Foundations

Classical dynamics of [redacted] particles

$$m\ddot{\vec{x}}_i = \vec{F}_i(x_1, \cdots, x_N) = -\nabla_{\vec{x}_i} V(\vec{x}_1, \cdots, \vec{x}_N)$$

More generally $\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{q}_i} = \frac{\partial \mathcal{L}}{\partial q_i}$

$\mathcal{L} = T - V$. This is the Lagrangian formulation

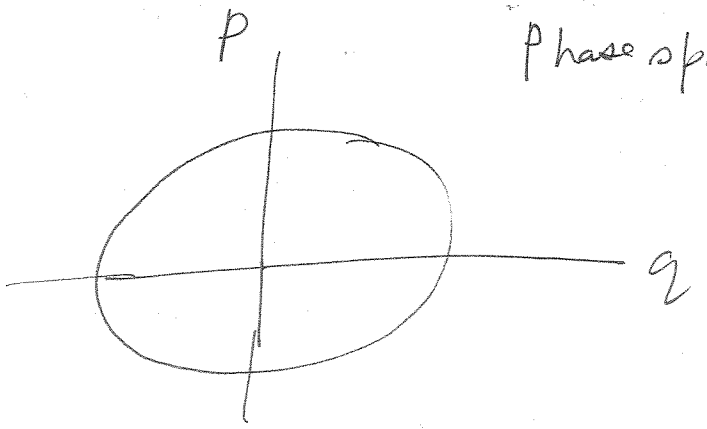
Ex: Usual Newtonian laws $\Longleftrightarrow$ $T = \frac{1}{2}\sum_i m_i \dot{\vec{x}}_i^2$ $V = V(\vec{x}_1, \cdots, \vec{x}_N)$

In the hamiltonian version: $p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i}$

$\mathcal{H} = p_i \dot{q}_i - \mathcal{L}$.

Ex: When $T = \frac{1}{2}\sum_i m_i \dot{\vec{x}}_i^2$ $\vec{p}_i = m_i \dot{\vec{x}}_i$

$$\mathcal{H} = \frac{1}{2}\sum_i m_i \dot{\vec{x}}_i^2 + V(x_1, \cdots, x_N) = \sum_i \frac{\vec{p}_i^2}{2m_i} + V(x_1, \cdots, x_N)$$



Phase space 6N dim

$$\boxed{\begin{aligned} \dot{p}_i &= \frac{\partial \mathcal{H}}{\partial q_i} \\ \dot{q}_i &= -\frac{\partial \mathcal{H}}{\partial p_i} \end{aligned}}$$

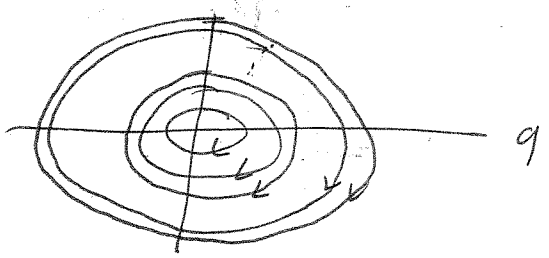
$$\dot{\mathcal{H}} = \dot{p}_i \frac{\partial \mathcal{H}}{\partial p_i} + \dot{q}_i \frac{\partial \mathcal{H}}{\partial q_i} = -\dot{p}_i \dot{q}_i + \dot{q}_i \dot{p}_i = 0$$

Also note that Hamiltonian flows are volume preserving

$$\text{div(flow)} = \sum_i (\partial_{q_i} v_{q_i} + \partial_{p_i} v_{p_i}) = \sum_i \left\{ \partial_{q_i} \left(\frac{\partial H}{\partial p_i} \right) + \partial_{p_i} \left(-\frac{\partial H}{\partial q_i} \right) \right\} = 0$$

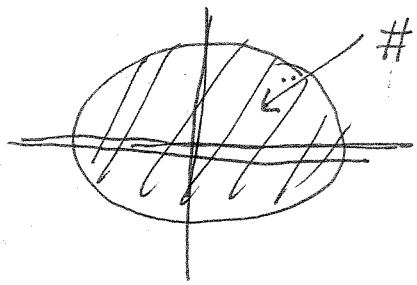
Example 1d Harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2} q^2$$



In semiclassical picture the nth state corresponds to the condition

$$n\hbar = \oint p\,dq, \quad \hbar \text{ is Planck's constant}$$



# of quantum states in this region

$$= \frac{\text{Area}}{\hbar}$$

A bunch of decoupled oscillators

$$H = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m_i} + \frac{m\omega_i^2}{2} q_i^2 \right)$$

Note

States specified by $(n_1 \cdots n_N)$, $n_i \hbar = \oint p_i\,dq_i$

The region inside $\frac{p_i^2}{2m_i} + \frac{m\omega_i^2}{2} q_i^2 < e_i$ for $i = 1, \cdots, N$

ellipse x ellipse x ....

