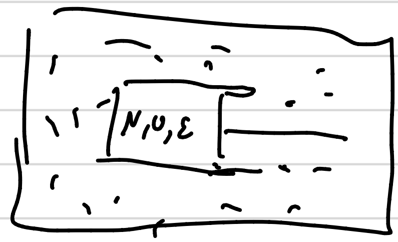
Lecture 4 – thermo review

microcanonical examples

Basic thermo reminder

1st law: conservation of energy. Change in internal energy of a system is equal to the amount of heat transferred to the system − work done by the system

Common setup would be
small change eg move piston would give



$$d\mathcal{E} = \delta q - \delta w$$, put δ b/c depends on path taken from state a to b

different kinds of work include changing volume at const pressure, and changing number of particles w/ or against chemical gradient

$$\mathcal{E}(b) - \mathcal{E}(a) = \int_a^b (\delta q - \delta w) = \int_a^b (\delta q - P\,dV + \mu\,dN)$$

$\mathcal{E}$ is a state function

- 2nd law of Thermodynamics

(1) "Heat is not a state function but exists a quantity $dS = \delta Q/T$ that is a state function

ie $S(b) - S(a) = \int_a^b \delta Q/T$ for any path from a to b rearranging first law, $\delta Q = d\mathcal{E} + dw = d\mathcal{E} - \sum_i F_i \, d\lambda_i$

where $F_i = -\partial \mathcal{E} / \partial \lambda_i$

So $dS = \delta Q / T = \frac{1}{T} d\mathcal{E} - \frac{1}{T} \sum F_i \, d\lambda_i$

for microcanonical ensemble, S is a function of $N, V, \mathcal{E}$, so

$dS = 1/T \, d\mathcal{E} + P/T \, dV - \mu/T \, dN$

$$dS = \left(\partial S / \partial \mathcal{E}\right)_{N,V} d\mathcal{E} + \left(\partial S / \partial V\right)_{N,\mathcal{E}} dV + \left(\frac{\partial S}{\partial N}\right)_{V,\mathcal{E}} dN$$

(chain rule)

so $\left(\frac{\partial S}{\partial \mathcal{E}}\right)_{N,V} = \frac{1}{T}$ $\left(\frac{\partial S}{\partial V}\right)_{N,\mathcal{E}} = P/T$ $\left(\frac{\partial S}{\partial N}\right)_{V,\mathcal{E}} = -\mu/T$

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(2) Quasistatic process on isolated system,

$\Delta S = 0$ (no heat flow)

(3) Non-quasi static process in an isolated system, $\Delta S \geq 0$

Next we will return to stastical mechanics. There we will deal with large numbers of particles, often indistinguishable

We already saw a bit how if we have N indistinguishable things, we may have factors of $N! = N \cdot (N-1) \cdot (N-2) \cdots (1)$

for even small numbers of particles, this is a large number, how fast does it grow

$N! \sim N^N \rightarrow$ what is N^N

important relation $e^{\log(x)} = x$, $x^a = \left(e^{\log(x)}\right)^a = e^{a\log(x)}$

so $N^N = e^{N\log N}$, grows faster than exponentially in N

but $N!$ is clearly a little smaller than N^N

In fact, we have Stirlings Approximation

$N! \approx N^N e^{-N}$ for large N, or

$\log_e(N!) \approx N\log N - N$ [better approx $N\log N - N + \frac{1}{2}\log 2\pi N$]

we will use this later

Another (generalized) definition of $N!$

$$\Gamma(N+1) = N!, \qquad \Gamma(z+1) \equiv \int_0^\infty x^z e^{-x} dx$$

why?

$$\Gamma(1) = \int_0^\infty x^0 e^{-x} dx = 1$$

Recall integration by parts $\int u\,dv = uv - \int v\,du$

$$\Gamma(z+1) = \int_0^\infty \underbrace{x^z}_{u} \underbrace{e^{-x} dx}_{dv}$$

$$= \underbrace{\left[-x^z e^{-x}\right]}_{0-0}\Big|_0^\infty - \int_0^\infty -e^{-x} z x^{z-1} dx$$

$$= +z \int x^{z-1} e^{-x} dx = z\,\Gamma(z)$$

Recursive definition of $N!$

$$\Gamma(N+1) = N\,\Gamma(N) = N(N-1)\,\Gamma(N-1) \quad \cdots$$

untill $\Gamma(1) = 1$

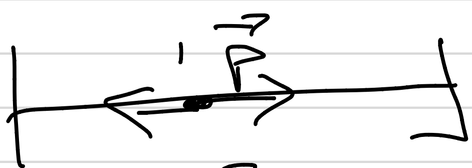
What can we do w/ the microcanonical ensemble:

