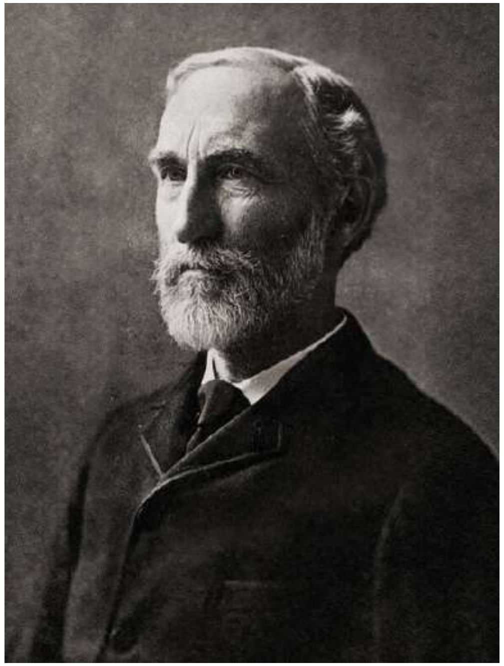
CH 576: Statistical Mechanics



Josiah Willard Gibbs
(1839-1903)

James Clerk Maxwell
(1831-1879)

Ludwig Edward Boltzmann
(1844-1906)

Statistical Mechanics

Classical Mechanics
Quantum Mechanics } Not enough !!

$\{q, p\} \rightsquigarrow$ { Newtonian Mechanics →
Lagrangian →
Hamiltonian →

they are equivalent

q = position co-ordinate

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

$\ddot{q} = \frac{d^2q}{dt^2}$

$m\ddot{q} = F$ → $F = -V'(q) \equiv -\frac{dV}{dq}$

Second order differential equation

Initial position $q(0)$
Initial velocity $\dot{q}(0)$ } $q(t)$

"DETERMINISTIC"

Wavefunction $\psi(q, t) \rightsquigarrow$ All the information of the system

Probabilistic

↓

$\psi^* \psi \to$ prob. density

$$i\hbar \frac{\partial \psi(q,t)}{\partial t} = \hat{H}\psi(q,t) \longrightarrow \psi(q,t) = e^{-\frac{i\hat{H}t}{\hbar}}\psi(q,0)$$

if it has no explicit time dependence

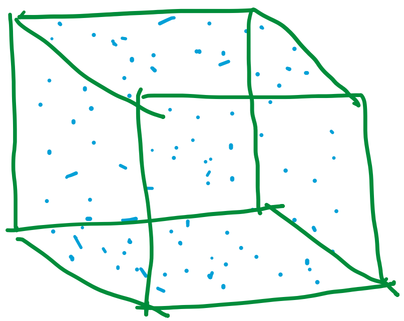
Statistical Mechanics gives a prescription to calculate macroscopic (thermodynamic) quantities, starting from a microscopic description of the system.

Calculate $\rightarrow$ Pressure, Entropy, free energy . . . .

Microscopic Description

Classical Mechanics

Postulates and Hypothesis



CM

$(q_k, p_k) \rightarrow$ k^{th} molecule / atom

$\{q_k, p_k\}$

Classical Mechanics

– Deterministic –

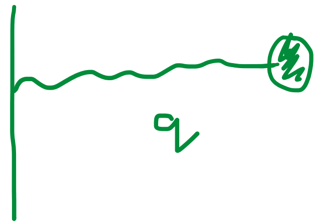
$$F = m\ddot{q} \qquad \text{"Newton"}$$

$$F = -\frac{\partial V}{\partial q}$$

Example: Simple Harmonic Oscillator (SHO)

$$V = \frac{1}{2}k(q-q_0)^2$$

k; $(q-q_0)$: Displace-ment



$$m\ddot{q} = -k(q-q_0)$$

$$(q-q_0) = \xi$$

$$\dot{q} = \dot{\xi}$$

$$\ddot{q} = \ddot{\xi}$$

$$m\frac{d^2\xi}{dt^2} = -k\xi$$

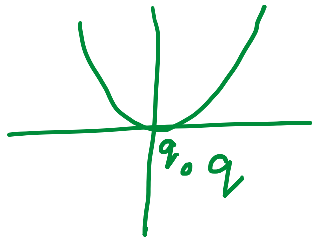
$$\frac{d^2\xi}{dt^2} + \frac{k}{m}\xi = 0$$

$$\xi(t) = A\sin\omega t + B\cos\omega t$$

$$\omega = \left(\frac{k}{m}\right)^{\frac{1}{2}}$$

$$2\pi\nu = \left(\frac{k}{m}\right)^{\frac{1}{2}}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$



Lagrangian Approach: 1 particle

$$\underbrace{K}_{\text{Kinetic energy}}(\underbrace{\dot{x}, \dot{y}, \dot{z}}_{\text{velocities}}) = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

It is not a f^n of (x, y, z) but a f^n of $(\dot{x}, \dot{y}, \dot{z})$

$$L(x, y, z, \dot{x}, \dot{y}, \dot{z}) = K(\dot{x}, \dot{y}, \dot{z}) - V(x, y, z)$$

only a f^n of (x, y, z)

L → Lagrangian

$$\frac{\partial L}{\partial \dot{x}} = \frac{\partial K}{\partial \dot{x}} = \frac{m}{2} 2\dot{x} = m\dot{x}$$

$$\frac{\partial L}{\partial x} = -\frac{\partial V}{\partial x} \qquad \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) = m\ddot{x}$$

$$m\ddot{x} = F = -\frac{\partial V}{\partial x}$$

L. eq^n of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) = \left(\frac{\partial L}{\partial x}\right) \rightarrow \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) = \left(\frac{\partial L}{\partial q_j}\right)$$

$j = 1, 2, 3, \ldots$

Hamiltonian Approach:

$$H(p_1, p_2, p_3, q_1, q_2, q_3) = \sum_{j=1}^{3} p_j \dot{q}_j - L(\dot{q}_1, \dot{q}_2, \dot{q}_3, q_1, q_2, q_3)$$

$$\underbrace{\text{"Hamiltonian"}}$$

$$K = \sum_{j=1}^{3N} a_j (q_1, q_2, q_3 \dots) \dot{q}_j^2$$

→ depends on position but not on velocity

K. E. for N particle system.

$$\frac{\partial L}{\partial \dot{q}_j} = m\dot{q}_j = p_j = \frac{\partial K}{\partial \dot{q}_j} = 2a_j \dot{q}_j$$

$m\dot{q}_j$

$$a_j = \frac{m}{2}$$

$$H = \sum_j p_j \dot{q}_j - L$$

$$= \sum_j \underline{2a_j \dot{q}_j} \dot{q}_j - L$$

$$= 2 \sum_j \underbrace{a_j \dot{q}_j^2}_{K} - L = 2K - L = 2K - (K - V) = K + V$$

$$= \underline{\text{Total energy}}$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) = \left(\frac{\partial L}{\partial q_j}\right)$$

$$p_j = \frac{\partial L}{\partial \dot{q}_j}$$

$$H = \sum_{j=1}^{3} p_j \dot{q}_j - L$$

$$dH = d\left(\sum_{j=1}^{3} p_j \dot{q}_j\right) - dL$$

$$= \sum_{j=1}^{3} p_j \, d\dot{q}_j + \sum_{j=1}^{3} \dot{q}_j \, dp_j -$$

$$L = L(\dot{q}_j, q_j)$$

$$dL = \sum_{j=1}^{3} \frac{\partial L}{\partial q_j} dq_j + \sum_{j=1}^{3} \frac{\partial L}{\partial \dot{q}_j} d\dot{q}_j$$

$$= \sum_j \underbrace{\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right)}_{\dot{p}_j} dq_j + \sum p_j \, d\dot{q}_j$$

$$= \sum \dot{p}_j \, dq_j + \sum p_j \, d\dot{q}_j$$

$$dH = \sum_j \dot{q}_j \, dp_j - \sum_j \dot{p}_j \, dq_j$$

$$H = H(p_j, q_j)$$

$$dH = \sum \frac{\partial H}{\partial q_j} dq_j + \sum \frac{\partial H}{\partial p_j} dp_j$$

Comparing

$$\left.\begin{aligned} \frac{\partial H}{\partial p_j} = \dot{q}_j \; ; \quad \frac{\partial H}{\partial q_j} = -\dot{p}_j \end{aligned}\right\} \text{Hamilton's eq}^n \text{ of motion}$$

Simple Harmonic Oscillator

$$m\ddot{x} = -kx$$
$$= m\dot{v}$$
$$= \dot{p}$$

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

$$\frac{\partial H}{\partial p} = \frac{p}{m} = \dot{x}$$

$$\frac{\partial H}{\partial x} = \frac{1}{2}2kx = -(-kx)$$
$$\parallel$$
$$-\dot{p}$$

$H(q_j, p_j)$

$$\frac{dH}{dt} = \underbrace{\sum\left(\frac{\partial H}{\partial q_j}\right)\frac{\partial q_j}{\partial t} + \sum\left(\frac{\partial H}{\partial p_j}\right)\frac{\partial p_j}{\partial t}}_{} + \frac{\partial H}{\partial t}$$

$\frac{\partial H}{\partial t} \rightarrow$ Partial derivative

$\frac{\partial H}{\partial t} \rightarrow = 0$ (no explicit time dependence)

$$= \underbrace{\sum -\dot{p}_j \dot{q}_j + \sum \dot{q}_j \dot{p}_j}_{=0} + 0 = 0$$

$\rightsquigarrow$ Hamiltonian is constant of motion

$\hookrightarrow$ Total energy of the system is conserved

Newton's equation:

$$m\ddot{q} = F = -\frac{dV}{dq}$$

→ Conservative force → Derivative of a potential

Lagrangian approach:

Define $L(\dot{q}, q) \equiv K(\dot{q}) - V(q)$

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

$$\frac{\partial L}{\partial q} = -\frac{\partial V}{\partial q}$$

Thus, $\boxed{\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) = \frac{\partial L}{\partial q}}$

$$m\ddot{q} = F$$

Newton's equation in terms of Lagrangian

Hamiltonian Approach:

$$H(p, q) = p\dot{q} - L(\dot{q}, q)$$

$$\frac{\partial H}{\partial p} = \dot{q} \qquad \frac{\partial H}{\partial q} = -\dot{p}$$

Hamilton's equation of motion

Thermodynamics:

Work done by the system

$$W = \int_A^B P\,dV$$

Heat absorbed by the system

$$Q = \int_A^B dq$$

$$\underbrace{Q - W}_{\text{path functions}} = \underbrace{\Delta E}_{\text{State } f^n} \rightarrow \text{Change in internal energy}$$

$\rightsquigarrow$ First law of thermodynamics

Change in entropy $\Delta S = \int_A^B \frac{dq_{rev}}{T}$ for a reversible process

Second law

for all other processes $\Delta S > \int_A^B \frac{dq}{T} \Rightarrow$ $\boxed{dS \geq \frac{dq}{T}}$

$$S - S_0 = \int_0^T \frac{dq_{rev}}{T} = S \quad \text{as} \quad S_0 = 0$$

(S at T=0 is zero)

"third law"

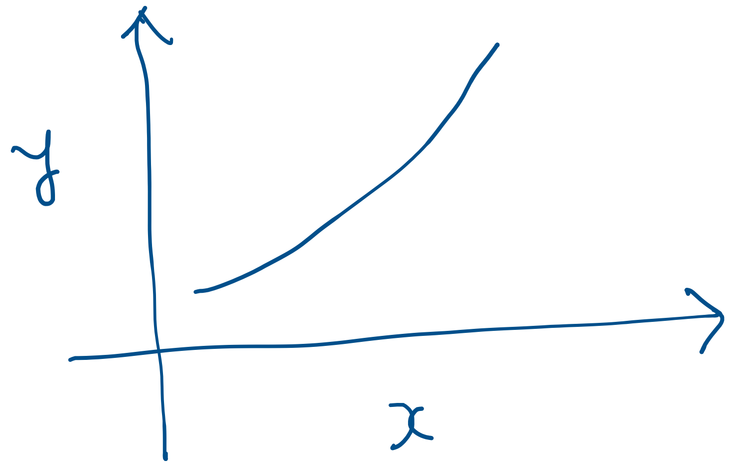
$$dE = đQ - đW$$

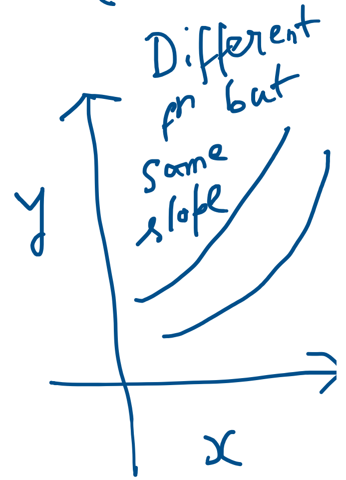
First law

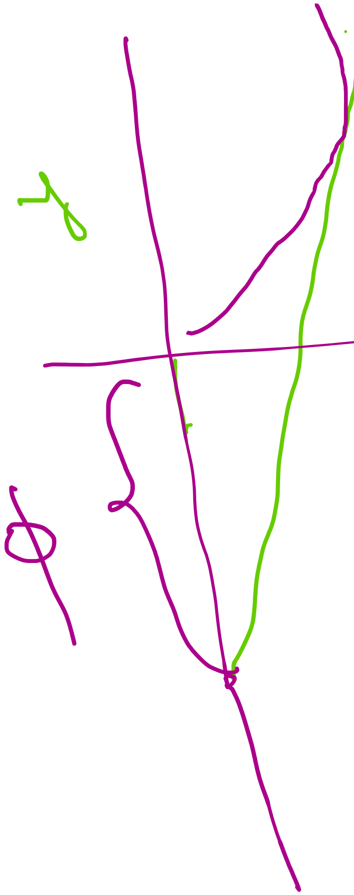
$$dE = T\,dS - P.dV \rightsquigarrow$$

(S, V) are the natural variables for $E \equiv E(S, V)$

$$\left(\frac{\partial E}{\partial S}\right)_V = T \qquad \left(\frac{\partial E}{\partial V}\right)_S = -P$$







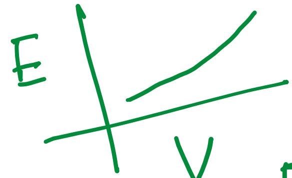
Slope:

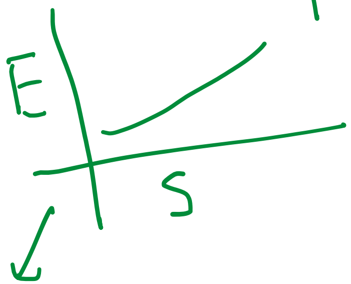
$$p = \frac{y-\phi}{x-0} \Rightarrow \boxed{\phi(p) = y - px}$$

slope (not pressure or momentum)

$$y(x) \Leftrightarrow \phi\left(p = \frac{dy}{dx}\right)$$

Legendre transformation





$$E(S,V) \Rightarrow f(T,V)$$

$$E(S) \Rightarrow f(T)$$

$$f(T) = E - TS = A(T,V)$$

→ Helmholtz free

$$dE = TdS - P\cdot dV$$

$$\left(\frac{\partial E}{\partial S}\right)_V = T \; ; \; \left(\frac{\partial E}{\partial V}\right)_S = -P$$

$$g = E - \left(\frac{\partial E}{\partial V}\right)_S V = \underbrace{E + PV}_{\rightarrow \text{enthalpy}}$$

$$H(p,q) = p\dot{q} - L(\dot{q},q)$$

$$H(p) = p\dot{q} - L(\dot{q})$$

$$f(p) = L(\dot{q}) - \left(\frac{\partial L}{\partial \dot{q}}\right)\dot{q}$$

$$f(p) = L(\dot{q}) - p\dot{q}$$

$$\underbrace{-f(p)}_{\to\, H(p)} = p\dot{q} - L(\dot{q})$$

$\rightarrow$ They are related by Legendre transformations

$$\phi(p) = y - px$$

Not momentum

$$p = \frac{dy}{dx}$$

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

Quantum Mechanics:

Probabilistic

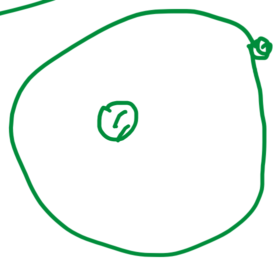
$\psi(x,t)$ $\psi(q,t)$

$\int dx\, \psi^*(x,t)\,\psi(x,t) \rightarrow$ Probability density

$\downarrow$

Total probability

H-atom



Simple Harmonic Oscillator (SHO)

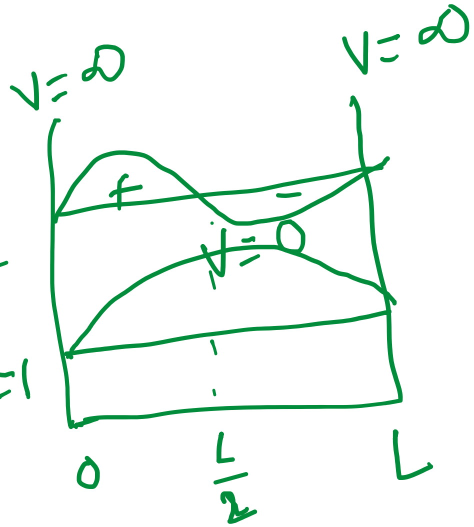
Rigid Rotors

Time independent Schrödinger's equation

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$$

$$\hookrightarrow \psi = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right)$$

Particle in a box: n=2



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

Phase Space

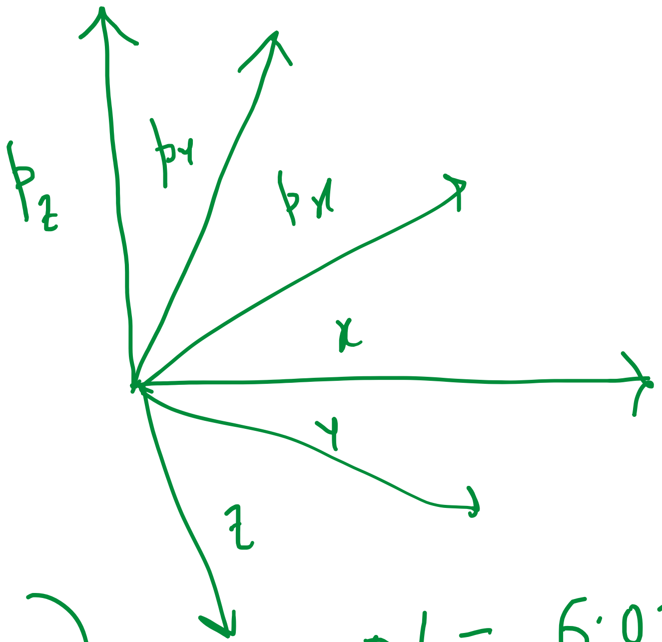
Single particle

(q, p)

$q \rightarrow x, y, z$

$p \rightarrow p_x, p_y, p_z$

~~6-co-ordinates~~



Think of N particles

$3N \rightarrow$ position co-ordinates

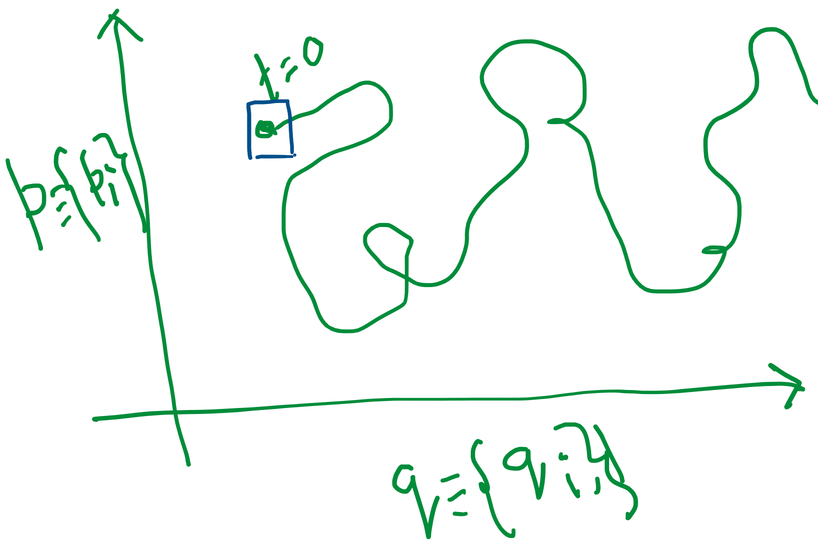
$3N \rightarrow$ momentum co-ordinates

$N = 6.023 \times 10^{23}$

$6N = \underbrace{36 \cdots\cdots \times 10^{23}}_{\text{Huge No.}}$

at some given time

$\{p_i, q_i\}$ or $\{q_i, p_i\} \Rightarrow$ phase space $\longrightarrow$ 6 N dimensional



$\longleftarrow$ Phase Space trajectory

What is rule the system follows in this phase space?

Each of these particles is following Newton's equation

No computer in this world can store

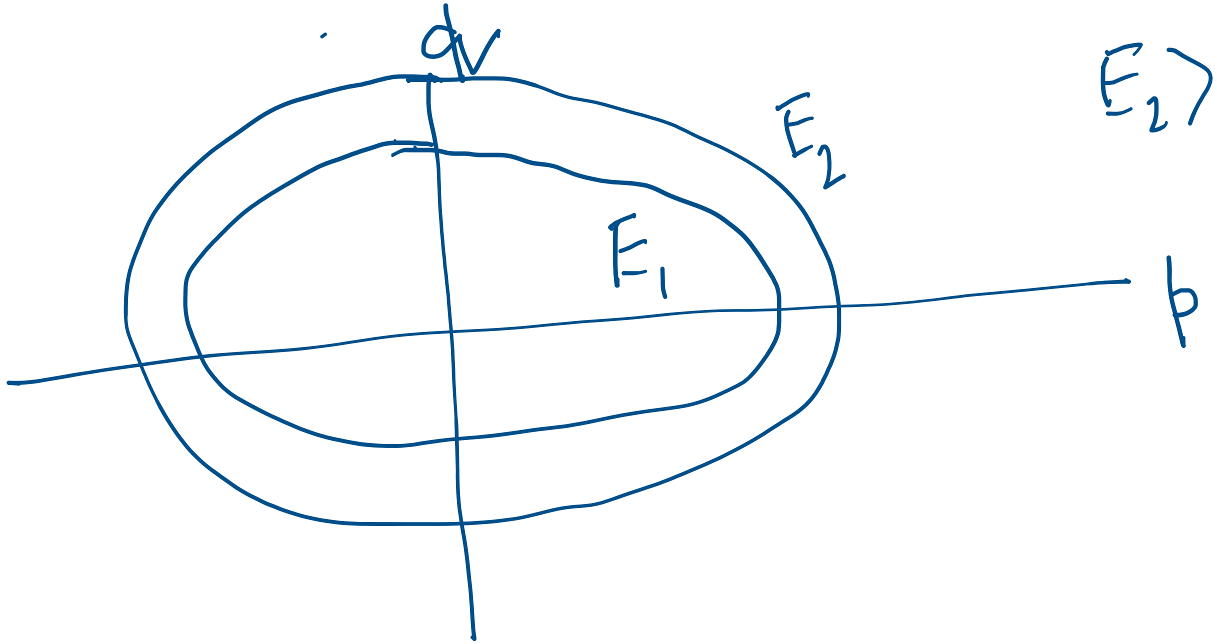
$\longrightarrow$ Phase space distribution $f^n \to f(p_i, q_i; t)$

$\hookrightarrow$ follows some $eq^n \to$ Liouville's eq^n.