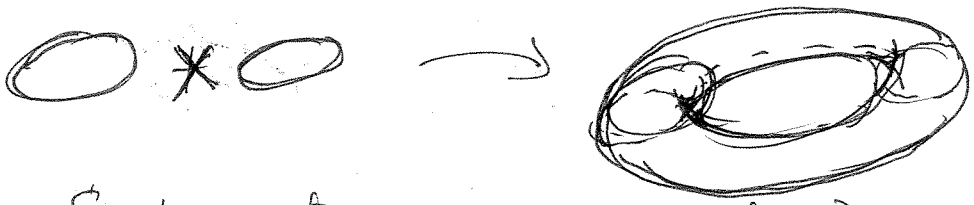
The number of states in $\frac{\int d^N p\, d^N q}{\hbar^N} = \frac{\text{Volume}}{\hbar}$

So $\frac{d^N p\, d^N q}{\hbar^N}$ is a natural measure of volume in the phase space

Note that the N oscillator system has N constants of motion in a 2N dim phase space

$$I_i = \frac{p_i^2}{2m_i} + \frac{m\omega_i^2 q_i^2}{2}$$ is constant of motion

The trajectory lives on a torus.
Circle cross circle cross circle.



Such systems are called integrable.

In fact a bunch coupled oscillators

$$H = \sum_i p_i^2/2m_i + \sum_{ij} K_{ij} q_i q_j$$

Could be reduced to a bunch of decoupled oscillators: normal modes.

In the same way generic integrable systems could be broken into action-angle variables, actions I_i being conserved. The angle variables (taking values) when on a compact set give rise to the N-torus again.

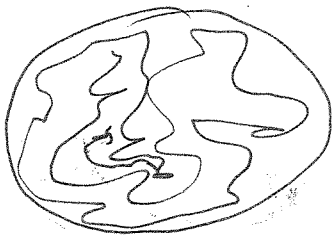
Example: Planetary motion.

The $H(p,q) = E$ is a $2N-1$ dim subspace. The trajectory of an integrable system stays in a N dimensional subspace of the $2N-1$ dim space.

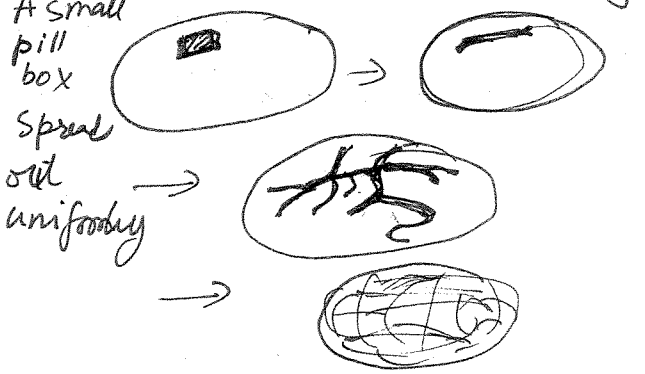
Notes: No invariant subset (measurable) smaller than the whole set ⇔ ergodic

Mixing: After a long time the points in set B coming from set A, occupy a fraction proportional to P(A) (stationary measure)

At the opposite end of the spectrum are ergodic systems where a typical trajectory meanders arbitrarily close to every point on the constant energy surface



In fact some systems would be mixing



In such systems

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T dt\, O(p,q) = \frac{\int d^N p\, d^N q\, O(p,q)\, \delta(H(p,q)-E)}{\int d^N p\, d^N q\, \delta(H(p,q)-E)}$$

This is the ergodic hypothesis in statistical mechanics. It is pretty hard to prove for a particular system, even it is true. We often need a leap of faith.

Quite strangely we will often apply this calculation tools to Hamiltonian that are clearly ~~ergodic~~ integrable [ideal gas, harmonic oscillations in lattice, ...].

How could this be?

May be $H_{ergodic} = H_{integrable} + \underbrace{H_{perturbation}}_{\text{small ?}}$

Unfortunately small perturbations of integrable systems (like a few weak anharmonic terms added to the coupled oscillators) keeps on behaving like an integrable system. That is the content of KAM results. This is why the planetary system, despite many additional interactions, beyond the sun-planet $1/r$ interaction, does not go crazy.

