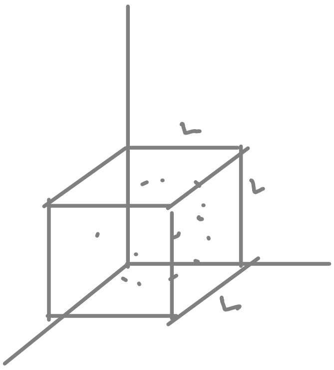
↳ system study approaches

- Energy thermo
- Matter stat mech, solid state
- Waves EM, quantum
- Mathematical Modelling Diffusion, Random Walk.

— x —

STAT MECH

— x —



System: N particles

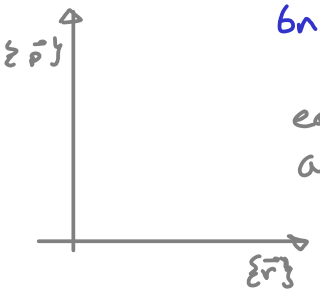
$x_i, y_i, z_i \in [0, L] \quad \forall i$

$V = L^3$

$\{\vec{r}_i\} = (x_i, y_i, z_i)$

● $|\{\vec{r}\}| = |\{\vec{p}\}| = 3n$

State Space



6n dimensional space

each point defines a microstate.

● Hamiltonian function Gives total energy of the system

$$H(\{\vec{r}\}, \{\vec{p}\}) = U(\{\vec{r}\}) + K(\{\vec{p}\})$$

Hamilton's Equations

Isolated System: No energy exchange with surroundings.

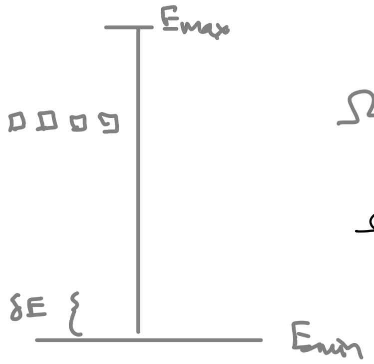
$$\frac{d}{dt} H(\{\vec{r}\}, \{\vec{p}\}) = 0$$

$$\Rightarrow \sum_{i=1}^{N} \left\{ \frac{\partial H}{\partial \vec{r}_i} \frac{\partial \vec{r}_i}{dt} + \frac{\partial H}{\partial \vec{p}_i} \cdot \frac{\partial \vec{p}_i}{\partial t} \right\} = 0.$$

$$\frac{\partial r_i}{\partial t} = \left(\frac{d}{dt} x_i, \frac{d}{dt} y_i, \frac{d}{dt} z_i \right)$$

$$\left. \begin{aligned} ● \quad \frac{\partial H}{\partial \vec{r}_i} &= - \overbrace{\frac{\partial \vec{p}_i}{\partial t}}^{\text{force}} \\ ● \quad \frac{\partial H}{\partial \vec{p}_i} &= \underbrace{\frac{d \vec{r}_i}{dt}}_{\text{Velocity.}} \end{aligned} \right\} \text{Hamilton's Equations} \; ●$$

Energy Ladder



$\Omega(E_i)$ = no. of cells with energy E_i

$\Omega(E_1) = 1$ for ice.

Boltzmann entropy

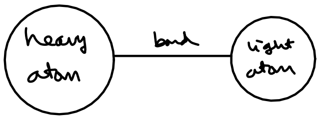
Microscopic definition of entropy.

$$S \propto \ln(\Omega(E_i))$$
$$S = k_B \ln(\Omega(E_i))$$

CALCULATIONS IN AN ISOLATED SYSTEM

1. 1D Harmonic Oscillation

Calculate $\Omega(E)$

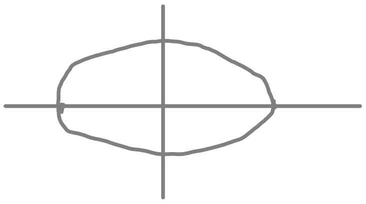


m = mass of light atom

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}k(x-x_0)^2 = E$$

Reorganising,

$$\frac{p^2}{\sqrt{2mE}} + \frac{(x-x_0)^2}{\left(\sqrt{\frac{2E}{k}}\right)^2} = 1 \xrightarrow[\text{ellipse}]{\text{squashing}}$$