Simple Harmonic Oscillator

SHO

$$H = \frac{p^2}{2m} + \frac{1}{2}kq^2 = E_{total}$$

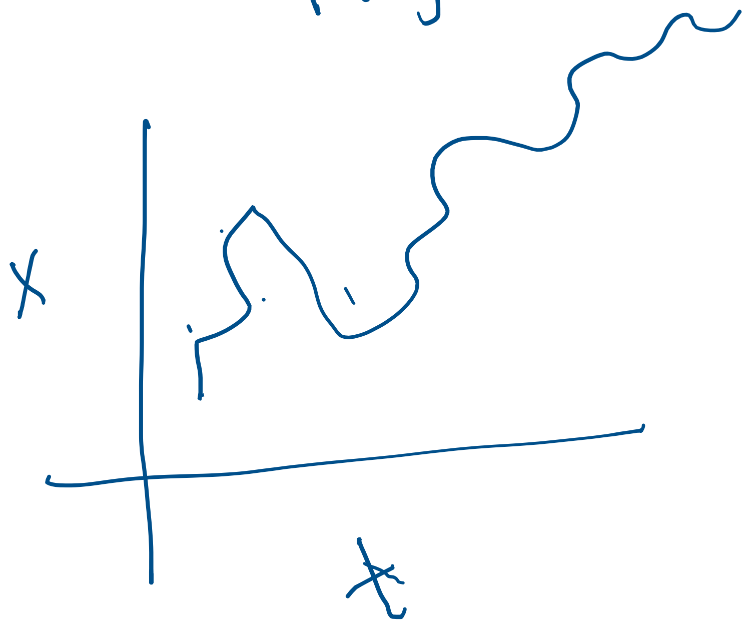


$E_2 > E_1$

Time Average:

$$\bar{X} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} ds\, X(s) \longrightarrow \text{time average over a long trajectory}$$

$$\bar{X} = \lim_{t \to \infty} \frac{1}{t} \int_{t_0}^{t_0+t} dt'\, X(t')$$



Ensemble & Ensemble average:

Microstate of a system $\rightarrow (p_i, q_i)$

Macrostate $\Rightarrow$ Many microstates can correspond to a single macrostate

$\vec{H}$ $\uparrow$

Magnetic system (three tiny magnets)

External magnetic field

$$E = -\vec{\mu}\cdot\vec{H}$$

$$\begin{array}{cccl}
\uparrow & \uparrow & \uparrow & E = -3\mu H \\
-\mu H & -\mu H & -\mu H & \\
\uparrow & \downarrow & \uparrow & E = -\mu H \\
\downarrow & \uparrow & \uparrow & E = -\mu H
\end{array}$$

two microstates $\leftarrow$

same macrostate

Time Average:

$$\bar{X} = \lim_{\tau\to\infty} \frac{1}{\tau}\int_{t_0}^{t_0+\tau} X(s)\,ds$$

$$\bar{X} = \lim_{\tau\to\infty} \frac{1}{\tau}\int_{0}^{\tau} X(s)\,ds$$

$X(t)$

First postulate of Statistical Mechanics:

$$\bar{X} = \langle X \rangle$$

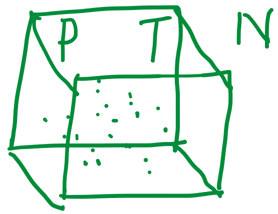
Time average = Ensemble average

Ensemble Average:

$$\langle X \rangle = \lim_{N\to\infty} \frac{1}{N}\sum_{i=1}^{N} p_i X_i$$

Macrostate of a system:

$$\underset{\downarrow\ \text{Macrostate}}{M}\ \underbrace{(N, P, T)}_{\text{Variables State}}$$



$3N \to$ position

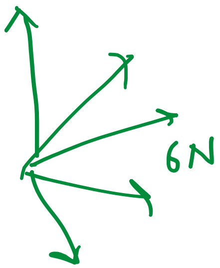
$3N \to$ momenta

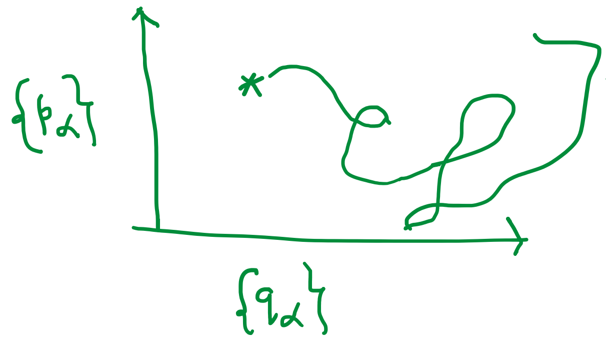
$6N$

$\sim 10^{24}$

Microstate $\longrightarrow$ position and the momentum co-ordinates of all the constituents

Phase space $\to$ 6N dimensional space





← Phase space trajectory

$M \rightarrow$ 1 microstate

$\downarrow$

another copy of $M \rightarrow$ 1 microstate

An ensemble

N, P, T	N, P, T	N, P, T	$\cdots \mathcal{N}$

such macro-states

N_M no. of macrostates (mental copies of) $\rightsquigarrow$ N_M no. of microstates

$\mathcal{N} \rightarrow$ No. of microstates

$\rho(\underline{p}, \underline{q})$ → 3N momenta co-ordinates; → 3N position coordinates

$\downarrow$

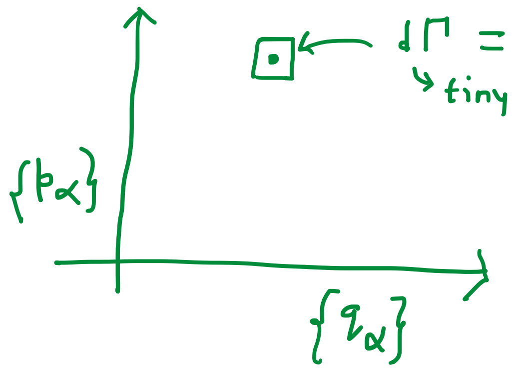
Ensemble density

$\underline{p} \equiv p_1, p_2, \ldots\ldots$

$\underline{q} \equiv q_1\ q_2 \ldots\ldots$

Gibbs Ensemble :⇝

$$\rho(\underline{p},\underline{q}) = \lim_{\mathcal{N}\to\infty} \frac{d\mathcal{N}}{\mathcal{N}\, d\Gamma}$$



$d\Gamma = \prod_{i=1}^{N} d^3p_i\, d^3q_i$

↳ tiny vol^m element

↳ Within this $d\Gamma$ vol^m there are $d\mathcal{N}$ no. of microstates

$$\int \rho(\underline{p},\underline{q})\, d\Gamma = \int \frac{d\mathcal{N}}{\mathcal{N}} = \frac{\mathcal{N}}{\mathcal{N}} = 1$$

↳ probability / density f^n → ensemble density

How this prob. density f^n evolve in time?

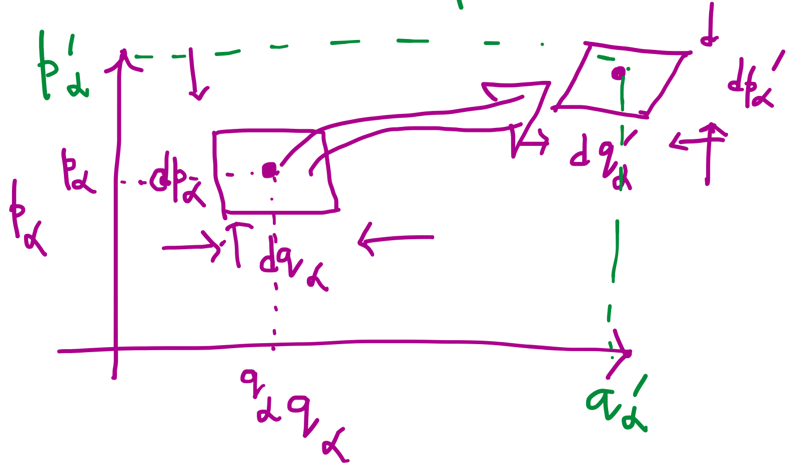
$$\langle X \rangle = \int x\, P(x)\, dx$$

$$\langle O(\underline{p},\underline{q}) \rangle = \int O(\underline{p},\underline{q})\, \rho(\underline{p},\underline{q},t)\, d\Gamma$$

↓ Ensemble average

in general it depends on time

Time evolution of $\rho(\underline{p}, \underline{q}, t)$ is given by "Liouville's theorem"



$d\Gamma$ (at time t)

$d\Gamma'$ (at time $t+dt$)

↳ Distorted

$$\boxed{q'_\alpha = q_\alpha + \dot{q}_\alpha dt} + \cancel{O(dt^2)} \to \sim 0$$

$$\boxed{p'_\alpha = p_\alpha + \dot{p}_\alpha dt} + \cancel{O(dt^2)} \to \sim 0$$

$$d\Gamma = dp_\alpha dq_\alpha$$

$$d\Gamma' = dp'_\alpha dq'_\alpha$$

$$dq'_\alpha = dq_\alpha + \underbrace{\left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha}\right) dq_\alpha dt}_{\text{Derivative of the velocity with respect to the separation multiplied by the separation}} + O(\ldots\ldots)$$

$$dp'_\alpha = dp_\alpha + \left(\frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right) dp_\alpha dt + O(\ldots\ldots)$$

$$d\Gamma' = dp_\alpha dq_\alpha \left[1 + \left\{\left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha}\right) + \left(\frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right)\right\} dt + \underbrace{\cancel{O(\ldots)}}_{0}\right]$$

$$d\Gamma' = \underbrace{dp_\alpha dq_\alpha}_{d\Gamma}\left[1 + \left\{\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right\}dt + \cancel{O(dt^2 \ldots)}\right] \qquad d\Gamma = \prod_i d^3 p_i \, d^3 q_i$$

$$\cancel{O(dt^2 \ldots)} \to 0$$

Hamilton's equation of motion

$$\frac{\partial H}{\partial p_\alpha} = \dot{q}_\alpha \qquad \frac{\partial H}{\partial q_\alpha} = -\dot{p}_\alpha$$

$$d\Gamma' = d\Gamma\left[1 + \left(\cancel{\frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha}} - \cancel{\frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha}}\right)dt\right] \Rightarrow$$

Phase Space volume is Conserved Under Hamiltonian Dynamics

$$\prod_\alpha dp_\alpha dq_\alpha = \prod_\alpha dp'_\alpha dq'_\alpha$$

$\rightsquigarrow$ Density does not change $\rightsquigarrow$ Incompressible fluid

$$\vec{\nabla} \cdot \vec{v} = 0$$

↳ Divergence of velocity field is zero.

$$\rho(\underline{p}', \underline{q}', t+dt) = \rho(\underline{p}, \underline{q}, t)$$

$$\rho(\underline{p}', \underline{q}', t+dt) = \rho(\underline{p} + \underline{\dot{p}}\,dt, \underline{q} + \underline{\dot{q}}\,dt, t+dt)$$

$$= \rho(\underline{p}, \underline{q}, t) + \underbrace{\left[\sum_\alpha \left(\dot{p}_\alpha \frac{\partial \rho}{\partial p_\alpha} + \dot{q}_\alpha \frac{\partial \rho}{\partial q_\alpha}\right) + \frac{\partial \rho}{\partial t}\right]}_{\cancel{0}} dt$$

$$0 \quad \frac{\{\rho(\underline{p}', \underline{q}', t+dt) - \rho(\underline{p}, \underline{q}, t)\}}{dt}$$

__Recall__

$$\frac{df(\underline{p}, \underline{q}, t)}{dt} = \frac{\partial f}{\partial t} + \sum_\alpha \left(\frac{\partial f}{\partial p_\alpha} \cdot \dot{p}_\alpha + \frac{\partial f}{\partial q_\alpha} \dot{q}_\alpha\right)$$

Total derivative of the f^n f

Streamline derivative

Partial derivative

$$\frac{d\rho}{dt} = 0 \rightarrow \text{Like incompressible fluid}$$

$$\boxed{\frac{\partial \rho}{\partial t} + \left[\sum_\alpha \left(\dot{p}_\alpha \frac{\partial \rho}{\partial p_\alpha} + \dot{q}_\alpha \frac{\partial \rho}{\partial q_\alpha}\right)\right] = 0}$$

$$\frac{\partial \rho}{\partial t} + \underbrace{\sum_\alpha \left\{ \left(\frac{\partial \rho}{\partial p_\alpha}\right)\dot{p}_\alpha + \left(\frac{\partial \rho}{\partial q_\alpha}\right)\dot{q}_\alpha \right\}} = 0$$

$$\dot{p}_\alpha = -\frac{\partial H}{\partial q_\alpha}$$

$$\dot{q}_\alpha = \frac{\partial H}{\partial p_\alpha}$$

$$\{A, B\} = \sum_\alpha \left(\frac{\partial A}{\partial q_\alpha}\frac{\partial B}{\partial p_\alpha} - \frac{\partial B}{\partial q_\alpha}\frac{\partial A}{\partial p_\alpha} \right)$$

↳ Poisson Bracket

$$\frac{\partial \rho}{\partial t} + \underbrace{\sum_\alpha \left\{ \frac{\partial \rho}{\partial p_\alpha}\left(-\frac{\partial H}{\partial q_\alpha}\right) + \left(\frac{\partial \rho}{\partial q_\alpha}\right)\left(\frac{\partial H}{\partial p_\alpha}\right) \right\}}_{\{\rho, H\}}$$

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

or $$\frac{\partial \rho}{\partial t} = -\{\rho, H\} = \{H, \rho\}$$

$$\boxed{\frac{\partial \rho}{\partial t} = \{H, \rho\}}$$

Liouville's theorem or equation.

What is equilibrium in this perspective?

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}$$

$\rho = \rho(H)$ → If the phase space density a function of the Hamiltonian

$$\{\rho, H\} = \{\rho(H), H\}$$

$$= \sum_\alpha \left(\underbrace{\frac{\partial \rho}{\partial H}}_{\rho'} \frac{\partial H}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \underbrace{\frac{\partial \rho}{\partial H}}_{\rho'} \frac{\partial H}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right)$$

$$= \rho' \{H, H\}$$

$$= 0$$

$$\frac{\partial \rho}{\partial t} = 0$$

↳ ρ has no explicit time dependence

$$\underbrace{\langle O(\underline{p}, \underline{q}) \rangle}_{\text{time-independent if}} = \int d\Gamma\, \rho(\underline{p}, \underline{q}, t)\, O(\bar{p}, \bar{q})$$

time-independent if $\rho(\underline{p}, \underline{q}, t) = \rho(\underline{p}, \underline{q}) \equiv \rho(H)$ ⇝ is a f^n of H → Definition of equilibrium

$\rho_{eq} = \rho(H)$

$L(\underline{p}, \underline{q})$

$\{L, H\} = 0$

Say for a system $\rightarrow$ Angular momentum is also conserved

$$\frac{dL(\underline{p}, \underline{q})}{dt} = 0$$

$$= \sum_{\alpha} \left(\frac{\partial L}{\partial p_\alpha} \dot{p}_\alpha + \frac{\partial L}{\partial q_\alpha} \dot{q}_\alpha \right)$$

$$= \sum_{\alpha} \frac{\partial L}{\partial p_\alpha} \left(-\frac{\partial H}{\partial q_\alpha} \right) + \frac{\partial L}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha}$$

$$= 0$$

$\rho_{eq}(H, L)$

$\rho_{eq}(H(\underline{p}, \underline{q}), L(\underline{p}, \underline{q}))$

$$\{\rho_{eq}, H\} = \rho_1' \{H, H\} + \rho_2' \{L, H\}$$

$$= 0$$

Isolate system

Energy is conserved

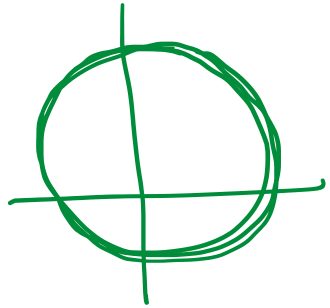
E

} Microcanonical ensemble

$$\rho(H) \sim \delta(H-E)$$

$f(H)$

Eq^m distribution



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

Canonical

Closed system $\rightsquigarrow$ Boltzmann distribution $\rho_{eq}(H) \sim e^{-\beta H}$

Phase space volume is conserved:

$$\frac{d\rho(\underline{p},\underline{q},t)}{dt} \rightarrow$$ Total time derivative of phase space density is zero

What is equilibrium:

$$\underbrace{\langle O(\underline{p},\underline{q}) \rangle}_{\text{Ensemble average}} = \text{Time independent}$$

$$= \int \underbrace{\rho(\underline{p},\underline{q},t)}_{\rho_{eq}(\underline{p},\underline{q})} O(p,q)\, d\Gamma$$

$\rho_{eq} \equiv \rho_{eq}(H) \rightarrow$ Hamiltonian of the system

$H \rightarrow$ Constant of motion $\quad \frac{dH}{dt} = 0$

Microcanonical ensemble

Isolated System

(N, V, E)

$E = H \Rightarrow \rho_{eq} \sim \delta(H-E)$

Canonical ensemble, $\quad \rho_{eq} \sim e^{-\beta H} \quad \beta = \frac{1}{k_B T}$ $\rightarrow$ Boltzmann distribution

First Postulate of Statistical Mechanics:

Time average = Ensemble average

→ Distribution f^n $\rho(\underline{p}, \underline{q})$ → System following classical Mechanics

But if the System is quantum mechanical
→ eigenfunctions and energy eigen values

$$\langle X \rangle = \frac{1}{N} \sum_{i=1}^{N} p_i X_i$$

$$\langle x \rangle = \frac{\sum p_i x_i}{\sum p_i} \qquad \sum p_i = N$$

Postulate of equal apriori

Microcanonical ensemble:

Systems of the ensemble are distributed uniformly, that is with equal probability over all possible microscopic states of the system. In the language of time trajectory, each state is visited on equal number of times if waited enough.

$E = -\mu H$

$H \rightarrow$ Magnetic field
$\mu \rightarrow$ Magnetic moment

$\uparrow\ \uparrow\ \downarrow \qquad \uparrow\ \downarrow\ \uparrow \qquad \downarrow\ \uparrow\ \uparrow \qquad \uparrow H$

$$\underbrace{\begin{matrix} -\mu H - \mu H + \mu H & -\mu H & -\mu H \\ = -\mu H & & \end{matrix}}_{\text{All are equally probable}}$$

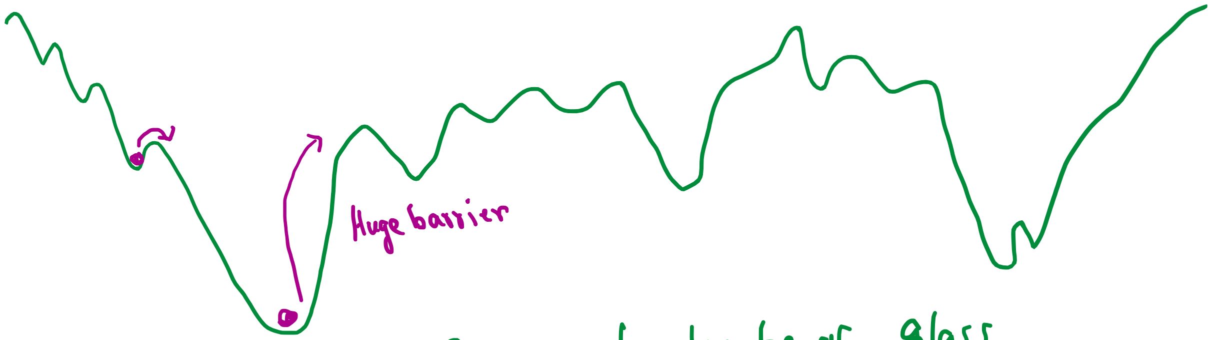
Ergodic Hypothesis: During its trajectory, in phase space, a system is free to explore all the microscopic states and given a sufficiently long period of time, spends time in a state that is proportional to the vol^m of the phase space.

state in

$dp\,dq \sim h$ ← Planck's const

→ smallest vol^m element

$d^{3N}p\, d^{3N}q \sim h^{3N}$



Energy landscape of glass

(Rugged energy landscape)

"Non-ergodic"

"Supercooled liquid"

n possible outcomes, each with probability p_j, where $j = 1, 2, \dots, n$

↳ Discrete prob. distribution

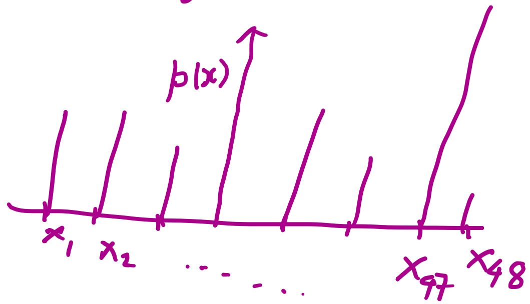
If the experiment is repeated indefinitely,

$$p_j = \lim_{N \to \infty} \frac{N_j}{N} \qquad j = 1, 2, \cdots n$$

$$\sum_{j=1}^{n} N_j = N \qquad \sum_{j=1}^{n} p_j = 1$$

$N_j \rightarrow$ is the # of times of outcome j

$N \rightarrow$ total # of repetitions of the expt.