Given the previous statements, we should be able to compute e.g. T or P of a system

$\boxed{\text{Sec 3.5}}$

System of obvious interest, N molecules/particles in a box, b/c dilute system actually acts like this –

Let's start w/ a simpler problem, 1 particle



L

$$\mathcal{H} = p^2/2m$$

Recall $$\Omega(N, V, E) = \underbrace{\frac{\mathcal{E}_0}{h^{3N} N!}}_{C/N!} \int d\vec{x}\, \delta(\mathcal{H}(x) - E)$$

not fully discussed

for 1 particle, $$\Omega = C \int dq\, dp\, \delta(p^2/2m - E)$$

$$= CL \int_{-\infty}^{\infty} dp\, \delta(p^2/2m - E)$$

$p = \sqrt{2m}\, y$, $dp = \sqrt{2m}\, dy$

$$= CL\sqrt{2m} \int_{-\infty}^{\infty} dy\, \delta(y^2 - E)$$

Appendix A.15, $\delta(x^2-a^2) = \frac{1}{2|a|}\left(\delta(x-a)+\delta(x+a)\right)$

[General formula $\delta(f(x)) = \sum_{k} \frac{\delta(x-x_k)}{|f'(x_k)|}$]

roots, $f(x_k)=0$

So $\Omega = C\sqrt{2m}\,L\int_{-\infty}^{\infty} dy\; \delta\left((y-\sqrt{E})(y+\sqrt{E})\right)$

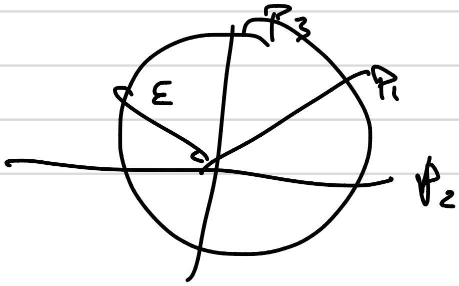
$$= C\sqrt{2m}\,\frac{L}{2\sqrt{E}}\cdot\int dy\; \delta(y-\sqrt{E}) + \delta(y+\sqrt{E})$$

$$= C\sqrt{2m}\,L/\sqrt{E} = \underline{\underline{\frac{\varepsilon_0 L}{h}\sqrt{\frac{2m}{E}}}}$$

Now lets get to the real problem

$H = \sum_{i=1}^{N} \vec{p}^{\,2}/2m$, in 3d

$$\Omega(N,0,E) = \frac{\varepsilon_0}{h^{3N}N!}\int dq^{3N}\int dp_1\cdots p_{3N}\;\delta\left(\frac{\sum p_i^2}{2m} - E\right)$$



$\therefore$ $\int dq^{3N} f(p) = L^{3N} f(p)$

$= V^{N} f(p)$

do the same multidimensional substitution

for $\vec{P}^2/2m$ $\quad$ $p_i = \sqrt{2m}\, y_i \quad d\vec{p}_i = \sqrt{2m}\, d\vec{y}_i$

$$\Omega = \frac{\varepsilon_0 V^N (2m)^{3N/2}}{h^{3N} N!} \int_{-\infty}^{\infty} dy^{3N}\, \delta(y^2 - \varepsilon)$$

If we have $\int dx\,dy\,dz \rightarrow \int dr\,d\theta\,d\phi\, r^2 \sin\theta$

$\Rightarrow 4\pi \int dr\, r^2$

$\leftarrow$ surface area of unit sphere

in higher dimension

$$dx_1 dx_2 \ldots dx_{3N} = r^{n-1}\, dr\, S_{n-1}$$

and it turns out (how?) we can solve $\int dS_{n-1}$ in a similar way to homework on gaussian intervals