Using ellipse model,

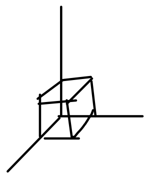
$\Omega(E_i)$ = circumference of ellipse / δE.

or $\Omega(E_i) \propto \pi \left(\sqrt{\frac{2E}{K}} + \sqrt{2mE} \right)$

or $\Omega(E_i) \propto \sqrt{E_i}$

2. Ideal Gas

Calculate $\Omega(E)$ dependence on N



Volume of 6N-d cell

$= \delta\{r\}\,\delta\{p\}$

$= h^{3n}$

h= arbitrary

h= Planck's contant in QM

$\delta(H-E) = 1$ if $H == E$
$ 0$ otherwise.

Krone
~~Dirac~~ cker
Delta

$$\Omega(N,V,E) = \frac{1}{h^{3n}} \int_{\{\vec{r}\}} \int_{\{\vec{p}\}} \delta(H-E)\, \delta\{\vec{r}\}\, \delta\{\vec{p}\}$$

Hamiltonian fnct.
$H(r\,p) = \frac{1}{2m} \sum \vec{p}_i \cdot \vec{p}_i$

$$= \frac{1}{h^{3N}} V^N \int_{\{\vec{p}\}} \delta(H-E)\, \delta\{p\}$$

Now, $\sum p^2 = (\sqrt{2mE})^2 \Rightarrow$ sphere.

surface area $\propto \left(\sqrt{2mE}\right)^{3N-1}$

$\propto E^{\frac{3N-1}{2}}$

$$\Omega\ N, V, E \propto \frac{1}{h^{3N}} V^N E^{\frac{3N-1}{2}}$$

CALCULATIONS IN A CLOSED SYSTEM

- $P(E_i) \propto e^{-\beta E_i}$, $\beta = \frac{1}{K_B T}$
- $P(E_i) = \frac{e^{-\beta E_i}}{Z}$ $\qquad Z = \frac{e^{-\beta E_i}}{P(E_i)}$

- $Z = \frac{1}{h^{3N}} \int_{\{\vec{r}\}} \int_{\{\vec{p}\}} e^{-\beta H(\{\vec{r}\},\{\vec{p}\})} \, d\{\vec{r}\} \, d\{\vec{p}\}$

1. 1D Harmonic Oscillator $\langle E \rangle$

$$Z = \sum e^{-\beta E_i}$$

$$\ln Z = \ln \sum e^{-\beta E_i}$$

$$\frac{\partial}{\partial \beta}(\ln Z) = -\frac{1}{\sum e^{-\beta E_i}} \sum E_i e^{-\beta E_i}$$

$$= - \sum E_i \left(\frac{e^{-\beta E_i}}{Z} \right)$$

$$= - \sum E_i P(E_i)$$

$$\boxed{-\frac{\partial}{\partial \beta}(\ln Z) = \langle E \rangle}$$

2. Covariance and C_V

$$\frac{\partial}{\partial \beta}\left[\sum E_i e^{-\beta E_i}\right] = \frac{\partial}{\partial \beta}\left(-Z \frac{\partial}{\partial \beta}(\ln Z)\right)$$

$$+\sum E_i^2 e^{-\beta E_i} = +\left[Z \frac{d^2}{d\beta^2}(\ln Z) + \frac{\partial Z}{\partial \beta} \frac{\partial}{\partial \beta}(\ln Z)\right]$$

$$\langle E_i^2 \rangle = \frac{d^2}{d\beta^2}(\ln Z) + \left[\frac{d}{d\beta}(\ln Z)\right]^2$$

$$\langle E_i^2\rangle - \langle E_i\rangle^2 = \frac{d^2}{d\beta^2}(\ln Z)$$

Now,

$$\langle E^2\rangle - \langle E\rangle^2 = \frac{-\frac{\partial}{\partial T}\langle E\rangle}{\frac{\partial}{\partial T}\beta} = \frac{-C_v}{-\frac{1}{k_B T^2}}$$

$$= C_v k_B T^2$$

$$\frac{\partial^2}{d\beta^2}\ln Z = -\frac{\partial}{\partial\beta}\langle E\rangle$$

