*Recap from L9

Use statistical ensembles (many mental copies of the system that have the same specified macro properties, but in different microstates)

$$\boxed{\begin{aligned} p_i &= \text{probability a randomly drawn system from ensemble is in microstate } i \\ \langle O \rangle &= \sum_i p_i O_i \end{aligned}}$$

① Microcanonical (fixed E, V, N)

$$P(i) = \begin{cases} \frac{1}{\Omega(E,V,N)} & \text{if } i \text{ has } E_i = E,\ V_i = V,\ N_i = N \\ 0 & \text{else} \end{cases}$$

$$S(E,V,N) = k_B \log \Omega(E,V,N)$$

② Canonical (fixed T, V, N)

$$P(i) = \frac{1}{Z} e^{-\beta E_i} \qquad \left(\beta = \frac{1}{k_B T}\right)$$

$$Z = \sum_j e^{-\beta E_j} \qquad \text{"Partition function"}$$

Connecting common quantities from thermodynamics to microscopic statistical mechanics (focus on canonical ensemble)

TD Property	in Stat. Mech. language
① Internal Energy E	$\langle E \rangle = \frac{1}{Z} \sum_i E_i e^{-\beta E_i}$ $= -\frac{\partial}{\partial \beta} \log Z$
② Helmholtz $F = E - TS$	$F = -\frac{1}{\beta} \log Z$
③ Pressure $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$	$P = \frac{1}{Z} \sum_i -\left(\frac{\partial E_i}{\partial V}\right) e^{-\beta E_i}$ $= \sum_i -\left(\frac{\partial E_i}{\partial V}\right) p(i)$ $= \sum_i P_i \, p(i)$ i.e., $P =$ avg. of $-\left(\frac{\partial E_i}{\partial V}\right)$ over ensemble
④ Entropy $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$	$S = -k_B \sum_i p(i) \log p(i)$

* We ended by trying to understand the meaning of

$$\otimes \quad \boxed{S = -k_B \sum_i p(i) \log p(i)} \qquad \left(p(i) = \frac{1}{Z} e^{-\beta E_i} \right)$$

* We showed that if we pretend all $E_i = E^*$, then we recover the Boltzmann/Microcanonical result that $S = k_B \log \Omega(E^*)$.

$\therefore$ Eq. $\otimes$ seems to be the natural extension from a closed system at fixed E, to a system at fixed T that can sample all possible E_i with probability $p(i)$.

To <u>really</u> drive this home, let's show that eqn. $\otimes$ is consistent with

$$T\,dS = đQ$$

as demanded by thermodynamics

proof that $TdS = đQ$ for $S = -k_B \sum_i p(i) \log p(i)$

Consider $E_{TD} = \langle E \rangle = \sum_i p(i) E_i$

$$dE_{TD} = \sum_i \left(dp(i) E_i + p(i) dE_i \right)$$

$$= đQ - PdV \quad \text{(by 1st Law)}$$

* Intuitively, we expect if we <u>fix V</u> but heat/cool the system, the energy levels won't change (after all, what does $H\psi = E\psi$ know about temperature)

but $p(i)$ <u>will change</u> (Since T changes & thus $e^{-\beta E_i}$ changes)

$$\Rightarrow \boxed{đQ = \sum_i dp(i) E_i}$$

* Now if we <u>quasi-statically</u> change V (want it slow so there's no transitions and so $p(i)$ doesn't change), then

$$-PdV = \sum_i p(i) dE_i = \sum_i p(i) \frac{\partial E_i}{\partial V} dV$$

$$\Rightarrow \boxed{đW = -PdV = \sum_i p(i) \left(-P_i \right) dV}$$

OK. Back to TdS:

$$TdS = -k_B T \sum_i \left[dp_i \log p_i + \cancel{p_i} \frac{dp_i}{\cancel{p_i}} \right]$$

* but must have $\sum_i dp_i = 0$ by cons. of probability

$$\therefore TdS = -k_B T \sum_i dp_i \log p_i$$

$$= \sum_i dp_i \left(E_i + \frac{1}{\beta} \log Z \right)$$

Since $p_i = \frac{1}{Z} e^{-\beta E_i}$
$\Rightarrow \log p_i = -\beta E_i - \log Z$