Average x $\qquad \langle x \rangle = \sum_{j=1}^{n} x_j p_j$

↓

First moment of this distribution

$$\langle x^2 \rangle = \sum_{j=1}^{n} x_j^2 p_j$$

↳ second moment

Second central moment or Variance:

$$\sigma_x^2 = \langle (x-\langle x\rangle)^2\rangle = \sum_{j=1}^{n} (x_j-\langle x\rangle)^2 p_j \rightarrow \geq 0 \text{ (positi b definition)}$$

↳ measure of the spread of the distribution

$$\sigma_x^2 = \sum_{j=1}^{n} \left(x_j^2 - 2x_j\langle x\rangle + \langle x\rangle^2\right)p_j = \underbrace{\sum_{j=1}^{n} x_j^2 p_j}_{\langle x^2\rangle} - 2\underbrace{\sum_{j=1}^{n} x_j p_j}_{\langle x\rangle}\langle x\rangle + \langle x\rangle^2 \underbrace{\sum_{j=1}^{n} p_j}_{1}$$

$$= \langle x^2\rangle - 2\langle x\rangle^2 + \langle x\rangle^2 = \langle x^2\rangle - \langle x\rangle^2 \geq 0$$

$$\langle x^2\rangle \geq \langle x\rangle^2$$

Continuous distribution

$$\text{Prob}(x, x+dx) = p(x)\,dx$$

$$-\infty \le x \le \infty$$

$$\int_{-\infty}^{+\infty} p(x)\,dx = 1 \quad (\text{normalized / total prob} = 1)$$

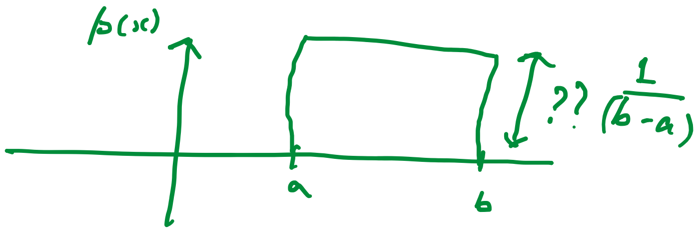
$$\int_{-\infty}^{+\infty} x\,p(x)\,dx = \langle x \rangle \qquad \int_{-\infty}^{+\infty} x^2 p(x)\,dx = \langle x^2 \rangle$$

$$\int_{-\infty}^{+\infty} x^n p(x)\,dx = \langle x^n \rangle \rightarrow n^{th} \text{ moment}$$

Example:

$$p(x) = A \qquad a \le x \le b$$

$$= 0 \qquad \text{otherwise}$$



$$\int_a^b p(x)\,dx = A\int_a^b dx = 1 \Rightarrow A(b-a) = 1$$

$$\text{or} \quad A = \frac{1}{(b-a)}$$

$$\langle x \rangle = \frac{1}{(b-a)}\int_a^b x\,dx = \frac{1}{(b-a)}\frac{x^2}{2}\Big|_a^b = \frac{b^2-a^2}{2(b-a)} = \frac{1}{2}(b+a)$$

$$\langle x^2 \rangle = \frac{1}{b-a}\int_a^b x^2\,dx = \frac{1}{(b-a)}\frac{1}{3}(b^3-a^3) = \frac{(b-a)(b^2+ab+a^2)}{3(b-a)} = \frac{1}{3}(b^2+ab+a^2)$$

variance $\quad \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{3}(b^2+ab+a^2) - \frac{1}{4}(b^2+2ab+a^2)$

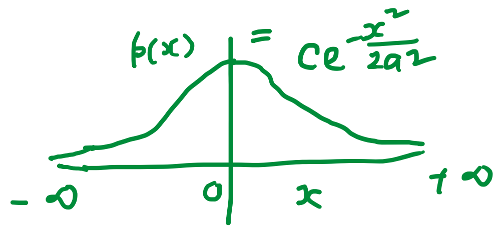
$$= \frac{(b-a)^2}{12}$$

$\sqrt{\sigma_x^2}$ = Standard deviation

$$= \frac{1}{\sqrt{12}}(b-a)$$

* Most common continuous prob. distribution → Gaussian or a normal distribution

$$p(x) = c\,e^{-x^2/2a^2} \qquad -\infty < x < \infty$$



$$\int_{-\infty}^{+\infty} p(x)\,dx = 1 \quad = \quad C\int_{-\infty}^{+\infty} e^{-\frac{x^2}{2a^2}}\,dx$$

$$\alpha \equiv \frac{1}{2a^2}$$

<u>Standard Integral</u>

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2}\,dx = \left(\pi/\alpha\right)^{\frac{1}{2}}$$

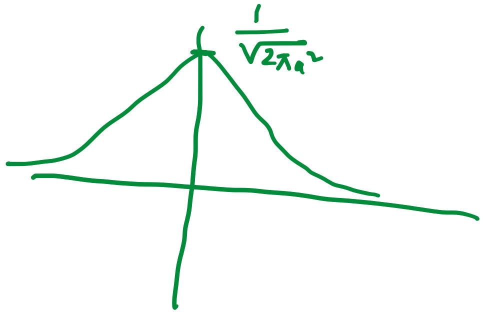
$$1 = C\sqrt{\pi}\,\frac{1}{\sqrt{\frac{1}{2a^2}}}$$

$$1 = C\sqrt{\pi}\sqrt{2}\,a$$

$$\Rightarrow \quad C = \frac{1}{\sqrt{2\pi a^2}}$$

$$p(x) = \frac{1}{\sqrt{2\pi a^2}}\,e^{-\frac{x^2}{2a^2}}$$

at $x=0$ $\qquad p(0) = \frac{1}{\sqrt{2\pi a^2}}$



$\langle x\rangle = ?$ $\qquad \langle x^3\rangle = 0$ $\qquad \langle x^n\rangle = 0$ if n is odd (Integration of an odd integrand within symmetric limits)

$$\langle x^2\rangle = \int_{-\infty}^{+\infty} x^2 \frac{1}{\sqrt{2\pi a^2}} e^{-\frac{x^2}{2a^2}} dx = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{+\infty} x^2 e^{-x^2/2a^2} dx$$

$$I = \int_{-\infty}^{+\infty} e^{-\alpha x^2} = (\pi/\alpha)^{\frac{1}{2}}$$

$$\frac{dI}{d\alpha} = \int_{-\infty}^{+\infty} -x^2 e^{-\alpha x^2} \Rightarrow \int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} = -\frac{dI}{d\alpha} = +\frac{1}{2}\sqrt{\pi}\, \alpha^{-3/2}$$

$$= \frac{1}{2\alpha}(\pi/\alpha)^{\frac{1}{2}}$$

$$\alpha \equiv \frac{1}{2a^2}$$

$$\langle x^2\rangle = \frac{1}{\sqrt{2\pi a^2}} \frac{1}{2 \cdot \frac{1}{2a^2}} \left(\pi/\tfrac{1}{2a^2}\right)^{\frac{1}{2}} = \frac{1}{\sqrt{2\pi a^2}} a^2 \sqrt{2\pi a^2} = a^2$$

$$\sigma_x^2 = \langle x^2\rangle - \langle x\rangle^2 = a^2 - 0 = a^2 \Rightarrow p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$$

$\sigma^2 \equiv$ variance

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$$

More general $\langle x \rangle = \mu$ (non-zero)

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \sqrt{\pi/\alpha}$$

$$p(x) = \frac{1}{\sqrt{2\pi\sigma_x^2}} e^{-\frac{(x-\mu)^2}{2\sigma_x^2}}$$

is this normalize?

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$\frac{x-\mu}{\sqrt{2}\sigma_x} = y$$

$$dx = dy\,\sqrt{2}\,\sigma_x$$

$$\int_{-\infty}^{+\infty} p(x)\,dx = \int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi\sigma_x^2}} e^{-y^2} \sqrt{2}\,\sigma_x\,dy = \frac{\sqrt{2}\,\sigma_x}{\sqrt{2}\,\sigma_x\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{-y^2} dy$$

$$= \frac{1}{\sqrt{\pi}} \sqrt{\pi} = 1 \text{ (normalized)}$$

$$\left.\begin{array}{l}\langle x \rangle = \mu \qquad \langle x^2 \rangle = \sigma_x^2 + \mu^2\end{array}\right\} \text{check}$$

$$x - \mu = z \qquad x = z + \mu$$

$$dx = dz$$

$$\langle x \rangle = \int_{-\infty}^{+\infty} x\,p(x) = \int_{-\infty}^{+\infty} dz\,(z+\mu)\,e^{-z^2/2\sigma_x^2}\left(\frac{1}{\sqrt{2\pi\sigma_x^2}}\right) = \underbrace{\frac{1}{\sqrt{2\pi\sigma_x^2}}\int_{-\infty}^{+\infty} z\,e^{-z^2/2\sigma_x^2}}_{0} + \underbrace{\frac{1}{\sqrt{2\pi\sigma_x^2}}\int_{-\infty}^{+\infty} dz\,e^{-z^2/2\sigma_x^2}}_{1}\,\mu = \mu$$

odd integrand

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} dx\, x^2 \frac{1}{\sqrt{2\pi\sigma_x^2}} e^{-\frac{(x-\mu)^2}{2\sigma_x^2}} = \int_{-\infty}^{+\infty} (z+\mu)^2 \frac{dz}{\sqrt{2\pi\sigma_x^2}} e^{-\frac{z^2}{2\sigma_x^2}} = \int_{-\infty}^{+\infty} dz\, z^2 \frac{1}{\sqrt{2\pi\sigma_x^2}} e^{-z^2/2\sigma_x^2} + \mu^2 \underbrace{\int_{-\infty}^{+\infty} \frac{dz}{\sqrt{2\pi\sigma_x^2}} e^{-z^2/2\sigma_x^2}}_{=1} + 2\mu \underbrace{\int_{-\infty}^{+\infty} \frac{dz}{\sqrt{2\pi\sigma_x^2}}\, z e^{-z^2/2\sigma_x^2}}_{0}$$

$$\langle x^2 \rangle = \mu^2 + \frac{1}{\sqrt{2\pi\sigma_x^2}} \int_{-\infty}^{+\infty} z^2 e^{-z^2/2\sigma_x^2} dz$$

Let, $\frac{z}{\sqrt{2}\sigma_x} = \tilde{z}$

$dz = \sqrt{2}\sigma_x \, d\tilde{z}$

$$\frac{1}{\sqrt{2\pi\sigma_x^2}} \int_{-\infty}^{+\infty} \tilde{z}^2 (2\sigma_x^2)\, e^{-\tilde{z}^2} d\tilde{z}\, (\sqrt{2}\sigma_x)$$

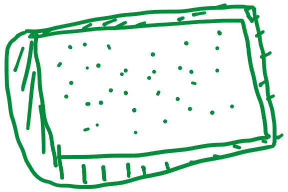
$$= \frac{1}{\sqrt{\cancel{2}\pi\cancel{\sigma_x^2}}} 2\sigma_x^2 \cancel{\sqrt{2}}\cancel{\sigma_x} \int_{-\infty}^{+\infty} \tilde{z}^2 e^{-\tilde{z}^2} d\tilde{z}$$

$$= \frac{2}{\sqrt{\pi}} \sigma_x^2 \frac{1}{2}\sqrt{\pi} = \sigma_x^2$$

$$\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha}\left(\pi/\alpha\right)^{\frac{1}{2}}$$

$\langle x^2 \rangle = \mu^2 + \sigma_x^2$ (checked)

Microcanonical Ensemble:



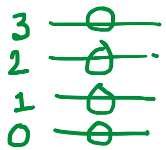
$dQ = 0 \quad dW = 0$

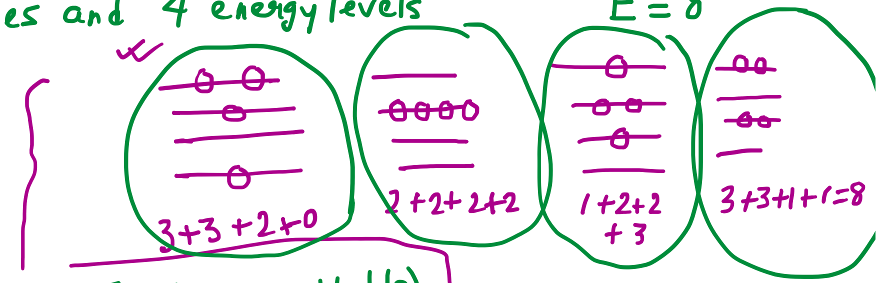
$dE = 0$ (Isolated System)

$M \equiv (N, V, E) \rightarrow$ fixed

$\hookrightarrow$ Macrostate

4 particles and 4 energy levels $\quad E = 8$





$3+2+1+0 = 6 \neq E$ (Not acceptable)

"4 microstate"

Each of these arrangements represent a microstate

"Postulate of equal apriori"

$\Omega(N, V, E) \rightarrow \dfrac{1}{\Omega(N,V,E)} \rightarrow$ prob. of finding the system in i th microstate

$\downarrow$ No. of microstates

Gibbs $\rightarrow$ $S = -k_B \sum_i p_i \ln p_i = -k_B \langle \ln p \rangle$

$k_B \rightarrow$ Boltzmann constant

$\downarrow$ Shannon's entropy

$$S = -k_B \sum_i \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right)$$

$$S = -k_B \frac{\Omega}{\Omega} (\ln 1 - \ln \Omega)$$

$$\boxed{S = k_B \ln \Omega} \rightarrow \text{"Boltzmann entropy"}$$

Third law:

$\Omega = 1$ (only one microstate)

$S = 0$

Cyclic Relation

$x = f(y, z)$ $\qquad y = f(x, z)$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad \cdots \quad (1)$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \quad \cdots \quad (2)$$

$$dx = \left(\frac{\partial x}{\partial z}\right)_y dz + \underbrace{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z}_{1} dx + \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x dz$$

$$dx = \left(\frac{\partial x}{\partial z}\right)_y dz + \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x dz + dx \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x dz = -\left(\frac{\partial x}{\partial z}\right)_y dz$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

S, V, E $\qquad \left(\frac{\partial S}{\partial V}\right)_{N,E}\left(\frac{\partial V}{\partial E}\right)_{N,S}\left(\frac{\partial E}{\partial S}\right)_{N,V} = -1$

$$E = TS - PV + \mu N$$

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = T \qquad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -P$$

$$\left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu \text{ (chemical potential)}$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = -\frac{1}{\left(\frac{\partial V}{\partial E}\right)_{N,S}\left(\frac{\partial E}{\partial S}\right)_{N,V}}$$

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

S, N, E $\qquad \left(\frac{\partial S}{\partial N}\right)_{E,V}\left(\frac{\partial N}{\partial E}\right)_{S,V}\left(\frac{\partial E}{\partial S}\right)_{N,V} = -1$

$$\Rightarrow \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{1}{\left(\frac{\partial N}{\partial E}\right)_{S,V}\left(\frac{\partial E}{\partial S}\right)_{N,V}}$$

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

$S(N, V, E)$

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

$$dS = -\frac{\sum_\alpha \mu_\alpha dN_\alpha}{T} + \frac{P dV}{T} + \frac{dE}{T}$$

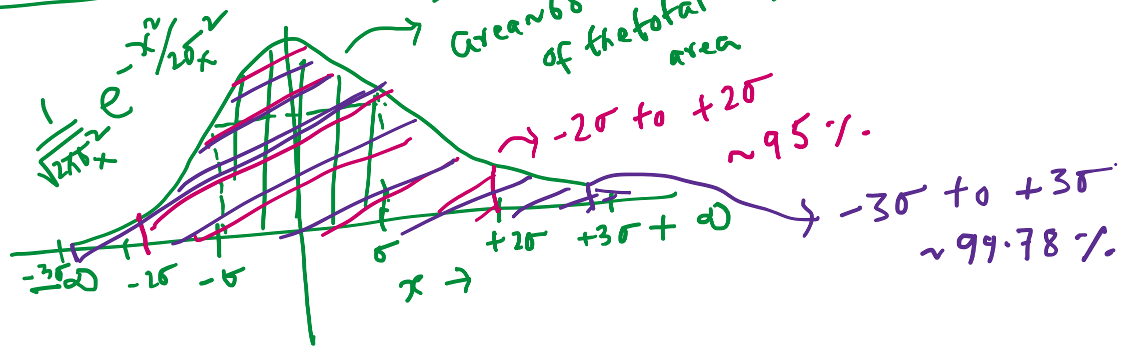
$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{\partial}{\partial E}(k_B \ln \Omega)_{V,N} = k_B \left(\frac{\partial \ln \Omega}{\partial E}\right)_{V,N}$$

Definition of temperature

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E} = k_B \left(\frac{\partial \ln \Omega}{\partial V}\right)_{E,N}$$

$$-\frac{\mu_i}{T} = \left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_{\alpha \neq i}} = k_B \left(\frac{\partial \ln \Omega}{\partial N_i}\right)_{E,V,N_{\alpha \neq i}}$$

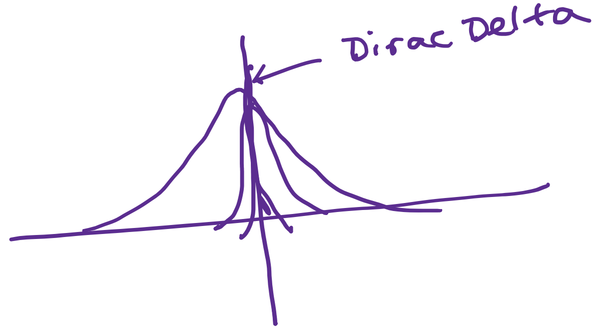
Gaussian Distribution:



3σ rule:

$\sigma_x \to 0 \quad p(x) \sim \delta(x)$

↳ Dirac-Delta function



$$f(x) = \infty \qquad x = 0$$
$$= 0 \qquad \text{Otherwise}$$

$\delta(x) \rightarrow$ Dirac-Delta function.

$\delta(x-a)$ peaked at $x = a$

$$\int_{-\infty}^{+\infty} \delta(x)\, dx = 1 \quad \text{(normalized)}$$

Dimension of Dirac-Delta function is $\frac{1}{\text{argument}}$

$$\delta(x) \sim \frac{1}{x}$$
$$\delta(t) \sim \frac{1}{t}$$

$$\int_{-\infty}^{+\infty} dx\, f(x)\,\delta(x) = f(0) \qquad \int_{-\infty}^{+\infty} dx\, f(x)\,\delta(x-a) = f(a)$$

$\delta(-x) = \delta(x)$ even function

Revisiting $\Omega(N,V,E)$

$H(\underline{p},\underline{q}) = E$ (constraint)

↳ is a f^n of 6N-co-ordinates

Recall Liouville's theorem

Equilibrium probability distribution in microcanonical ensemble

$$\rho_{eq}(H(\underline{p},\underline{q})) = N_c\,\delta(H(\underline{p},\underline{q}) - E)$$

(6N-1) dimensional hypersurface

$\Omega(N,V,E)$

↳ Number of allowed microstates ≡ measure of the amount of phase space available

$\Omega(N,V,E) = \tilde{N} \int \cdots d^3p_N \int d^3q_N \, \delta(H(\underline{p},\underline{q}) - E)$ → integration over entire phase space

<u>Quantum mechanics:</u>

$\Delta p \, \Delta q \sim h$ (Planck's constant)

- Heisenberg uncertainty principle -

We divide the entire phase space into hypervolumes, each with vol^m $\Delta\Gamma = \Delta p \, \Delta q = h^{3N}$, such that, each of these hypervolumes contain ONLY one (1) microstate.

Mark E Tuckerman

Statistical Mechanics

$$\Omega(N,V,E) = \sum_{\substack{\text{hypervol}^m \\ E < H(\underline{p},\underline{q}) < E+E_0}} \frac{\Delta\Gamma}{h^{3N}}$$

$d\Gamma = \int \cdots \int d^3p_N \int d^3q_N$

$\Delta\Gamma$ is small compared to the entire phase space vol^m

$$\Omega(N,V,E) = \frac{1}{h^{3N}} \int_{E<H<E+E_0} d\Gamma \quad \rightsquigarrow \text{Approximate} = \frac{E_0}{h^{3N}} \int \cdots d^3p_N \, d^3q_N \, \delta(H(\underline{p},\underline{q}) - E)$$

$$\Omega(N,V,E) = \frac{E_0}{h^{3N} N!} \int \cdots\cdots d^3p_N \, d^3q_N \, \delta(H(\underline{p},\underline{q}) - E)$$

$\tilde{M}$

Since the particles are indistinguishable

Particles are distinguishable

$$\text{prob.} = \frac{p_i}{\sum p_i}$$

$$\rho_{eq} = \frac{1}{\Omega(N,V,E)} \times \tilde{M} \, \delta(H(\underline{p},\underline{q}) - E)$$

Microcanonical ensemble

$$\rho_{eq} = \frac{\cancel{\tilde{M}} \, \delta(H(\underline{p},\underline{q}) - E)}{\cancel{\tilde{M}} \int \cdots\cdots d^3p_N \, d^3q_N \, \delta(H(\underline{p},\underline{q}) - E)} = \frac{\delta(H(\underline{p},\underline{q}) - E)}{\int \cdots d^3p_N \, d^3q_N \, \delta(H(\underline{p},\underline{q}) - E)}$$

$$\langle A(\underline{p},\underline{q})\rangle = \frac{\int A(\underline{p},\underline{q})\,\delta(H(\underline{p},\underline{q})-E)\,d\Gamma}{\int d\Gamma\,\delta(H(\underline{p},\underline{q})-E)}$$

$\left\{ \begin{matrix} 3.2.22 \\ \text{in} \\ \text{MT.} \\ \text{SM} \end{matrix} \right\}$ Page 80

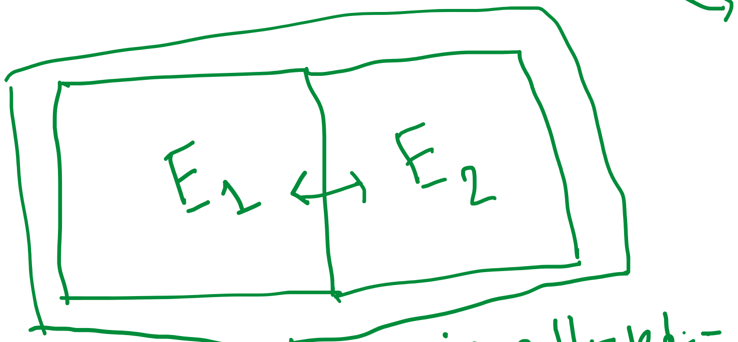
$\Omega(N,V,E) \rightsquigarrow$ Microcanonical partition function

$$\Omega(N,V,E) \equiv \Omega(E,X) \equiv \Omega(E)$$

X → generalized displacement co-ordinate

$$S_1 = k_B \ln \Omega(E_1)$$

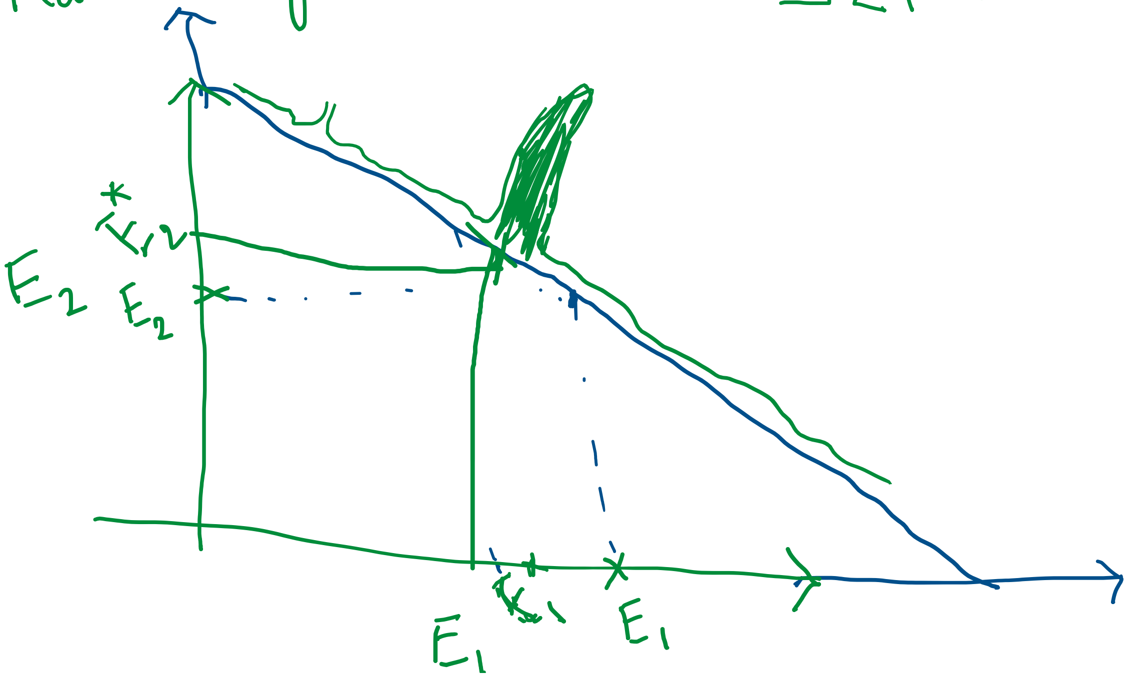
$$S_2 = k_B \ln \Omega(E_2)$$



- Heat exchange is allowed -

$$E_1 + E_2 = E \quad \text{(constant)}$$

$\Omega(E) \to$ Accessible no. of microstates for the combined system



$$\Omega(E) = \int dE_1 \Omega(E_1)\Omega(E-E_1) = \int dE_1 \exp\left[\frac{S_1(E_1)}{k_B} + \frac{S_2(E_2)}{k_B}\right] \simeq \underbrace{\exp\left[\frac{S_1(E_1^*)}{k_B} + \frac{S_2(E_2^*)}{k_B}\right]}_{\text{Approximate}}$$

$$\underbrace{k_B \ln \Omega(E)}_{} = k_B \ln \Omega(E_1^*) + k_B \ln \Omega(E_2^*)$$

$$S(E) = S_1(E_1^*) + S_2(E_2^*)$$ — extensivity of entropy —

$E = E_1 + E_2$

$E_1 = E - E_2$

$\frac{\partial}{\partial E_1} = -\frac{\partial}{\partial E_2}$

Extremise the exponent with respect to E_1

$$\frac{\partial}{\partial E_1}\left[\frac{S_1(E_1)}{k_B} + \frac{S_2(E_2)}{k_B}\right] = 0$$

$$\left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{X_1} + \left.\frac{\partial S_2(E_2)}{\partial E_1}\right|_{X_2} = 0 \rightarrow \left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{X_1} - \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{X_2} = 0$$