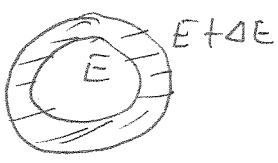
So we really have to add quite a strong perturbation to get the system to be ergodic and yet hope that calculations based on the integrable system remain a good approximation.

Thus we could start discussing the microcanonical ensemble. The measure is uniform on the constant energy surface and zero elsewhere.

Let us now define the "area/volume" of the constant energy subspace

$$\Omega(E) = \int \frac{d^N p\, d^N q}{h^n}\, \delta(H(p,q) - E)$$

Based on the semiclassical picture, we could have said the # of quantum states between E and $E+\Delta E$ is $\Omega(E)\Delta E$.



Now comes the most amazing insight from Boltzman

$$S(E) = k_B \ln \Omega(E)$$

If we identify E with total internal energy U we could start cooking

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

$$\frac{\partial \ln \Omega(E)}{\partial E} = \frac{1}{k_B T(E)} \quad \text{and} \quad P = T\left(\frac{\partial S}{\partial V}\right)_U$$

One could then get $F = U - TS$

$$= E - T(E)S(E)$$

etc etc.

~~If we know $F = F(V,T)$ we know everything~~

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad \text{etc}$$

Comment on Second Law

$$\Omega_1(E_1 - \epsilon)\,\Omega_2(E_2 + \epsilon)$$
$$= \Omega_1(E_1)\, e^{-\frac{\epsilon}{k_B T_1} + O(\epsilon^2)}\, \Omega_2(E_2)\, e^{+\frac{\epsilon}{k_B T_2}} + \epsilon^2$$
$$= \Omega_1(E_1)\Omega_2(E_2)\, e^{\left(\frac{1}{k_B T_2} - \frac{1}{k_B T_1}\right)\epsilon + O(\epsilon^2)}$$

$T_2^{-1} > T_1^{-1}$, $\epsilon > 0$

At this point we are itching to do this in practice. What about looking at ideal gas?

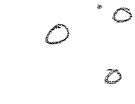
Example I. Ideal gas:

$$H = \frac{1}{2}\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$$

$$\Omega(E) \stackrel{?}{=} \int \frac{d^{3N}p\, d^{3N}q}{h^{3N}}\, \delta\left(\sum_i \frac{p_i^2}{2m} - E\right)$$

$\Omega_R \Omega_B \Omega_G$

Identical $\frac{1}{3!}\Omega_R \Omega_B \Omega_G$



$$\Omega(E) = \int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}}\, \delta\left(\sum_i p_i^2/2m - E\right)$$

$$= \frac{V^N}{N!\, h^{3N}} W(E)$$

$$W(E) = \int d^{3N}p \quad \delta\left(\sum_i \frac{p_i^2}{2m} - E\right)$$

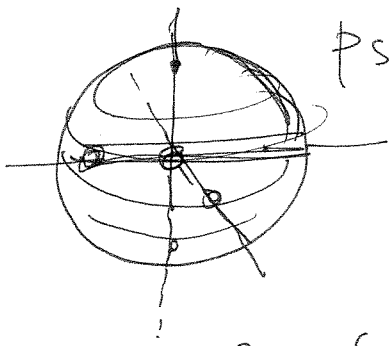
Remember

$$\int \delta(\lambda x)\,dx = \int \frac{1}{\lambda}\delta(y)\,dy = \frac{1}{\lambda}$$

$$\delta(\lambda x) = \frac{1}{\lambda}\delta(x)$$

$$\delta(f(x) - f(a)) = \frac{1}{f'(a)}\delta(x-a)$$

$$\delta\left(\sum \frac{p^2}{2m} - E\right) = 2m\,\delta(\Sigma p^2 - 2mE) = 2m \times \frac{1}{2\sqrt{2mE}}\,\delta\left(\sum p^2 - \sqrt{2m}\right) = \frac{m}{\sqrt{2E}}\,\delta\left(\sum p^2 - \sqrt{2}\right)$$



p space sphere area

d dim Sphere Radius R

$$\frac{d\,\pi^{d/2}}{\Gamma\left(\frac{d}{2}+1\right)} R^{d-1}$$ surface area

gamma fn $\rightarrow \Gamma\left(\frac{d}{2}+1\right)$

In this case $$W(E) = \frac{\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} (2mE)^{\frac{3N-1}{2}} \times \frac{1}{2m} \times 2 \times \sqrt{E}$$

$$\ln \Omega(E) = \frac{3N}{2} \ln \frac{2\pi m E}{h^2} + N \ln V$$

Remember

$\ln N! = N\ln N - N + o(\ln N)$

$\Gamma(N) = (N-1)!$

$$= N\left[\frac{3}{2}\ln\left(\frac{4\pi m E}{3Nh^2}\right) + \frac{3}{2} + \ln\frac{V}{N} + o\left(\frac{\ln N}{N}\right)\right]$$

