- Last time, we learned about the Helmholtz free energy F. It can be thought of in two equivalent* ways:

(1.1) (a) $F = U - \tau\sigma$ ← (thermodynamic definition: purely macroscopic)

or

(1.2) (b) ⊛ $F = -\tau \underbrace{\log Z}$ ← this part is constructed from the microphysics via $\{\varepsilon_s\}$

We saw that knowing Z allows straightforward computation of entropy and pressure:

(1.3) $$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$$

(1.4) $$p = -\left(\frac{\partial F}{\partial V}\right)_\tau$$

- Notice that, since $F = -\tau \log Z$,

(1.5) $$\boxed{Z = e^{-F/\tau}}$$

so that $P(\varepsilon_s) = \dfrac{e^{-\varepsilon_s/\tau}}{e^{-F/\tau}}$

(1.6) i.e. $$\boxed{P(\varepsilon_s) = \exp\left[-(\varepsilon_s - F)/\tau\right]}$$ ← helps F-intuition

- Notice that $p = -\left(\frac{\partial F}{\partial V}\right)_\tau = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau$

intuitively reasonable (e.g. gas in bike pump...) ↗ ↖ less intuitive (but just as important)

try it!

* One way to see this is to prove that both definitions of F satisfy $\left(1 - \tau\frac{\partial}{\partial \tau}\right) F = U$.

$\boxed{F \text{ and Equilibrium}}$

- Consider a process at constant τ.

(2.1) $$dF = d(U - \tau\sigma) = dU - \tau\, d\sigma$$

- Recall our definition of τ: $\left(\frac{\partial\sigma}{\partial U}\right)_V = \frac{1}{\tau}$

(2.2) $\Rightarrow$ at $\underline{\text{constant } (\tau, V)}$, $dF = 0$
i.e. F is extremized.

$\underset{\sim}{Q}$: is it maximized or minimized ?!

- Recall the picture of $\mathcal{S}$ & $\mathcal{R}$.
We know that, overall,

(2.3) $$U = U_\mathcal{S} + U_\mathcal{R} = \text{constant}.$$

Also, we know that entropy is additive ($\mathcal{S}, \mathcal{R}$ indep.):

(2.4) $$\sigma = \sigma_\mathcal{R}(U_\mathcal{R}) + \sigma_\mathcal{S}(U_\mathcal{S})$$

and that
$$\tau \text{ same for } \mathcal{R} \,\&\, \mathcal{S}.$$

Now,

(2.5) $$\begin{aligned} \sigma_\mathcal{R}(U_\mathcal{R}) &= \sigma_\mathcal{R}(U - U_\mathcal{S}) \\ &\approx \sigma_\mathcal{R}(U) - U_\mathcal{S} \cdot \left(\frac{\partial\sigma_\mathcal{R}}{\partial U_\mathcal{R}}\right)_{U_\mathcal{S}=0} + \mathcal{O}(U_\mathcal{S}^2) \quad \text{(Taylor expansion)} \\ &= \sigma_\mathcal{R}(U) - \frac{U_\mathcal{S}}{\tau} \end{aligned}$$

so $$\sigma = \sigma_\mathcal{R}(U) - \frac{U_\mathcal{S}}{\tau} + \sigma_\mathcal{S}(U_\mathcal{S})$$

(2.6) $$= \underbrace{\sigma_\mathcal{R}(U)}_{\text{constant}} \ominus \frac{1}{\tau} \underbrace{F_\mathcal{S}}$$

(2.7) So $\boxed{\text{maximizing } \sigma(\mathcal{S} \cup \mathcal{R})}$ $\Leftrightarrow$ $\boxed{\text{minimizing } F_\mathcal{S}}$ ☺

(2.8) 🚩 $\boxed{F_\mathcal{S} \text{ is } \underline{\text{minimized}} \text{ at fixed } (\tau, V) \text{ at thermal equilibrium}}$ ⊛

Maxwell Relations

← cute math trick ☺
– with physics consequences!

Prototypical example

- Take function of 2 variables

(3.1) e.g. $F = F(\tau, V)$

- Look at first derivatives

(3.2) e.g. $\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V$, $p = -\left(\frac{\partial F}{\partial V}\right)_\tau$

- Find mixed partial second derivatives

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

⊛ Equality of mixed 2nd partials [(math issue; need topologically trivial space!)]

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

↳ has been tested experimentally; & it works! ☺

∃ many other examples.

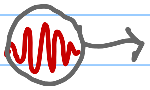
IDEAL GAS

– first go

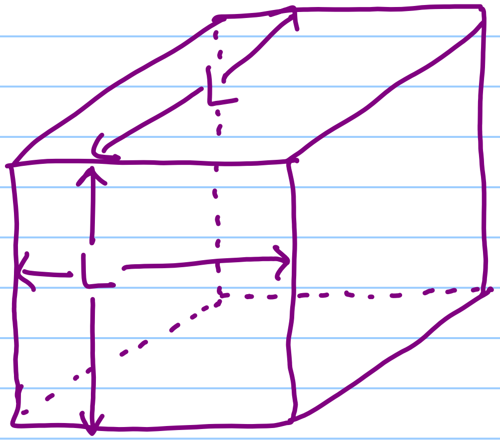
- In the rest of this lecture, we will derive the partition function for particles (e.g. molecules) of gas in a box. This will allow us to find $\varepsilon_s(V) \Rightarrow$ pressure next lecture ($\Rightarrow pV = N\tau$ ☺!)

⊛ To get started on this, we need to introduce a bit of Quantum Mechanics.

- wavicle



(4.1) Cubic box; Volume $V = L^3$.