(emperical temperature)

Condition for (thermal) eqm $\longleftarrow$ $$\left.\frac{\partial S_1(E_1)}{\partial E_1}\right|_{X_1} = \left.\frac{\partial S_2(E_2)}{\partial E_2}\right|_{X_2} = \frac{1}{T}$$

Zeorth law of Thermo-dynamics

First law of thermodynamics:

Changing the co-ordinate reversibly by δx

$$x \to x + \delta x$$

$$đW = J \cdot \delta x \quad \text{(work done)}$$

J → generalized force

$$S(E, x)$$

$$\downarrow$$

$$S(E + J\cdot\delta x, x + \delta x)$$

$$\delta S = S(E + J\cdot\delta x, x + \delta x) - S(E, x)$$

Change in entropy

$$= \cancel{S(E,x)} + \left.\frac{\partial S}{\partial E}\right|_x J\,\delta x + \left.\frac{\partial S}{\partial x}\right|_E \delta x - \cancel{S(E,x)}$$

$$\delta S = \left(\left.\frac{\partial S}{\partial E}\right|_x J + \left.\frac{\partial S}{\partial x}\right|_E\right)\delta x$$

$= 0$ (system is already in eq^m)

$$\Rightarrow \left.\frac{\partial S}{\partial E}\right|_x J\,\delta x = -\left.\frac{\partial S}{\partial x}\right|_E \delta x$$

$\left.\frac{\partial S}{\partial E}\right|_x \to \frac{1}{T}$

$$-\frac{J}{T} = \left.\frac{\partial S}{\partial x}\right|_E$$

$$dS(E,x) = \left.\frac{\partial S}{\partial E}\right|_x dE + \left.\frac{\partial S}{\partial x}\right|_E dx = \frac{dE}{T} - \frac{J\,dx}{T}$$

$$\Rightarrow \boxed{dE = T\,dS + J\,dx}$$

↳ 1st Law of thermodynamics

Second law of thermodynamics:

$$\underbrace{\Omega_1(E_1^*, x)\,\Omega_2(E_2^*, x)}_{\text{Eq}^m \text{ has a large no. of accessible states than any (other state) starting point}} \geqslant \Omega_1(E_1, x)\,\Omega_2(E_2, x)$$

$$\delta S = S_1(E_1^*) + S_2(E_2^*) - S_1(E_1) - S_2(E_2) \geqslant 0$$

$$\delta S = \left(\left.\frac{\partial S_1}{\partial E_1}\right|_{x_1} - \left.\frac{\partial S_2}{\partial E_2}\right|_{x_2} \right) \delta E_1 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta E_1 \geqslant 0$$

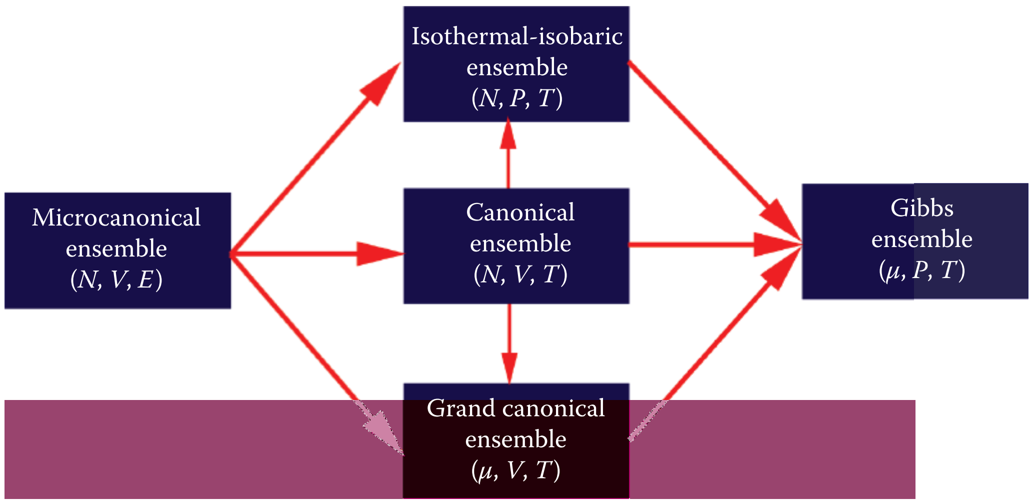
heat flows from hot to cold body $\rightarrow$ 2nd law of thermodynamics

Ensemble

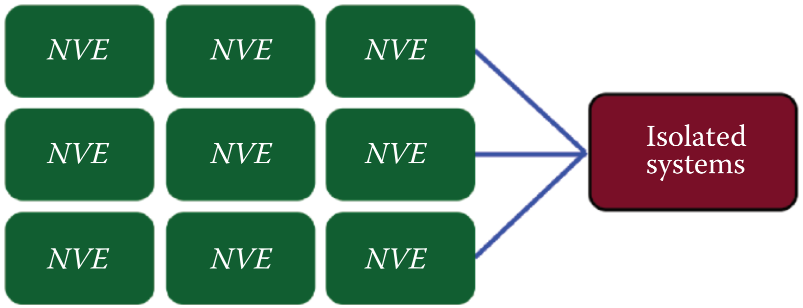
The concept of an ensemble is a brilliant mental construct

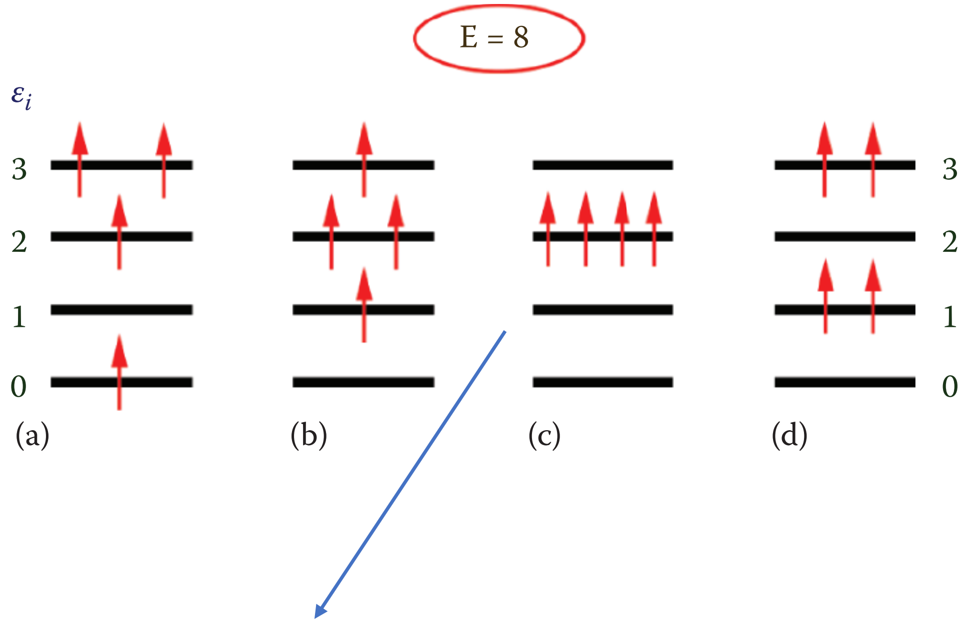
System must have a large number of microscopic states (positions and momenta), and natural motion of system at non-zero temperature takes the system through a finite fraction of these states in a time comparable to time of measurement of the macroscopic properties.

Different types of Ensembles



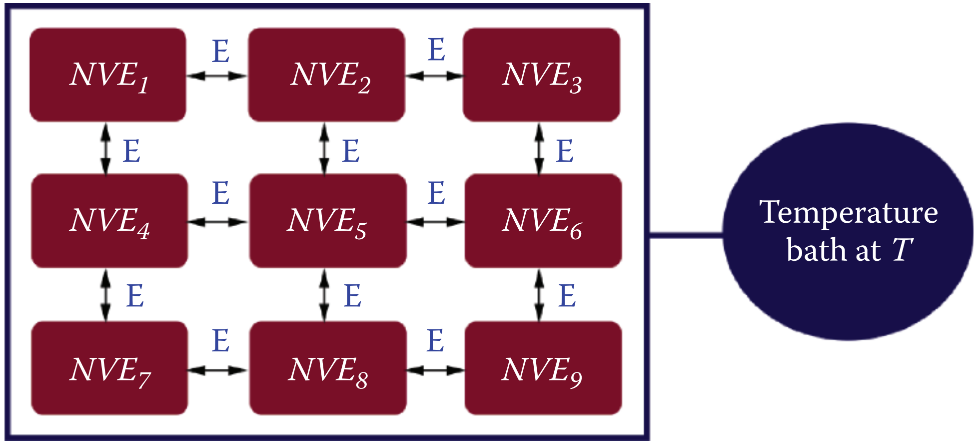
A microcanonical ensemble consists of mental replicas of the original (NVE) system (Isolated System)

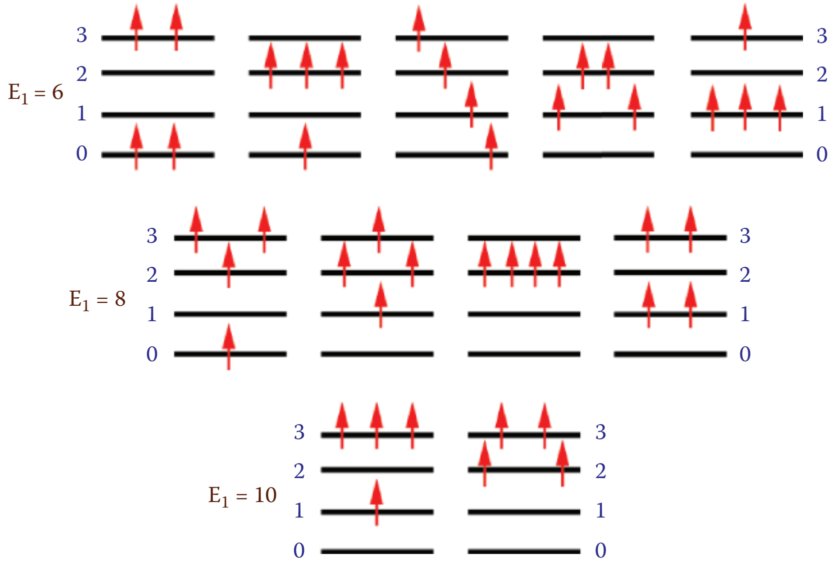




Four arrangements giving rise to same total energy (these are microstates)

Canonical ensemble





Canonical ensemble, where energy of each system can fluctuate. The systems are kept at temperature T by putting the super-system in a bath and establishing thermal contacts between the individual systems

$N_s \rightarrow$ Total no. of systems

$N \rightarrow$ No. of particles in each System

Super-System

(Isolated)

$N_t = N_s N$
$\hookrightarrow$ total no. of particles

$V_t = N_s V$
$\hookrightarrow$ total volume

E_t = Total energy

$(N_t, V_t, E_t) \rightarrow$ then we can construct a microcanonical ensemble starting here

$$\sum_j n_j = N_s \qquad \sum_j n_j E_j = E_t$$

$\rightarrow$ constraints

If the particles are distinguishable

$$\Omega(\{n_j\}) = \frac{N_s!}{n_1!\, n_2!\, n_3! \ldots\ldots} \quad \text{(elaborate this later)} \quad \ldots\ldots (1)$$

→ No. of ways ....

* Biman Bagchi
* Mc.Quarrie

[In general, there are many distributions that are consistent with $\sum_j n_j = N_s$]

Probability of observing a given state n_j with energy E_j:

$$p_j = \frac{\bar{n}_j}{N_s} = \frac{1}{N_s} \boxed{\frac{\sum_j n_j \Omega(\{n_j\})}{\sum_j \Omega(\{n_j\})}} \rightarrow \bar{n}_j \quad \ldots\ldots (2)$$

$$\simeq \frac{1}{N_s} \frac{n_j^* \Omega(\{n_j^*\})}{\Omega(\{n_j^*\})} = \frac{n_j^*}{N_s}$$

→ Most probable value

$n_j^* \rightarrow$ is the value of n_j that maximises $\Omega(\{n_j\})$

In any particular distribution, $\frac{n_j}{N_s}$ is the fraction of systems of the canonical ensemble in the j-th energy state. The overall probability p_j that a system is in the j-th energy state is obtained by averaging $\frac{n_j}{N_s}$ over all the allowed distributions, giving equal weight to the each one

principle of equal a priori probabilities

$$\frac{\partial}{\partial n_j}\Big(\underbrace{\ln\Omega(\{n_j\})}_{} - \alpha\sum_j n_j - \beta\sum n_j E_j\Big) = 0$$

LUM

$N_s = \sum n_j$

$\sum n_j E_j = E_t$

$\ln N! \simeq N\ln N - N$

(Stirling Approximation)

$$\Big(0 - n_j \frac{1}{\cancel{n_j}} - \ln n_j^* - \alpha - \beta E_j\Big) = 0$$

$$-1 - \ln n_j^* - \alpha - \beta E_j = 0$$

or, $\ln n_j^* = -(1+\alpha) - \beta E_j \qquad \alpha' = 1+\alpha$

$$= -\alpha' - \beta E_j$$

$$\ln\Omega(\{n_j\}) = \ln N_s! - \ln\prod_j n_j!$$

$$= N_s\ln N_s - N_s - \sum_j \ln n_j! \qquad \Big[\, n_1!\, n_2! \ldots = \prod_j n_j! \,\Big]$$

$$= N_s\ln N_s - \cancel{N_s} - \sum_j n_j\ln n_j + \sum_j n_j$$

N_s

$$\ln\Omega = N_s\ln N_s - \sum_j n_j\ln n_j$$

$$n_j^* = e^{-\alpha'} e^{-\beta E_j}$$

$$\sum n_j^* = N_s = e^{-\alpha'}\sum_j e^{-\beta E_j}$$

or, $$e^{+\alpha'} = \frac{\sum_j e^{-\beta E_j}}{N_s}$$

$$\Rightarrow \quad P_j = \frac{n_j^*}{N_s} = \frac{\cancel{N_s}}{\sum_j e^{-\beta E_j}} \cdot \frac{e^{-\beta E_j}}{\cancel{N_s}}$$

$$Q_N(V,T) = \sum_j e^{-\beta E_j}$$

canonical partition function

$$P_j = e^{-\beta E_j} \Big/ \sum_j e^{-\beta E_j}$$

Boltzmann distribution

What about β? → LATER and show $\beta = \frac{1}{k_B T}$

$$\bar{E} = \sum_j P_j E_j = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

$$d\bar{E} = \sum_j \left(E_j dP_j + P_j dE_j \right)$$

$$P_j = \frac{e^{-\beta E_j}}{Q}\ ; \quad \ln P_j = -\beta E_j - \ln Q$$

or,

$$E_j = -\frac{1}{\beta} \left(\ln P_j + \ln Q \right)$$

$$d\bar{E} = \sum_j \left(-\frac{1}{\beta}\right)\left(\ln P_j + \ln Q\right) dP_j + \sum_j P_j \left(\frac{\partial E_j}{\partial V}\right) dV$$

$$d\bar{E} = -\frac{1}{\beta} \sum_j \ln P_j \, dP_j - \frac{1}{\beta} \ln Q \underbrace{\cancel{\sum_j dP_j}}_{0} + \sum_j P_j \left(\frac{\partial E_j}{\partial V}\right) dV$$

$$d\bar{E} = -\frac{1}{\beta} \sum_j \ln P_j \, dP_j + \sum_j P_j \left(\frac{\partial E_j}{\partial V}\right) dV$$

$$S = -k_B \sum_j P_j \ln P_j$$

$$dS = -k_B \, d \sum_j P_j \ln P_j$$

$$= -k_B \left(\underbrace{\sum_j P_j \cancel{/P_j} \, dP_j}_{0} + \sum_j \ln P_j \, dP_j \right)$$

$$dS = -k_B \sum_j \ln P_j \, dP_j$$

$$\boxed{p = -\sum_j P_j \left(\frac{\partial E_j}{\partial V}\right)}$$

Thermodynamics

$$d\bar{E} = \left(-\frac{1}{\beta}\right)\left(-\frac{dS}{k_B}\right) + \sum_j P_j \left(\partial E_j / \partial V\right) dV$$

$$d\bar{E} = \frac{1}{\beta k_B} dS + \sum_j P_j \left(\partial E_j / \partial V\right) dV \quad \cdots (A)$$

$$dE = T dS - p \, dV \quad \cdots (B)$$

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

$$Q = \sum_j e^{-\beta E_j}$$

$$\ln Q = \ln\left(\sum_j e^{-\beta E_j}\right)$$

$$\frac{\partial \ln Q}{\partial \beta} = \frac{1}{\sum_j e^{-\beta E_j}} \sum_j (-E_j) e^{-\beta E_j} = -\sum_j E_j e^{-\beta E_j} \Big/ \sum_j e^{-\beta E_j}$$

$$\bar{E} = \sum_j P_j E_j \qquad P_j = \frac{e^{-\beta E_j}}{Q}$$

$$= -\bar{E}$$

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

$$\text{or } \frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$$

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta}$$

$$\bar{E} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

Internal energy

$$\frac{\partial \ln Q}{\partial V} = \frac{1}{\sum_j e^{-\beta E_j}} (-\beta) \sum_j e^{-\beta E_j} \left(\frac{\partial E_j}{\partial V}\right)$$

$$= \beta \left(- \frac{\sum_j e^{-\beta E_j} \left(\partial E_j / \partial V\right)}{Q} \right) = \beta p$$

Pressure

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

$$S = -k_B \sum_j P_j \ln P_j$$

$$= -k_B \sum_j \frac{e^{-\beta E_j}}{Q} \ln\left(\frac{e^{-\beta E_j}}{Q}\right) = -k_B \sum_j \frac{e^{-\beta E_j}}{Q}\left(-\beta E_j - \ln Q\right)$$

$$= k_B \beta \left(\frac{\sum e^{-\beta E_j} E_j}{Q}\right) + k_B \ln Q$$

$$S = \frac{1}{T}\bar{E} + k_B \ln Q = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_B \ln Q$$

$$A = E - TS$$

$\downarrow$

Helmholtz free energy

$$A = \cancel{k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}} - \cancel{k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}} - k_B T \ln Q$$

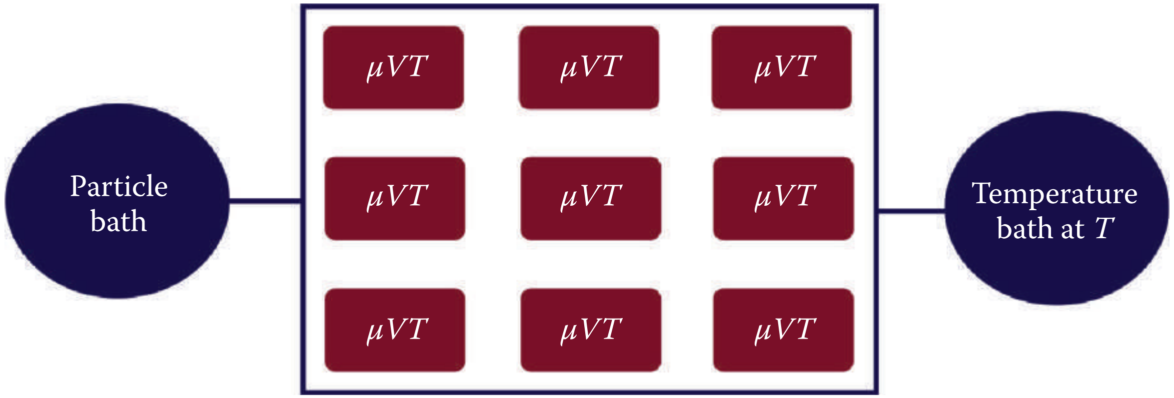
$$A = -k_B T \ln Q$$

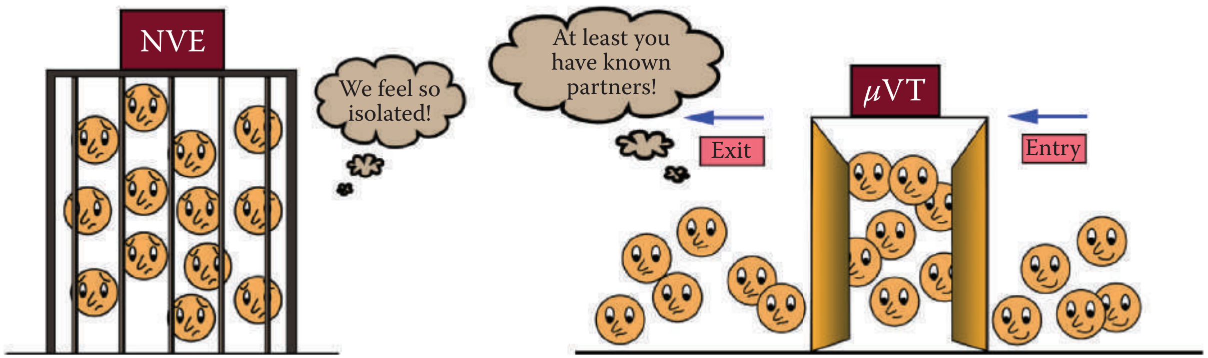
$\rightarrow$ Thermodynamic potential in canonical ensemble

$$S = k_B \ln \Omega$$

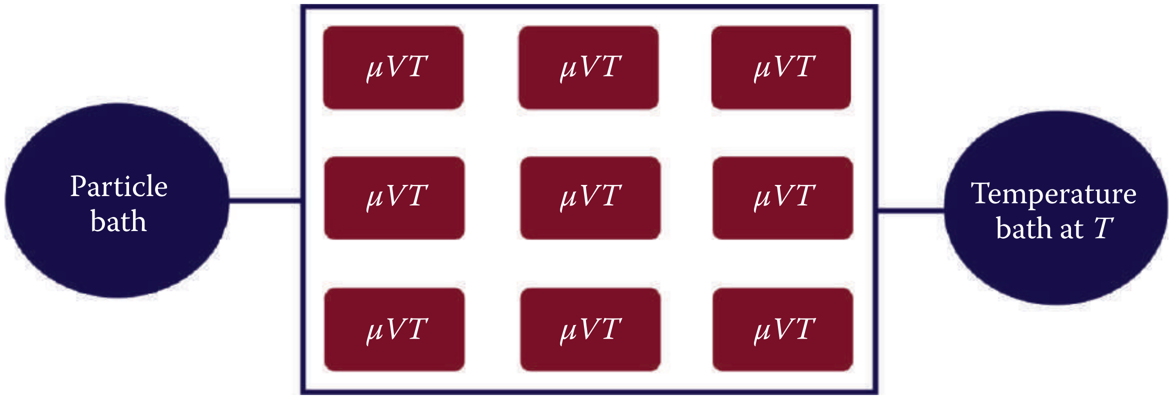
$\hookrightarrow$ T. P. in micro-canonical ensemble