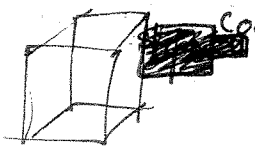
$$- N\ln N + N - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2} + o(\ln N)$$

Sackur Tetrode - eqn.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{3k_B N}{2E} \qquad P = T\left(\frac{\partial S}{\partial V}\right)_E = T\frac{Nk_B}{V} = \frac{2}{3}\frac{E}{V}$$

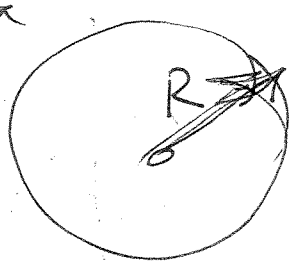
$$PV = Nk_BT = nRT \qquad \boxed{N_{Av}k_B = R}$$

This was a careful calculation which yielded all the additive constants right in a way so that if we do a quantum calculation for low temperature with entropy at $T=0$ being zero this classical formula would be the right high temperature limit. However, if we don't care about additive constants we could get it quite cheaply



coordinates $\rightarrow V^N C \left(\sqrt{2mE}\right)^{\frac{3N-1}{2}}$ ← momenta

$R = \sqrt{2mE}$



C_D

$\frac{1}{N!}$ from indistinguishability

$$S = k_B \log \left[\frac{V^N (3N)\, \pi^{\frac{3N}{2}}}{N! \left(\frac{3N}{2}\right)!} \left(\sqrt{2mE}\right)^{3N-1} \right]$$

$$= k_B \left[N \ln V - N \ln N + \frac{3N}{2} \ln E - \frac{3N}{2} \ln \frac{3N}{2} + N(\text{const}) \right]$$

$$= N k_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln \frac{E}{N} \right) + N k_B \text{Const} + O(\log N)$$

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2} \frac{N k_B}{E}} \qquad \boxed{\frac{P}{T} = \frac{\partial S}{\partial V} = \frac{N k_B}{V}}$$

ideal gas eqn of state

Equipartition energy $E = \frac{3}{2} N k_B T$ ↙ $\rightarrow PV = N k_B T$

I should show you how to get C_D.

One way is to write $dx_1 \ldots dx_D$ in polar coords for D dimension and do the angle integrals.

Short cut:

$$\prod_i \int \frac{e^{-x_i^2/2}}{\sqrt{2\pi}} dx_i = 1$$

$$1 = \int \frac{d^D x}{(2\pi)^{D/2}} e^{-R^2/2} = \frac{C_D}{(2\pi)^{\frac{D}{2}}} \int_0^\infty dR\, R^{D-1} e^{-R^2/2}$$

Call $R^2/2 = y$

$$1 = \frac{C_D}{(2\pi)^{\frac{D}{2}}} 2^{\frac{D-2}{2}} \int_0^\infty d\left(\frac{R^2}{2}\right) \left(\frac{R^2}{2}\right)^{\frac{D}{2}-1} e^{-R^2/2}$$

$$= \frac{C_D}{2(\pi)^{D/2}} \int_0^\infty dy\, y^{\frac{D}{2}-1} e^{-y}$$

$$= C_D \times \frac{\Gamma\left(\frac{D}{2}\right)}{2\pi^{D/2}}$$

$$C_D = \frac{2\pi^{D/2}}{\Gamma\left(\frac{D}{2}\right)} = \frac{D\,\pi^{\frac{D}{2}}}{\Gamma\left(\frac{D}{2}+1\right)} = \frac{D\pi^{\frac{D}{2}}}{\left(\frac{D}{2}\right)!}$$

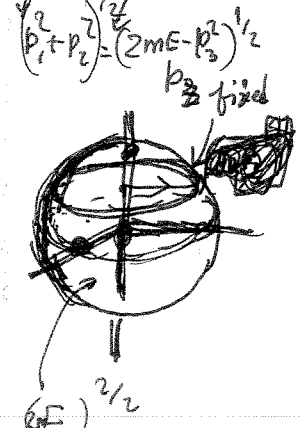
for even D.

Since $\Gamma(n+1) = n\Gamma(n)$ and $\Gamma(n+1) = n!$ for integer

Before we leave the ideal gas we would like a few more things calculated.

