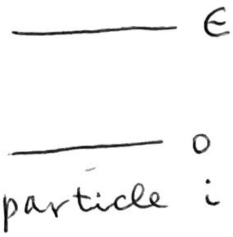
Lecture 7

Ex. N distinguishable indep. particles with a two-state energy spectrum:



$(i = 1, \dots, N)$

System state: $\nu = (n_1, \dots, n_N)$ $\quad n_i = (0, 1)$

$$E_\nu = \sum_{j=1}^{N} n_j \epsilon \quad \Rightarrow \quad E_\nu = \epsilon \underbrace{\left(\sum_{j=1}^{N} n_j\right)}_{\text{"}m\text{", the number of } n_j = 1 \text{ in the sum}}$$

<u>Microcanonical ensemble</u>:

$$\Omega(E, N) = \frac{N!}{(N-m)!\, m!} \leftarrow m = \frac{E}{\epsilon}$$

Next,
$$\begin{cases} S = k_B \log \Omega(E, N), \\ \beta = \left(\dfrac{\partial \log \Omega}{\partial E}\right)_N = \epsilon^{-1} \left(\dfrac{\partial \log \Omega}{\partial m}\right)_N \end{cases}$$

m assumed continuous

Stirling's approx.: $\log M! \underset{M \gg 1}{\simeq} M \log M - M$

Then
$$\frac{\partial}{\partial m} \log \frac{N!}{(N-m)!\, m!} \simeq -\frac{\partial}{\partial m}\Big[(N-m)\log(N-m) - (N-m) - m \log m + m\Big] = -\left[-\log(N-m) - \frac{N-m}{N-m} - \log m - 1 + 2\right] = \log\left(\frac{N}{m} - 1\right).$$

So, $\beta\epsilon = \log\left(\frac{N}{m} - 1\right)$, or

$$\frac{N}{m} = 1 + e^{\beta\epsilon} \Rightarrow \underbrace{\frac{m}{N}}_{\substack{\text{fraction of excited}\\ \text{states}}} = \frac{1}{1+e^{\beta\epsilon}}$$

Finally, $E = m\epsilon = \dfrac{N\epsilon}{1+e^{\beta\epsilon}}$ (*)

$T \to 0$: $E \to 0$ (ground state)

$T \to \infty$: $E \to \frac{N\epsilon}{2}$ (all states equally likely)

<u>Canonical ensemble</u>:

$$-\beta A = \log Q = \log\left(\sum_\nu e^{-\beta E_\nu}\right).$$

Then $Q(\beta, N) = \sum_{n_1,\ldots,n_N} e^{-\beta\sum_{j=1}^{N}\epsilon n_j} =$

$$= \prod_{j=1}^{N}\sum_{n_j=0,1} e^{-\beta\epsilon n_j} = \left(1+e^{-\beta\epsilon}\right)^N, \text{ giving}$$

$$-\beta A = \overbrace{N\log(1+e^{-\beta\epsilon})}^{\log Q}.$$

Finally, $\langle E\rangle = \left(\dfrac{\partial\log Q}{\partial(-\beta)}\right)_N = N\dfrac{\epsilon e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}} =$

$$= \frac{N\epsilon}{1+e^{\beta\epsilon}}, \text{ just as (*) above.}$$

recall that $N \gg 1$ in the microcanonical ensemble

Generalized ensembles

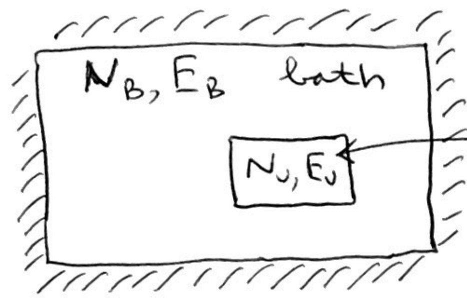
Recall that $dE = T\,dS + \vec{f}\cdot d\vec{X}$, or

$$\underbrace{k_B^{-1}\,dS}_{d(\log\Omega)} = \beta\,dE \underbrace{-\beta\vec{f}}_{``\vec{\xi}"}\cdot d\vec{X} \qquad (++)$$

$\Rightarrow$ if $X = N$, $f = \mu$ and $\xi = -\beta\mu$, etc.