Result will have a gamma function

$$\Gamma(N+1) = N! = \int_0^{\infty} x^N e^{-x}\, dx$$

$$\int dS_{\underset{\uparrow\, 3N}{n-1}} = \frac{2\pi^{n/2}}{\Gamma(n\ \ )}$$

so

$$\Omega(N, V, \mathcal{E}) = \underbrace{\frac{\mathcal{E}_0 (2m)^{3N/2} V^N}{N!\, h^{3N}}} \frac{2\pi^{3N/2}}{\Gamma(3N/2)}$$

$$\times \int_0^\infty r^{3N-1} \underbrace{\delta(r^2 - \mathcal{E})}_{\frac{1}{2\sqrt{\mathcal{E}}}\left[\delta(r-\sqrt{\mathcal{E}}) + \delta(r+\sqrt{\mathcal{E}})\right]} dr$$

$$= \frac{\mathcal{E}_0}{N!} \frac{(2m)^{3N/2} V^N}{h^{3N}} \frac{\cancel{2}\pi^{3N/2}}{\Gamma(3N/2)} \cdot \frac{\mathcal{E}^{3N/2}}{\cancel{2}\mathcal{E}}$$

$$= \frac{\mathcal{E}_0}{\mathcal{E}} \frac{1}{N!} \cdot \frac{1}{\Gamma(3N/2)} \left[V \left(\frac{2\pi m \mathcal{E}}{h^2} \right)^{3/2} \right]^N$$

Now $\mathcal{E}^{3N/2 - 1} \approx \mathcal{E}^{3N/2}$

and $\Gamma(3N/2) = (3N/2 - 1)! \approx \left(\frac{3N}{2}\right)!$

$$\approx \left(\frac{3N}{2}\right)^{3N/2} e^{-3N/2}$$

So $\Omega \approx \frac{\mathcal{E}_0}{N!} \cdot \left[V \left(\frac{4\pi m \mathcal{E}}{3N} e \right)^{3/2} \right]^N$

this came from indisting of particles
keep for now

Finally, we can show something familiar / useful / interesting ...

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

$$\frac{1}{k_B T} = \left(\frac{\partial \log \Omega}{\partial E}\right)_{N,V}$$

$$\log \Omega = \log\left(E^{3N/2}\right) + \log(\text{other})$$

$$\frac{1}{k_B T} = \frac{3N}{2} \frac{d \log E}{dE} = \frac{3N}{2E}$$

$$\Rightarrow \boxed{E = \frac{3}{2} N k_B T = 3/2\, nRT}$$

$$P/T = k_B\left(\frac{\partial \log \Omega}{\partial V}\right)_{N,E}, \quad \log \Omega = N \log V + \dots$$

$$= N k_B / V, \quad \Rightarrow \boxed{PV = N k_B T = nRT}$$

In full

$$S(N,V,E) = N k_B \log\left[V/h^3 \left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3}{2} Nk - k \log N!$$

subbing in E

$$= N k_B \log\left[V \left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right] + \frac{3Nk}{2} - k \log N!$$

$$\hat{}\ \text{QM}$$

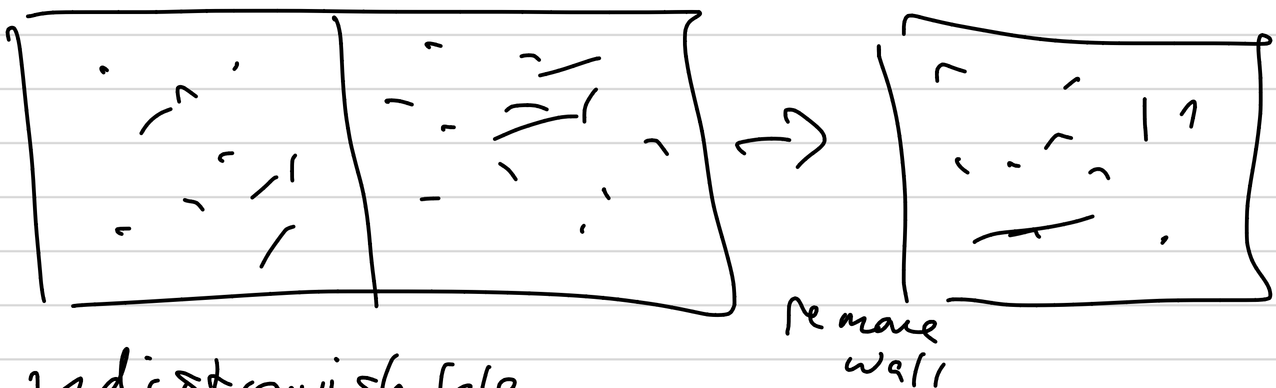
$$\approx \boxed{N k_B \log\left[\frac{V}{N}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right] + 5/2\, Nk}$$ Sackur Tetrode

thermal wavelength $\Lambda = \sqrt{\dfrac{h^2}{2\pi m k_B T}}$

So entropy depends on V/Λ^3

Gibbs paradox, entropy of mixing

what if we didn't have $1/N!$



indistinguishable

HW: what is entropy of mixing w/ and w/o indistinguishability factor $1/N!$