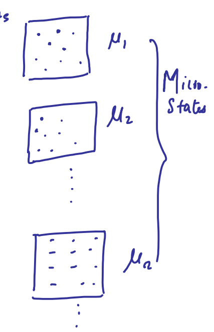
Chapter 2. Classical Statistical Mechanics

Systems at Equilibrium.

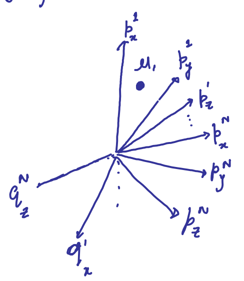
$$\left.\begin{array}{c}(N, V, E) \\ (N, P, T) \\ \vdots\end{array}\right\}$$ Macrostates

$(N, V, E) \xrightarrow{\text{consists}}$



Phase space corresponds to $(\underset{p}{3N} + \underset{q}{3N} = 6N)$ dimensional

No. of micro-states are very large.



Not required to time evolve the coordinates!

$$H(\{q_i, p_i\})$$

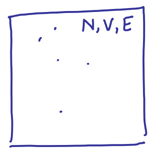
$$-\dot{p}_i = \frac{\partial H}{\partial q_i}$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

Instead, we study distribution functions

for $\underbrace{(N, V, E)}_{\text{Micro canonical}}$, $\underbrace{(N, P, T)}_{\text{Canonical}}$, $\underset{\text{Gibbs-Canonical}}{(\mu, V, T)}$ . .

(1) Micro-canonical Ensemble:



$N \sim 10^{23}$
$V \sim 100\,L$
$E \sim X$ Joule

Macrostate : $\mathcal{H}(\mu) = E$

$$p_M(\mu) = \frac{1}{\Omega(E, V)}, \quad \mathcal{H}(\mu) = E$$

. .

$= 0 \quad , \mathcal{H}(\mu) \neq E$

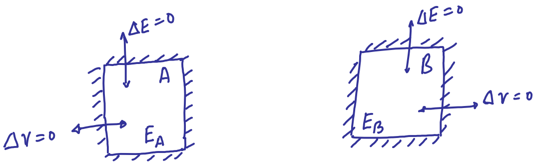
$\Omega(E,V) \equiv$ No. of microstates accessible

$$p_M(\mu) = \frac{1}{\Omega(E,V)} \quad , \mathcal{H}(\mu) = E$$

Assuming equal a priori probability distribution.

Boltzmann Entropy: $S = k_B \ln \Omega$

(I) Zeroth Law of Thermodynamics:

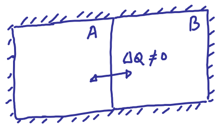


A, B are in thermal & Mechanical equilibrium

$\boxed{E = E_A + E_B}$

$S_A = k_B \ln \Omega_A$ $\qquad$ $S_B = k_B \ln \Omega_B$

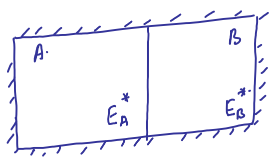
connect these systems



A, B can exchange Energy now.

$S_A(E_A) + S_B(E_B) = $ Total Entropy

...... Wait to equilibrate .....



$$S(E) = S_A(E_A^*) + S_B(E_B^*)$$

Q: What is the condition for equilibrium.

$$\delta S_A = \left.\frac{\partial S_A}{\partial E_A}\right|_{V_A} \delta E_A$$

$$\delta S_B = \left.\frac{\partial S_B}{\partial E_B}\right|_{V_B} \delta E_B$$

$$\delta S = \delta S_A + \delta S_B = \left.\frac{\partial S_A}{\partial E_A}\right|_{V_A} \delta E_A + \left.\frac{\partial S_B}{\partial E_B}\right|_{V_B} \delta E_B$$

