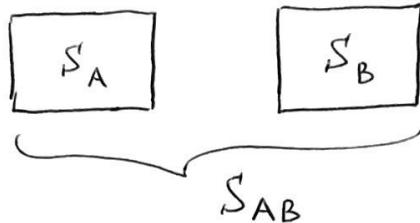


Lecture 8

Alternative derivation of equilibrium distribution functions

Start with $S = -k_B \sum_j P_j \log P_j$.



$$S_{AB} = -k_B \sum_{\substack{J_A, \\ J_B}} P_{AB}(J_A, J_B) \log P_{AB}(J_A, J_B) \quad \text{①}$$

" $P_A(J_A) P_B(J_B)$, indep. systems

$$\text{①} \Rightarrow -k_B \sum_{J_A} P_A(J_A) \log P_A(J_A) - k_B \sum_{J_B} P_B(J_B) \log P_B(J_B) \quad \text{②}$$

$\nearrow$
 $\sum_{J_A} P_A(J_A) = 1$, $\sum_{J_B} P_B(J_B) = 1$

$$\text{②} \Rightarrow S_A + S_B \quad \leftarrow \text{extensivity}$$

Conversely, if we impose $S_{AB} = S_A + S_B$,

$$S = \sum_j P_j f(P_j) = \langle f(P) \rangle \quad \text{has to have } f(P_j) = C \log(P_j), \text{ where } C = \text{const.}$$

Microcanonical ensemble: $E, N, V = \text{const}$

$$(SS)_{E, V, N} = 0 \quad , \quad S = \max \text{ @ equil.}$$

Vary S under the $\sum_j P_j = 1$ constraint:

$$\delta(S + \gamma(\sum_j P_j - 1)) = 0.$$

Note that this is the only constraint,

$$\text{since } \begin{cases} \langle E \rangle = \sum_j E_j P_j = E, \\ \langle N \rangle = \sum_j N_j P_j = N \text{ trivially.} \end{cases}$$

$\underbrace{E_j}_{=E}$
 $\underbrace{N_j}_{=N}$

$$\frac{\partial}{\partial P_i} \left[-k_B \sum_j P_j \log P_j + \gamma \sum_j P_j \right] =$$

$$= -k_B + \gamma - k_B \log P_i = 0, \text{ or}$$

$$\log P_i = \text{const} \Rightarrow P_i = \text{const}.$$

$$\sum_i P_i = 1 \text{ gives } P_i = \frac{1}{\underbrace{\Omega(N, E, V)}_{\substack{\# \text{ states} \\ \text{with } E, N, V}}} \text{ as before.}$$

$$\text{Finally, } P_i = \begin{cases} \Omega^{-1} & E_i = E \\ 0 & \text{otherwise} \end{cases}$$

$$S' = k_B \sum_{i=1}^{\Omega} \frac{1}{\Omega} \log \Omega = k_B \log \Omega \text{ as before.}$$

Canonical ensemble: $N, V, T = \text{const}$
 E fluctuates

Now, we need

$$\delta(S + \gamma(\sum_j P_j - 1) + \lambda(\sum_j P_j E_j - \langle E \rangle)) = 0, \quad \text{yielding}$$

$$\frac{\partial}{\partial P_i} \left[-k_B \sum_j P_j \log P_j + \gamma \sum_j P_j + \lambda \sum_j P_j E_j \right] =$$

$$= -k_B(1 + \log P_i) + \gamma + \lambda E_i = 0, \text{ or}$$

$$\log P_i = \frac{\lambda E_i + \gamma - k_B}{k_B}$$

$\Downarrow$

$$P_i \sim e^{\frac{\lambda E_i}{k_B}}$$

$$\sum_i P_i = 1 \Rightarrow P_i = \frac{e^{\frac{\lambda E_i}{k_B}}}{Q} \quad \text{where } Q = \sum_j e^{\frac{\lambda E_j}{k_B}}$$

$$\text{But then } S = -k_B \sum_i P_i \log P_i =$$

$$= -k_B \sum_i P_i \left[\frac{\lambda E_i}{k_B} - \log Q \right] =$$

$$= k_B \log Q - \lambda \langle E \rangle.$$

$$\left(\frac{\partial S}{\partial \langle E \rangle} \right)_{V, N} = \frac{1}{T} \Rightarrow \lambda = -\frac{1}{T}.$$

hence $P_i = \frac{e^{-\frac{E_i}{k_B T}}}{Q} \Leftarrow \text{Boltzmann distribution}$
 $\nwarrow$
 canonical partition function

