

Statistical Mechanics: It is a probabilistic approach to equilibrium macroscopic properties of a system with large degrees of freedom.

Keywords: "probabilistic approach" $p(\mu) \equiv \mu\text{-state probability}$
"equilibrium macroscopic properties" T, E, P const.
"large degrees of freedom" $N \sim 10^{23}$

Microstate $\mu \equiv \{ \vec{r}_i, \vec{p}_i \} \quad i \in (1, N)$

Macrostate $M \equiv (N, V, T), (N, P, T), (N, V, E)$ etc.

Microcanonical ensemble:

This happens when a system is both mechanically and adiabatically isolated. Since no heat/work exchange takes place, the macrostate is specified by

$$M \equiv (E, \vec{x})$$

\vec{x} is a generalized coordinate such as N, V, L, \dots etc.

The Hamiltonian equations conserve the total energy of the system, all microstates are confined to the surface $H(\mu) = E$ in phase space.

If there are no other conserved quantities, so that all points on this surface are mutually accessible, the equilibrium probability distribution is:

$$p_{(E, \vec{x}^0)}(\mu) = \frac{1}{\Omega(E, \vec{x}^0)}, \text{ if } E - \Delta E \leq H(\mu) \leq E + \Delta E$$

$$= 0, \text{ otherwise}$$

Some observations are immediately made as below:

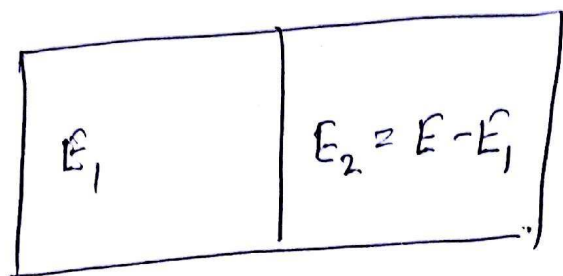
(1) the unbiased probability estimate is a direct consequence of constant total energy. This is the Boltzmann's equal a priori equilibrium probabilities.

(2) the normalization constant $\Omega(E, \vec{x}^0)$ is the volume of the shell of thickness $2\Delta E$ around the surface of constant energy E . Ω depends exponentially on E , as long as $\Delta E \sim O(E^0)$ (or independent of E)

(3) the entropy of this probability distribution is

$$S(E, \vec{x}^0) = k_B \ln \Omega(E, \vec{x}^0)$$

Zeroth law: Bring two microcanonical systems with energies E_1 and E_2 into thermal contact



$$E_1 + E_2 = \text{constant}$$

Joint system is mechanically & thermally isolated.

Microstate: $\mu = \mu_1 \otimes \mu_2$

Hamiltonian: $H(\mu) = H(\mu_1) + H(\mu_2)$

Probability distribution:
$$p_E(\mu_1 \otimes \mu_2) = \frac{1}{\Omega(E, H)} \mathbb{1}_{E - \Delta E \leq H(\mu) \leq E + \Delta E}$$

$$= 0, \text{ otherwise}$$

Therefore, total allowed phase space volume is:

$$\Omega(E) = \int dE_1 \Omega_1(E_1) \Omega_2(E - E_1) = \int dE_1 e^{(S_1(E_1) + S_2(E - E_1))/k_B}$$

Since S_1 and S_2 are extensive quantities ($\sim N$), above integral is approximated using saddle point method.

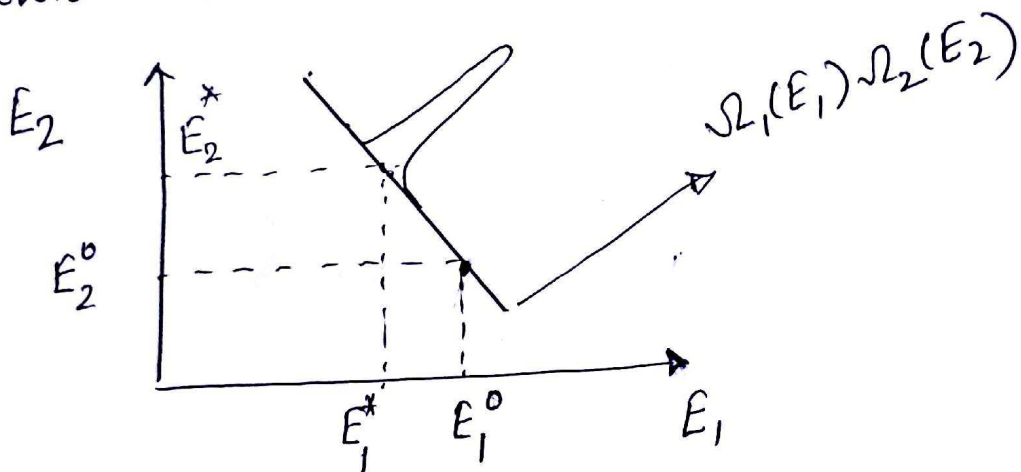
$$\Omega(E) \approx e^{(S_1(E_1^*) + S_2(E_2^*))/k_B}$$