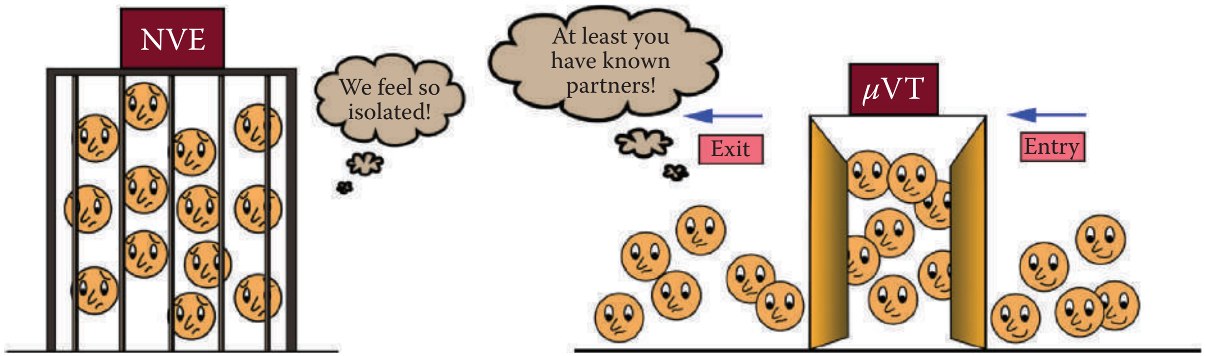
Grand-canonical ensemble





Grand-canonical ensemble





$n_{Nj} \rightarrow$ No. of Systems in the ensemble that contain N molecules/particles that are in the state j

$\{n_{Nj}\}$ is a distribution

$$\sum_N \sum_j n_{Nj} = N_s \rightsquigarrow \text{Total no. of Systems in the ensemble}$$

$$\sum_N \sum_j n_{Nj} E_{Nj} = E_t \rightsquigarrow \text{Total energy of the ensemble}$$

$$\sum_N \sum_j n_{Nj} N = \mathcal{N}^{\circ} \rightsquigarrow \text{Total no. of molecules (particles) in the ensemble}$$

No. of States

$$\Omega(\{n_{Nj}\}) = \frac{N_s!}{\prod_N \prod_j a_{Nj}!}$$

The distribution that maximizes $\Omega(\{n_{Nj}\})$ subjected to appropriate Constraints completely dominates all others.

$$\ln \Omega(\{n_{N_j}\}) = \ln N_s! - \ln \prod_N \prod_j n_{N_j}!$$

$$\ln \Omega(\{n_{N_j}\}) = N_s \ln N_s - N_s - \sum_N \sum_j \ln n_{N_j}!$$

$$\ln \Omega = N_s \ln N_s - \cancel{N_s} - \sum_N \sum_j n_{N_j} \ln n_{N_j} + \underbrace{\sum_N \sum_j n_{N_j}}_{N_s}$$

$$\ln \Omega(\{n_{N_j}\}) = N_s \ln N_s - \sum_N \sum_j n_{N_j} \ln n_{N_j}$$

$$\frac{\partial}{\partial n_{N_j}}\left[N_s \ln N_s - \sum_N \sum_j n_{N_j} \ln n_{N_j} - \alpha \sum_N \sum_j n_{N_j} - \beta \sum_N \sum_j n_{N_j} E_{N_j} - \gamma \sum_N \sum_j n_{N_j} N \right] = 0$$

$$\Rightarrow \quad 0 - \frac{n_{N_j}}{n_{N_j}} - \ln n^*_{N_j} - \alpha - \beta E_{N_j} - \gamma N = 0$$

$$\ln n^*_{N_j} = -(1+\alpha) - \beta E_{N_j} - \gamma N = -\alpha' - \beta E_{N_j} - \gamma N$$

$$n^*_{N_j} = e^{-\alpha'} e^{-\beta E_{N_j}} e^{-\gamma N} \qquad P_{N_j}(V, \beta, \gamma) = \frac{n^*_{N_j}}{N_s}$$

$$N_s = \sum_N \sum_j n^*_{N_j}$$

$$N_s = \sum_N \sum_j e^{-\alpha'} e^{-\beta E_{N_j}(V)} e^{-\gamma N} = e^{-\alpha'} \sum_N \sum_j e^{-\beta E_{N_j}(V)} e^{-\gamma N}$$

$$P_{N_j}(V,\beta,\gamma) = \frac{n^*_{N_j}}{N_s} = \frac{\cancel{e^{-\alpha'}} e^{-\beta E_{N_j}(V)} e^{-\gamma N}}{\cancel{e^{-\alpha'}} \sum_N \sum_j e^{-\beta E_{N_j}(V)} e^{-\gamma N}} = \frac{e^{-\beta E_{N_j}(V)} e^{-\gamma N}}{\Xi(V,\beta,\gamma)}$$

$\Xi(V,\beta,\gamma) \rightarrow$ grand canonical partition f^n

$$\bar{E} = \langle E \rangle = \bar{E}(V,\beta,\gamma) = \frac{1}{\Xi} \sum_N \sum_j E_{N_j} e^{-\beta E_{N_j}(V)} e^{-\gamma N}$$

$$\ln \Xi = \ln \left(\sum_N \sum_j e^{-\beta E_{N_j}(V)} e^{-\gamma N} \right)$$

$$\left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{V,\gamma} = \frac{1}{\underbrace{\sum_N \sum_j e^{-\beta E_{N_j}(V)} e^{-\gamma N}}_{\Xi}} \times \sum_N \sum_j (-E_{N_j}) e^{-\beta E_{N_j}(V)} e^{-\gamma N} = -\bar{E}(V,\beta,\gamma)$$

$$\bar{E} = \langle E \rangle = -\left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{V,\gamma}$$

$$\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta,\gamma} = \frac{1}{\sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}} \beta \sum_N \sum_j \left(-\frac{\partial E_{Nj}}{\partial V}\right) e^{-\beta E_{Nj}(V)} e^{-\gamma N} = \bar{p} = \langle p \rangle \rightarrow \text{Thermodynamic pressure}$$

$$\left\langle -\beta \frac{\partial E_{Nj}}{\partial V} \right\rangle$$

$$\bar{N} = \langle N \rangle$$

$$\left(\frac{\partial \ln \Xi}{\partial \gamma}\right)_{\beta, V} = \frac{1}{\Xi} (-1) \sum_N \sum_j N e^{-\beta E_{Nj}(V)} e^{-\gamma N} = -\bar{N} = -\langle N \rangle$$

$$\bar{N} = \langle N \rangle = -\left(\frac{\partial \ln \Xi}{\partial \gamma}\right)_{\beta, V}$$

$$\beta = \frac{1}{k_B T} \quad \text{(can be shown)}$$

$$\ln \Xi = f\left(\beta, \gamma, \{E_{Nj}(V)\}\right) = \ln \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}$$

$$df = \left(\frac{\partial f}{\partial \beta}\right)_{\gamma, \{E_{Nj}\}} d\beta + \left(\frac{\partial f}{\partial \gamma}\right)_{\beta, \{E_{Nj}\}} d\gamma + \sum_N \sum_j \left(\frac{\partial f}{\partial E_{Nj}}\right)_{\beta, \gamma, E_{Nj}'} dE_{Nj}$$

$$\ln \Xi = \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}$$

$$\frac{\partial \ln \Xi}{\partial E_{Nj}} = \frac{1}{\Xi}(-\beta) e^{-\beta E_{Nj}(V)} e^{-\gamma N}$$

$$= -\beta P_{Nj}$$

$$df = -\bar{E}\, d\beta - \bar{N}\, d\gamma - \beta \underbrace{\sum_N \sum_j P_{Nj}\, dE_{Nj}}$$

Ensemble average reversible work done by the system

$$df = -\bar{E}\, d\beta - \bar{N}\, d\gamma + \beta \bar{p}\, dV$$

Adding $d(\beta \bar{E}) + d(\gamma \bar{N})$ to both sides of this eq^n.

$$d(f + \beta \bar{E} + \gamma \bar{N}) = -\cancel{\bar{E}\, d\beta} - \cancel{\bar{N}\, d\gamma} + \beta \bar{p}\, dV + \beta\, d\bar{E} + \cancel{\bar{E}\, d\beta} + \gamma\, d\bar{N} + \cancel{\bar{N}\, d\gamma}$$

$$d(f + \beta \bar{E} + \gamma \bar{N}) = \beta \bar{p}\, dV + \beta\, d\bar{E} + \gamma\, d\bar{N}$$

$$d(f+\beta\bar{E}+\gamma\bar{N}) = \beta\bar{p}\,dV + \beta\, d\bar{E} + \gamma\, d\bar{N} \qquad \beta = \frac{1}{k_B T}$$

$$T\,dS = dE + p\,dV - \mu\, dN \quad \text{(thermodynamics)} \quad \ldots\ldots \text{(I)}$$

$$k_B T\, d(f+\beta\bar{E}+\gamma\bar{N}) = \bar{p}\,dV + d\bar{E} + k_B T\gamma\, d\bar{N}$$

$$T\, d\left(k_B f + \frac{\bar{E}}{T} + k_B\gamma\bar{N}\right) = \bar{p}\,dV + d\bar{E} + k_B T\gamma\, d\bar{N} \quad \ldots \text{(II)}$$

Compair (I) & (II)

$$-\mu = k_B T\gamma \Rightarrow \gamma = -\mu/k_B T$$

$$S = k_B f + \frac{\bar{E}}{T} + k_B\bar{N}\left(-\mu/k_B T\right) = k_B \ln\Xi + \frac{\bar{E}}{T} - \frac{\bar{N}\mu}{T}$$

$$\boxed{S = \frac{\bar{E}}{T} - \frac{\bar{N}\mu}{T} + k_B \ln\Xi}$$

- Entropy in Grand Canonical ensemble -

$$\Xi(V,T,\mu) = \sum_N \sum_j e^{-E_{Nj}(V)/k_BT} e^{\mu N/k_BT}$$

grand canonical ensemble partition function

$$Q(N,V,T) = \sum_j e^{-E_j/k_BT}$$

canonical partition function

$$S = \frac{\bar{E}}{T} + k_B \ln \Xi - \frac{\mu \bar{N}}{T}$$

$$S = \frac{\bar{E}}{T} + k_B \ln Q$$

$$A = -k_B T \ln Q$$

$$\Xi(V,T,\mu) = \sum_{N=0}^{\infty} Q(N,V,T) e^{\mu N/k_BT}$$

$$\lambda = e^{\mu/k_BT}$$

$$\Xi = \sum_{N=0}^{\infty} Q(N,V,T) \lambda^N$$

$$G = \mu N = E + pV - TS$$

Gibbs free energy

$$\Rightarrow \mu N + TS - E = pV$$

$$TS = \bar{E} + k_B T \ln \Xi - \mu \bar{N}$$

$$k_B T \ln \Xi = TS + \mu \bar{N} - \bar{E} = \bar{p} V$$

$$\Rightarrow \quad pV = k_B T \ln \Xi$$

Isothermal-Isobaric ensemble:

(N, P, T)

$$\Delta(N,T,p) = \sum_E \sum_V \Omega(N,V,E)\, e^{-E/k_B T - pV/k_B T}$$ ← "Check"

Isothermal-Isobaric partition function

$$\boxed{G = -k_B T \ln \Delta(N,T,p)}$$

Gibbs free energy

Canonical Ensemble

(N,V,T)

$$\bar{E} = \langle E \rangle = \frac{1}{Q(N,V,T)} \sum_j E_j e^{-\beta E_j}$$

$$\bar{E^2} = \langle E^2 \rangle = \frac{1}{Q(N,V,T)} \sum_j E_j^2 e^{-\beta E_j}$$

Mean Square Standard deviation

$$\sigma_E^2 = \langle (E - \langle E \rangle)^2 \rangle$$

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2$$

$$C_V(T) = \left(\frac{d\langle E \rangle}{dT}\right)_V$$

Heat capacity at constant volume

$$\langle E^2\rangle = \overline{E^2}$$

$$= \frac{1}{Q}\sum_j E_j^2 e^{-\beta E_j}$$

$$= -\frac{1}{Q}\frac{\partial}{\partial\beta}\underbrace{\sum_j E_j e^{-\beta E_j}}_{\langle E\rangle Q}$$

$$= -\frac{1}{Q}\frac{\partial}{\partial\beta}\left(\langle E\rangle Q\right)$$

$$= -\frac{1}{Q} Q \frac{\partial\langle E\rangle}{\partial\beta} - \frac{1}{Q}\langle E\rangle\frac{\partial Q}{\partial\beta}$$

$$= -\frac{\partial\langle E\rangle}{\partial\beta} - \langle E\rangle \frac{\partial \ln Q}{\partial\beta} \rightarrow -\langle E\rangle$$

$$\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial\beta}\right)_{N,V}$$

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

$$\langle E^2\rangle = -\frac{\partial\langle E\rangle}{\partial\beta} + \underbrace{\langle E\rangle\langle E\rangle}_{\to\,\langle E\rangle^2}$$

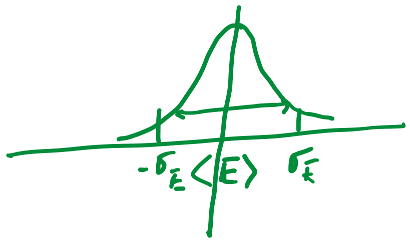
$$\Rightarrow \langle E^2\rangle - \langle E\rangle^2 = \sigma_E^2 = -\frac{\partial\langle E\rangle}{\partial\beta}$$

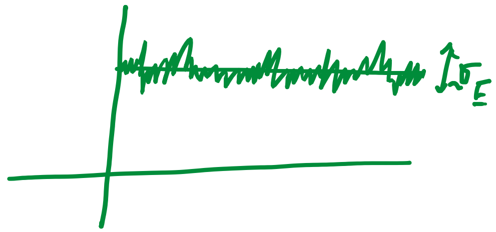
$$\Rightarrow \sigma_E^2 = k_B T^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} = k_B T^2 C_V$$

$$\Rightarrow C_V(k_B T^2) = \sigma_E^2$$

$\Rightarrow$ Heat Capacity at constant volume.

$\dfrac{\sigma_E}{\langle E \rangle} \sim$ How does it depend on the no. of particles $\left(\sim \dfrac{1}{\sqrt{N}}\right)$





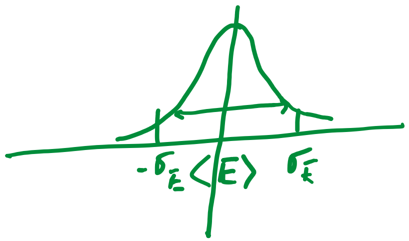
↓

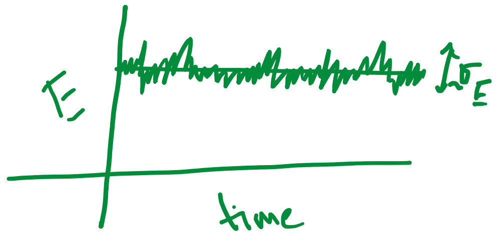
Relative fluctuation

$$\frac{\sigma_E}{\langle E \rangle} \sim \frac{(k_B T^2 C_V)^{\frac{1}{2}}}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

(signature of equilibrium fluctuation)

$\dfrac{\sigma_E}{\langle E\rangle}$ ~ How does it depend on the no. of particles $\left(\sim \dfrac{1}{\sqrt{N}}\right)$





$\downarrow$

Relative fluctuation

$$\frac{\sigma_E}{\langle E\rangle} \sim \frac{(k_B T^2 C_V)^{\frac{1}{2}}}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

(Signature of equilibrium fluctuation)

$C_V \rightarrow$ Heat capacity at constant volm
(Response function)
(N, V, T)

$C_p \rightarrow$ Heat capacity at constant pressure
(N, p, T)

$$\boxed{k_B T^2 C_V = \sigma_E^2}$$

$$\Delta = \sum_{j,V} e^{-\beta(E_j + pV)}$$

$\downarrow$

A partition f^n in (N, p, T) ensemble

$$\Delta(N,p,T) = \sum_{jV} e^{-\beta(E_j + pV)}$$

$$\langle H \rangle = \frac{\sum_{jV} (E_j + pV) e^{-\beta(E_j + pV)}}{\sum_{j,V} e^{-\beta(E_j + pV)}} \leftarrow \text{Average enthalpy} \qquad \langle H \rangle = \langle E_j + pV \rangle$$

$$\frac{\partial \langle H \rangle}{\partial \beta} = \frac{\sum_{jV} -(E_j + pV)^2 e^{-\beta(E_j + pV)} \left(\sum_{jV} e^{-\beta(E_j + pV)}\right) - \sum_{jV} -(E_j + pV) e^{-\beta(E_j + pV)} \sum_{jV} (E_j + pV) e^{-\beta(E_j + pV)}}{\left(\sum_{j,V} e^{-\beta(E_j + pV)}\right)^2}$$

$$\frac{d}{dx}\left(\frac{f(x)}{g(x)}\right) = \frac{f'(x) g(x) - g'(x) f(x)}{g(x)^2}$$

$$= \frac{-\sum_{jV} (E_j + pV)^2 e^{-\beta(E_j + pV)}}{\sum_{jV} e^{-\beta(E_j + pV)}} + \left\{\left(\frac{\sum_{jV} (E_j + pV) e^{-\beta(E_j + pV)}}{\left(\sum_{j,V} e^{-\beta(E_j + pV)}\right)}\right)\right\}^2$$

$$= -\langle H^2 \rangle \qquad + \langle H \rangle^2$$

$$\frac{\partial \langle H \rangle}{\partial \beta} = \langle H \rangle^2 - \langle H^2 \rangle$$

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

$$\frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$$

$$k_B T^2 \underbrace{\frac{\partial \langle H \rangle}{\partial T}}_{C_p} = \langle H^2 \rangle - \langle H \rangle^2 = \sigma_H^2$$

$$\boxed{k_B T^2 C_p = \sigma_H^2}$$

Average vol^m

$$\langle V\rangle = \frac{\sum_{jV} V e^{-\beta(E_j+pV)}}{\sum_{jV} e^{-\beta(E_j+pV)}}$$

$$\frac{\partial\langle V\rangle}{\partial p} = \frac{\sum_{jV} V(-\beta V)e^{-\beta(E_j+pV)}\sum_{jV} e^{-\beta(E_j+pV)} - \sum_{jV} e^{-\beta(E_j+pV)}(-\beta V)\sum_{jV} Ve^{-\beta(E_j+pV)}}{\left(\sum_{jV} e^{-\beta(E_j+pV)}\right)^2}$$

$$= (-\beta)\left[\frac{\sum_{jV} V^2 e^{-\beta(E_j+pV)}}{\sum_{jV} e^{-\beta(E_j+pV)}} - \frac{\left(\sum_{jV} e^{-\beta(E_j+pV)}V\right)^2}{\left(\sum_{jV} e^{-\beta(E_j+pV)}\right)^2}\right] = -\beta\left[\langle V^2\rangle - \langle V\rangle^2\right]$$

Isothermal Compressibility $\quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \Rightarrow \boxed{\kappa = \frac{\sigma_V^2}{V k_B T}}$

Canonical Ensemble

1 single particle → Structureless (point particle)

$\underbrace{\text{N such particles (Non-interacting)}}$ ⇝ vol^m V, temperature T

↓

"ideal monatomic gas"

(N, V, T)

$$Q(N,V,T) = \sum_j e^{-\beta E_j^a} \times \sum_j e^{-\beta E_j^b} \cdots$$ ← particle index

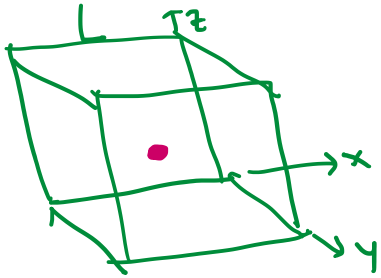
Single particle

$q_{trans} = ?$

Only translational motion

How to calculate q_{trans}?