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

$$\frac{d\beta}{dT} = -\frac{1}{k_B T^2}$$

◇ Entropy for a closed system

$$S = -K_B \sum P_i \ln P_i = -K_B \langle \ln P\rangle$$

3. Hemholtz free energy

$$S = -K_B \sum_i \left(\frac{e^{-\beta E_i}}{Z}\right)\left(-\beta E_i - \ln Z\right)$$

$$= \beta K_B \sum E_i P_i + K_B \ln Z \sum P_i$$

$$S = \frac{\langle E\rangle}{T} + K_B \ln Z$$

or

$$-K_B T \ln Z = \langle E\rangle - TS$$

Thermodynamics

Laws : ① $dU = dQ + dW$

② $(\Delta S)_{total} = (\Delta S)_{system} + (\Delta S)_{surroundings}$

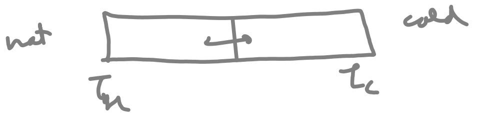
In spontaneous process, $(\Delta S)_{total} \geq 0$

Quasi-static : $(\Delta S)_T = 0$

Clausius inequality: $(\Delta S)_{system} \geq \dfrac{dQ}{dT}$

③ As $T \to 0$, $S \to 0$

Spontaneity : Heat flow.



$T_H >> T_c$

Assume H : $T_c \to T_H$

$\therefore (\Delta S)_{cold} = -\dfrac{dQ}{dT_c}$

$(\Delta S)_H = \dfrac{dQ}{dT_H}$

$(\Delta S)_T = dQ \left(\dfrac{1}{T_H} - \dfrac{1}{T_c} \right)$

≤ 0

$\therefore$ Not spontaneous
cold

$\Rightarrow$ $H \to C$ is spontaneous.

Thermodynamic Potentials

U, H, A, G

i) <u>Const V</u> $(dV = 0)$

$dU = dq$

$dW = 0$

$dS \geq \dfrac{dq}{dt} = \dfrac{dU}{dt}$

$TdS - dU \geq 0$

ii) <u>Const S</u> $dU = dq + dw$

$H = U + PV$

$dH = dU + PdV + VdP$

$= dq - PdV + PdV + VdP$

$dH = dq + VdP$

$(dH)_{P,S} = dq$

$TdS - dH = 0$

Lagrangian Mechanics

- Lagrangian: $L(q, \dot{q}, t)$

generalised coordinates

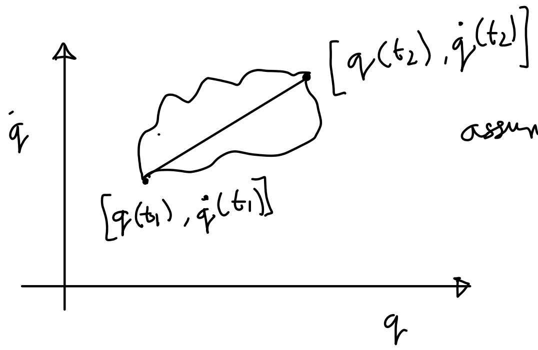
generalised velocity

$$\dot{q} = \frac{dq}{dt}$$

dependence on time is implicit.

$$L = K(\dot{q}) - U(q)$$

- In statespace:

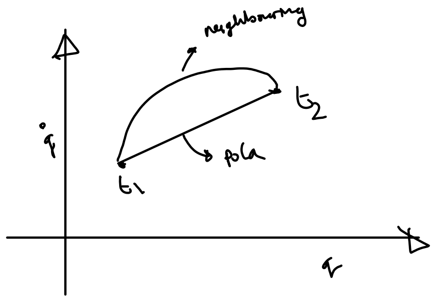


assume $t_2 > t_1$.

