization}}$ of Entropy at const. N,V,E implies $\underline{\text{minimization}}$ of Energy at const. S,V,N

Assume a system with an internal variable ξ (e.g. position of a piston)

$S(E,V,N,\xi)$ is max $\rightarrow$ $\left.\frac{\partial S}{\partial \xi}\right)_{E,V,N} = 0 \quad \left.\frac{\partial^2 S}{\partial \xi^2}\right)_{E,V,N} < 0$

$$\left.\frac{\partial E}{\partial \xi}\right)_S \underset{\substack{\uparrow \\ \text{xyz-1 rule}}}{=} -\left.\frac{\partial E}{\partial S}\right)_\xi \left(\frac{\partial S}{\partial \xi}\right)_E = -T\left.\frac{\partial S}{\partial \xi}\right)_E$$

$\Rightarrow$ if system is at S extremum also at E extremum

$$\left.\frac{\partial^2 E}{\partial \xi^2}\right)_S = \frac{\partial}{\partial \xi}\left[-\left.\frac{\partial E}{\partial S}\right)_\xi \left.\frac{\partial S}{\partial \xi}\right)_E\right]_S = -\left.\frac{\partial E}{\partial S}\right)_\xi \frac{\partial}{\partial \xi}\left[\left.\frac{\partial S}{\partial \xi}\right|_E\right]_S$$

$$\underbrace{\cancel{-\left.\frac{\partial S}{\partial \xi}\right)_E}}_{0\ @\ S\max} \frac{\partial}{\partial \xi}\left[\left.\frac{\partial E}{\partial S}\right)_\xi\right]_S = -T\frac{\partial}{\partial \xi}\left[\left.\frac{\partial S}{\partial \xi}\right)_E\right]_S \quad (1)$$

To evaluate this derivative, consider a function $x(E,\xi)$

$dx = \left(\frac{\partial x}{\partial E}\right)_\xi dE + \left(\frac{\partial x}{\partial \xi}\right)_E d\xi$ } take ξ derivative at constant S:

$$\left.\frac{\partial x}{\partial \xi}\right)_S = \left.\frac{\partial x}{\partial E}\right)_\xi \left.\frac{\partial E}{\partial \xi}\right)_S + \left.\frac{\partial x}{\partial \xi}\right)_E$$

} Let $x = \left.\frac{\partial S}{\partial \xi}\right)_E$

$$\therefore \frac{\partial}{\partial \xi}\left[\left.\frac{\partial S}{\partial \xi}\right)_E\right]_S = \frac{\partial^2 S}{\partial E\partial \xi}\underbrace{\cancel{\left.\frac{\partial E}{\partial \xi}\right)_S}}_{0 \text{ at extremum}} + \left.\frac{\partial^2 S}{\partial \xi^2}\right)_E \quad \overrightarrow{(1)}$$

$$\Rightarrow \left.\frac{\partial^2 E}{\partial \xi^2}\right)_S = -T\left.\frac{\partial^2 S}{\partial \xi^2}\right)_E > 0 \quad \text{QED}$$

Differential form

$$\boxed{\begin{aligned} dS &= \frac{1}{T}\,dE + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN \\ dE &= T\,dS - P\,dV + \mu\,dN \end{aligned}}$$

(Entropy representation)

(Energy ″)

derivatives of the F.E. determine equilibrium conditions

$$\left.\frac{\partial E}{\partial S}\right)_{V,N} = T(S,V,N) \qquad \left.\frac{\partial E}{\partial V}\right)_{S,N} = -P(S,V,N) \qquad \left.\frac{\partial E}{\partial N}\right)_{S,V} = \mu(S,V,N)$$

S, E, V, N : extensive, prop. to size of system

T, P, μ : intensive, independent of size

The F.E. is homogeneous of 1st order with respect to its variables

Euler's Theorem: if $f(\lambda x, \lambda y) = \lambda f(x,y)$

then $f = \left.\frac{\partial f}{\partial x}\right)_y x + \left.\frac{\partial f}{\partial y}\right)_x y$

Proof: $f(\lambda x, \lambda y) = \lambda f(x,y) \underset{\partial/\partial\lambda}{\Longrightarrow} \frac{\partial f}{\partial x}\frac{\partial \lambda x}{\partial \lambda} + \frac{\partial f}{\partial y}\frac{\partial \lambda y}{\partial \lambda}$

$= f(x,y) \Longrightarrow \qquad x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} = f(x,y)$ QED

Applying to E:

$$\boxed{E = TS - PV + \mu N}$$

Integrated form — Confusing, appears to have T, S, P, V, μ, N as variables?

! $T(S,V,N)$ $P(S,V,N)$ $\mu(S,V,N)$ are still not independent variables