

Chapter 2.5: Microcanonical Equilibrium

in general $S(E)$ increases with E

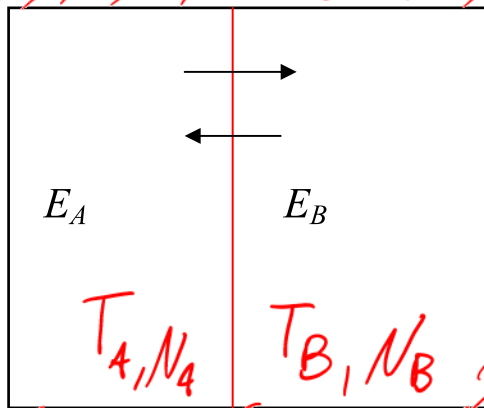
Def. 2.7:

Two systems with energies E_A and E_B are in energetic equilibrium if the total number of states $\Omega_{tot}(E_A, E_B) = \Omega_A(E_A)\Omega_B(E_B)$ is maximal.

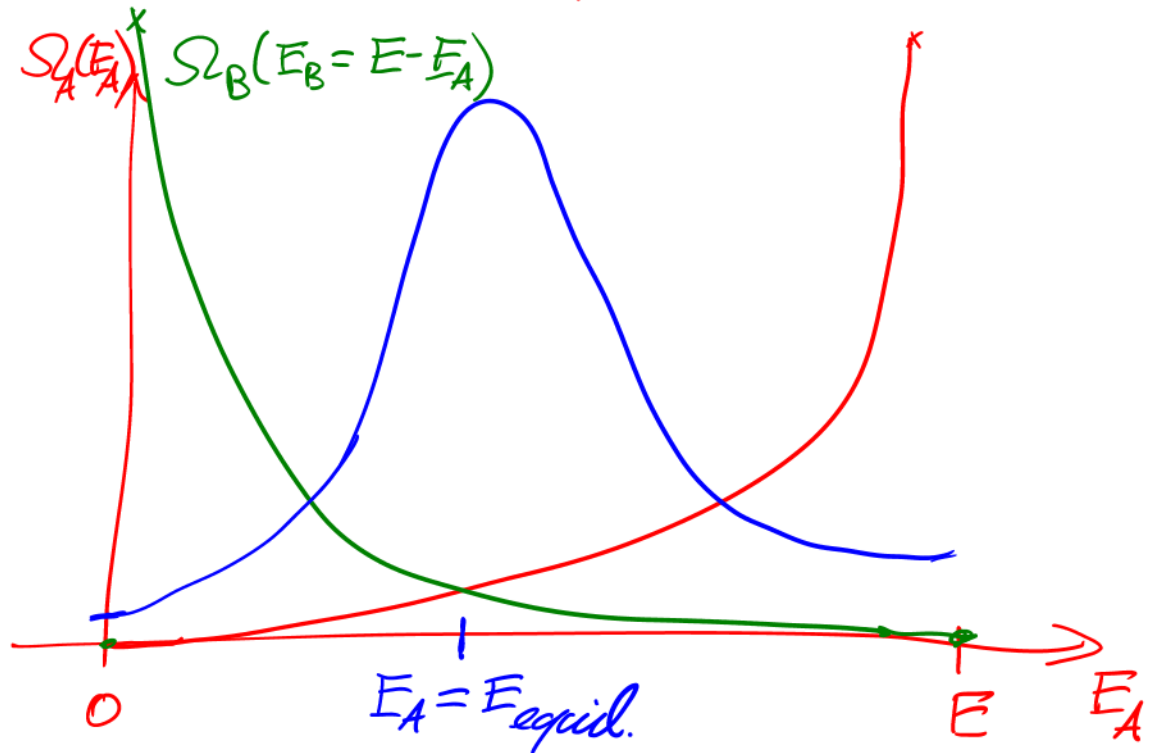
(zeroth law of thermodyn.)

all microstates are equally probable, even non-equilibrium situation

total $E = E_A + E_B$ conserved



$$\Omega(E_A, E_B) = \Omega_A(E_A)\Omega_B(E_B)$$



interpretation:

equilibrium state is "most likely"