Taking the least action path.

$$\text{Action}(S) = \int_{t_1}^{t_2} L(q, \dot{q}, t)\, dt$$

DERIVING LAGRANGE'S EQUATIONS OF MOTION



- Consider 2 paths: least Action, and something else.

$(q(t), \dot{q}(t)) \longrightarrow$ least action path.

$(q(t) + \delta q(t), \dot{q}(t) + \delta \dot{q}(t)) \longrightarrow$ other path.

- The paths must meet at t_1 and t_2.

$$\delta q(t_1) = \delta q(t_2) = 0$$

- S for least Action: $\int_{t_1}^{t_2} L(q, \dot{q}, t)\, dt$

- Change in S: $\int_{t_1}^{t_2} L(q + \delta q, \dot{q} + \delta \dot{q}, t)\, dt - \int_{t_1}^{t_2} L(q \quad \dot{q} \quad t)\, dt = \boxed{\delta S}$

$$\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\delta \dot{q}$$

$$= \delta \int_{t_1}^{t_2} L(q, \dot{q}, t)\, dt$$

$\updownarrow =$ how?

$$= \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q}\delta q + \frac{\partial L}{\partial \dot{q}}\delta \dot{q} \right) dt.$$

$$\delta \dot{q} = \frac{d}{dt}(\delta q)$$

$$\text{or } \delta S = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q}\delta q + \underline{\frac{\partial L}{\partial \dot{q}} \frac{d}{dt}(\delta q)} \right) dt$$

$$\int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}} \frac{d}{dt}(\delta q)\, dt$$

$$\boxed{\begin{aligned} \int uv\,dx &= u.V - \int u'V\,dx \\ V &= \int v\,dx. \end{aligned}}$$

Integrating by parts

$$0 = \left[\frac{\partial L}{\partial \dot q}\delta q\right]_{t_1}^{t_2} - \int_{t_1}^{t_2}\frac{d}{dt}\left(\frac{\partial L}{\partial \dot q}\right)\delta q\,dt.$$

Since $\delta q = 0$ @ t_1, t_2.

$$\left|\frac{\partial L}{\partial \dot q}\delta q\right|_{t_1}^{t_2} - \int_{t_1}^{t_2}\frac{d}{dt}\left(\frac{\partial L}{\partial \dot q}\right)\delta q\,dt$$

$$\delta S = \int_{t_1}^{t_2}\frac{\partial L}{\partial q}\delta q\,dt - \int_{t_1}^{t_2}\frac{d}{dt}\left(\frac{\partial L}{\partial \dot q}\right)\delta q\,dt$$

$$\delta S = \int_{t_1}^{t_2}\left(\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot q}\right)\right)\delta q\,dt$$

In path of least action:

$$\delta S = 0 \ \forall\ \delta q$$

or

$$\boxed{\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot q}\right) = 0.}$$

LAGRANGE'S EQUATION OF MOTION.

Again, $\frac{\partial L}{\partial q} = -\underset{\text{force}}{\underset{\downarrow}{\frac{\partial U}{\partial q}}}$ (from $L = K - U$) $\Rightarrow \frac{d}{dt}\left(\frac{\partial L}{\partial q}\right) =$ rate of change of generalised momentum.

