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 of more piston would give

\[ dE = dq - \delta w \]

put \( \delta w \) depends on path taken from state a to b.

Different kinds of work include changing volume at constant pressure, and changing number of particles \( U \) or against chemical gradient.

\[ E(b) - E(a) = \int_a^b (dq - \delta w) = \int_a^b (dq - P \delta V + \mu \delta N) \]

\( E \) is a state function.

2nd law of Thermodynamics

Heat is not a state function but exists a quantity \( dS = \frac{dQ}{T} \) that is a state function.

\[ S(b) - S(a) = \int_a^b \frac{dQ}{T} \]

for any path from a to b.
rearranging first law,

\[ S = dE + dS = dE - \sum F_i \, d\lambda_i \]

where \( F_i = -\frac{\partial E}{\partial \lambda_i} \).

So,

\[ dS = \frac{S}{T} = \frac{1}{T} \, dE - \frac{1}{T} \sum F_i \, d\lambda_i \]

for microcanonical ensemble, \( S \) is a function of \( N, U, E \), so

\[ dS = \left( \frac{\partial S}{\partial E} \right)_N, U \, dE + \left( \frac{\partial S}{\partial U} \right)_N, E \, dU + \left( \frac{\partial S}{\partial N} \right)_E, U \, dN \]

(Chain rule)

So,

\[ \left( \frac{\partial S}{\partial E} \right)_N, U = \frac{1}{T} \left( \frac{\partial S}{\partial U} \right)_N, E = \frac{P}{T} \left( \frac{\partial S}{\partial N} \right)_E, U = -\frac{M}{T} \]

\( \square \)

(2) Quasi-static process on isolated system,

\[ \Delta S = 0 \quad \text{(no heat flow)} \]

(3) Non-quasi-static process in an isolated system, \( \Delta S \geq 0 \).
Next we will return to statistical 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?

$N! \approx N^N \rightarrow$ what is $N^N$?

Important relation $e^{(\log x)} = x$, $x^a = (e^{\log x})^a = e^{a \log x}$.

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 **Stirling's Approximation**

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

$\log_e(N!) \approx N \log N - N \quad [\text{better approx } N \log N - N + \frac{1}{2} \log 2\pi N]$.
Another (generalized) definition of $N!$.

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

why?

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

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

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

$$
= \left[ -x^z e^{-x} \right]_0^\infty - \int_0^\infty -e^{-x} \cdot z x^{z-1} \, dx
$$

$$
= 0 + 2 \int_0^\infty x^{z-1} e^{-x} \, dx = 2 \Gamma(z)
$$

Recursive definition of $N!$.

$$
\Gamma(N+1) = N \Gamma(N) = N(N-1) \Gamma(N-1) \ldots
$$

until $\Gamma(1) = 1$
What can we do with the microcanonical ensemble:

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

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

\[
\mathcal{H} = p^2 / 2m
\]

Recall $\mathcal{Z}(N, 0, \varepsilon) = \frac{\varepsilon^N}{\hbar^{3N}N!} \int d^3x \mathcal{S}(\mathcal{H}(x) - \varepsilon)$

not fully discussed

For 1 particle, $\mathcal{Z} = C \int d\rho \mathcal{S}(\rho^2 / 2m - \varepsilon)$

\[
= CL \int_{-\infty}^{\infty} d\rho \mathcal{S}(\rho^2 / 2m - \varepsilon)
\]

\[
= CL \sqrt{2m} \int_{-\infty}^{\infty} dy \mathcal{S}(y^2 - \varepsilon)
\]
Appendix A.15, \[ S(x^2-a^2) = \frac{1}{2a} (S(x-a) + S(x+a)) \]

General formula \[ S(f(x)) = \sum_{k \text{ roots } f(x_k) = 0} \frac{S(x-x_k)}{|f'(x_k)|} \]

So \[ S_r = C \sqrt{2m} \int_{-\infty}^{\infty} dy \ S(y-\delta E)(y+\delta E) \]
\[ = C \sqrt{2m} L \frac{\delta E}{2 \sqrt{\delta E}} \int dy \ S(y-\delta E) + S(y+\delta E) \]
\[ = C \sqrt{2m} L / \delta E = \frac{C_0 L}{\hbar} \sqrt{\frac{2m}{\delta E}} \]

Now let's get to the real problem
\[ h = \sum_{i=1}^{N} \frac{p_i^2}{2m}, \text{ in 3d} \]

\[ \Sigma \left( N , 10 , \delta E \right) = \frac{E_0}{h^{3N} N!} \int d^3 p_1 \cdots d^3 p_N \ S\left( \frac{\delta E - 3N \sum_{i=1}^{N} E_i}{2m} \right) \]

\[ \int d^3 p = 4\pi^2 a^3 \]
\[ \int d^3 p = 4\pi^2 a^3 \]
\[ \int d^3 q = 4\pi^2 a^3 \]

\[ f(q) = \frac{E_0}{h^{3N} N!} \]
\[ = \frac{E_0}{h^{3N} N!} \]
do the same multidimensional substitution for \( \mathcal{P}_{2/2} \),  
\[ p_i = \frac{\mathcal{P}_{2/2}}{\mathcal{P}_{2/2}} y_i, \quad dp_i = \frac{\mathcal{P}_{2/2}}{\mathcal{P}_{2/2}} dy_i \]

\[ \mathcal{N} = \frac{\mathcal{E}_0 \psi(2\pi)^{3n/2}}{\hbar^{3n} N!} \int_{-\infty}^{\infty} \mathcal{N} dy^n S(y^2 - 3) \]