Now imagine a system in which both E & X (e.g., both E & N) can fluctuate:

T=const (equil.)



system << bath but macroscopic

$$\begin{cases} E_\nu \ll E \\ N_\nu \ll N \end{cases} \qquad \begin{cases} E = E_\nu + E_B = \text{const}, \\ N = N_\nu + N_B = \text{const} \end{cases}$$

Then $\underbrace{P_\nu}_{\text{prob. to observe system in state } \nu} \sim \Omega(E - E_\nu, N - N_\nu) = e^{\log\Omega(E-E_\nu, N-N_\nu)} \approx$

$$\approx e^{\log\Omega(E) - E_\nu \underbrace{\frac{d\log\Omega}{dE}}_{``\beta" \text{ from before}} - N_\nu \underbrace{\frac{d\log\Omega}{dN}}_{-\beta\mu}} \sim$$

$$\sim e^{-\beta E_\nu + \beta\mu N_\nu}.$$

$$\sum_\nu P_\nu = 1 \Rightarrow P_\nu = \frac{e^{-\beta E_\nu + \beta\mu N_\nu}}{\Sigma}, \text{ where}$$

$$\Sigma = \sum_\nu e^{-\beta(E_\nu - \mu N_\nu)}$$ is the grand canonical partition function.

$\Sigma = \Sigma(\beta, \mu, V)$ since $E_\nu = E_\nu(V)$

More generally,

$$\begin{cases} P_\nu = \dfrac{e^{-\beta E_\nu - \xi X_\nu}}{\Sigma}, \\ \Sigma = \sum_\nu e^{-\beta E_\nu - \xi X_\nu}. \end{cases}$$

$$\langle E \rangle = \sum_\nu P_\nu E_\nu = \left(\frac{\partial \log \Sigma}{\partial(-\beta)} \right)_{\xi, X_\nu}$$

$$\langle X \rangle = \sum_\nu P_\nu X_\nu = \left(\frac{\partial \log \Sigma}{\partial(-\xi)} \right)_{\beta, E_\nu}$$

But then $d(\log \Sigma) = -\langle E \rangle d\beta - \langle X \rangle d\xi$.

Now, if we define $\tilde{S} = -k_B \sum_\nu P_\nu \log P_\nu$,

we obtain: $\tilde{S} = -k_B \sum_\nu P_\nu \left[-\beta E_\nu - \xi X_\nu - \log \Sigma \right] =$

$= k_B \left[\log \Sigma + \beta \langle E \rangle + \xi \langle X \rangle \right]$.

So, $\tilde{S}$ is the Legendre transform of

$\log \Sigma$: $d\tilde{S} = k_B d(\log \Sigma) + k_B \left[d\beta \langle E \rangle + \beta d\langle E \rangle + \right.$

$\left. + d\xi \langle X \rangle + \xi d\langle X \rangle \right] = \underline{-k_B \langle E \rangle d\beta} - \underline{k_B \langle X \rangle d\xi} +$

$+ \underline{k_B \langle E \rangle d\beta} + k_B \beta d\langle E \rangle + \underline{k_B \langle X \rangle d\xi} + k_B \xi d\langle X \rangle =$

$= k_B \beta d\langle E \rangle + k_B \xi d\langle X \rangle$

$k_B^{-1} d\tilde{S}$ = RHS from Eq. (++)

Thus, $\tilde{S}$ is in fact $= S$ and

$$\boxed{S = -k_B \sum_\nu P_\nu \log P_\nu}$$ gibbs entropy formula

For the grand canonical ensemble,
we have:

$$S = -k_B \sum_\nu P_\nu \left[-\log \Sigma - \beta E_\nu + \beta \mu N_\nu\right] =$$

$$= k_B \log \Sigma + \underbrace{k_B \beta}_{\frac{1}{T}} \underbrace{\langle E \rangle}_{\text{"}TS - pV + \mu N} - \overbrace{k_B \beta}^{1/T} \mu \langle N \rangle \quad \text{, or}$$

$$k_B \log \Sigma - \frac{p}{T} V + \cancel{\frac{\mu}{T} N} - \cancel{\frac{\mu}{T} \langle N \rangle} = 0,$$

$$\underline{\log \Sigma = \beta p V}$$

Fluctuations: $\langle (\delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 =$

