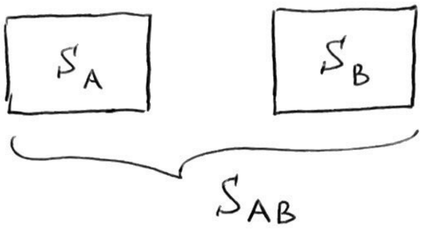
Lecture 8

Alternative derivation of equilibrium distribution functions

Start with $S = -k_B \sum_{\nu} P_\nu \log P_\nu$.



$$S_{AB} = -k_B \sum_{\substack{\nu_A,\\ \nu_B}} \underbrace{P_{AB}(\nu_A, \nu_B)}_{\overset{\shortparallel}{P_A(\nu_A)\, P_B(\nu_B)}\text{, indep. systems}} \log P_{AB}(\nu_A, \nu_B) \textcircled{=}$$

$$\textcircled{=} - k_B \sum_{\nu_A} P_A(\nu_A) \log P_A(\nu_A) - k_B \sum_{\nu_B} P_B(\nu_B) \log P_B(\nu_B) \boxed{=}$$

↗

$$\sum_{\nu_A} P_A(\nu_A) = 1 \ , \quad \sum_{\nu_B} P_B(\nu_B) = 1$$

$\boxed{=}\ S_A + S_B$ ← extensivity

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

$S = \sum_{\nu} P_\nu f(P_\nu) = \langle f(P) \rangle$ has to have $f(P_\nu) = C \log(P_\nu)$, where $C = \text{const}$.

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

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

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

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

Note that this is the only constraint,

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

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

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

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

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

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

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

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

Now, we need

$$\delta\left(S+\gamma\left(\sum_{\nu} P_{\nu}-1\right)+\alpha\left(\sum_{\nu} P_{\nu} E_{\nu}-\langle E\rangle\right)\right)=0,$$

yielding

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

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

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

$$\Downarrow$$

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

$$\sum_i P_i=1 \implies P_i=\frac{e^{\frac{\alpha E_i}{k_B}}}{\underbrace{Q}_{=\sum_j e^{\frac{\alpha E_i}{k_B}}}}.$$

But then $S=-k_B\sum_i P_i\log P_i=$

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

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

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

Hence $P_i=\dfrac{e^{-\frac{E_i}{k_BT}}}{Q}$ ⇐ Boltzmann distribution

↖ canonical partition function

Moreover,

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

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

$$\hookrightarrow \; Q = e^{-\beta A} \quad \Rightarrow \quad P_i = e^{-\beta(E_i - A)}$$

$$[\log Q = -\beta A]$$

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

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

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

Systems of non-interacting particles

We need to compute $\sum_{\nu} e^{-\beta E_\nu}$ or $\sum_{\nu} e^{-\beta(E_\nu - \mu N_\nu)}$

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

Note that if $\overset{\text{state label}}{\underset{\underset{(n,m)}{\shortparallel}}{E_\nu}} = E_n^{(1)} + E_m^{(2)}$,

$$Q = \sum_\nu e^{-\beta E_\nu} = \sum_{n,m} e^{-\beta(E_n^{(1)} + E_m^{(2)})} =$$

$$= \left(\sum_n e^{-\beta E_n^{(1)}}\right)\left(\sum_m e^{-\beta E_m^{(2)}}\right) \equiv \underbrace{Q^{(1)} Q^{(2)}}_{\text{factorization}}$$

* * *

$$\langle E^{(1)} E^{(2)} \rangle = Q^{-1} \sum_{n,m} E_n^{(1)} E_m^{(2)} e^{-\beta(E_n^{(1)} + E_m^{(2)})} =$$

$$= \left(\sum_n E_n^{(1)} \frac{e^{-\beta E_n^{(1)}}}{Q^{(1)}}\right)\left(\sum_m E_m^{(2)} \frac{e^{-\beta E_m^{(2)}}}{Q^{(2)}}\right) =$$

$$= \langle E^{(1)} \rangle \langle E^{(2)} \rangle$$, no correlations.

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

Occupation numbers

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

If the particles are non-interacting, Ψ_ν will be a $\underbrace{\text{symmetric}}_{\text{bosons}}$ or $\underbrace{\text{antisymmetric}}_{\text{fermions}}$

product of $\underbrace{\varphi_1(\vec{r}), \varphi_2(\vec{r}), \ldots}_{\text{single-particle wavefunctions}}$

E.g., with $N=2$

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

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

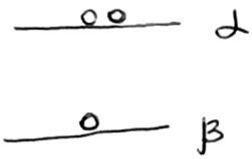
fermions:
$$\underbrace{\Psi(\vec{r}_1, \vec{r}_2)}_{=\,-\Psi(\vec{r}_2, \vec{r}_1)} = \frac{1}{\sqrt{2}}\left[\varphi_i(\vec{r}_1)\,\varphi_j(\vec{r}_2) - \varphi_i(\vec{r}_2)\,\varphi_j(\vec{r}_1)\right]$$

Note that if $i=j$, $\underset{\substack{\Uparrow\\ \text{pauli exclusion principle}}}{\Psi(\vec{r}_1, \vec{r}_2) = 0}$

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.



$n_\alpha = 2$ $\Rightarrow J = (n_\alpha, n_\beta)$

$n_\beta = 1$

$N = 3$

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

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

Finally, fermions: $n_j = 0, 1$ only

bosons: $n_j = 0, 1, 2, \dots$

Photon gas

$n = 0, 1, 2, \dots$ $$E_n = \left(n + \frac{1}{2}\right) \underbrace{\hbar \omega}_{\substack{\epsilon,\ \text{single-photon} \\ \text{energy}}}$$

Omit zero-point energy:

$$E_n \to n\hbar\omega = n\epsilon$$

For a spectrum of frequencies,

$$e^{-\beta A} = Q = \sum_J e^{-\beta E_J} = \sum_{\substack{n_1=0\\ n_2=0\\ \cdots\\ n_j=0\\ \cdots}}^{\infty} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)} ⊜$$

$\Uparrow$ Total # photons is indefinite: $\mu = 0$

$$\underline{\epsilon_j = \hbar\omega_j}$$

$$⊜ \prod_j \underbrace{\left(\sum_{n_j=0}^{\infty} e^{-\beta n_j \epsilon_j}\right)}_{\text{geom. series}} = \underline{\underline{\prod_j \frac{1}{1-e^{-\beta\epsilon_j}}}}.$$

Next, $\langle n_j \rangle = \dfrac{\sum_J n_j e^{-\beta E_J}}{\sum_J e^{-\beta E_J}} = \dfrac{\partial(\log Q)}{\partial(-\beta\epsilon_j)} =$

$$= \frac{\partial}{\partial(-\beta\epsilon_j)}\left\{-\sum_{j'}\log(1-e^{-\beta\epsilon_{j'}})\right\} =$$

$$= -\frac{-e^{-\beta\epsilon_j}}{1-e^{-\beta\epsilon_j}} = \underline{\underline{\frac{1}{e^{\beta\epsilon_j}-1}}}.$$

Planck distribution

Internal energy: $\overset{\langle E \rangle}{\overset{\shortparallel}{U}} = -\dfrac{\partial \log Q}{\partial \beta} =$

$$= \underline{\underline{\sum_j \underbrace{\epsilon_j}_{\hbar\omega_j} \langle n_j \rangle}}.$$