Cubic box



$$q_{trans} = \sum_j e^{-\beta E_j}$$

$$E_{n_x,n_y,n_z} = \frac{(n_x^2+n_y^2+n_z^2)h^2}{8mL^2}$$

(particle in 3D box)

$\underbrace{n_x, n_y, n_z}_{1, 2, \ldots\ldots}$

If the particles are distinguishable

$$Q(N,V,T) = q_{trans}^a \, q_{trans}^b \cdots$$

$$Q(N,V,T) = (q_{trans})^N$$

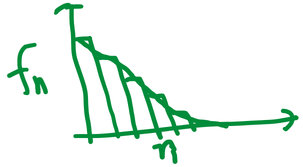
m ⇒ mass of the particle

$$e^{abc} = e^a e^b e^c$$

$$q_{trans} = \sum_{n_x,n_y,n_z} e^{-\beta\frac{(n_x^2+n_y^2+n_z^2)h^2}{8mL^2}}$$

$$= \sum_{n_x} e^{-\frac{\beta n_x^2 h^2}{8mL^2}} \sum_{n_y} \cdots \sum_{n_z} \cdots$$

$$q_{trans} = \sum_{n_x} e^{-\beta \frac{n_x^2 h^2}{8mL^2}} \sum_{n_y} e^{-\frac{\beta n_y^2 h^2}{8mL^2}} \sum_{n_z} e^{-\frac{\beta n_z^2 h^2}{8mL^2}} = \left(\sum_n e^{-\frac{n^2 h^2 \beta}{8mL^2}} \right)^3$$



$$\simeq \left\{ \int_0^\infty dn \, e^{-\frac{n^2 h^2 \beta}{8mL^2}} \right\}^3$$

$$= \left\{ \int_0^\infty dn \, e^{-\frac{n^2 h^2}{8mL^2 k_B T}} \right\}^3$$

Recall

$$\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = (\pi/\alpha)^{\frac{1}{2}}$$

$$q_{trans} = \left\{ \frac{1}{2} \int_{-\infty}^{\infty} \cdots\cdots \right\}^3 = \left\{ \frac{1}{2} \left(\frac{\pi \, 8mL^2 k_B T}{h^2} \right)^{\frac{1}{2}} \right\}^3$$

$$8^{1/2} = (2 \cdot 2 \cdot 2)^{1/2} = 2\sqrt{2} = 2^{3/2}$$

$$q_{trans} = \frac{1}{8} 8^{3/2} L^3 \left(\frac{\pi m k_B T}{h^2} \right)^{3/2}$$

$L^3 \to V$ (vol^m of cubic box)

$$\boxed{q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V}$$

Then C_v (per particle)

$$C_v = \frac{\partial \langle E \rangle}{\partial T}$$

$$\langle E \rangle = k_B T^2 \frac{\partial \ln q_{trans}}{\partial T}$$

$$= k_B T^2 \frac{\partial}{\partial T} \left[\ln T^{3/2} + \cdots \right]$$

independent of T

$$\boxed{\langle E \rangle = k_B T^2 \frac{3}{2} \frac{1}{T} = \frac{3}{2} k_B T}$$

Equipartition theorem

$$Q(N,V,T) = q_{trans}^{N}$$

$$Q = V^N \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}$$

$$\langle E \rangle = \frac{3}{2} N k_B T$$

$$C_V = \frac{\partial}{\partial T}\langle E \rangle = \frac{3}{2} N k_B$$

if $N = N_A$ $\quad C_V = \frac{3}{2} R$

Entropy:

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

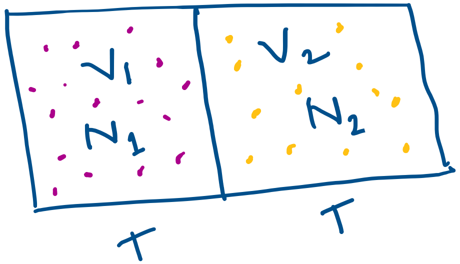
$$= k_B \ln(q_{trans}^{N}) + k_B T \frac{\partial}{\partial T} \ln(q_{trans}^{N})$$

$$= N k_B \ln q_{trans} + N k_B T \frac{\partial}{\partial T}(\ln q_{trans})$$

$$= N k_B \ln q_{trans} + N k_B T \frac{3}{2}\frac{1}{T} = N k_B \ln q_{trans} + \underbrace{\frac{3}{2} N k_B}_{N k_B \ln(e^{3/2})}$$

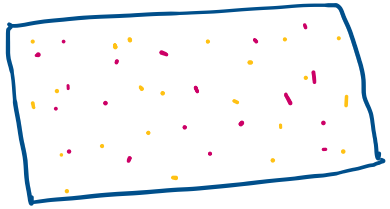
$$S = N k_B \ln\left[\left(\frac{2\pi m k_B T e}{h^2}\right)^{3/2} V\right] = N k_B \ln V + N k_B \underbrace{\ln\left[\left(\frac{2\pi m k_B T e}{h^2}\right)^{3/2}\right]}_{\sigma \text{ (say)}}$$

$$S = N k_B \ln V + N k_B \sigma$$



Distinct gas molecules
(atoms)

"Remove the partition"



"Mixing"

$\Delta S_{mix} > 0$ (Should be positive)

<u>When the partition is on:</u>

$$S_i = S_1 + S_2 = N_1 k_B \ln V_1 + \sigma_1 N_1 k_B + N_2 k_B \ln V_2 + \sigma_2 N_2 k_B$$

Entropy of the initial state

$$S_f = N_1 k_B \ln(V_1+V_2) + N_2 k_B \ln(V_1+V_2) + (N_1\sigma_1 + N_2\sigma_2) k_B$$

(after removing the partition)

$$\Delta S_{mix} = S_f - S_i$$

$$= N_1 k_B \ln(V_1 + V_2) + N_2 k_B \ln(V_1 + V_2) - N_1 k_B \ln V_1 - N_2 k_B \ln V_2$$

$$V_1 + V_2 = V, \quad N_1 + N_2 = N$$

$$= N_1 k_B \ln\left(\frac{V}{V_1}\right) + N_2 k_B \ln\left(\frac{V}{V_2}\right) > 0$$

$$V > V_1, \quad V > V_2$$

$$\Delta S_{mix} = -N k_B \left[\frac{N_1}{N} \ln\left(\frac{V_1}{V}\right) + \frac{N_2}{N} \ln\left(\frac{V_2}{V}\right)\right]$$

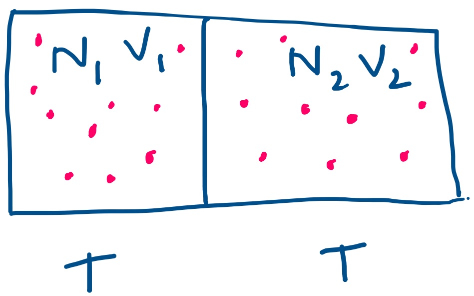
One can generalize the above expression

$$\Delta S_{mix} = -N k_B \sum_\alpha \left(\frac{N_\alpha}{N}\right) \ln\left(\frac{V_\alpha}{V}\right)$$

monatomic identical (indistinguishable) ideal gas

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}$$

$$\left.\begin{array}{l} N = N_1 + N_2 \\ V = V_1 + V_2 \end{array}\right\}$$



$\rightsquigarrow$ Now we remove the partition

What do you expect in terms of entropy (change)?

$\Delta S_{mix} = 0$ (should be)

But if we use the formula (we used few minutes back)

$\Delta S > 0$

"Gibbs Paradox"

$$Q(N,V,T) = \frac{q_{trans}^N}{N!} \leftarrow \text{Divide by } N!$$

Non-interacting

indistinguishable (identical) particles

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$S = k_B \ln\left(\frac{q_{trans}^N}{N!}\right) + k_B T \frac{\partial}{\partial T} \ln\left(\frac{q_{trans}^N}{N!}\right)$$

$$= N k_B \ln q_{trans} - k_B \ln N! + \frac{3}{2} N k_B$$

$$S = N k_B \ln q_{trans} - N k_B \ln N + N k_B + \frac{3}{2} N k_B$$

$$S = N k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \left(V/N\right)\right] + \frac{5}{2} N k_B$$

$$S = N k_B \ln\left(\frac{Ve}{N}\right) + N k_B \underbrace{\ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]}_{\sigma}$$

$$S = N k_B \ln\left(\frac{Ve}{N}\right) + N k_B \sigma$$

$$V = V_1 + V_2$$
$$N = N_1 + N_2$$

$$S_i = N_1 k_B \ln\left(\frac{V_1 e}{N_1}\right) + N_1 k_B \sigma + N_2 k_B \ln\left(\frac{V_2 e}{N_2}\right) + N_2 k_B \sigma$$

$$S_f = N_1 k_B \ln\left(\frac{Ve}{N_1}\right) + N_1 k_B \sigma + N_2 k_B \ln\left(\frac{Ve}{N_2}\right) + N_2 k_B \sigma$$

(if Distinct gas particles) (particle type 1 has available vol^m $V_1 + V_2 = V$)

$$\Delta S_{mix} = S_f - S_i = N_1 k_B \ln\left(\frac{V\cancel{e}}{\cancel{N_1}} \cdot \frac{\cancel{N_1}}{V_1 \cancel{e}}\right) + N_2 k_B \ln\left(\frac{V\cancel{e}}{\cancel{N_2}} \cdot \frac{\cancel{N_2}}{V_2 \cancel{e}}\right)$$

$$= -N k_B \left[\frac{N_1}{N} \ln(V_1/V) + \frac{N_2}{N} \ln(V_2/V)\right] > 0$$

But particles are identical !!

$$S_f = (N_1+N_2)k_B \ln\left(\frac{e\overbrace{(V_1+V_2)}^{V}}{\underbrace{(N_1+N_2)}_{N}}\right) + N_1 k_B \sigma_1 + N_2 k_B \sigma_2$$

$\sigma_1 = \sigma_2$

$\downarrow$

$$S_i = N_1 k_B \ln\left(\frac{V_1 e}{N_1}\right) + N_1 k_B \sigma_1 + N_2 k_B \ln\left(\frac{V_2 e}{N_2}\right) + N_1 k_B \sigma_2$$

ΔS_{mix}

$$= N_1 k_B \ln\left(\frac{\cancel{e}V}{N}\cdot\frac{N_1}{\cancel{e}V_1}\right) + N_2 k_B \ln\left(\frac{\cancel{e}V}{N}\cdot\frac{N_2}{V_2\cancel{e}}\right)$$

Now

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V} \quad \text{(density is uniform)}$$

$$\Delta S_{mix} = N_1 k_B \ln\Big(\underbrace{\frac{V}{N}\cdot\frac{N_1}{V_1}}_{1}\Big) + N_2 k_B \ln\Big(\underbrace{V/N\cdot\frac{N_2}{V_2}}_{1}\Big) = 0$$

(What we expect)

N - non-interacting, indistinguishable (identical) particles/molecules

Canonical ensemble

$$\boxed{Q = \frac{q^N}{N!}}$$

q = Molecular partition function

Non-interacting but distinguishable

Total energy of the System

particle no.

$$E_l(N,V) = \underbrace{\varepsilon_i^a(V) + \varepsilon_j^b(V) + \cdots + \varepsilon_k^c(V) + \cdots}_{N \text{ such terms}}$$

Energy levels/particle

Total partition f^n of the system

$$\boxed{Q(N,V,T) = \sum_l e^{-\beta E_l}} = \sum_{i,j,k} e^{-\beta(\varepsilon_i^a(V) + \varepsilon_j^b(V) + \cdots\cdots)}$$

l → Sum is all possible configurations / States

particles are distinguishable

$$= \sum_i e^{-\beta\varepsilon_i^a} \sum_j e^{-\beta\varepsilon_j^b} \sum_k e^{-\beta\varepsilon_k^c} \cdots = q_a(V,T)\, q_b(V,T)\, q_c(V,T) \cdots$$

$$q(V,T) = \sum_i e^{-\beta\varepsilon_i}$$

Molecular p.f^n

Non-interacting (independent) indistinguishable particles:

Two non-interacting Fermions (example: electron) $\rightarrow$ $\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4$ $\rightarrow$ Available particle energy levels

$$Q(2, V, T) = \sum_{i,j=1}^{4} e^{-\beta(\varepsilon_i + \varepsilon_j)}$$

$\hookrightarrow$ 16 terms in this sum

* Additional restriction
$\rightarrow$ for a given ε_i, occupation no. is 0 or 1

But 4 terms are unacceptable $\rightarrow$ As these are Fermions

12 terms seem acceptable

$$\underbrace{\begin{matrix} \varepsilon_1+\varepsilon_2 & \varepsilon_2+\varepsilon_3 \\ \varepsilon_1+\varepsilon_3 & \varepsilon_2+\varepsilon_4 \\ \varepsilon_1+\varepsilon_4 & \varepsilon_3+\varepsilon_4 \end{matrix}}_{6} \qquad \underbrace{\begin{matrix} \varepsilon_2+\varepsilon_1 & \varepsilon_3+\varepsilon_2 \\ \varepsilon_3+\varepsilon_1 & \varepsilon_4+\varepsilon_2 \\ \varepsilon_4+\varepsilon_1 & \varepsilon_4+\varepsilon_3 \end{matrix}}_{6}$$

Are they acceptable

As these particles are indistinguishable

$$\frac{12}{2!} = 6 \text{ terms}$$

Bosons ? no. restriction on occupation no.
But they are still indistinguishable

In general

Collection of N particles

$$E = \underbrace{\varepsilon_2 + \varepsilon_{10} + \varepsilon_{10} + \varepsilon_{10} + \cdots + \varepsilon_{10}}_{\text{N particles, hence N terms}}$$

Position of ε_2 is not important as particles are indistinguishable

$$E = \underbrace{\varepsilon_{10} + \varepsilon_2 + \varepsilon_{10} + \varepsilon_{10} + \cdots + \varepsilon_{10}}_{\text{N terms}}$$

It represents the same state

ε_2 can be located in any of the N positions

$$\boxed{E = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \cdots + \varepsilon_N}$$

N! possible permutations !!

$$Q = \frac{q^N}{N!}$$ (to restrict overcounting)

Electronic partition function:

$$q_{elec} = \sum_i \omega_{e_i} e^{-\beta \varepsilon_i}$$

$\omega_{e_i} \rightarrow$ Degeneracy

Fix the arbitary zero of energy

Say the lowest electronic state $\equiv$ zero state

$$q_{elec} = \omega_{e_1} e^{0} + \omega_{e_2} e^{-\beta \underbrace{(\varepsilon_2 - \varepsilon_1)}_{\Delta\varepsilon_{12} = \varepsilon_2}} + \cdots\cdots$$

$\varepsilon_1 = 0$ (by definition)

He atom

fraction of atoms in the lowest triplet state $^3S_1$ is given by (first excited state)

$$f_2 = \frac{\omega_{e_2} e^{-\beta \Delta\varepsilon_{12}}}{\omega_{e_1} e^{-0} + \omega_{e_2} e^{-\beta \Delta\varepsilon_{12}} + \cdots} \simeq \frac{3 e^{-\beta \Delta\varepsilon_{12}}}{\omega_{e_1} + 3 e^{-\beta \Delta\varepsilon_{12}} + \omega_{e_3} e^{-\beta \Delta\varepsilon_{13}} + \cdots}$$

At 300K, $\beta \Delta\varepsilon_{12} \simeq 770 \rightarrow f_2 \sim 10^{-334}$ (almost zero) 3000K, $f_2 \sim 10^{-33}$ (still small)

A good apporximation

$$q_{elec} = \omega_{e_1} + \underbrace{\omega_{e_2} e^{-\beta\Delta\varepsilon_{12}}}_{\text{may or may not be required}}$$

F atoms

T (K)	f_2
200	0.027
400	0.105
⋮	
2000	0.272

$$q_{elec} \simeq \omega_{e_1} + \omega_{e_2} e^{-\beta\Delta\varepsilon_{12}}$$

Nuclear partition function:

Nuclear energy levels are separated by millions of electron volts

$q_n = \omega_{n1}$ (ground state (nuclear) energy is taken to be zero) → Many times omitted

Ideal Monatomic gas

$$Q = \frac{(q_{trans}\, q_{elec}\, q_{nucle})^N}{N!}$$

$$q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

$$q_{trans} = \frac{V}{\Lambda^3}$$

Helmholtz free energy:

$$\ln\left(\frac{1}{N!}\right) = -\ln N! = -N\ln N + N$$
$$= -(N\ln N - N)$$

$$A = -k_B T \ln Q = -k_B T \ln\left\{\left(\frac{q_{trans}\, q_{elec}}{N!}\right)^N\right\}$$

$$= -N k_B T \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{Ve}{N}\right] - \underbrace{N k_B T \ln\left(\omega_{e_1} + \omega_{e_2} e^{-\beta \Delta \varepsilon_{12}}\right)}_{\text{Small contribution}}$$

$$q_{elec} = \omega_{e_1} + \omega_{e_2} e^{-\beta \Delta \varepsilon_{12}} \Rightarrow \ln q_{elec} = \ln(\ldots\ldots)$$

Thermodynamic (internal) energy:

$$E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = + N k_B T^2 \left(\frac{3}{2}\right)\frac{1}{T} + \text{electronic part}$$

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

$$N k_B T^2 \frac{1\left(0 + \omega_{e_2}(-\Delta\varepsilon_{12}) e^{-\beta\Delta\varepsilon_{12}} \left(-\frac{1}{k_B T^2}\right)\right)}{\left(\omega_{e_1} + \omega_{e_2} e^{-\beta\Delta\varepsilon_{12}}\right)}$$

$$E = \frac{3}{2} N k_B T + \underbrace{\frac{N \omega_{e_2} \Delta\varepsilon_{12}\, e^{-\beta\Delta\varepsilon_{12}}}{q_{elec}}}_{\text{Very small contribution}}$$

Entropy

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$S = \frac{3}{2} N k_B + N k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{Ve}{N}\right] + N k_B \ln\left(\omega_{e_1} + \omega_{e_2} e^{-\beta \Delta\varepsilon_{12}}\right) + \frac{N k_B \omega_{e_2} \beta \Delta\varepsilon_{12} e^{-\beta\Delta\varepsilon_{12}}}{q_{elec}}$$

"Sackur-Tetrode equation"

S_{elec}

Contribution from electronic part of the partition function.

The chemical potential

$$q = q_{trans}\, q_{elec}\, q_n$$

$$\mu(T,p) = -k_BT\left(\frac{\partial \ln Q}{\partial N}\right)_{V,T} = -k_BT\frac{\partial}{\partial N}\left\{\ln\left(\frac{q^N}{N!}\right)\right\}$$

$$= -k_BT\frac{\partial}{\partial N}\left[N\ln q - \ln N!\right]$$

$$= -k_BT\frac{\partial}{\partial N}\left[N\ln q - N\ln N + N\right]$$

$$\mu(T,p) = -k_BT\left[\ln q - \cancel{N/N} - \ln N + \cancel{1}\right] = -k_BT\ln(q/N)$$

$$\mu(T,p) = -k_BT\ln\left[\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}\frac{V}{N}\right] - k_BT\ln q_{elec}q_n$$

$$\frac{V}{N} \rightarrow \frac{k_BT}{p}$$

$$\mu(T,p) = \underbrace{-k_BT\ln\left[\left(\frac{2\pi m k_BT}{h^2}\right)^{3/2}k_BT\right] - k_BT\ln q_{elec}q_n}_{\mu_0(T)} + k_BT\ln p$$

$$\mu(T,p) = \mu_0(T) + k_BT\ln p$$

Ideal (non-interacting) diatomic gas:

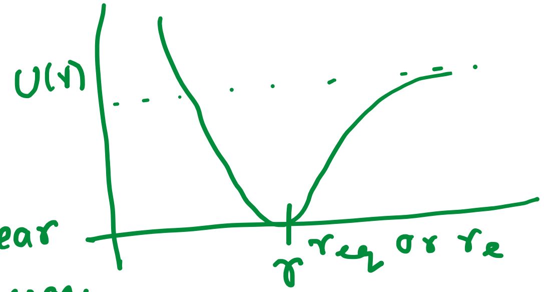
Rigid Rotor - Harmonic Oscillator approximation

$$\underbrace{m_1 + m_2}_{\text{Total mass}}$$

Born-Oppenheimer Approximation

fixed nuclei (heavy)

$U(r)$
↓
internuclear pot energy



$$H = H_{trans} + H_{int} \text{ (internal)}$$

H ↓ Hamiltonian

H_{trans} ↳ for the motion of the whole body

H_{int} ↳ Relative co-ordinate

$$q_{trans} = \left[\left(\frac{2\pi(m_1+m_2)k_BT}{h^2}\right)^{3/2}\right]V$$

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{int}$$

(Diatomic)

$$U(r) = U(r_e) + (r-r_e)\cancel{\left(\frac{\partial U}{\partial r}\right)_{r=r_e}} + \frac{1}{2!}(r-r_e)^2 \overbrace{\left(\frac{\partial^2 U}{\partial r^2}\right)_{r=r_e}}^{k} + \cdots$$

$\left(\frac{\partial U}{\partial r}\right)_{r=r_e} \to 0$

(Taylor expansion)

k = force constant

$$\underbrace{U(r) \simeq U(r_e) + \frac{k}{2}(r-r_e)^2}_{\text{Harmonic}} + \underbrace{\cdots}_{\text{Anharmonic (not included)}}$$

for the internal motion

$$H_{int} = H_{rot,vib} = H_{rot} + H_{vib}$$

H_{rot} → Rigid Rotor

H_{vib} → Simple Harmonic oscillator

$$\varepsilon_{rot,vib} = \varepsilon_{rot} + \varepsilon_{vib}$$

$$q_{rot,vib} = q_{rot}\, q_{vib}$$

Let us consider vibration first

$$\varepsilon_{vib} = \left(n + \frac{1}{2}\right) h\nu$$

$n = 0, 1, 2, \ldots$ → vibrational quantum number

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

→ 1000 cm^{-1}

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

→ Reduced mass

$k \sim 10^5 - 10^6$ dynes/cm

The vibrational partition function:

$$\varepsilon_n = \left(n + \tfrac{1}{2}\right)h\nu$$

$$q_{vib}(T) = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)h\nu} = e^{-\frac{\beta h\nu}{2}} \sum_{n=0}^{\infty} e^{-n\beta h\nu}$$

Let us assume $y = \sum_{n=0}^{\infty} e^{-n\beta h\nu} = \left(1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + e^{-3\beta h\nu} + \cdots\cdots\right)$

Let, $e^{-\beta h\nu} = x$

$$y = 1 + x + x^2 + x^3 + \cdots$$

$$= 1 + x\underbrace{\left(1 + x + x^2 + \cdots\cdots\right)}$$

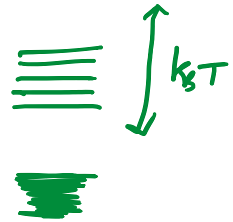
$$y = 1 + xy$$

$$\Rightarrow y(1-x) = 1 \Rightarrow y = \frac{1}{1-x}$$

$$q_{vib} = e^{-\beta h\nu/2}\left(\frac{1}{1-e^{-\beta h\nu}}\right)$$

If temperature is high $\beta h\nu << 1$

$\frac{h\nu}{k_BT}$ is small



$$q_{vib}(T) \approx \int_0^\infty e^{-\beta h\nu/2}\, e^{-n\beta h\nu}\, dn = e^{-\beta h\nu/2} \int_0^\infty e^{-n\beta h\nu}\, dn$$

$$= e^{-\beta h\nu/2} \left. \frac{e^{-\beta h\nu n}}{(-\beta h\nu)} \right|_0^\infty$$

$$= e^{-\beta h\nu/2} \frac{\left(e^{-\infty} - e^{0}\right)}{(-\beta h\nu)} = \frac{e^{-\beta h\nu/2}}{\beta h\nu}$$

$e^{-\beta h\nu/2} \approx 1$

$$q_{vib}(T) \simeq \frac{1}{\beta h\nu} = \left(\frac{k_BT}{h\nu}\right)$$

$$q_{vib}(T) = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}$$

$\beta h\nu << 1$

$$\simeq \frac{1 - \cancel{\beta h\nu/2}^{\,0}}{1-1+\beta h\nu} \simeq \frac{1}{\beta h\nu} = \left(\frac{k_BT}{h\nu}\right)$$

Vibrational Contribution to the internal energy:

$$E_{vib} = Nk_BT^2 \frac{d \ln q_{vib}}{dT} = -N \frac{d \ln q_{vib}}{d\beta}$$

$$q_{vib} = \frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}$$

$$\ln q_{vib} = -\beta h\nu/2 - \ln\left(1-e^{-\beta h\nu}\right)$$

$$\frac{d \ln q_{vib}}{d\beta} = -h\nu/2 - \frac{1}{(1-e^{-\beta h\nu})}\left(0 + h\nu e^{-\beta h\nu}\right)$$

$$-N\frac{d \ln q_{vib}}{d\beta} = +Nh\nu/2 + \frac{Nh\nu\, e^{-\beta h\nu}}{1-e^{-\beta h\nu}} = E_v$$

Let, $\Theta_v = \frac{h\nu}{k_B}$ → vibrational temp

$$\beta h\nu = \frac{\Theta_v}{T}$$

$$\boxed{E_v = Nk_B\left(\frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v/T}-1}\right)}$$

$C_{V,vib}$ → Next

$$E_\nu = Nk_B\left(\frac{\Theta_\nu}{2} + \frac{\Theta_\nu}{e^{\Theta_\nu/T}-1}\right)$$

$$\frac{d}{dx}\left(\frac{f(x)}{g(x)}\right) = \frac{f'(x)g(x)-g'(x)f(x)}{g(x)^2}$$

Vibrational contribution to the heat capacity

$$C_{V,vib} = \left(\frac{\partial E_\nu}{\partial T}\right)_{N,V}$$

$$\left(\frac{\partial E_\nu}{\partial T}\right)_{N,V} = Nk_B \times 0 + Nk_B \frac{\left(0 - \left(e^{\Theta_\nu/T}\left(-\frac{\Theta_\nu}{T^2}\right) - 0\right)\right)}{\left(e^{\Theta_\nu/T}-1\right)^2}$$

$$\boxed{C_{V,vib} = Nk_B\left(\frac{\Theta_\nu}{T}\right)^2 \frac{e^{\Theta_\nu/T}}{\left(e^{\Theta_\nu/T}-1\right)^2}}$$

$$C_{V,vib} \simeq (Nk_B)\left(\frac{\Theta_\nu}{T}\right)^2\left(\frac{1+\Theta_\nu/T+\cdots}{\left(\cancel{1}+\Theta_\nu/T+\cdots-\cancel{1}\right)^2}\right)$$

$$\simeq (Nk_B)\left(\frac{\Theta_\nu}{T}\right)^2\left(\frac{T}{\Theta_\nu}\right)^2(1+\cdots) = Nk_B \quad \text{(checked)}$$

$$E_\nu\Big|_{T\to\infty} = Nk_B\left(\frac{\Theta_\nu}{2}+\frac{\Theta_\nu}{1+\Theta_\nu/T-1\cdots}\right)$$

$$= Nk_B\left(\frac{\Theta_\nu}{2}+\frac{\cancel{\Theta_\nu}}{\cancel{\Theta_\nu}}T\right)$$

$$\simeq Nk_BT \qquad T \gg \Theta_\nu$$

(checked)

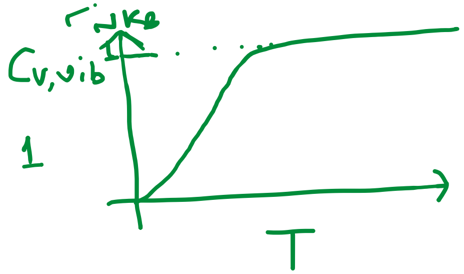
What happens at high temperature?