Deriving:

Langrangian ⟶ Hamiltonian

$$\frac{dL}{dt} = \sum_{i=1}^{N}\frac{\partial L}{\partial q_i}\dot q_i + \sum_{i=1}^{N}\frac{\partial L}{\partial \dot q_i}\ddot q_i$$

$$= \sum_{i=1}^{N}\frac{d}{dt}\left(\frac{\partial L}{\partial \dot q_i}\right)\dot q_i + \sum_{i=1}^{N}\frac{\partial L}{\partial \dot q_i}\ddot q_i$$

$$= \sum_{i=1}^{N}\frac{d}{dt}\left(\dot q_i\frac{\partial L}{\partial \dot q_i}\right)$$

$$\sum_{i=1}^{N}\frac{d}{dt}\left(\dot q_i\frac{\partial L}{\partial \dot q_i}\right) - \frac{dL}{dt} = 0$$

$$\frac{d}{dt}\left[\sum_{i=1}^{N}\dot q_i\frac{\partial L}{\partial \dot q_i} - L\right] = 0$$

or

$$\boxed{\underbrace{\sum_{i=1}^{N}\dot q_i\frac{\partial L}{\partial \dot q_i} - L}_{\text{Hamiltonian}} = \text{const}}$$

Prove:

$$\sum_{i=1}^{N}\dot q\frac{\partial L}{\partial \dot q} - L = H$$

$$\frac{\partial L}{\partial \dot q} = \frac{\partial K}{\partial \dot q}$$

$$= m\dot q$$

$$\Rightarrow \underbrace{\sum_{i=1}^{N}\dot q(m\dot q) - L}_{} = \text{Const}$$

$$= 2K - (K - U)$$

$$= K + U$$

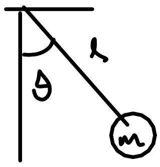
$$= H$$ QED

Eg: Simple Pendulum

Step 1: Construct L

$K(\dot{\theta}),\ U(\theta)$

$$L(\theta,\dot{\theta}) = K(\dot{\theta}) - U(\theta)$$



Step 2: $\frac{\partial L}{\partial \theta}$ and $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right)$

$$\frac{\partial L}{\partial \theta} = -mgl\sin\theta$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{\theta}}\right) = ml^2\ddot{\theta}$$

?? Redo

Mathematical Modelling

The process: Diffusion. Model: Random walk.

1D Random Walk:

$\overset{l}{\leftarrow} \quad \overset{r}{\rightarrow}$

P(finding at point p after t steps) is a gaussian distribution

N = total steps

n_1 = " " $\rightarrow$

n_2 = " " $\leftarrow$

Displacement, $m = (n_1 - n_2) l$

l = length of each step

$$P(n_1 \text{ steps to the right}) = \frac{N!}{n_1!\, n_2!} p^{n_1} q^{n_2} = W_N(n_1)$$

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} p^{\frac{N+m}{2}} q^{\frac{N-m}{2}}.$$

$$\langle n_1 \rangle = \sum_{n_1=0}^{N} W_N(n_1)\, n_1$$

$$= \sum_{n_1=0}^{N} \frac{N!}{n_1!\,(N-n_1)!} p^{n_1} q^{(N-n_1)} n_1 \longrightarrow \boxed{n_1 p^{n_1} = p \frac{\partial}{\partial p} p^{n_1}}$$

$$= \sum \frac{N!}{n_1!\,(N-n_1)!} q^{(N-n_1)} \left[p \frac{\partial}{\partial p} p^{n_1} \right]$$

$$= p \frac{\partial}{\partial p} \left[\sum \frac{N!}{n_1!\,(N-n_1)!} q^{N-n_1} p^{n_1} \right]$$

$$= p \frac{\partial}{\partial p} (p+q)^N = pN(p+q)^{N-1}$$

or

$$\langle n_1 \rangle = Np$$

$$\langle n_2 \rangle = Nq$$

Quantum Mechanics

Motivations

1. Black Body Radiation
2. Photoelectric effect
3. Hydrogen Spectrum
4. Heat capacity of solids (at low temps)
5. Diffraction of electrons by crystals
6. Spin Angular Momentum.