Moreover,

$$k_B \log Q = S + \frac{\langle E \rangle}{T} = S - \frac{\langle E \rangle}{T}, \text{ or}$$

$$\underbrace{-k_B T \log Q}_{\text{free energy } A} = \langle E \rangle - T S$$

$$\hookrightarrow Q = e^{-\beta A} \Rightarrow P_i = e^{-\beta(E_i - A)}$$
$$[\log Q = -\beta A]$$

$\log Q$ (or A) tells us everything about the thermodynamics of the system.

$$\text{For ex., } \left(\frac{\partial (\log Q)}{\partial V} \right)_{T, N} = -\beta \underbrace{\left(\frac{\partial A}{\partial V} \right)_{T, N}}_{-p} = \beta p,$$

$$\left(\frac{\partial (\log Q)}{\partial \beta} \right)_{V, N} = -\langle E \rangle, \text{ etc.}$$

Systems of non-interacting particles

We need to compute $\sum_j e^{-\beta E_j}$ or $\sum_j e^{-\beta(E_j - \mu N_j)}$

The # states contributing appreciably to these sums grows with T , usually very rapidly.

Note that if $E_j = E_n^{(1)} + E_m^{(2)}$,
state label
" (n,m)

$$\begin{aligned} Q &= \sum_j e^{-\beta E_j} = \sum_{n,m} e^{-\beta(E_n^{(1)} + E_m^{(2)})} = \\ &= \left(\sum_n e^{-\beta E_n^{(1)}} \right) \left(\sum_m e^{-\beta E_m^{(2)}} \right) \equiv \underbrace{Q^{(1)} Q^{(2)}}_{\text{factorization}} \end{aligned}$$

—o—

$$\begin{aligned} \langle E^{(1)} E^{(2)} \rangle &= Q^{-1} \sum_{n,m} E_n^{(1)} E_m^{(2)} e^{-\beta(E_n^{(1)} + E_m^{(2)})} = \\ &= \left(\sum_n E_n^{(1)} \frac{e^{-\beta E_n^{(1)}}}{Q^{(1)}} \right) \left(\sum_m E_m^{(2)} \frac{e^{-\beta E_m^{(2)}}}{Q^{(2)}} \right) = \\ &= \langle E^{(1)} \rangle \langle E^{(2)} \rangle, \text{ no correlations.} \end{aligned}$$

If there are N identical uncorrelated systems, $Q = Q^{(1)} Q^{(2)} \dots Q^{(N)} = [Q^{(1)}]^N$.

Occupation numbers

Consider $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ = wavefunction for an N -part. system

If the particles are non-interacting,

Ψ will be a symmetric or antisymmetric
bosons fermions

product of $\underbrace{\Psi_1(\vec{r}), \Psi_2(\vec{r}), \dots}_{\text{single-particle wavefunctions}}$

E.g., with $N=2$

bosons: $\underbrace{\Psi(\vec{r}_1, \vec{r}_2)}_{\Psi(\vec{r}_2, \vec{r}_1)} = \frac{1}{\sqrt{2}} [\underbrace{\Psi_i(\vec{r}_1)}_{\substack{\uparrow \\ \text{single-particle} \\ \text{quantum state}}} \Psi_j(\vec{r}_2) + \Psi_i(\vec{r}_2) \Psi_j(\vec{r}_1)]$

$\int d^3r |\Psi_j(\vec{r})|^2 = 1, \forall j$

fermions: $\underbrace{\Psi(\vec{r}_1, \vec{r}_2)}_{\Psi(\vec{r}_2, \vec{r}_1)} = \frac{1}{\sqrt{2}} [\Psi_i(\vec{r}_1) \Psi_j(\vec{r}_2) - \Psi_i(\vec{r}_2) \Psi_j(\vec{r}_1)]$

Note that if $i=j$, $\Psi(\vec{r}_1, \vec{r}_2) = 0$
 $\Rightarrow$ Pauli exclusion principle

In general, a quantum state of a system of non-interacting particles is fully described by $(n_1, n_2, \dots, \underbrace{n_j}_{\substack{\text{\# particles} \\ \text{in state } j}}, \dots) = J$

Note that particles in the same state are completely indistinguishable.

Ex. $\begin{array}{c} \text{oo} \\ \hline \end{array} \alpha \quad n_\alpha = 2$
 $\begin{array}{c} \text{o} \\ \hline \end{array} \beta \quad n_\beta = 1$
 $N = 3 \Rightarrow J = (n_\alpha, n_\beta)$

$\underbrace{N_J}_{\substack{\text{total \# part. in} \\ \text{state } J}} = \sum_j n_j \quad (= 2 + 1 = 3 \text{ in the ex.})$

$E_J = \sum_j \epsilon_j n_j$
 $\quad \quad \quad \uparrow$
 $\quad \quad \quad \text{single-part. energy}$

Finally, fermions: $n_j = 0, 1$ only
bosons: $n_j = 0, 1, 2, \dots$