If we have  
\[ \int dx dy dz \Rightarrow \int dr d\theta d\phi r^2 \sin \theta \]

in higher dimension
\[ dx_1 dx_2 \ldots dx_5 = r^{n-1} dr \cdot dS_{n-1} \]

and it turns out (hw?) we can solve \( \int dS_{n-1} \)

in a similar way to homework on Gaussian integrals

Result will have a gamma function
\[ (N+1) = N! = \int_0^\infty x^n e^{-x} dx \]

\[ \int_{S_{n-1}} p_{n-1} = \frac{2\pi^{n/2}}{\Gamma(n)} \quad \text{so} \]
\[ \mathcal{N}(N, \nu, \varepsilon) = \frac{E_0 (2\pi)^{3N/2} \nu^N}{N! \pi^{3N} / \Gamma(3N/2)} \]

\[ \times \int_{0}^{\infty} \int_{0}^{\infty} \frac{8(\varepsilon^2 - \varepsilon)}{\pi^2} \frac{1}{2\varepsilon} \left[ \delta(r - \nu \varepsilon) + \delta(r + \nu \varepsilon) \right] \]

\[ = \frac{E_0}{N!} \frac{(2\pi)^{3N/2} \nu^N}{\pi^{3N} / \Gamma(3N/2)} \cdot \frac{3N/2}{\pi \nu \varepsilon} \]

\[ = \frac{E_0}{\pi \varepsilon} \frac{1}{N!} \cdot \frac{1}{\Gamma(3N/2)} \left[ V \left( \frac{2\pi m \varepsilon}{\hbar^2} \right)^{3/2} \right]^N \]

Now, \( \nu^{3N/2-1} \propto \nu^{3N/2} \)

and \( \Gamma(3N/2) \approx (3N/2)^{3N/2} \frac{\pi}{2} \)

So \( \mathcal{N} \approx \frac{E_0}{N!} \frac{1}{\pi \varepsilon} \left[ V \left( \frac{2\pi m \varepsilon}{\hbar^2} \right)^{3/2} \right]^N \)

\[ \approx \left( \frac{3N/2 \nu}{\pi} \frac{E_0}{\varepsilon} \right)^{3N/2} \]

This can be interpreted as the indistinguishability of particles, keep this in mind.

Finally, we can show something familiar:

\[ \text{useful | interesting} \]
\[ S(N_1, v, \varepsilon) = k_B \log \mathcal{R} \]
\[ \frac{1}{k_B T} = \left( \frac{\partial \log \mathcal{R}}{\partial \varepsilon} \right)_{N_1, v} \]
\[ \log \mathcal{R} = \log (e^{3\varepsilon/2}) + \log \text{(other)} \]
\[ \frac{1}{k_B T} = \frac{3N}{2} \frac{\partial \log \mathcal{R}}{\partial \varepsilon} = \frac{3N}{2} \varepsilon \]
\[ \Rightarrow \mathcal{E} = \frac{3}{2} N k_B T = \frac{3}{2} k_B T \]
\[ P_U = k_B \left( \frac{\partial \log \mathcal{R}}{\partial U} \right)_{N_1, v} \quad \log \mathcal{R} = N \log v + \ldots \]
\[ = N k_B / v, \quad \Rightarrow \quad P_U = N k_B T = n k_B T \]

In full:
\[ S(N_1, v, \varepsilon) = N k_B \log \left[ \frac{U^{1/3} \left( \frac{4 \pi m \varepsilon}{3N} \right)^{3/2}}{N} \right] + \frac{3}{2} N k - k \log N! \]

Subbing in \( \mathcal{E} \)
\[ \mathcal{E} = \frac{3}{2} N k_B T \]

\[ \mathcal{E} = N k_B \log \left[ \frac{U}{N} \left( \frac{2 \pi m k_B T}{h^2} \right)^{3/2} \right] + \frac{3}{2} N k - k \log N! \]

\[ \sim N k_B \log \left[ \frac{U}{N} \left( \frac{2 \pi m (\frac{\varepsilon}{k_B T})}{h^2} \right)^{3/2} \right] + \frac{5}{2} N k \]

Sackur–Tetrode
thermal wavelength \( \Lambda = \sqrt{\frac{\hbar^2}{2\pi m k_B T}} \)

So entropy depends on \( V / \Lambda^3 \)

Gibbs paradox, entropy of mixing
what if we didn’t have \( \frac{1}{N!} \)?

\[
\begin{array}{c}
\text{indistinguishable}
\end{array}
\]

HW: what is entropy of mixing w/ and w/o indistinguishability factor \( \frac{1}{N!} \)