1) What is the distribution of momenta of a single gas molecule.

$$\frac{\int \frac{d^{3N}q}{h^{3N}} \int \prod_{i=2}^{N} d^3p_i \; \delta\left(\frac{1}{2m}\sum_{i=2}^{N}\vec{p}_i^{\,2} - \left(E - \frac{\vec{p}_1^{\,2}}{2m}\right)\right)}{\int \frac{d^{3N}q}{h^{3N}} \int \prod_{i=1}^{N} d^3p_i \; \delta\left(\frac{1}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2} - E\right)}$$



$$= \frac{3(N-1)}{\Gamma\left(\frac{3(N-1)}{2}+1\right)} \frac{\pi^{\frac{3(N-1)}{2}}}{\sqrt{2\left(E-\frac{\vec{p}_1^{\,2}}{2m}\right)}} \left(2m\left(E-\frac{\vec{p}_1^{\,2}}{2m}\right)\right)^{\frac{3N-4}{2}}$$

$$\frac{3N\,\pi^{\frac{3N}{2}}}{\Gamma\left(\frac{3N}{2}+1\right)} \sqrt{\frac{m}{2E}} \left(2mE\right)^{\frac{3N-1}{2}}$$

$$\simeq \frac{1}{\pi^{3/2}} \frac{\Gamma\left(\frac{3N}{2}+1\right)}{\Gamma\left(\frac{3N}{2}+\frac{1}{2}\right)} \sqrt{\frac{E}{E-\frac{p_1^2}{2m}}} \times \frac{1}{(2mE)^{\frac{3}{2}}} \left(1-\frac{\vec{p}_1^{\,2}}{2mE}\right)^{\frac{3N-4}{2}}$$

$$\simeq \frac{1}{\pi^{3/2}}\left(\frac{3N}{2}\right)^{\frac{3}{2}} \frac{1}{\left(\sqrt{2mE}\right)^3} e^{-\frac{\vec{p}_1^{\,2}}{2mE}\times\frac{3N}{2}}$$

$$\simeq \left(\frac{3N}{4\pi mE}\right)^{3/2} e^{-\frac{\vec{p}_1^{\,2}}{4mE/3N}}$$

Remember that $\frac{3}{2}k_BT = \frac{E}{N} \iff \frac{2E}{3N} = k_BT$

$$P(\vec{p}) = \left(\frac{1}{2\pi m k_BT}\right)^{3/2} e^{-\frac{\vec{p}^{\,2}}{2mk_BT}}, \text{ Maxwell distribution}$$

In fact typical momentum $\sim \sqrt{m k_B T}$

In Q. Mech $p = \hbar k = \frac{h}{\lambda} \Rightarrow \lambda = \frac{h}{p} \sim \left(\frac{h^2}{m k_B T}\right)^{1/2}$

If we define $\boxed{\lambda_T = \left(\frac{h^2}{2\pi k_B T}\right)^{1/2}}$ the Sackur-Tetrode formula becomes

$$S = N k_B \left[\ln \frac{V}{N \lambda_T^3} + \frac{5}{2}\right] = N k_B \left[\ln \left(\frac{r_s}{\lambda_T}\right)^3 + \frac{5}{2}\right]$$

where r_s is the spacing between the particles

2) What is the chemical potential of ideal gas

$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$ How do I keep S const.

$$dS = N k_B \left[\ln \frac{V}{N \lambda_T^3} + \frac{5}{2}\right] - 3 N k_B \, d(\ln \lambda_T) - k_B dN$$

$$= k_B dN \left(\ln \frac{V}{N \lambda_T^3} + \frac{5}{2}\right) + 3 N k_B \, d \ln \sqrt{\frac{E}{N V}} - k_B dN$$

$$= k_B dN \left(\ln \frac{V}{N \lambda_T^3} + \frac{5}{2}\right) + \frac{3 N k_B}{2E} dE - \frac{3}{2} k_B dN - k_B dN$$

$$= k_B dN \left(\ln \frac{V}{N \lambda_T^3}\right) + \frac{dE}{T}$$

If $dS = 0$

$$\frac{dE}{dN} = k_B T \ln \frac{N \lambda_T^3}{V}$$

$$= k_B T \ln (\rho \lambda_T^3)$$

BTW, $G = U - TS + PV = \frac{3}{2} N k_B T - N k_B T \left[\ln \frac{V}{N \lambda_T^3} + \frac{5}{2}\right] + N k_B T$

$$G/N = -k_B T \ln \frac{V}{N\lambda_T^3} = k_B T \ln P\lambda_T^3$$

[Note that for multicomponent system $\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V}$
$G = \sum_i N_i \mu_i$]

Comment on def: How to keep entropy fixed while adding particles.