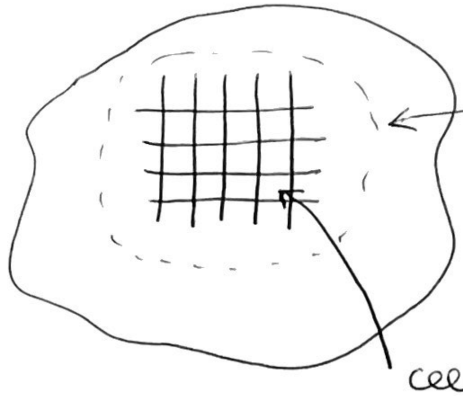
$$= \left(\frac{\partial \langle N \rangle}{\partial (\beta \mu)} \right)_{\beta, V} = \left(\frac{\partial^2 \log \Sigma}{\partial (\beta \mu)^2} \right)_{\beta, V}.$$

Since $\langle (\delta N)^2 \rangle \geq 0 \Rightarrow \left(\frac{\partial \langle N \rangle}{\partial (\beta \mu)} \right)_{\beta, V} \geq 0$, or

$\frac{\partial \langle N \rangle}{\partial \mu} \geq 0$, same as $\frac{\partial n}{\partial \mu} \geq 0$
from thermodynamic stability

Consider

$N_{tot} = \text{Const}$



Cells are small + density is low: only 0 or 1 particle per cell.

$$\begin{cases} n_i = 1 & \text{if a particle is in cell } i \\ n_i = 0 & \text{otherwise} \end{cases}$$

$(n_1, n_2, \dots, n_m)$ fully describes the region of interest

$$N = \sum_{i=1}^{m} n_i \quad , \quad \text{yielding}$$

$$\langle (\delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = \sum_{i,j=1}^{m} \left[\langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle \right]$$

Uncorrelated particles: $\langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle, \quad i \neq j$

Low density: $\langle n_i \rangle \ll 1 \; , \forall i$

Finally,

$$\langle n_i^2 \rangle = \langle n_i \rangle = \underbrace{\langle n_1 \rangle}_{\text{by cell equivalence}}$$

Then $$\langle (\delta N)^2 \rangle = \sum_{i=1}^{m} \left[\langle n_i^2 \rangle - \langle n_i \rangle^2 \right] =$$

$$= m \langle n_1 \rangle (1 - \langle n_1 \rangle) \underset{\langle n_1 \rangle \ll 1}{\simeq} m \langle n_1 \rangle = \langle N \rangle.$$

But $\langle (\delta N)^2 \rangle = \left(\frac{\partial \langle N \rangle}{\partial(\beta\mu)} \right)_{\beta, V} = \langle N \rangle$.

Further, $\left(\frac{\partial \rho}{\partial(\beta\mu)} \right)_{\beta, V} = \rho$, or

$\frac{\langle N \rangle}{V} = \rho$

$$\left(\frac{\partial(\beta\mu)}{\partial \rho} \right)_{\beta} = \rho^{-1}.$$

$$\Downarrow$$

$$\beta\mu = \log \rho + \text{const}.$$

Now, from (1.14) we have:

$$\left(\frac{\partial \mu}{\partial v} \right)_T = v \left(\frac{\partial p}{\partial v} \right)_T, \text{ or}$$

$v = \rho^{-1}$

$$\left(\frac{\partial \mu}{\partial(\frac{1}{\rho})} \right)_T = \frac{1}{\rho} \left(\frac{\partial p}{\partial(\frac{1}{\rho})} \right)_T,$$

$$\left(\frac{\partial p}{\partial \rho} \right)_\beta = \rho \left(\frac{\partial \mu}{\partial \rho} \right)_\beta.$$

But then $\left(\frac{\partial(\beta p)}{\partial \rho} \right)_\beta = \rho \underbrace{\left(\frac{\partial(\beta\mu)}{\partial \rho} \right)_\beta}_{\rho^{-1}} = 1,$

$$\beta p = \rho + \cancel{\text{const}}$$ since $p \to 0$ as $\rho \to 0$

$$\Downarrow$$

$$\boxed{pV = nRT}$$, ideal gas law

$R = k_B N_0$, N_0 = Avogadro's #

In summary, for a one-component system at low density (s.t. there are no correlations):

$$\begin{cases} \rho \sim e^{\beta\mu}, \\ \dfrac{\beta P}{\rho} = 1 \end{cases}$$