Recap

Helmholtz free Energy $\boxed{F = -\tau \log Z}$

We found that

$$\boxed{F = U - \tau\sigma}$$

Also, we had

$$\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_\tau = -p$$

* New trick :

$$\frac{\partial^2 F}{\partial \tau \partial V} = \frac{\partial^2 F}{\partial V \partial \tau}$$

$$\Rightarrow \boxed{\left(\frac{\partial \sigma}{\partial V}\right)_\tau = \left(\frac{\partial p}{\partial \tau}\right)_V}$$

(for Math types: we always work on simply connected domains $\mathbb{R}^3$!)

This is called a Maxwell Relation and there are many more general examples!

For example, we also had

$$dU = \tau d\sigma - p dV \Rightarrow \left(\frac{\partial U}{\partial \sigma}\right)_V = \tau \ , \ \left(\frac{\partial U}{\partial V}\right)_\sigma = -p$$

$$\frac{\partial^2 U}{\partial \sigma \partial V} = \frac{\partial^2 U}{\partial V \partial \sigma} \Rightarrow \left(\frac{\partial \tau}{\partial V}\right)_\sigma = -\left(\frac{\partial p}{\partial \sigma}\right)_V$$

☺.

Consider a constant τ, constant V process and recall our system (s) + reservoir (R) story.

For the system, @ $\tau = \text{const}$,

$$dF_s = dU_s - \tau\, d\sigma_s$$

Earlier, we learned

$$\left(\frac{\partial \sigma}{\partial U}\right)_V \equiv \frac{1}{\tau} \quad \text{, so @ const } \tau \,\&\, V, \quad d\sigma . \tau = dU$$

$$\Rightarrow \quad dF_s = 0 \quad @ \text{ const } \tau, V.$$

$\therefore$ Extremize F – maximize or minimize?

for $R + s$, $U_R + U_s = \text{const}$
$= U$

Entropy is always additive $\Rightarrow \sigma = \sigma_R(U_R) + \sigma_s(U_s)$

For the reservoir,

$$\sigma_R(U - U_s) \cong \sigma_R(U) - U_s \left(\frac{\partial \sigma_R}{\partial U_R}\right)_V + \text{h.o.t.}$$

But $\left(\frac{\partial \sigma_R}{\partial U_R}\right)_V = \frac{1}{\tau_R} = \frac{1}{\tau_s}$ .. @equilibrium (v.g. approx to $\left(\frac{\partial \sigma_R}{\partial V}\right) \cdots$)

so

$$\sigma = \sigma_R(U) - \frac{U_s}{\tau} + \sigma_s = \underbrace{\sigma_R(U)}_{\text{constant}} - \frac{F_s}{\tau}$$

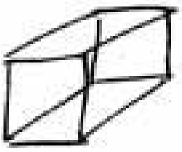
σ maximized $\Rightarrow$ $\boxed{F_s \text{ minimized}}\ \boxed{@ \text{ const } \tau, V}$

IDEAL GAS : FIRST GO

Simplest case: single atom in a box!
This is not thermodynamically interesting, of course, but finding its partition function will enable us to do Z for a box of N particles in gaseous form.

- Atom mass M, cubical box volume $V = L^3$.

Non-relativistic wave equation is



$$H\psi = \epsilon\psi$$

i.e. $\left(-\frac{\hbar^2\nabla^2}{2M}\right)\psi = \epsilon\psi$

Solution is standing waves = linear combination of Right- & Left-moving plane waves.

In x-direction, standing wave is $\psi_x = \sin\left(\frac{n_x\pi x}{L}\right)$

($\sin(ax)$ is zero when $ax = n\pi$; we need $\psi_x(x=L) = 0$ always $\because$ of boundary condition of box. (no leaking out!)
So $aL = n\pi$, i.e. $a = \frac{n\pi}{L}$ $\blacksquare$).

$$\Rightarrow \psi = A \sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

So

$$-\frac{\hbar^2}{2M}\nabla^2\psi = +\frac{\hbar^2}{2M}\left(\frac{n_x^2\pi^2}{L^2}+\frac{n_y^2\pi^2}{L^2}+\frac{n_z^2\pi^2}{L^2}\right)\psi$$

$$\Rightarrow \quad \varepsilon = \frac{\hbar^2\pi^2}{2ML^2}\left(n_x^2+n_y^2+n_z^2\right)$$