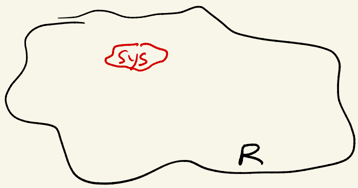
$$= \sum_i dp_i E_i$$ (since $\sum_i dp_i = 0$ once more)

$\therefore$ We see that our microscopic Stat. Mech. definitions for $S = -k_B \sum_i p_i \log p_i$ and $đQ = \sum_i dp_i E_i$ are consistent with the general TD relation $đQ = TdS$.

$$\boxed{\begin{array}{l}\textbf{Bottom line:} \text{ Our SM def. } F = -k_B T \log Z \\ \text{+ corresponding expressions for } S, P \\ đQ, đW, dE \text{ are all consistent} \\ \text{with TD relations, but with} \\ \text{a much deeper microscopic} \\ \text{underpinning} \end{array}}$$

Equivalence of Canonical + Microcanonical Ensembles as $N \to \infty$

* In our derivation of $p(i)$ for the canonical ensemble, no assumptions were made on the size of our system that is connected to a much larger heat bath or reservoir



i.e, the system S could be a single or a few particles

* Now let's see what happens when we take S macroscopic (i.e, $N >> 1$, say $N \sim 10^{23}$ or something)

$$Z = \sum_i e^{-\beta E_i} = {\sum_E}' \Omega(E)\, e^{-\beta E}$$

Sum over distinct quantum states i

Sum over distinct energy levels

degeneracy / multiplicity for each level E

* $\Omega(E)$ rapidly grows with N $(\sim E^N)$
* $e^{-\beta E}$ rapidly shrinks with N (since $E \sim N$)

$\therefore$ There will be some sharp maximum at energy E^*

i.e., E^* maximizes $e^{-\beta E}\, \Omega(E) = e^{-\beta\left(E - \frac{1}{\beta}\log \Omega(E)\right)}$

or minimizes $E - T k_B \log \Omega(E)$ — where have we seen this before?

* Extremum condition to find E^*

$$\frac{d}{dE}\left(E - TK_B \log \Omega(E)\right)\Big|_{E=E^*} = 0$$

$$\Rightarrow \frac{d}{dE}\log \Omega(E)\Big|_{E=E^*} = \beta$$

(i.e., just the condition we derived for equilibrium if put 2 closed systems in thermal contact)

* So then,

$$Z = \sum_E{}' \Omega(E) e^{-\beta E} = \sum_E{}' e^{-\beta(E - TK_B \log \Omega(E))}$$

$$= \sum_E{}' e^{-\beta F_{\text{microcan}}(E)} = e^{-\beta F}$$

$$F_{\text{microcan}}(E) = E - TS_{\text{microcan}} = E - T K_B \log \Omega(E)$$

(aka Landau free energy F_L)

* Now, separating out the maximal term at E^*

$$\boxed{Z = e^{-\beta F} = e^{-\beta F_L(E^*)} + \sum_{E \neq E^*}{}' e^{-\beta F_L(E)}}$$

* Everything is exact so far. But noting that

(1) $F_L(E) \propto N$ (extensive)

(2) we're assuming $N \sim 10^{23}$ (macroscopic system)

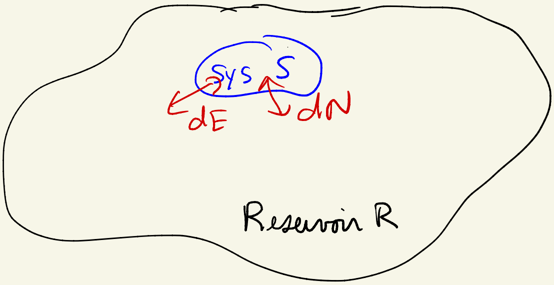
$$\Rightarrow \boxed{Z = e^{-\beta F} \approx e^{\beta F_L(E^*)}}$$

(i.e., $\sum'_{E \neq E^*} e^{-\beta F_L(E)} \ll e^{-\beta F_L(E^*)}$. We made more or less the same point in our 9/27 activity sheets.)

ex: Even if $N = 10^6$ (say), $e^{-N \times 1.0}$ + $e^{-N \times (1.0001)}$ differ tremendously (~43 orders of magnitude!)