$\psi(x,t)$

PD: $\psi^{*}(x,t) \cdot \psi(x,t)$

$$\hat{p} = -i \hbar \frac{\partial}{\partial x}$$

$$\boxed{\hbar = \frac{h}{2\pi}}$$

$$\hat{K} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

$$\hat{H} = \hat{K} + \hat{U}$$

$$= \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x)$$

Schrod Eq:

$$H(\psi(x,t)) = E \cdot \psi(x,t)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x,t) + U(x)\psi(x,t) = E\psi(x,t)$$

1D Model:

Inside box: $U(x) = 0$.

$$\boxed{-\frac{\hbar^2}{2m}} \frac{\partial^2}{\partial x^2} \psi(x,t) = E\psi(x,t)$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

$$k^2 \psi(x,t) + \frac{\partial^2}{\partial x^2}\psi(x,t) = 0$$

SHM

$$\psi = A \cos kx + B \sin kx$$

Prove quantization $\psi(x=0, L) = 0.$

$A = 0$

$B \neq 0$

$\sin kL = 0$

$kL = n\pi$

$k = \frac{n\pi}{L}$

" " energy:

$$k = \sqrt{\frac{2mE}{\hbar^2}} \qquad E = \frac{k^2\hbar^2}{2m}$$

$$E = \frac{n^2 \cancel{\pi^2}}{L^2} \frac{h^2}{4\cancel{\pi^2}} \cdot \frac{1}{2m}$$

$$\boxed{E = \frac{n^2h^2}{8mL^2}}$$

$$\Rightarrow \psi(x,t) = B \sin\left(\frac{n\pi x}{L}\right)$$

Now,

P(electron in world)=1

$$\int \psi^*(x)\, \psi(x)\, dx = 1$$

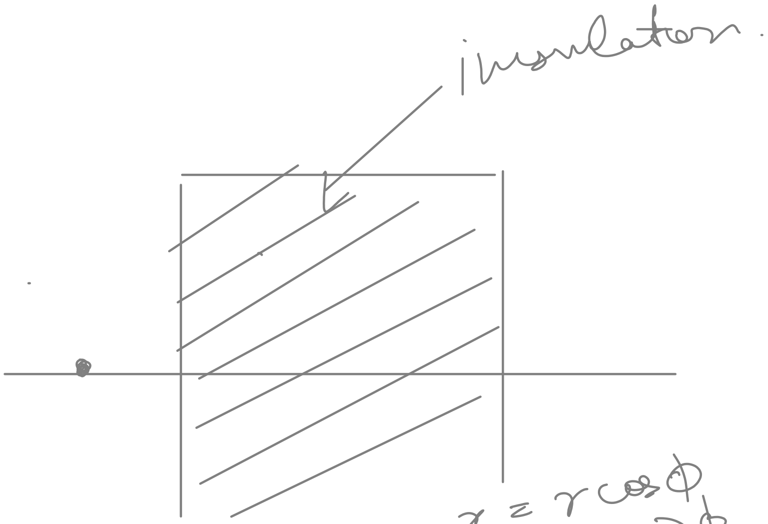
⋮

$$\boxed{B = \sqrt{2/L}}$$

$$E = \frac{n^2h^2}{8mL^2} \qquad \psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi}{L}x\right)$$

2D box,

- $-\frac{\hbar}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]$
- $\psi(x,y) = X(x)\,Y(y)$
- $E = E_1+E_2 = (n_1^2+n_2^2)\,\frac{h^2}{8mL^2}$
- $\psi(x,y) = \frac{2}{L}\sin\left(\frac{n_1\pi}{L}x\right)\sin\left(\frac{n_2\pi}{L}x\right)$



$y = r \sin\phi$

$x = r \cos\phi$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r} \cos\phi + \frac{\partial f}{\partial \phi} \times \frac{\partial \phi}{\partial x}$$

$$\frac{\partial \phi}{\partial x} = \frac{1}{r}(-\sin\phi)$$

$$f(x, y) = f(r, \phi).$$

$=$

$$\frac{x}{\partial r} = \cos\phi \quad \frac{d\phi}{\partial x} = -\sin\phi$$