* Pretend that the atom has no other labels to sum over (i.e. no spin, no other structure)

$$\Rightarrow \quad \underset{\substack{\uparrow \\ \text{single atom}}}{Z_1} = \sum_{n_x, n_y, n_z} \exp\left(-\frac{\hbar^2\pi^2}{2ML^2}\frac{(n_x^2+n_y^2+n_z^2)}{\tau}\right)$$

* Assume that the energy spacing $|\Delta\varepsilon| \ll \tau$

Then $\Sigma \rightarrow \int$

and

$$Z_1 = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \; e^{-(n_x^2+n_y^2+n_z^2)\tau_*/\tau}$$

where we defined $\tau_* \equiv \dfrac{\hbar^2\pi^2}{2ML^2}$

Note: for ${}^{4}_{2}\mathrm{He}$ $\quad \tau_* \cong \left(\dfrac{8\times10^{-42}}{L^2}\right)$ K

so for ordinary boxes & temperatures the assumption was just fine.

Notice that all 3 integrals are the same!

$$Z_1 = \left[\int_0^\infty dn \; e^{-n^2(\tau_*/\tau)} \right]^3$$

$$= \sqrt{\frac{\tau}{\tau_*}}^{\,3} \left(\int_0^\infty dw \; e^{-w^2} \right)^3$$

$$= \left(\frac{\tau}{\tau_*}\right)^{3/2} \left(\frac{\sqrt{\pi}}{2}\right)^3 = \frac{\tau^{3/2}\,\pi^{3/2}}{8} \left(\frac{2ML^2}{\hbar^2\pi^2}\right)^{3/2}$$

$$\boxed{Z_1 = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2} V} \;\; \boxed{\equiv n_Q V}$$

"Quantum Concentration"
(units of $1/V$.)

N.B. Z_1 $\begin{cases} \text{is proportional to the volume } V \\ \text{scales as } \tau^{3/2} \end{cases}$

physically

The quantum concentration is the concentration associated with one atom in a cubic box with side equal to the thermal de Broglie wavelength.

What is $\lambda_{t\,deB}$? $= \dfrac{\hbar}{M\sqrt{\langle v^2\rangle}}$

But what is $\sqrt{\langle v^2 \rangle}$? $\quad M\langle v^2\rangle \sim \tau \quad (= k_B T)$

$\uparrow$ units of energy

$\Rightarrow \sqrt{\langle v^2\rangle} \sim \sqrt{\tau/M}$

$\Rightarrow \lambda_{t\,deB} \sim \dfrac{\hbar}{\sqrt{M\tau}}$ and $n_Q \sim \dfrac{1}{(\lambda_{t\,deB})^3}$

Consider ${}^4_2\mathrm{He}$ @ room-T, $\sim 300\,\mathrm{K}$.
$\Rightarrow \tau \sim 4.14 \times 10^{-21}\,\mathrm{J}$

For this case, $\lambda_{t\,deB}$
$\sim 5 \times 10^{-11}\,\mathrm{m} \Rightarrow n_Q \sim 8 \times 10^{30}\,\mathrm{m}^{-3}$
$\sim 8 \times 10^{27}\,\mathrm{L}^{-1}$

C.f. at STP,

1 mole ($N_{av} \sim 6. \times 10^{23}$) of gas occupies 22.4 L

$\Rightarrow \sim 2.7 \times 10^{22}\,\mathrm{L}^{-1} \quad \Rightarrow \quad \dfrac{n}{n_Q} \sim 3 \times 10^{-6} \ll 1$

If $\boxed{\dfrac{n}{n_Q} \ll 1}$ we say gas is in <u>classical régime</u>

← def^{n}s

If in addition atoms of gas don't interact, then it's called an <u>ideal gas</u>

* <u>N particles!</u>

Assume All independent. If all distinguishable,

$Z_N \overset{?}{=} Z_1^{\,N}$. (energies additive ∵ non-interacting!)

But this overcounts ∵ $N!$ ways of arranging any state with a given total energy.

$$\Rightarrow \boxed{Z_N = \frac{Z_1^{\,N}}{N!}} = \frac{(n_Q V)^N}{N!} \quad \text{where } n_Q \sim \tau^{3/2}.$$