2.5-2 Microcanonical equilibrium

Claim: equilibrium is overwhelmingly likely

Ideal gas $N_A = N_B = N$

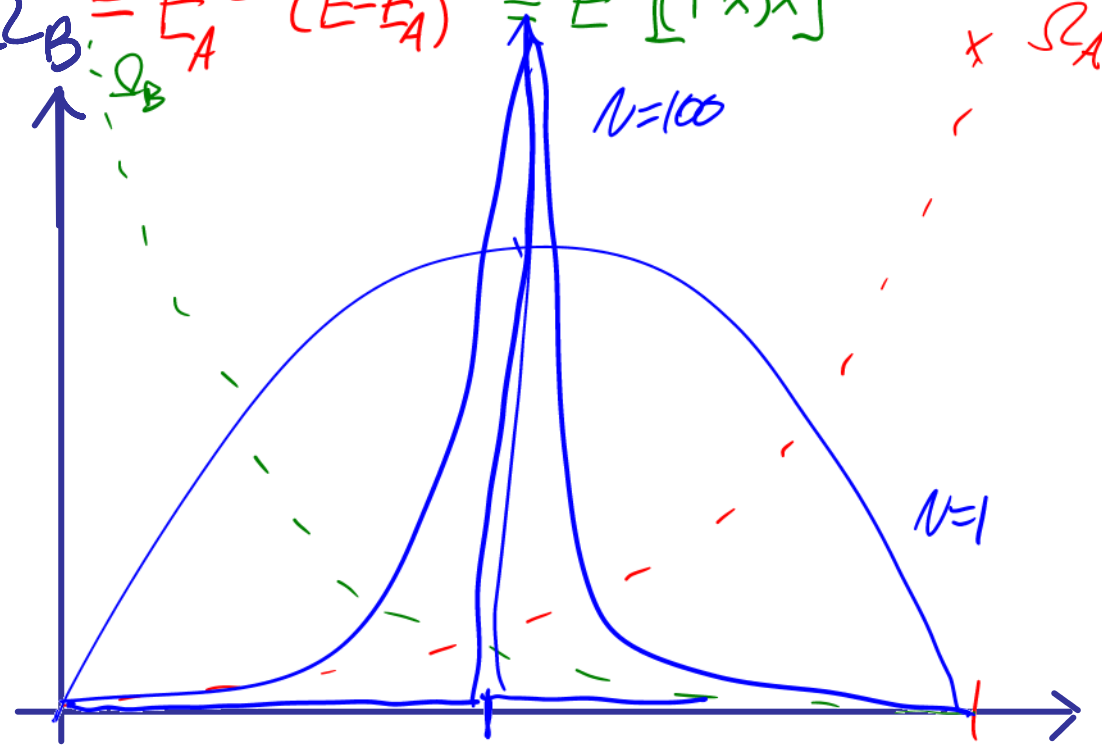
$$\Omega_A \propto E_A^{\frac{3}{2}N}$$

$$\Omega_B \propto E_B^{\frac{3}{2}N} = (E - E_A)^{\frac{3}{2}N}$$

In the limit of large systems, the maximum may become very sharp

$$\Omega = \Omega_A \Omega_B = E_A^{\frac{3}{2}N} (E - E_A)^{\frac{3}{2}N} = E^{\frac{3}{2}N} [(1-x)x]^{\frac{3}{2}N}$$

$$x = \frac{E_A}{E}$$



very sharp for $N \sim 10^{23}$ $x = 1/2$

$$E_A = E - E_B$$

2.5-3 Microcanonical equilibrium

Example: Two systems of three oscillators each $\varepsilon_j = \hbar\omega(n_j + 1/2)$, $j = 1, 2, 3, 4, 5, 6$

$$E = E_A + E_B = \sum_{j=1}^3 \varepsilon_j + \sum_{j=4}^6 \varepsilon_j$$

assume $R = R_A + R_B = 4$

$E = E_A + E_B = 7$ two fixed

R_A	R_B	Ω_A	Ω_B	$\Omega = \Omega_A \Omega_B$
0	4	1	15	15
1	3	3	10	30
2	2	6	6	36
3	1	10	3	30
4	0	15	1	15

→ most likely "equilibrium"

2.5-4 Microcanonical equilibrium

Mathematical condition for the maximum number of states $\Omega = \Omega_A(E_A) \Omega_B(E - E_A)$
 should be max as function E_A

$$0 = \frac{\partial \Omega}{\partial E_A} = \frac{\partial \Omega_A}{\partial E_A} \Omega_B + \Omega_A \frac{\partial \Omega_B}{\partial E_A}$$

$$\Omega_B(E_B) = \Omega_B(E - E_A)$$

$$= \frac{\partial \Omega_A}{\partial E_A} \Omega_B - \Omega_A \frac{\partial \Omega_B}{\partial E_B}$$

$$\frac{\partial \Omega_B}{\partial E_B} = - \frac{\partial \Omega_B}{\partial E_A}$$

$$\frac{1}{\Omega_A} \frac{\partial \Omega_A}{\partial E_A} = \frac{1}{\Omega_B} \frac{\partial \Omega_B}{\partial E_B}$$

equilibrium conditions

$$\beta_A = \frac{\partial \ln \Omega_A}{\partial E_A} = \frac{\partial \ln \Omega_B}{\partial E_B} = \beta_B \quad \text{equilibrium parameter } \beta$$

Remember $\left(\frac{\partial \Omega}{\partial E}\right)_{\text{rest}} = \frac{1}{T} = k_B \frac{\partial \ln \Omega}{\partial E}$

$$\Rightarrow \beta = \frac{1}{k_B T}$$

Equilibrium parameter

$$\beta = \frac{1}{k_B T}$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{rest}$$

Def. 2.8:

The temperature of a system is defined by the equilibrium parameter

$$\beta = \frac{1}{k_B T} = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{rest}$$

Therefore

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{rest}$$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV + \dots$$

Entropy is additive for indep. systems

$$\begin{aligned} S &= k_B \ln \Omega = k_B \ln \Omega_A \Omega_B = k_B (\ln \Omega_A + \ln \Omega_B) \\ &= S_A + S_B \end{aligned}$$