

1) Macroscopic and microscopic states

Macro: E, V, N $N \sim 10^{23}$

micro: $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, t)$

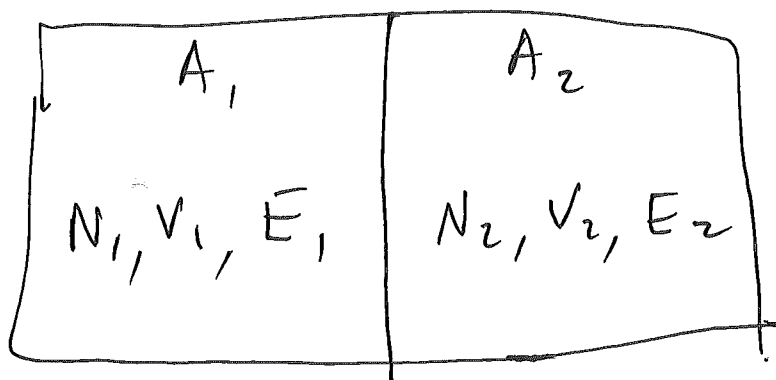
or $\vec{r}_1(t), \vec{p}_1(t), \dots, \vec{r}_N(t), \vec{p}_N(t)$

$\Omega(N, V, E) = \#$ of microstates
consistent with our knowledge
of macrostate

Principle of equal a priori
probabilities.

2) Contact between 2 systems

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$$A = A_1 + A_2$$

$$E = E_1 + E_2$$

$$N = N_1 + N_2$$

$$V = V_1 + V_2$$

$$\Omega = \Omega_1 \Omega_2$$

i) suppose A₁ & A₂ can exchange energy through a conductive partition.

Q: What is the most likely value of E₁ (and of E₂ = E - E₁)?

$$\Omega = \Omega_1(E_1) \Omega_2(E_2)$$

$$0 = \frac{d\Omega}{dE_1} = \frac{d\Omega_1}{dE_1} \Omega_2 + \Omega_1 \frac{d\Omega_2}{dE_2} \frac{dE_2}{dE_1}$$

$$E = E_1 + E_2 = \text{const.}$$

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$$0 = 1 + \frac{dE_2}{dE_1}, \quad \frac{dE_2}{dE_1} = -1$$

$$\Rightarrow 0 = \frac{d\Omega_1}{dE_1} \Omega_2 - \Omega_1 \frac{d\Omega_2}{dE_2}$$

$$\frac{1}{\Omega_1} \frac{d\Omega_1}{dE_1} = \frac{1}{\Omega_2} \frac{d\Omega_2}{dE_2}$$

$$\frac{d \ln \Omega_1}{dE_1} = \frac{d \ln \Omega_2}{dE_2}$$

cond. of max. probability

def. $\beta \equiv \left. \frac{\partial \ln \Omega(N, V, E)}{\partial E} \right|_{N, V}$

Entropy (Boltzmann)

$$S = k_B \ln \Omega$$

recall $\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{N, V}$

$\Rightarrow \beta = \frac{1}{k_B T}$ (inverse temperature)

(i) movable partition

$$\left. \frac{\partial \ln \Omega_1}{\partial V_1} \right|_{N_1, E_1} = \left. \frac{\partial \ln \Omega_2}{\partial V_2} \right|_{N_2, E_2}$$

$$\eta \equiv \left. \frac{\partial \ln \Omega(N, V, E)}{\partial V} \right|_{N, E}$$

(iii) permeable membrane

$$\left. \frac{\partial \ln \Omega_1}{\partial N_1} \right|_{V_1, E_1} = \left. \frac{\partial \ln \Omega_2}{\partial N_2} \right|_{V_2, E_2}$$

$$\xi \equiv \left. \frac{\partial \ln \Omega(N, V, E)}{\partial N} \right|_{V, E}$$

Thermodynamic relation

$$dE = T dS - P dV + \mu dN$$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\eta = \frac{P}{k_B T} \quad \xi = - \frac{\mu}{k_B T}$$

The most probable state in each case is referred to as the equilibrium state.

If the initial state differs from the equilibrium state, the system will relax toward the equilibrium (most probable) state.

i) Thermal equilibrium

$$T_1 = T_2$$

ii) Mechanical equilibrium

$$P_1 = P_2$$

iii) Diffusive equilibrium

$$\mu_1 = \mu_2$$

In place of the extensive variables N, V, E , we may wish to characterize the macrostate of the system by the corresponding intensive variables μ, P, T . This can be accomplished by a Legendre transformation:

def. $F = E - TS$
 Helmholtz free energy

$$\begin{aligned}
 dF &= dE - TdS - SdT \\
 &= (\cancel{TdS} - PdV + \mu dN) - \cancel{TdS} - SdT \\
 &= \mu dN - PdV - SdT \\
 F &= F(N, V, T) \quad (E \rightarrow T)
 \end{aligned}$$

$$\text{def. } \Omega = F - \mu N$$

Grand canonical potential

or

thermodynamic potential

$$d\Omega = \cancel{\mu dN} - p dV - S dT - \cancel{\mu dN} - N d\mu$$

$$\Omega = \Omega(\mu, V, T) \quad (N \rightarrow \mu)$$