Recap from L10

① Microcanonical ensemble (fixed E, V, N)

$$p(i) = \frac{1}{\Omega(E,V,N)} \quad ; \quad S = k_B \log \Omega(E,V,N)$$

$$F_{MC} = E - TS(E,V,N)$$

② Canonical Ensemble (fixed T, V, N)

$$p(i) = \frac{e^{-\beta E_i}}{Z}$$

$$Z = \sum_i e^{-\beta E_i} = e^{-\beta F_c}$$

$$F_c = -\frac{1}{\beta} \log Z$$

$$S = -k_B \sum_i p(i) \log p(i)$$

* Showed for large N,

$$e^{-\beta F_c} = \sum_i e^{-\beta E_i} = \sum_E{}' e^{-\beta\left(E_i - \frac{1}{\beta}\log \Omega(E)\right)} = \sum_E{}' e^{-\beta F_{MC}(E)} \approx e^{-\beta F_{MC}(E^*)}$$

$\therefore$ CE/MCE equivalent for large N

③ Grand Canonical Ensemble (fixed T, V, μ)

$$\rho(i,N) = \frac{1}{Z_{GCE}} e^{-\beta(E_i - \mu N)}$$

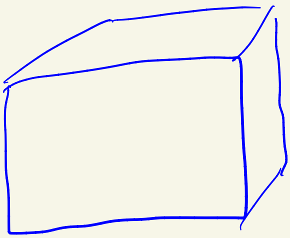
where $$Z_{GCE} = \sum_N \sum_{i(N)} e^{-\beta(E_i - \mu N)} = e^{-\beta \mathcal{G}(T,V,\mu)}$$

$$d\mathcal{G} = -S\,dT - P\,dV - N\,d\mu \quad \text{(grand potential)}$$

* As before, you can show for macroscopic systems ($N \to \infty$), the sum for Z_{GCE} sharply peaked at N^*, E^*

$$\Rightarrow \quad \underline{\underline{MCE \simeq CE \simeq GCE}}$$

Ideal Gas (Canonical Ensemble)



large box $V = L^3$
with N free particles

$$\hat{H} = \sum_{j=1}^{N} \frac{\vec{p}_j^{\,2}}{2m} \Rightarrow \Psi(\vec{x}_1, \vec{x}_2, \ldots \vec{x}_N) = \psi(\vec{x}_1)\,\psi(\vec{x}_2) \cdots \psi(\vec{x}_N)$$

(No assumptions on identical particles or Bose/Fermion symmetry of Ψ. More on this later...)

$$\Psi_\alpha(\vec{x}_1, \ldots \vec{x}_N) = (x) \prod_{i=1}^{N} \sin k_i^x x_i \, \sin k_i^y y_i \, \sin k_i^z z_i$$

where the box B.C.'s enforce quantized wave vectors

$$\vec{k}_j = \frac{\pi}{L}\left(n_j^x, n_j^y, n_j^z\right) \qquad n_j^x = 1, 2, 3, \ldots \text{ etc.}$$

$$E_\alpha = \frac{\hbar^2}{2m} \sum_{j=1} \vec{k}_j^{\,2}$$

(here α is shorthand for the $(\vec{n}_1, \vec{n}_2, \ldots \vec{n}_N)$
where $\vec{n}_1 = (n_1^x, n_1^y, n_1^z)$ etc.)

Technical aside:

* We often have sums like $\sum_{n_x n_y n_z} f\left(\frac{\pi}{L}n_x, \frac{\pi}{L}n_y, \frac{\pi}{L}n_z\right)$

* For large L, $\frac{\pi}{L}n_x$ & $\frac{\pi}{L}(n_x+1)$ are very close to each other

$\therefore$ $\Delta n = 1$ results in a small/infinitesimal change in $\vec{k}$

$\Downarrow$

Suggests $\displaystyle\sum_{n=1}^{\infty} f\left(\frac{\pi}{L}n\right) \simeq \int_0^{\infty} dn\, f\left(\frac{\pi}{L}n\right)$

$$= \int_0^{\infty} \frac{dn}{dk} dk\, f(k)$$

$$= \frac{L}{\pi}\int_0^{\infty} dk\, f(k)$$

$$= \frac{L}{2\pi}\int_{-\infty}^{\infty} dk\, f(k)$$

letting $p = \hbar k$

$$\boxed{\Rightarrow \sum_{n=1}^{\infty} f\left(\frac{\pi}{L}n\right) \longrightarrow L\int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} f(p)}$$

we'll use this dictionary over & over to convert $\vec{k}$-mode sums to integrals