∴ while in general the microcanonical / canonical ensembles give different predictions for modest / small N, as N approaches macroscopic sizes the canonical ensemble for all practical purposes becomes identical to the microcanonical.

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



* energy + particle # can fluctuate

* as before, make no assumptions other than $R \gg S$

* Derivation is the same as canonical ensemble case (see L9 notes for details)

$\Downarrow$

* Following the same initial steps, we arrive at

$$p(i, N) \propto \Omega_R(E_{TOT} - E_i, N_{TOT} - N)$$

* Under analogous assumptions ($E_i \ll E_{TOT}$, $N \ll N_{TOT}$) we Taylor expand

$$\log \Omega_R(E_T - E_i, N_T - N) \approx \Omega_R(E_T, N_T) - E_i \left(\frac{\partial \log \Omega_R}{\partial E}\right)_{N_R, E = E_T} - N \left(\frac{\partial \log \Omega_R}{\partial N_R}\right)_{\substack{N_R = N_T \\ E_R}}$$

$$= \Omega_R(E_T, N_T) - E_i \beta - \underset{\sim}{N \mu \beta}$$

$$\left(\text{Since } \left(\frac{\partial S}{\partial N}\right)_{N,E} = \frac{\mu}{T}\right)$$

$\therefore$ $p(i,N) \propto e^{-\beta(E_i - \mu N)}$ (E_i should really be labelled E_i^N, but most books don't)

$\therefore$ Normalizing $\sum_N \sum_{i(N)} p(i,N) = 1$

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

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

$$\langle N \rangle = \sum_{N, i(N)} p(i,N)\, N$$

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

$$\langle N \rangle = \frac{1}{Z_{GCE}} \frac{1}{\beta} \frac{\partial}{\partial \mu} Z_{GCE} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_{GCE}$$

* In analogy to the canonical case $Z = \sum_i e^{\beta E_i} = e^{-\beta F(N,T,V)}$

here we can show

$$Z_{GCE} = e^{-\beta \Omega(\mu,T,V)}$$

"Grand Potential" from earlier

$$d\mathcal{G} = -S\,dT - P\,dV - N\,d\mu$$

$\Rightarrow$ so get S, P, N from various derivatives of $\log Z_{GCE}$

* Same remarks hold as in our discussion of Z_{CE} for large N $\quad Z_{CE} \simeq e^{-\beta F_L(E^*)}$

$$F_L(E^*) = E^* - TS(E^*)$$

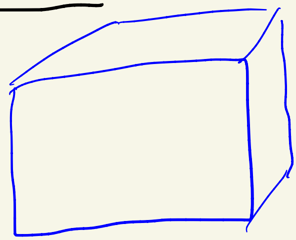
so $F_L(E^*) = F$

(canonical = microcanonical)

i.e., $Z_{GCE} \simeq e^{-\beta(E^* - TS(E^*) - \mu N^*)}$

So again in large N systems, the GCE will match onto the microcanonical

Ideal Gas



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

$$\hat{H} = \sum_{j=1}^{N} \frac{\vec{p}_j^{\,2}}{2m}$$

$\Downarrow$ solve Sch. eqn.

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

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

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

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

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

(here α is shorthand for the $(n_1^x, n_1^y, n_1^z, \dots n_N^x, n_N^y, n_N^z)$)

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

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

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

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

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

Canonical Ensemble treatment

$$Z_N = \left[\sum_{\nu=1}^{\infty} e^{-\beta \frac{\pi \hbar^2}{2mL^2}\nu^2}\right]^{3N}$$

(used $Z_N = Z(1)Z(2)\cdots Z(N)$ since non-interacting. Then used $Z(1) = Z_x Z_y Z_z$)

$$\approx \left[\frac{L}{2\pi\hbar}\int_{-\infty}^{\infty} dp\, e^{-\beta\frac{p^2}{2m}}\right]^{3N}$$

Nice Gaussian Integral

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}$$

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

(I have $k_B = 1$)

$$\equiv \left(\frac{V}{\ell_Q^3}\right)^N$$

$$\ell_Q \equiv \sqrt{\frac{2\pi\hbar^2}{mT}}$$

"Thermal de Broglie wavelength"

(Will be a measure of when quantum effects come in if $\ell \ll \ell_Q$ where ℓ = avg particle spacing)