Quantum Mechanical Version

$$\langle \mathcal{O}(t) \rangle = \langle \psi(t) | \hat{\mathcal{O}} | \psi(t) \rangle$$

Statmech $\sum_r p_n \langle \psi_n(t) | \hat{\mathcal{O}} | \psi_n(t) \rangle$ complete $|\psi_n\rangle$'s basis

$$\mathrm{Tr}\left(\hat{\mathcal{O}}\rho(t)\right) = \langle \mathcal{O}(t) \rangle$$

where $$\rho(t) = \sum_r p_r |\psi_n(t)\rangle\langle\psi_n(t)|$$

Typically mixed state. Pure state $|\psi\rangle\langle\psi|$

General condn $\rho^2 = \rho$

$$\frac{d}{dt}\rho(t) = \sum_r p_r \left[\frac{d}{dt}|\psi_n\rangle\langle\psi_n| + |\psi_n\rangle \frac{d}{dt}\langle\psi_n|\right]$$

$$= \sum_r p_r \left[\frac{H}{i\hbar}|\psi_n\rangle\langle\psi_n| - |\psi_n\rangle\langle\psi_n|\frac{H}{i\hbar}\right]$$

$$= \frac{1}{i\hbar}[H, \rho(t)]$$

$\rho = \rho(H)$ $\qquad \frac{d}{dt}\rho = 0$

Microcanonical ensemble

P_n is the same for all energy eigenstates $|\psi_n\rangle$ with $E < E_n < E + \Delta E$.

$$P_n = \frac{1}{\Omega(E)\Delta E} \qquad \sum_n P_n = \frac{1}{\Omega(E)\Delta E}\Omega(E)\Delta E = 1$$

$$\text{Shannon entropy} = \sum_n P_n \ln \frac{1}{P_n} = [\quad] \ln(\Omega(E)\Delta E)$$

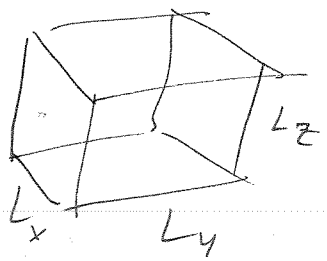
$$= \ln \Omega(E) + [\quad] \text{const}$$

not scaling as N

Missing the factor k_B from Boltzmann.

Back to ideal gas: Quantum version

$$\psi_{\vec{k}} = e^{i\left(\sum_{j=1}^{N} \vec{k}_j \cdot \vec{x}_j\right)}$$

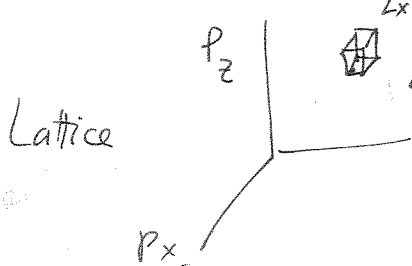


Non-deg.: each k distinct.: permutations [when k's are the same, quantum statistics matters] eqvt.

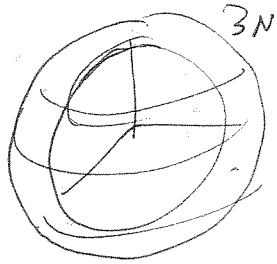
For each particle $k_x = \frac{2\pi n_x}{L_x}$ $\quad k_y = \frac{2\pi n_y}{L_y}$ $\quad k_z = \frac{2\pi n_z}{L_z}$

$p_x = \hbar k_x = \frac{h n_x}{L_x}$

Lattice



$\frac{h^3}{L_x L_y L_z} = \frac{h^3}{V}$ $\quad \left(\frac{h^3}{V}\right)^N$



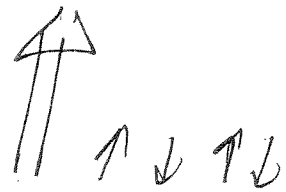
How many pill boxes in the shell

$\frac{\text{Vol}}{\text{pill box}}$

$$\frac{1}{N!}\int \frac{d^{3N}p}{\left(\frac{h^3}{V}\right)^N} \qquad \delta\left(\sum_i \frac{\vec{p}_i^{\,2}}{2m} - E\right)\Delta E$$

Origin of $\frac{dpdq}{h}$ rule $\Leftarrow$ $\frac{V^N}{h^{3N}}\int d^{3N}p \;\delta\left(\sum_i \frac{\vec{p}_i^{\,2}}{2m} - E\right)\Delta E$ $\Rightarrow$ Reduces to the classical calculation

Example II: (Non-interacting) Spins in a magnetic field.