Partition function

$$Z_N = \sum_\alpha e^{-\beta E_\alpha} = \sum_{\vec{n}_1 \vec{n}_2 \cdots \vec{n}_N} e^{-\beta(\varepsilon_{\vec{n}_1} + \varepsilon_{\vec{n}_2} + \cdots + \varepsilon_{\vec{n}_N})}$$

where $\varepsilon_{\vec{n}} = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$

$$\therefore Z_N = \sum_{\vec{n}_1} e^{-\beta \varepsilon_{\vec{n}_1}} \times \sum_{\vec{n}_2} e^{-\beta \varepsilon_{\vec{n}_2}} \times \cdots \sum_{\vec{n}_N} e^{-\beta \varepsilon_{\vec{n}_N}}$$

$$= \left[\sum_{\vec{n}} e^{-\beta \varepsilon_{\vec{n}}}\right]^N$$

$$\boxed{Z_N = (Z_1)^N}$$

$$\therefore Z_1 = \sum_{n_x n_y n_z} e^{-\beta \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)}$$

$$Z_1 = \left[\sum_n e^{-\beta \frac{\hbar^2 \pi^2}{2mL^2} n^2}\right]^3 = (Z_{1,x})^3$$

$$Z_{1,x} = \sum_n e^{-\beta \frac{\hbar^2 \pi^2}{2mL^2} n^2} \longrightarrow \frac{L}{2\pi\hbar}\int_{-\infty}^{\infty} dp\, e^{-\frac{\beta p^2}{2m}}$$

$$\Rightarrow \boxed{Z_{1,x} = \frac{L}{2\pi\hbar} \times \sqrt{\frac{2m\pi}{\beta}} = \frac{L}{2\pi\hbar}\sqrt{2\pi m k_B T}}$$

$$\therefore \quad Z_N = \left(Z_{1,x}\right)^{3N}$$

$$= \left(\frac{L}{2\pi\hbar}\right)^{3N} \times \left(2\pi k_B T m\right)^{3N/2}$$

$$= L^{3N} \times \left[\sqrt{\frac{2\pi k_B T m}{(2\pi\hbar)^2}}\right]^{3N}$$

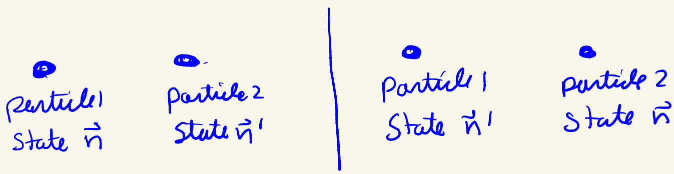
$$= L^{3N} \times \left[\sqrt{\frac{k_B T m}{2\pi \hbar^2}}\right]^{3N}$$

$$\boxed{Z_N = \left(\frac{L}{l_Q}\right)^{3N} = \left(\frac{V}{l_Q^3}\right)^N \qquad l_Q \equiv \sqrt{\frac{2\pi\hbar^2}{k_B T m}}}$$

"Thermal de-Broglie wavelength"

expect QM effects to dominate when particle spacing $\lesssim l_Q$

* So far, we've not worried about the identity of the N particles (i.e., we know from QM if they are identical, then they are <u>indistinguishable</u>, so that



are <u>not</u> distinct states

* Therefore, we expect for identical particles our Z_N above runs afoul of this.

Ad Hoc Correction

$$Z_N = \sum_\alpha e^{-\beta E_\alpha} = \sum_{\vec{n}_1 \vec{n}_2 \cdots \vec{n}_N} e^{-\beta(\varepsilon_{\vec{n}_1} + \varepsilon_{\vec{n}_2} + \cdots + \varepsilon_{\vec{n}_N})}$$

unrestricted sum "overcounts" states that merely differ by permutations of the particle labels

If the system is dilute $\left(\frac{V}{N}\right)^{1/3} \gg \ell_Q$ and at high T so that most s.p. states are unoccupied, and those that are have at most 1 particle in them, then an approximate fix is

$$Z_N \longrightarrow \frac{1}{N!} Z_N$$

$$\boxed{\therefore\ Z_N^{\text{corrected}} = \frac{1}{N!}\left(\frac{V}{\ell_Q^3}\right)^N}$$

for N identical particles

*Later, when we introduce statistical ensembles in QM Hilbert space, we'll see how to handle this issue exactly (i.e., not just for dilute & high T)

$$F = -k_B T \log Z = k_B T N \log\left(\frac{\ell_\alpha^3}{V}\right) + \underbrace{k_B T N \log N - k_B T N}_{\text{from } \frac{1}{N!} \text{ correction (applied Stirling's approx.)}}$$

* Now it's just a matter of taking derivatives of F to get TD props

$\Downarrow$

Omitting the intermediate algebra (you fill it in!)
(Setting $k_B = 1$)

$(n = \frac{N}{V})$

① $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = N\left(\frac{5}{2} - \log\left[n \ell_\alpha^3\right]\right)$

② $E = F + TS = \frac{3}{2} N T$

③ $P = -\left(\frac{\partial F}{\partial T}\right)_{T,N} = \frac{NT}{V}$

④ $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = T \log\left[n \ell_\alpha^3\right]$

⑤ $C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{3}{2} N$

⑥ $C_P = \frac{\partial}{\partial T}(E + PV)\Big|_P = \frac{5}{2} N$

⑦ $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} = \frac{1}{P}$

⑧ $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = \frac{N}{PV} = \frac{1}{T}$

Note 1: $S = N\left(\frac{5}{2} - \log[n\ell_Q^3]\right) < 0$ (Unphysical!)

when $\log[n\ell_Q^3] > \frac{5}{2}$

or

$$\boxed{n > e^{5/2}\ell_Q^{-3}}$$

This goes back to our ad hoc $\frac{1}{N!}$ correction to Z_N.
This approximate correction only works if $\langle n_{\vec{k}} \rangle \ll 1$
(here $n_{\vec{k}}$ = occupation # for s.p. state $\vec{k}$)
which is a dilute/high T regime.