Equipartition theorem (classical)

$$C_{V,vib} = Nk_B \qquad T\to\infty$$

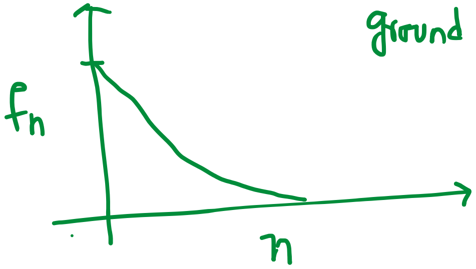
$$E_{vib} = Nk_BT$$

$$\frac{\Theta_\nu}{T} \ll 1$$



Fraction of molecules in the excited vibration state(s)

In state "n"
$$f_n = \frac{e^{-\beta h\nu(n+\frac{1}{2})}}{q_{vib}(T)}$$



Most molecules are in the ground vibrational state

$$\Theta_\nu = \frac{h\nu}{k_B}$$ ← Molecular property

$$f_{n>0} = \sum_{n=1}^{\infty} \frac{e^{-\beta h\nu(n+\frac{1}{2})}}{q_{vib}(T)}$$
$$= \frac{e^{-\beta h\nu/2}}{q_{vib}(T)} \sum_{n=1}^{\infty} e^{-\beta h\nu n}$$
$$= \frac{e^{-\beta h\nu/2}}{q_{vib}(T)} \left(1 + \sum_{n=1}^{\infty} e^{-\beta h\nu n} - 1\right)$$
$$= \frac{e^{-\beta h\nu/2}}{q_{vib}(T)} \left(\frac{1}{1-e^{-\beta h\nu}} - 1\right)$$
$$= \frac{1}{q_{vib}(T)} \left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}} - e^{-\beta h\nu/2}\right) = 1 - \frac{e^{-\beta h\nu/2}}{q_{vib}(T)} = (1-f_0) =$$

Θ_ν	Molecule
H_2	6215
HCl	4227
I_2	310
Cl_2	810

$$f_0 = \frac{e^{-\beta h\nu/2}}{q_{vib}(T)}$$

$$1 - f_0 = 1 - \frac{\cancel{e^{-\beta h\nu/2}}}{\frac{\cancel{e^{-\beta h\nu/2}}}{1-e^{-\beta h\nu}}}$$
$$= 1 - (1 - e^{-\beta h\nu})$$
$$f_{n>0} = e^{-\beta h\nu} = e^{-\Theta_\nu/T}$$

Rotational partition function of a heteronuclear Diatomic:

$$q_{rot}(T) = \sum_{J=0}^{\infty} (2J+1)\, e^{-\beta J(J+1)\bar{B}}$$

$\frac{\bar{B}}{k_B} = \Theta_r \rightarrow$ Characteristic temperature of rotation

usually, $\frac{\Theta_r}{T}$ is quite small at ordinary temperatures

then above sum can be replaced by an integral

Let, $\frac{\Theta_r}{T} J(J+1) = y$

$(2J+1)\frac{\Theta_r}{T}\, dJ = dy$

$$q_{rot}(T) = \int_0^{\infty} dJ\,(2J+1)\, e^{-\frac{\Theta_r J(J+1)}{T}}$$

$$= \int_0^{\infty} dy \left(\frac{T}{\Theta_r}\right) e^{-y} = \frac{T}{\Theta_r}\int_0^{\infty} e^{-y}\, dy = \frac{T}{\Theta_r}\left.\frac{e^{-y}}{-1}\right|_0^{\infty} = \frac{T}{\Theta_r}(-0+1)$$

$$q_{rot}(T) = \frac{T}{\Theta_r}$$

$\frac{\Theta_r}{T} << 1$

"High temperature limit"

For low temperatures (molecules with high value of Θ_r, HD, $\Theta_r = 42.7\,K$)

One cannot use integration to evaluate the partition function

$$q_{rot}(T) = \left(1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + \cdots\cdots\right)$$

Euler-Maclaurin Summation formula

$$\frac{\Theta_r}{T} \gg 1$$

$$\frac{\Theta_r}{T} \ll 1$$

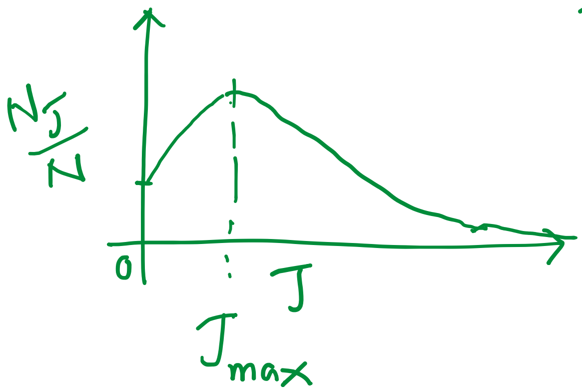
$$E_{rot} = N \frac{\partial \ln q_{rot}(T)}{\partial T}(k_B T^2) = Nk_B T^2 \frac{\partial}{\partial T}\left(\ln\left(T/\Theta_r\right)\right)$$

$$E_{rot} = Nk_B T^2 \left(\frac{1}{T}\right) = Nk_B T$$ (equipartition theorem)

$$C_{V,rot} = Nk_B$$

$$\frac{N_J}{N} = \frac{(2J+1)\,e^{-\theta_r J(J+1)/T}}{q_{rot}(T)}$$

↳ A plot of this vs J



J_{max} ? How to calculate?

$$\frac{\partial}{\partial J}\left(\frac{N_J}{N}\right) = 0$$

$$\frac{1}{q_{rot}(T)}\,\underbrace{\frac{\partial}{\partial J}\left((2J+1)\,e^{-\theta_r J(J+1)/T}\right)}_{(2\cdot 1+0)\,\cancel{e^{-\theta_r J(J+1)/T}} + (2J+1)\,\cancel{e^{-\theta_r J(J+1)/T}}\left(-\frac{\theta_r}{T}\right)(2J+1)} = 0$$

$$(2\cdot 1+0)\,\cancel{e^{-\theta_r J(J+1)/T}} + (2J+1)\,\cancel{e^{-\theta_r J(J+1)/T}}\left(-\frac{\theta_r}{T}\right)(2J+1) = 0$$

$$2 + (2J+1)^2\left(-\frac{\theta_r}{T}\right) = 0$$

$$\Rightarrow (2J+1)^2\left(\frac{\theta_r}{T}\right) = 2 \Rightarrow (2J+1) = \left(\frac{2T}{\theta_r}\right)^{\frac{1}{2}}$$

$$J_{max} = \frac{1}{2}\left(\frac{2T}{\theta_r}\right)^{1/2} - \frac{1}{2}$$

$$J_{max} = \left(\frac{T}{2\theta_r}\right)^{\frac{1}{2}} - \frac{1}{2}$$

$$= \left(\frac{T}{2B/k_B}\right)^{1/2} - \frac{1}{2} \simeq \left(\frac{k_B T}{2B}\right)^{1/2}$$

Homonuclear Diatomic Molecule (partition f^n for rotation):

H_2 $\qquad \psi_{total} = \psi_{trans}\,\psi_{rot}\,\psi_{vib}\,\psi_{elec}\,\psi_{nucl}$

Let us do a two step operation

1. An inversion of all the particles, electrons and nuclei, through the origin
2. An inversion of just electrons back through the origin

This two step process is equivalent to an exchange of nuclei

Translational wavefunction: → Not affected by inversion

electronic wavefunction: ⇝ that depends on the symmetry of that electronic state

ground electronic state Σ_g^+ (Symmetric under both the operations)

ψ_{vib} depends on $\underset{\substack{\downarrow \\ \text{magnitude of}}}{}(r - r_e)$ → Unaffected by any inversion operation

Rotation

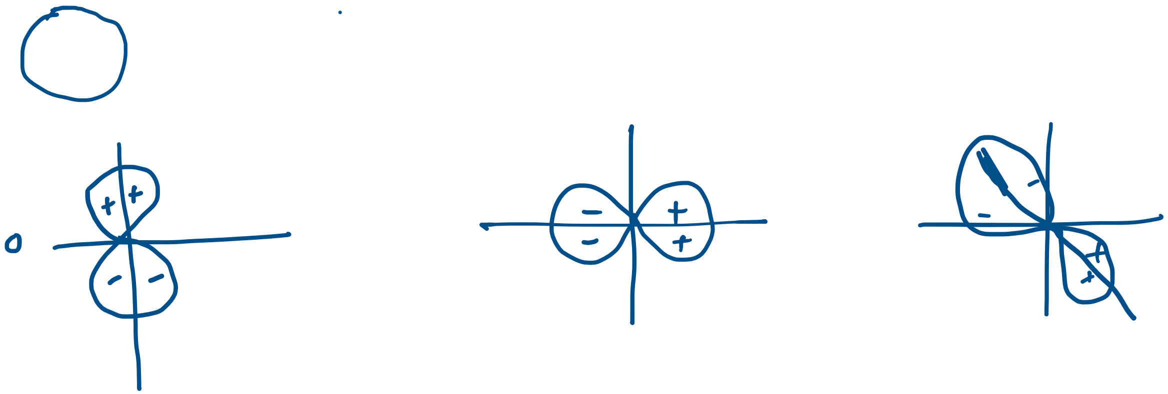
rotational wave functions (Solve rigid-rotor problem) These wavef^{n}s will get affected by inversion

$J=0$

$M=0$

$J=1$

$M=0$



$J =$ even

$J =$ odd

$$(r, \theta, \phi) \longrightarrow (r, \pi-\theta, \phi+\pi)$$

nuclear part of the wavef^n (nuclear spin)

H-H molecule

$\uparrow \uparrow$

$$\left.\begin{array}{l} \alpha\alpha \\ \beta\beta \\ \frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha) \end{array}\right\} \text{Symmetric}$$

$$\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha) \rightarrow \text{Antisymmetric}$$

H_2 molecule in the ground electronic state Σ_g^+

In general

$I \rightarrow$ nuclei spin

Each nuclei would have $(2I+1)$ states (spin)

Diatomic molecule

$\overset{o}{(2I+1)}$ $\quad$ $\overset{o}{(2I+1)}$

Total no. of spin state (Diatomic)

$(2I+1)^2$

$(2I+1)\left(\frac{2I}{2}\right) \rightarrow$ No. of antisymmetric spin states

$\frac{1}{\sqrt{2}}\left(\alpha_i(1)\alpha_j(2) - \alpha_j(2)\alpha_i(1)\right)$

$i < j \quad i \leq 2I+1$

No. of symmetric spin states

$$(2I+1)^2 - (2I+1)\left(2I/_2\right) = (I+1)(2I+1)$$

for H_2 $\quad I = \frac{1}{2}$

$$\left(2\cdot\frac{1}{2}+1\right)\left(\frac{2\cdot 1/2}{2}\right) = \frac{2}{2} = 1$$

$$\left(\frac{1}{2}+1\right)\left(2\cdot\frac{1}{2}+1\right) = 3$$

I Integral Spins: (Total wavef^n has to be symmetric)

(Bosons)

$I(2I+1)$ Antisymmetric nuclear spin f^{n}s combine with J odd

$(I+1)(2I+1)$ Symmetric nuclear spin f^{n}s combine with J even

$$\longrightarrow \quad q_{rot,nucl}(T) = (I+1)(2I+1)\sum_{J\,even}(2J+1)e^{-J(J+1)\Theta_r/T} + I(2I+1)\sum_{J\,odd}\cdots\cdots$$

Half-Integral Spins

(Fermions)

(Antisymmetric)

Example H_2 molecule

$I(2I+1)$ Antisymmetric nuclear spin f^{n}s × J even

$I(2I+1)$ Antisymmetric nuclear spin f^{n}s × J odd

$(I+1)(2I+1)$ Symmetric " " " × J odd

$$q_{rot,nucl}(T) = (I+1)(2I+1)\sum_{J\,odd}\cdots\cdots + I(2I+1)\sum_{J\,even}\cdots\cdots$$

$$q_{rot,nucl} \neq q_{rot}\,q_{nucl}$$

At ordinary temperatures $\Theta_r \ll T$

$$\sum_{J\,even} \approx \sum_{J\,odd} \simeq \frac{1}{2}\int_0^\infty (2J+1)\, e^{-\Theta_r J(J+1)/T} = \frac{1}{2}\frac{T}{\Theta_r}$$

For Integral Spins

$$q_{rot,nucl}(T) = (I+1)(2I+1)\cdot\frac{1}{2}\frac{T}{\Theta_r} + I(2I+1)\frac{1}{2}\frac{T}{\Theta_r}$$

$$= \frac{1}{2}\frac{T}{\Theta_r}(2I+1)(I+1+I)$$

"High temp"

$$q_{rot,nucl}(T) = \underbrace{\frac{1}{2}\frac{T}{\Theta_r}}_{q_{rot}}\ \underbrace{(2I+1)^2}_{q_{nucl}}$$

$$q_{rot,nucl}(T) = I(2I+1)\frac{1}{2}T/\Theta_r + (I+1)(2I+1)\frac{1}{2}T/\Theta_r$$

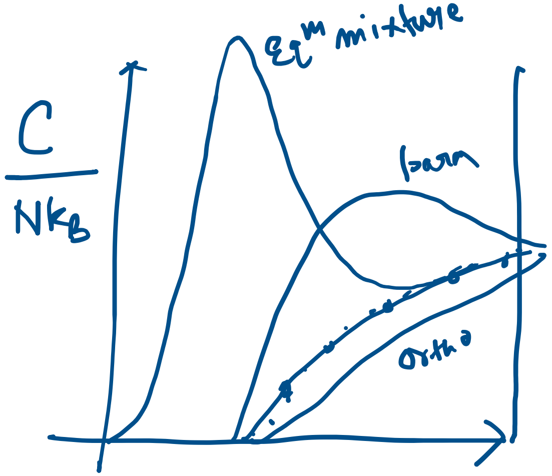
$$= \frac{1}{2}\frac{T}{\Theta_r}(2I+1)^2$$

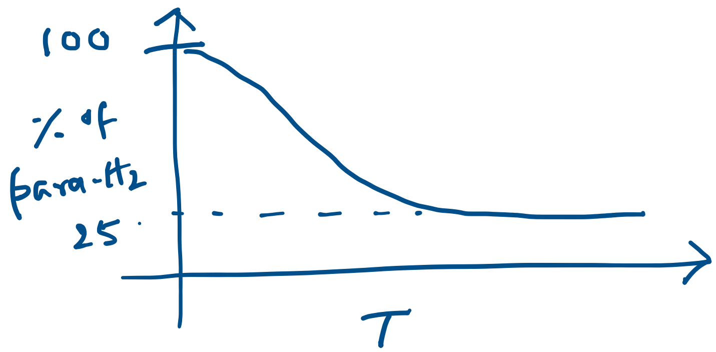
q_{rot} (Homonuclear diatomic) $= \frac{1}{2}\frac{T}{\Theta_r}$ → 2: Symmetry no.

H_2

$$q_{rot,nucl} = \underbrace{\sum_{J\,even} (2J+1) e^{-J(J+1)\theta_r/T}}_{para} + 3\underbrace{\sum_{J\,odd} (2J+1) e^{-J(J+1)\theta_r/T}}_{ortho}$$

$$\frac{N_{ortho}}{N_{para}} = \frac{3\sum_{J\,odd} \cdots\cdots}{1\sum_{J\,even} \cdots\cdots} \rightsquigarrow 3 \text{ as } T \text{ increases}$$





" SM
"Mc. Quarrie"

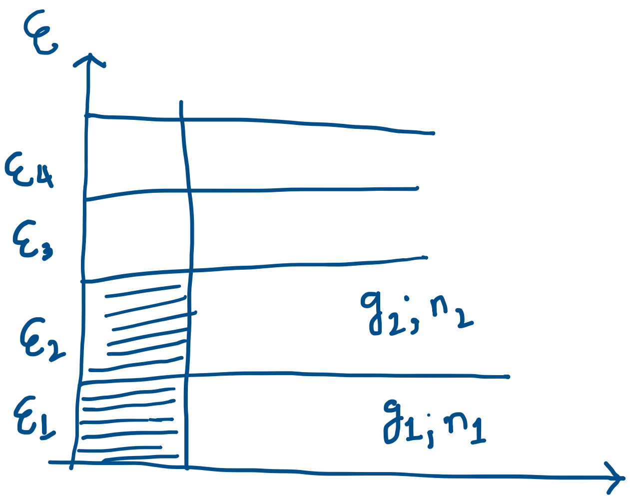
Quantum Statistics

N indistinguishable particles (Quantum)

"Fermions" "Bosons"

Microcanonical Ensemble (N, V, E)

"Single particle energy levels"



"grouping into cells"

n_1 particles in first cell

n_2 " " second cell

$g_i \to$ Degeneracy

$$\boxed{\sum_i n_i = N \; ; \; (\mathrm{i}) \qquad \sum_i n_i \varepsilon_i = E \; (\mathrm{ii})}$$

$$\Omega(N, V, E) = \sum_{\{n_i\}}' W\{n_i\}$$

$\downarrow$ No. of distinct microstates accessible to the system under the macrostate N, V, E

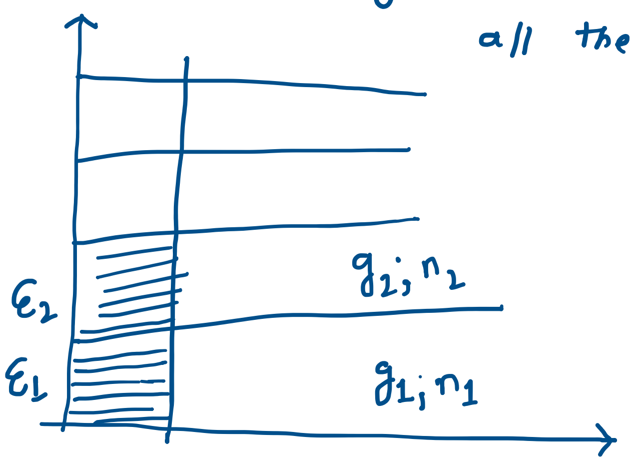
$W\{n_i\} \to$ No. of distinct microstates associated with the distribution set $\{n_i\}$

$' \to$ Due to constraints (i) & (ii)

$$W\{n_i\} = \prod_i \omega(i)$$

→ The product goes over all the cells in the spectrum

$\omega(i)$ is the no. of distinct microstates associated with ith cell of the spectrum (the cell contains n_i particles to be accommodated among g_i levels)



$\omega(i)$ is the number of distinct ways in which the n_i identical and indistinguishable particles can be distributed among the g_i levels of the cell.

Fermions (follow Fermi-Dirac distribution) $\quad n_i = 0$ or $1 \qquad g_i \geq n_i$ (Fermions)

$$\omega_{F.D}(i) = \frac{g_i!}{n_i!\,(g_i-n_i)!} \qquad W_{F.D} = \prod_i \frac{g_i!}{n_i!\,(g_i-n_i)!}$$

Bosons (follow Bose-Einstein Statistics):

$n_i = 0, 1, 2, 3, \ldots \ldots$

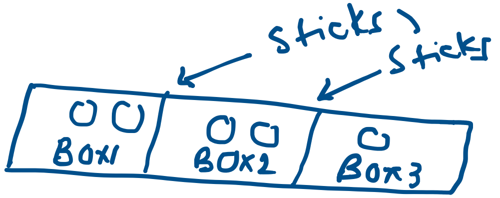
$n_i^{max} = \infty \quad (N \to \infty)$

B-E statistics will allow much more no. of configurations than that for F.D statistics while satisfying the same constraints.

$n_i = 5$

$g_i = 3$

$(g_i - 1)$ no. of sticks



ONE Possibility

(These balls are indistinguishable)

$\rightarrow$ Other possibilities $\rightarrow$ can be generated by moving sticks

$(\underbrace{n_i}_{\text{No. of particles}} + \underbrace{g_i - 1}_{\text{No. of Sticks}})$ no. of things to be arranged to generate configurations

$n_i = 5, \; g_i = 3$

$$\omega_{BE} = \frac{(5+3-1)!}{5!\,2!} = \underbrace{21}_{\text{Possibilities}}$$

$$\omega_{B.E}(i) = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$$

$n_i = 2, \; g_i = 3$

$$\omega_{BE} = \frac{4!}{2!\,2!} = 6 \; ; \; \omega_{FD} = \frac{3!}{2!\,1!} = 3$$

Classical particles:
(Distinguishable)

n_i particles may be put into any of the g_i levels, independently of one another and the resulting states may be counted as distincts

The no. of these states is clearly $(g_i)^{n_i}$

$$\frac{N!}{n_1!\, n_2! \cdots} \rightsquigarrow \text{weight factor } \frac{1}{n_1!\, n_2! \cdots} = \prod_i \frac{1}{n_i!}$$

$$W_{MB}\{n_i\} = \prod_i \frac{(g_i)^{n_i}}{n_i!}$$

Maxwell-Boltzmann

Entropy: $S = k_B \ln \Omega(N, V, E)$

$$= k_B \ln \left[\sum_{\{n_i\}}{}' W\{n_i\} \right] \simeq k_B \ln W(\{n_i^*\})$$

(Approximately equal to the logarithm of the longest term in the sum)

"Most probable".