$$\therefore S(E) \approx S_1(E_1^*) + S_2(E_2^*)$$

E_1^*, E_2^* can also be found as:

$$\left. \frac{\partial S_1}{\partial E_1} \right|_{E_1=E_1^*, \vec{x}_1} = \left. \frac{\partial S_2}{\partial E_2} \right|_{E_2=E_2^*, \vec{x}_2} \quad \because dE_1 = -dE_2$$

The energy redistribution between the two systems that start from (E_1^0, E_2^0) and evolve upto (E_1^*, E_2^*) is shown below:



Realizing $\frac{\partial S_1}{\partial E_1} = \frac{1}{T}$ we make the following observation

"The systems exchange heat energy until the empirical temperature becomes same for both"

First law: We now look for variations in $S(E, \vec{x})$ with \vec{x}

Suppose we do reversible work $d.W = \vec{J} \cdot d\vec{x}$.
This change E to $E + \vec{J} \cdot \delta\vec{x}$

The first order change in entropy is

$$\delta S = S(E + \vec{J} \cdot \delta \vec{x}, \vec{x} + \delta \vec{x}) - S(\vec{x}, E)$$

$$= \left(\left. \frac{\partial S}{\partial E} \right|_{\vec{x}} \vec{J} + \left. \frac{\partial S}{\partial \vec{x}} \right|_E \right) \cdot \delta \vec{x}$$

This change will happen spontaneously, taking the system to a more probable state.

Identifying $\left. \frac{\partial S}{\partial x_i} \right|_E, x_j \neq i = -\frac{J_i}{T}$ $\left\{ \because \left. \frac{\partial S}{\partial E} \right|_{\vec{x}} = \frac{1}{T} \right\}$

$$\therefore dS(E, \vec{x}) = \frac{dE}{T} - \frac{\vec{J} \cdot d\vec{x}}{T}$$

$$\Rightarrow T ds = dE - \vec{J} \cdot d\vec{x}$$

$$\Rightarrow dE = T ds + \vec{J} \cdot d\vec{x}$$

$\underbrace{\hspace{2cm}}$
 dQ (heat input)

this is law of conservation of energy.

Second Law: Since the statistical definition rests on the presence of large N ($N \gg 1$), the resulting number of accessible states at equilibrium has much larger count than what we start with.

Mathematically \bar{u} means:

$$\Omega_1(E_1^*, \vec{x}_1) \Omega_2(E_2^*, \vec{x}_2) \gg \Omega_1(E_1, \vec{x}_1) \Omega_2(E_2, \vec{x}_2)$$

The change (irreversible) in entropy is then

$$\delta S = S(E_1^*) + S(E_2^*) - (S_1(E_1) + S_2(E_2)) \gg 0$$

$$= (S_1(E_1^*) - S_1(E_1)) + (S_2(E_2^*) - S_2(E_2)) \gg 0$$

$$= \left. \frac{\partial S_1}{\partial E_1} \right|_{\vec{x}_1} \delta E_1 + \left. \frac{\partial S_2}{\partial E_2} \right|_{\vec{x}_2} \delta E_2 \gg 0$$

$$= \left(\left. \frac{\partial S_1}{\partial E_1} \right|_{\vec{x}_1} - \left. \frac{\partial S_2}{\partial E_2} \right|_{\vec{x}_2} \right) \delta E_1 \gg 0 \quad \because \delta E_1 = -\delta E_2$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_1 \gg 0$$

Thus heat flows from hotter body to cooler body.

Stability conditions: Since (E_1^*, E_2^*) maximize $S(E)$, the second derivative of $S(E)$ must be negative.

$$\therefore \left. \frac{\partial^2 S_1}{\partial E_1^2} \right|_{\vec{x}_1} + \left. \frac{\partial^2 S_2}{\partial E_2^2} \right|_{\vec{x}_2} \leq 0$$