.... Recall that $E = E_A + E_B = E_A^* + E_B^*$

$$\delta E = 0 = \delta E_A + \delta E_B$$

$$\Rightarrow \delta E_A = -\delta E_B$$

$$\delta S = \left.\frac{\partial S_A}{\partial E_A}\right|_{V_A} \delta E_A + \left.\frac{\partial S_B}{\partial E_B}\right|_{V_B} (-\delta E_A)$$

$$\delta S = \underbrace{\left(\left.\frac{\partial S_A}{\partial E_A}\right|_{V_A} - \left.\frac{\partial S_B}{\partial E_B}\right|_{V_B} \right)}_{=0} \underbrace{\delta E_A}_{\text{arbitrary.}}$$

If thermal equilibrium is achieved, $\delta S = 0$

then, $$\left.\frac{\partial S}{\partial E_A}\right|_{V_A} = \left.\frac{\partial S}{\partial E_B}\right|_{V_B}$$

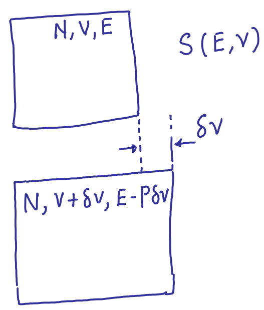
Defining $$\frac{1}{T_{A,B}} = \left.\frac{\partial S}{\partial E_{A,B}}\right|_{V_{A,B}}$$

Condition for equilibrium: $$\frac{1}{T_A} = \frac{1}{T_B}$$

$$\Rightarrow T_A = T_B$$

(2) First law of thermodynamics: Law of conservation of Energy.

Consider system at equilibrium



Allow Reversible work:

$đW = -P\delta V$

Change in entropy: $\delta S\,(E,V) = ?$

$$S(E-P\delta V,\, V+\delta V) = S(E,V) + \left.\frac{\partial S}{\partial E}\right|_V \delta E + \left.\frac{\partial S}{\partial V}\right|_E \delta V \qquad (1)$$

Recall, $\delta Q = 0$

hence $\delta E = đW = -P\delta V$

$$S(E-P\delta V,\, V+\delta V) - S(E,V) = \left.\frac{\partial S}{\partial E}\right|_V (-P\delta V) + \left.\frac{\partial S}{\partial V}\right|_E \delta V$$

$$\delta S = \left(\left.\frac{\partial S}{\partial E}\right|_V (-P) + \left.\frac{\partial S}{\partial V}\right|_E \right) \delta V$$

Recall that $\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V$

$$\delta S = \left(\frac{-P}{T} + \left.\frac{\partial S}{\partial V}\right|_E \right) \delta V$$ ↳ arbitrary

This variation is due to reversible work, $\delta S = 0$

$$\Rightarrow \quad P/T = \left.\frac{\partial S}{\partial V}\right|_E \qquad (2)$$

Rewriting eq^n (1) using (2),

$$\delta S = \frac{\delta E}{T} + \frac{P}{T}\delta V$$

Now including all variations,

$$dS = \frac{dE}{T} + \frac{P\,dV}{T}$$

$$\Rightarrow \underline{\underline{T\,dS}} = \underline{\underline{dE}} + \underline{\underline{P\,dV}}$$ — Ist law of thermodynamics.

(3) **IInd law of thermodynamics:**

Arrow of time

What is the direction of heat flow?

Total Entropy $= S = S_A + S_B$

Right after connection — At equilibrium

$$S_A(E_A) + S_B(E_B) < S_A(E_A^*) + S_B(E_B^*)$$

$\therefore$ Change:

$$\delta S = \underbrace{S_A(E_A^*) - S_A(E_A)} + \underbrace{S_B(E_B^*) - S_B(E_B)} \geq 0$$

Irreversible

$$\Rightarrow \left.\frac{\partial S_A}{\partial E_A}\right|_{V_A} \delta E_A + \left.\frac{\partial S_B}{\partial E_B}\right|_{V_B} \delta E_B \geq 0$$

$$\Rightarrow \frac{1}{T_A}\delta E_A + \frac{1}{T_B}\delta E_B \geq 0$$

Since $\delta E_A = -\delta E_B \quad (E_A + E_B = E \text{ (const)})$

$$\Rightarrow \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\delta E_A \geq 0$$

If $T_B > T_A$ B is hotter than A.

$$\frac{1}{T_A} - \frac{1}{T_B} > 0$$

implies $\delta E_A > 0$ A has recieved net flow of energy.