(can easily do rectangular-type box; cubic is just simpler. ☺)

- Physics of <u>one</u> particle in box is first step towards finding Z_N, partition function for N independent particles.

- Need to know energy ε_s of state "s".

(4.2) ► <u>QM</u> : $\hat{H}\psi = \varepsilon\psi$ ← eigenvalue equation

wavefunction $[P \propto |\psi|^2]$

energy (eigenvalue of $\hat{H}$)

(4.3) where, for free particle, $\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2$ (i.e. $\hat{H} = \frac{\vec{p}^{\,2}}{2m}$; $\vec{p} \leftrightarrow -i\hbar\vec{\nabla}$)

$\Rightarrow$ need to solve

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi = \varepsilon\psi$$

$$\nabla^2\psi = -\frac{2m\varepsilon}{\hbar^2}\psi$$

(4.4) or $\left[\vec{\nabla}^2 + \frac{2m\varepsilon}{\hbar^2}\right]\psi = 0$

- Solution : <u>waves</u>. Boundary conditions : $\psi \to 0$ at box walls (& outside box) $\Rightarrow$ probability of finding particle ($\propto |\psi|^2$) restricted to box interior ✓ ☺

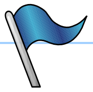
- Guess <u>standing wave</u> solution :

(5.1) $\psi(\vec{n}) = A \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$ (obeys B.C.)

$n_i \in \mathbb{N}$

Substitute into Schrödinger equation

$$\Rightarrow |\vec{n}|^2 \frac{\pi^2}{L^2} = \frac{2mE}{\hbar^2}$$

(5.2) i.e. 

$$\boxed{E_{\vec{n}} = \frac{\hbar^2 \pi^2}{2mL^2} |\vec{n}|^2}$$

(5.3) Each n_i component is 1, 2, 3, 4, ... : $n_i \in \mathbb{N}$
($n_i = 0$ means $\psi = 0$ i.e. <u>no</u> <u>particle</u>! ☺)

- The above equation is for <u>non-relativistic</u> particles and originates from the [NR] Schrödinger equation of Quantum Mechanics — i.e. <u>microphysics</u>.

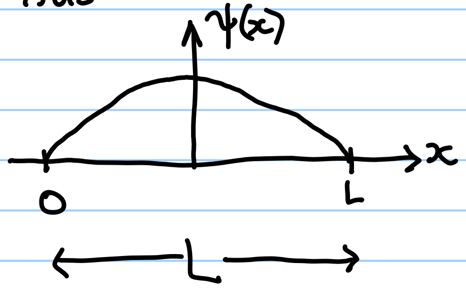
Depends on { mass of particle
volume, via $L = \sqrt[3]{V}$ (in 3 space dimensions).

(5.4) & Fundamental constant (of <u>QM</u>) $\hbar = \frac{h}{2\pi}$; $h \simeq 6.626 \times 10^{-34}$ Js
↑
dimensions of angular momentum.

★ [Also, $E_{\vec{n}}$ depends on $\vec{n}$, the vector telling us how many half-wavelengths fit in each direction of the box.

The lowest nonzero energy level has
(5.5) $\vec{n} = (1, 1, 1)$

A 1-d slice looks like :



- So! Let's now work on Z, the partition fn.

(6.1) In general, $Z = \sum_s e^{-\varepsilon_s/\tau}$, s = state label (for <u>microstates</u>)

Here, "s" is $\vec{n}$!
So

$$Z_1 = \sum_{\vec{n}} e^{-\varepsilon_{\vec{n}}/\tau}$$

(6.2) $$= \sum_{n_x=1}^{\infty} e^{-(\hbar^2\pi^2L^2/2m)\frac{n_x^2}{\tau}} \sum_{n_y}^{\infty} e^{-(\hbar^2\pi^2/2mL^2)\frac{n_y^2}{\tau}} \sum_{n_z}^{\infty} e^{-(\hbar^2\pi^2/2mL^2)\frac{n_z^2}{\tau}}$$

(6.3) $$= \left(\sum_{n=1}^{\infty} e^{-(\hbar^2\pi^2/2mL^2)\frac{n^2}{\tau}}\right)^3$$

i.e.

(6.4) $$\boxed{Z_1\,(3\text{-d}) = [Z_1\,(1\text{-d})]^3}$$ ☺

What is $Z_1(1\text{-d}) = \sum_{n=1}^{\infty} e^{-n^2(\hbar^2\pi^2/2mL^2\tau)}$?

- For temperatures τ such that adjacent energy

(6.5) levels have $\frac{|\Delta\varepsilon|}{\tau} \ll 1$, (good for typical molecule) (@ room T in ~1m box. <u>CHECK!</u>)

we may approximate the sum by an integral:

$$Z_1(1\text{-d}) = \int_0^{\infty} dn\, e^{-\alpha n^2} \quad , \quad \alpha := \frac{\hbar^2\pi^2}{2mL^2\tau}$$

$$= \frac{1}{\sqrt{\alpha}} \int_0^{\infty} dx\, e^{-x^2}$$

$$= \frac{1}{2}\frac{1}{\sqrt{\alpha}} \underbrace{\int_{-\infty}^{+\infty} dx\, e^{-x^2}}_{\sqrt{\pi}}$$

$$= \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} = \sqrt{\frac{\pi}{4\alpha}}$$

(6.6) ⇒ $$\boxed{Z_1\,(1\text{-d}) = \sqrt{\frac{m\tau}{2\pi\hbar^2}}\, L}$$ ← This is the <u>basic</u> "<u>Lego</u>" <u>block</u> for all of our ideal gas physics! ☺