N spins $\sigma_i = \pm 1$

$N = N_\uparrow + N_\downarrow$

$M = N_\uparrow - N_\downarrow$

$\frac{M}{N} = m$

$E = -h \sum \sigma_i = -hM$

2^N total conf. ${}^N C_{N_\uparrow}$ configur.'s

correspond to a particular M (and E, therefore)

$N_\uparrow = N\left(\frac{1+m}{2}\right)$ $N_\downarrow = N\left(\frac{1-m}{2}\right)$

$\ln {}^N C_{N_\uparrow} = \ln \frac{N!}{N_\uparrow! N_\downarrow!} = N \ln N - N$
$- N_\uparrow \ln N_\uparrow + N_\uparrow$
$- N_\downarrow \ln N_\downarrow + N_\downarrow$

$= -N\left[\frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2}\right]$

$E = -Nmh$

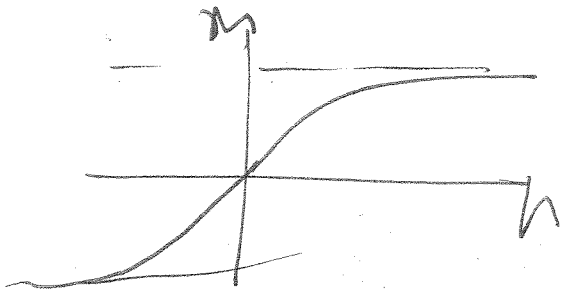
$\frac{\partial S}{\partial E} = \frac{Nk_B}{2}\left[\ln\left(\frac{1+m}{2}\right) - \ln\left(\frac{1-m}{2}\right)\right] \times \frac{dm}{dE}$

$\frac{1}{T} = -\frac{Nk_B}{2}\left(\ln \frac{1+m}{1-m}\right)\left(-\frac{1}{Nh}\right)$

$e^{\frac{2h}{k_B T}} = \frac{1+m}{1-m} \Rightarrow m = \frac{e^{2\beta h} - 1}{e^{2\beta h} + 1}$

$= \tanh \beta h$

$\frac{1}{k_B T} = \beta$



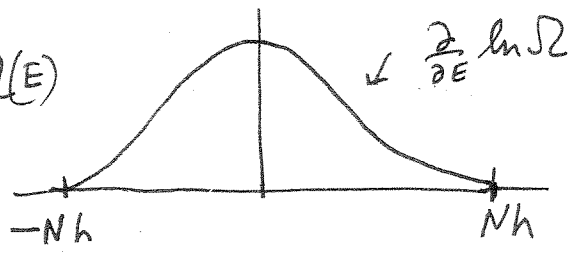
For small h $\quad m = \beta h$ so susceptibility $\chi \sim \beta \sim \frac{1}{T}$

[More carefully $E = -h\mu \sum \sigma_i$ and $m = \mu \sigma_i$

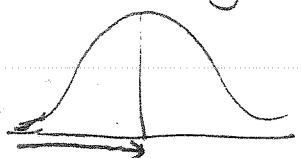
(μ = mag moment)

$$m = \mu \tanh \mu\beta h \Rightarrow \chi = \frac{\mu^2}{k_B T} \quad]$$

BTW $\Omega(E)$



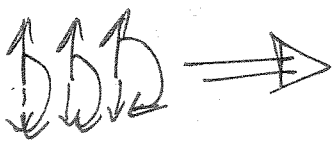
Increasing E decreases $\Omega(E)$ $\Rightarrow$ negative temp