Note 2: The V dependence of Z_N is independent of the s.p. dispersion relation $\epsilon(\vec{p}) = \frac{p^2}{2m}$

$\Downarrow$

expect any non-interacting gas w/ general $\epsilon(\vec{p})$ to obey

$$-T\log Z_N = -NT\log V + g(N,T)$$

$\Downarrow$

$$\boxed{-\left(\frac{\partial F}{\partial V}\right)_{T,N} = P = \frac{NT}{V} \quad \text{for \underline{any} non-int } \epsilon(\vec{p})}$$

Note 3: Can also think about the thermal average of some function of the velocity of one particle

$$\langle g(\vec{v}_i)\rangle = \frac{\int d^3\vec{p}_i\, g(\vec{v}_i)\, e^{-\beta \frac{\vec{p}_i^{\,2}}{2m}}}{\int d^3\vec{p}_i\, e^{-\beta\frac{\vec{p}_i^{\,2}}{2m}}}$$

$$= \int d^3\vec{v}_i\, g(\vec{v}_i) \underbrace{\left(\frac{m}{2\pi T}\right)^{3/2} e^{-\beta m \vec{v}_i^{\,2}/2}}_{}$$

$\rho(\vec{v}_i)$ = Maxwell-Boltzmann distribution for velocities in a gas

Note 4: Mixing Entropy + Gibbs Paradox

* If we don't make the $\frac{1}{N!}$ correction, (i.e., distinguishable particles)

$$S_{dist} = N\left[\frac{5}{2} - \log(n\ell_\alpha^3)\right] + N\log\left(\frac{N}{e}\right) \qquad (X)$$

$\Rightarrow$ Non-extensive due to term

* Imagine putting 2 boxes w/ $N_1 = N_2 = N$, $S_1 = S_2$, $V_1 = V_2$ together + removing a partition so they can mix (using eq. (X))

$$S_{TOT} = 2N\left[\frac{5}{2} - \log(n\ell_\alpha^3)\right] + 2N\log\left(\frac{2N}{e}\right)$$

$$= S_{①} + S_{②} + \underbrace{2N\log(2)}_{\text{“entropy of mixing”}}$$

* implies that removing the partition & letting the gas mix is irreversible (since $S_{TOT} > S_{①} + S_{②}$)

* Intuitively, one would expect this to be reversible (if the 2 boxes of gas are identical in all respects) since we could just close the partition & we're back to where we started.

This "paradox" is what led Gibbs to postulate the ad-hoc $\frac{1}{N!}$ correction factor

* On the other hand, if the particles truly are distinguishable (e.g. each box has N particles all of different species), then $S_{TOT} > S_{①} + S_{②}$ makes sense since our ignorance of the state has truly increased (i.e., before mixing we knew which particles were in box 1 & which ones were in 2, but after mixing we don't know this.)

Ensembles in Classical Phase Space

* all we've done so far has kind of assumed discrete QM microstates.

* But SM was developed well before QM came into being.

* How can we develop SM working entirely in classical phase space?

* Microstate $(q_1 \ldots q_{3N}, p_1 \ldots p_{3N})$ at some time t evolves via

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

* as before, we expect an enormous # of microstates (points in 6N-dim phase space) to be consistent w/a given macrostate.

* Imagine $\mathcal{N} \to \infty$ mental copies of these microstates distributed as a swarm of points in phase space.

let $\boxed{\rho(q,p;t)\, d^3q_1 \ldots d^3q_N\, d^3p_1 \ldots d^3p_N = \text{\# of points in volume about } (p,q)}$

Then the ensemble avg. of some qty. $f(q,p)$

$$\boxed{\langle f(t)\rangle = \frac{\int d^{3N}p\, d^{3N}q\, f(q,p)\, \rho(q,p;t)}{\int d^{3N}p\, d^{3N}q\, \rho(q,p;t)}}$$

∗ any function of (q,p) evolves via

$$\frac{d}{dt} f(q,p) = \frac{\partial f}{\partial t} + \sum_i \frac{\partial f}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial f}{\partial p_i}\frac{dp_i}{dt}$$

$$= \frac{\partial f}{\partial t} + \sum_i \frac{\partial f}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}$$

$$= \frac{\partial f}{\partial t} + \{f, \mathcal{H}\}_{PB}$$

poisson bracket

∴ We can ask how our swarm of ensemble members moves about in 6N-dim PS.