Typically heating up

But ⇅ Align ↑↑↑↑↑

than put a ⊥ mag pulse



$\beta_{neg} < \beta$

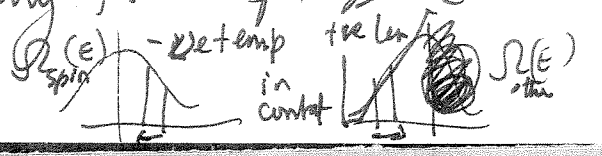
neg temp hotter than any temp

always gives heat to any +ve temp system

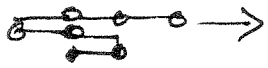
H

↓↓↓↓

Neg temperature system



Example II A pulled polymer (1-d)
No self avoidance

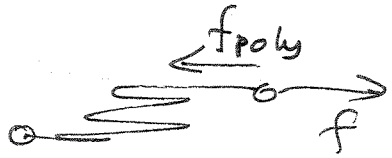


$X = L - R$

$N = L + R$

$H = -fX$ exact same math

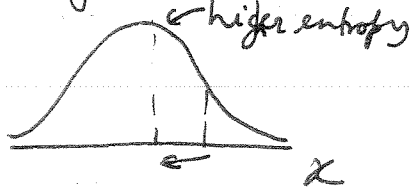
$x = \frac{X}{N} = \text{th}\,\beta f$



$f(x) = \frac{k_B T}{2} \ln \frac{1+x}{1-x}$

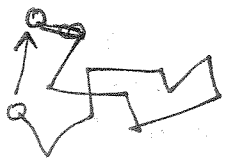
$\simeq k_B T x$ for small x

Entropic force $\propto T$

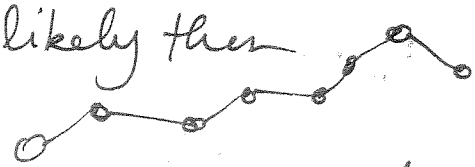


$f_{Poly} = -\overbrace{k_B T}^{\text{Spring con.}} x$

The same happens for polymer in 3d



More likely then



Many more ways of having the same end to end distance.

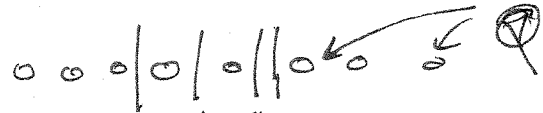
How does it go that way in reality? The water molecules in the solution kick it and fold it up. Hence $\propto$ proportional to T.

Example IV Einstein model of phonons

N noninteracting 3dim. harmonic oscillators with freq. ω. $\Rightarrow 3N$ one-dim Harmonic oscillators $E_n = (n+\frac{1}{2})\hbar\omega$

$$E = \hbar\omega \underbrace{\sum_{i=1}^{3N} n_i}_{Q} + \frac{3N}{2}\hbar\omega$$

Call $3N = N'$ Each state corresponds to partitioning Q in N' boxes.



$$\frac{(Q+N'-1)!}{Q!\,(N'-1)!}$$

$$S = k_B \left[(Q+N'-1)\ln(Q+N'-1) - Q\ln Q - (N'-1)\ln(N'-1) \right]$$

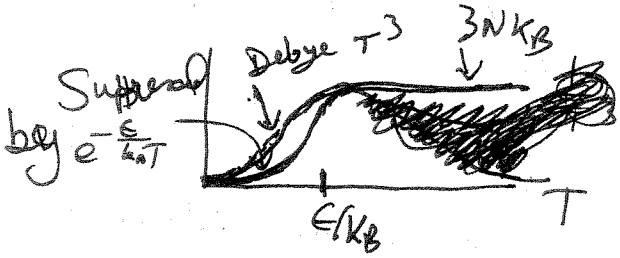
$$\frac{1}{T}\frac{\partial S}{\partial E} = \frac{\partial S}{\partial Q}\frac{1}{\hbar\omega} \Rightarrow \frac{\hbar\omega}{k_B T} = \ln(Q+N'-1)/Q$$

$$\Rightarrow \frac{Q}{N'-1} = \left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^{-1}$$

$$\Rightarrow \quad E = \hbar\omega Q + \frac{3N\hbar\omega}{2} = \frac{3N\hbar\omega}{e^{\frac{\hbar\omega}{k_BT}} - 1} + \frac{3N\hbar\omega}{2}$$

$$U = \frac{3N\epsilon}{2} + \frac{3N\epsilon}{e^{\frac{\epsilon}{k_BT}} - 1} \quad \text{where } \epsilon = \hbar\omega$$

$$C_V = \left(\frac{\partial U}{\partial T}\right) = \frac{3N\epsilon^2}{k_BT^2} \frac{e^{\epsilon/k_BT}}{\left(e^{\frac{\epsilon}{k_BT}} - 1\right)^2}$$



for small T $\quad C_V \approx \frac{3N\epsilon^2}{k_BT} \frac{e^{\epsilon/k_BT}}{e^{2\epsilon/k_BT}} = \frac{3N\epsilon^2}{k_BT} e^{-\epsilon/k_BT}$

For large T $\quad C_V \approx \frac{3N\epsilon^2}{k_BT^2} \frac{1}{\frac{\epsilon^2}{k_B^2T^2}} = 3Nk_B$

Equipartition $\frac{1}{2}k_BT$ for each momentum coordinate

$$U \sim 3N\left(\tfrac{3}{2} + \tfrac{3}{2}\right)k_BT = 3Nk_BT$$

$$C_V = 3Nk_B$$

Debye ϵ distributed as $\epsilon^2 d\epsilon$ for $0 \le \epsilon \le \epsilon_D$

Low temp $C_V \sim T^3$ for acoustic phonons