$\{n_i^*\}$ is the distribution set that maximizes the no. $W\{n_i^*\}$

$n_i^* \rightarrow$ is the the Most probable n_i.

(Do not forget the constraints)

Employing Lagrange's method of undetermined multipliers

$$\delta \ln W\{n_i\} - \alpha \sum_i \delta n_i - \beta \sum_i \varepsilon_i \delta n_i = 0$$

$$\delta \ln W\{n_i\} = \sum_i \delta \ln w^{(i)}(n_i)$$

F. D Statistics

$$\omega_{F.D}(i) = \frac{g_i!}{n_i!\,(g_i-n_i)!}$$

$$\ln \omega_{F.D}(i) = \ln g_i! - \ln n_i! - \ln (g_i-n_i)!$$

$$= g_i \ln g_i - \cancel{g_i} - n_i \ln n_i + \cancel{n_i} - (g_i-n_i)\ln(g_i-n_i) + \cancel{g_i} - \cancel{n_i}$$

$$= -g_i \ln\left(\frac{g_i-n_i}{g_i}\right) + n_i \ln\left(\frac{g_i-n_i}{n_i}\right)$$

$$\ln \omega_{F.D}(i) = -g_i \ln\left(1-\frac{n_i}{g_i}\right) + n_i \ln\left(\frac{g_i}{n_i} - 1\right)$$

$$\omega_{B.E}(i) = \frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}$$

$$\ln \omega_{B.E}(i) = \ln (n_i+g_i-1)! - \ln n_i! - \ln (g_i-1)!$$

$$= (n_i+g_i-1)\ln(n_i+g_i-1) - n_i \ln n_i + \cancel{n_i} - (g_i-1)\ln(g_i-1) + \cancel{g_i} - \cancel{1} - (\cancel{n_i}+\cancel{g_i}-\cancel{1})$$

$$g_i - 1 \simeq g_i$$

$$\ln \omega_{B.E}(i) \simeq$$

$$= n_i \ln\left(\frac{n_i+g_i-1}{n_i}\right) + (g_i-1)\ln\left(\frac{n_i+g_i-1}{g_i-1}\right)$$

$$\ln \omega_{BE}(i) \simeq n_i \ln\left(1 + g_i/n_i\right) + g_i \ln\left(\frac{n_i}{g_i} + 1\right)$$

In general

$$\boxed{\ln \omega(i) = n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \ln\left(1 - a \cdot \frac{n_i}{g_i}\right)}$$

$$\boxed{\ln \omega_{F.D}(i) = -g_i \ln\left(1 - \frac{n_i}{g_i}\right) + n_i \ln\left(\frac{g_i}{n_i} - 1\right)}$$

$$\boxed{\ln \omega_{BE}(i) \simeq n_i \ln\left(1 + g_i/n_i\right) + g_i \ln\left(\frac{n_i}{g_i} + 1\right)}$$

$a = -1$ for B.E

$a = 1$ for F.D

$a = 0$ for MB

$$\omega_{MB}(i) = \frac{(g_i)^{n_i}}{n_i!}$$

$$\ln \omega_{MB}(i) = n_i \ln g_i - n_i \ln n_i + n_i$$

$$= n_i \left(\ln\left(g_i/n_i\right) + 1\right)$$

$$\ln_{x \to 0}(1 - x) \simeq -x$$

$$\ln_{a \to 0}\left(1 - a\frac{n_i}{g_i}\right) = -a\frac{n_i}{g_i}$$

$$\left(-\cancel{g_i}/\cancel{a}\right)\left(-\cancel{a}\frac{n_i}{\cancel{g_i}}\right) = n_i$$

$$\boxed{\ln w(i) = n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \ln\left(1 - a \cdot \frac{n_i}{g_i}\right)}$$

$\delta \ln w(i)$

$$\hookrightarrow = \left[1 \cdot \ln\left(\frac{g_i}{n_i} - a\right) + n_i \frac{1}{\left(\frac{g_i}{n_i} - a\right)} \times \left(\frac{-g_i}{n_i^2}\right) - \frac{g_i}{a} \frac{1}{\left(1 - a\, n_i/g_i\right)} \cdot \left(0 - a/g_i\right)\right] \delta n_i$$

$$= \left[\ln\left(\frac{g_i}{n_i} - a\right) - \cancel{\frac{g_i}{n_i}\left(\frac{1}{\frac{g_i}{n_i} - a}\right)} + \cancel{\frac{1}{1 - a\, n_i/g_i}}\right] \delta n_i$$

$$= \ln\left(\frac{g_i}{n_i} - a\right) \delta n_i$$

Once we put the constraints $\quad \ln W(\{n_i\}) = \sum_i \delta \ln w(i)(n_i)$

$$\sum_i \left\{\ln\left(\frac{g_i}{n_i} - a\right) - \alpha - \beta \varepsilon_i\right\} \delta n_i = 0 \longrightarrow$$

Should be true for any arbitrary δn_i

Each term in the sum = 0

$$\ln\left(\frac{g_i}{n_i^*} - a\right) - \alpha - \beta\varepsilon_i = 0$$

or, $\ln\left(\frac{g_i}{n_i^*} - a\right) = \alpha + \beta\varepsilon_i$

or, $g_i/n_i^* - a = e^{\alpha+\beta\varepsilon_i}$

or, $g_i/n_i^* = a + e^{\alpha+\beta\varepsilon_i}$

or, $\frac{n_i^*}{g_i} = \frac{1}{a + e^{\alpha+\beta\varepsilon_i}} \Rightarrow n_i^* = \frac{g_i}{(a + e^{\alpha+\beta\varepsilon_i})}$

$a = 1$ for FD

$$n_{i\,FD}^* = \frac{g_i}{1 + e^{\alpha+\beta\varepsilon_i}}$$

$a = -1$ for BE

$$n_{i\,BE}^* = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} - 1}$$

$a = 0$ for M.B

$$n_{i\,MB}^* = g_i\, e^{-\alpha-\beta\varepsilon_i}$$

$$n_i^* = \frac{g_i}{(a + e^{\alpha + \beta \varepsilon_i})}$$

F.D. $a = 1$

B.E $a = -1$

M.B $a = 0$

$$\boxed{\ln \omega(i) = n_i \ln\left(\frac{g_i}{n_i} - a\right) - \frac{g_i}{a} \ln\left(1 - a \cdot \frac{n_i}{g_i}\right)}$$

$$S/k_B = \ln \Omega$$

Entropy

$$= \ln \sum_{\{n_i\}} W(\{n_i\}) \simeq \ln W(n_i^*) = \sum_i \ln \omega(i)(n_i^*)$$

$$\left[\ln(x/y) = -\ln(y/x) \right]$$

$$\frac{S}{k_B} = \sum_i n_i^* \ln\left(\frac{g_i}{n_i^*} - a\right) - \frac{g_i}{a} \ln\left(1 - a \frac{n_i^*}{g_i}\right)$$

$$= \sum_i \left\{ n_i^* \ln\left(\cancel{a} + e^{\alpha + \beta \varepsilon_i} - \cancel{a}\right) - \frac{g_i}{a} \ln\left(1 - \frac{a}{a + e^{\alpha + \beta \varepsilon_i}}\right) \right\}$$

$$= \sum_i \left\{ n_i^* (\alpha + \beta \varepsilon_i) - \frac{g_i}{a} \ln\left(\frac{\cancel{a} + e^{\alpha + \beta \varepsilon_i} - \cancel{a}}{a + e^{\alpha + \beta \varepsilon_i}}\right) \right\} = \sum_i \left\{ n_i^* (\alpha + \beta \varepsilon_i) + g_i/a \ln\left(\frac{a + e^{\alpha + \beta \varepsilon_i}}{e^{\alpha + \beta \varepsilon_i}}\right) \right\}$$

$$\frac{S}{k_B} = \sum_i \left\{ n_i^*(\alpha + \beta \varepsilon_i) + \frac{g_i}{a} \ln\left(1 + a e^{-\alpha - \beta \varepsilon_i}\right) \right\}$$

$$\frac{S}{k_B} = \alpha N + \beta E + \sum_i \frac{g_i}{a} \ln\left(1 + a e^{-\alpha - \beta \varepsilon_i}\right)$$

$$\sum_i \frac{g_i}{a} \ln\left(1 + a e^{-\alpha - \beta \varepsilon_i}\right) = \frac{S}{k_B} - \alpha N - \beta E$$

$$\alpha = -\mu/k_B T \; ; \; \beta = \frac{1}{k_B T} \quad \text{(Done earlier)}$$

$$\frac{S}{k_B} + \frac{\mu N}{k_B T} - \frac{E}{k_B T} = \sum_i \frac{g_i}{a} \ln\left(1 + a e^{-\alpha - \beta \varepsilon_i}\right)$$

$$\underbrace{TS + \mu N - E} = \frac{k_B T}{a} \sum_i g_i \ln\left(1 + a e^{-\alpha - \beta \varepsilon_i}\right)$$

$$\Rightarrow \quad PV = \frac{k_B T}{a} \sum_i g_i \ln\left(1 + a e^{-\alpha - \beta \varepsilon_i}\right)$$

Equation of State for a quantum ideal gas

$$\sum_i n_i^* = N$$

$$\alpha \sum_i n_i^* = \sum_i \alpha n_i^* = \alpha N$$

$$\beta \sum_i n_i^* \varepsilon_i = \beta E$$

$$\mu N = G \quad \text{(Gibbs Free energy)}$$
$$= E + PV - TS$$

$$PV = \frac{k_B T}{a} \sum_i g_i \ln(1 + \underbrace{a e^{-\alpha - \beta\varepsilon_i}}_{\text{"small"}})$$

In the Maxwell-Boltzmann Case

$a \to 0$

$$\lim_{x \to 0} \ln(1+x) = x$$

$$\simeq \frac{k_B T}{a} \sum_i g_i \, a e^{-\alpha - \beta\varepsilon_i}$$

$$= k_B T \sum_i \underbrace{g_i e^{-\alpha - \beta \varepsilon_i}}_{n_i^*(MB)} = k_B T \sum_i n_i^* = N k_B T$$

$$PV = N k_B T$$

"CLASSICAL" ideal gas law "MB"

Ideal Bose Gas (non-interacting collection of Bosons)

$a = -1$

$$\frac{PV}{k_B T} = -\sum_i g_i \ln(1 - e^{-\alpha - \beta\varepsilon_i})$$

$$e^{-\alpha} = e^{\mu/k_B T} = z$$

z ↓ fugacity

$$\frac{PV}{k_B T} = -\sum_i g_i \ln(1 - z e^{-\beta\varepsilon_i})$$

⇝ Sum is over energy levels

Replacing the sum over energy levels with the sum over states and replacing the sum with an integral giving a statistical weight to each state

[Either high temp or large volume]

$$\frac{PV}{k_BT} = -\sum_i g_i \ln(1 - e^{-\alpha - \beta\varepsilon_i})$$

$$= -\sum_i g_i \ln(1 - z e^{-\beta\varepsilon_i})$$

$g(\varepsilon).d\varepsilon \rightarrow$ No. of states betn ε and $\varepsilon + d\varepsilon$

$$\frac{PV}{k_BT} = -\int d\varepsilon \, \underbrace{g(\varepsilon)}_{\text{Density of states}} \ln(1 - z e^{-\beta\varepsilon})$$

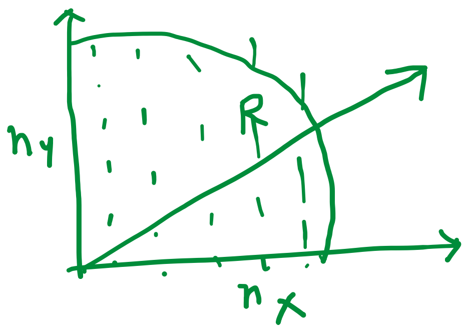
$$N = \sum_i \langle n_i \rangle = \sum_i \frac{g_i}{(e^{\alpha + \beta\varepsilon_i} - 1)} = \sum_i \frac{g_i}{(z^{-1} e^{\beta\varepsilon_i} - 1)}$$

$$N = \int \frac{d\varepsilon \, g(\varepsilon)}{(z^{-1} e^{\beta\varepsilon} - 1)}$$

How to calculate the density of states?

3D Box Particle in

$$E = \varepsilon = \frac{(n_x^2+n_y^2+n_z^2)}{8mL^2}h^2$$



Calculate the no. of lattice points

$$R^2 = \frac{8mL^2\varepsilon}{h^2} = n_x^2+n_y^2+n_z^2$$

$n_x, n_y, n_z \rightarrow$ Cannot be negative

$\phi(\varepsilon)$ No. of states with energy

$$= \frac{1}{8}\left(\frac{4}{3}\pi R^3\right) = \frac{1}{8}\,\frac{4}{3}\,\pi\left(\frac{8mL^2\varepsilon}{h^2}\right)^{3/2} = \frac{\pi}{6}\left(\frac{8mL^2\varepsilon}{h^2}\right)^{3/2}$$

only one octant

$$\phi'(\varepsilon) = \frac{d\phi}{d\varepsilon}$$

$$\phi(\varepsilon+\Delta\varepsilon) =$$

$\Delta\varepsilon/\varepsilon \ll 1$

$V = L^3$

$$\omega(\varepsilon,\Delta\varepsilon) = \phi(\varepsilon+\Delta\varepsilon) - \phi(\varepsilon)$$

$$\simeq \phi(\varepsilon) + \phi'(\varepsilon)\Delta\varepsilon - \phi(\varepsilon) = \phi'(\varepsilon)\Delta\varepsilon$$

$$= \frac{\pi}{6}\left(\frac{8mL^2}{h^2}\right)^{3/2}\frac{3}{2}\varepsilon^{3/2-1}\Delta\varepsilon = \frac{\pi}{4}\left(\frac{8m}{h^2}\right)^{3/2}\underbrace{L^3}_{=V}\varepsilon^{1/2}\Delta\varepsilon$$

$$\frac{PV}{k_BT} = -\int \ln(1 - z e^{-\beta \varepsilon})$$

$$g(\varepsilon)\,d\varepsilon = \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\,\varepsilon^{1/2}\,d\varepsilon \quad \text{(Please check)}$$

$$\langle n_k \rangle_{BE} = \frac{z e^{-\beta \varepsilon_k}}{(1 - z e^{-\beta \varepsilon_k})} \quad \text{Bosons}$$

$$\langle n_k \rangle_{FD} = \frac{z e^{-\beta \varepsilon_k}}{1 + z e^{-\beta \varepsilon_k}} \quad \text{Fermions}$$

What happens if T is high or density is low ($\rho = N/V$). $\Rightarrow$ No. of available energy states >> No. of particles $\rightarrow$ "CLASSICAL"

$\langle n_k \rangle_{FD/BE} \simeq 0 \;\rightsquigarrow\; z \to 0$

(Weakly degenerate case)

$$\langle n_k \rangle = z e^{-\beta \varepsilon_k}$$

$$\sum_k \langle n_k \rangle = z \sum_k e^{-\beta \varepsilon_k} = zq = N$$

$\hookrightarrow z = N/q$

$$\langle n_k \rangle = z e^{-\beta \varepsilon_k}$$

$$\langle n_k \rangle = \frac{N}{q} e^{-\beta \varepsilon_k}$$

$$z = e^{\mu / k_BT}$$

$z \to 0$ (Classical)

$z \gg 0$ (Quantum)

$$\boxed{\frac{\langle n_k \rangle}{N} = \frac{e^{-\beta \varepsilon_k}}{q}} \rightarrow \text{M.B}$$

Equation of State for the Bose gas (ideal Bose)

$$\frac{PV}{k_BT} = -\left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\int_0^\infty d\varepsilon\, \ln\left(1-ze^{-\beta\varepsilon}\right)\varepsilon^{1/2}$$

ONE Problem

The state $\varepsilon=0$ has been given zero weight when we replace the sum with the integral
we should take this state out and then replace the sum with the integral

New state of matter

As $T\downarrow$, the $\varepsilon=0$ level gets densely populated.

$$\frac{P}{k_BT} = -\left(\frac{2\pi}{h^3}\right)(2m)^{3/2}\int_0^\infty d\varepsilon\, \ln\left(1-ze^{-\beta\varepsilon}\right)\varepsilon^{1/2} - \frac{\ln(1-z)}{V}$$

BEC

$\boxed{\text{Bose-Einstein Condensation}}$

$z \ll 1$ (classical)

Similarly

$$\frac{N}{V} = \left(\frac{2\pi}{h^3}\right)(2m)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{\left(z^{-1}e^{\beta\varepsilon}-1\right)} + \underbrace{\frac{1}{V}\frac{1}{\left(z^{-1}-1\right)}}$$

$$\frac{1}{V}\left(\frac{z}{1-z}\right)$$

$$\frac{1}{V}\left(\frac{z}{1-z}\right) \sim \frac{1}{N}z$$

~ vanishing (small)

$$N = N_e + N_0$$

No. of particles in the ground state

$$N_0 = \frac{z}{1-z}$$

$$N_e = \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\int \cdots\cdots$$

$z \gg 0$ ~ approaching 1

T is small, $T\to 0$ ← $z\to 1$ $\quad \frac{1}{V}\left(\frac{z}{1-z}\right)$ will blow up!!

$$\frac{P}{k_BT} = -\left(\frac{2\pi}{h^3}\right)\frac{(2m)^{3/2}}{\beta^{3/2}}\int_0^\infty dx\, x^{1/2}\ln(1-ze^{-x})$$

$$\boxed{\frac{P}{k_BT} = \frac{1}{\lambda^3} g_{5/2}(z)} + \cdots$$

$$\frac{z}{1-z} = N_0 \Rightarrow \ln(1-z)\frac{1}{V}$$

$$z = \frac{N_0}{N_0+1} \qquad -\ln(1-z)\frac{1}{V}$$

$$= \ln\frac{1}{N_1+1}$$

$$= \frac{1}{V}\ln(N_0+1)$$

$$\sim \frac{1}{N}\ln N$$

~ 0 (thermodynamic limit)

$$\beta\varepsilon = \frac{p^2}{2mk_BT} = x$$

$$\beta\, d\varepsilon = dx$$

$$d\varepsilon = \frac{1}{\beta}dx$$

$$\varepsilon^{1/2} = \frac{x^{1/2}}{\beta^{1/2}}$$

$$\frac{N_e}{V} = \frac{N-N_0}{V} = \left(\frac{2\pi}{h^3}\right)(2m)^{3/2}\frac{1}{\beta^{3/2}}\int_0^\infty \frac{x^{1/2}dx}{(z^{-1}e^{x}-1)}$$

$$\boxed{\frac{N_e}{V} = \frac{1}{\lambda^3} g_{3/2}(z)}$$

$$\lambda = \frac{h}{(2\pi m k_BT)^{1/2}}$$

$g_\nu(z) \rightarrow$ Bose-Einstein functions

$$g_\nu(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty \frac{x^{\nu-1}dx}{(z^{-1}e^{x}-1)} = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \cdots$$

Upper bound of $(\nu = 3/2)$

$g_{3/2}(z)$

$$g_{3/2}(1) = \zeta(3/2)$$

$$= 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \cdots$$

$$\zeta(3/2) \simeq 2.62$$

$$N_e = \frac{V}{\lambda^3} g_{3/2}(z)$$

if fugacity is 1 (quantum)

$$N_e = \frac{V}{\lambda^3} \zeta(3/2)$$

$$N_e < \underbrace{\frac{V}{\lambda^3} \zeta(3/2)}_{\text{No. of particles in the excited states at } z=1 \ (T=0)}$$

$T > 0$

$$N_e = \frac{V}{\lambda^3} g_{3/2}(z)$$

if fugacity is 1 (quantum)

$$N_e = \frac{V}{\lambda^3} \zeta(3/2)$$

$$N_e \leq \underbrace{\frac{V}{\lambda^3} \zeta(3/2)}_{\text{No. of particles in the excited states at } z=1\ (T=0)}$$

$T > 0$

$$g_\nu(z) = 1 + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \cdots$$

$z = 1$ (Quantum)

$z = 0$ (Classical)

$$g_{3/2}(z) = 1 + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots$$

$z = 1$

$$g_{3/2}(1) \equiv \zeta(3/2) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \cdots > g_{3/2}(z)$$

$$g_{3/2}(z) \leq \zeta(3/2)$$

"upper bound"

$$N_e = \frac{V}{\lambda^3} g_{3/2}(z) = V \frac{(2\pi m k_B T)^{3/2}}{h^3} g_{3/2}(z) \leq \frac{V}{\lambda^3} \zeta(3/2)$$

No. of particles in the excited state ($\epsilon \neq 0, > 0$)

Any z

$z = 1$

No. of particles occupying the ground state ($\varepsilon = 0$)

$$N_0 = N - V \frac{(2\pi m k_B T)^{3/2}}{h^3} \zeta(3/2)$$

<u>Condition for the onset of BEC</u>

$$N > V \frac{(2\pi m k_B T)^{3/2}}{h^3} \zeta(3/2)$$

Total no. of particles exceeds the "upper bound" of the excited state

In terms of temperature??

"CRITICAL TEMPERATURE"

for a given N and V

$\varepsilon \to p$ $\quad$ $p^2/2m \sim \varepsilon$

What is special about BEC?

"Phase Transition"

* No intermolecular interaction!!
  (Purely quantum mechanical in origin)

* This is happening in momentum space
  (Not in co-ordinate state)

$$N = V \frac{(2\pi m k_B)^{3/2}}{h^3} \zeta(3/2) T_c^{3/2}$$

$$\Rightarrow \quad T_c = \left(\frac{h^2}{2\pi m k_B}\right)\left(\frac{N}{V} \frac{1}{\zeta(3/2)}\right)^{2/3}$$

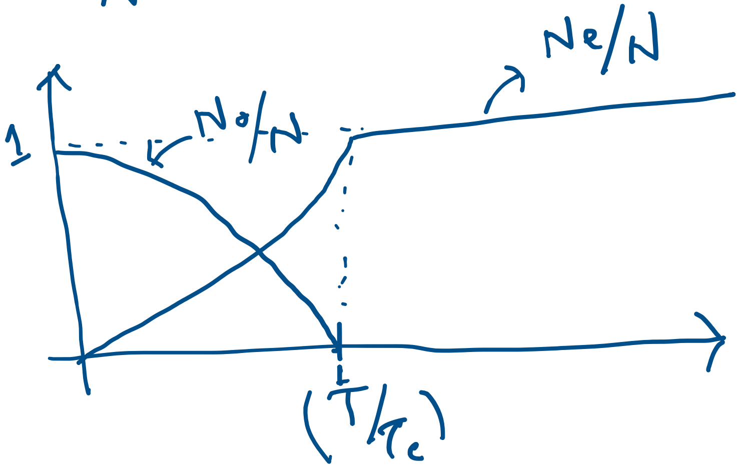
Below this C.T (T_c) → Two phases exist

(i) N_e particles in the excited state (ii) $N - N_e$ in the ground state

Complementary fractions

$$\frac{N_0}{N} = 1 - \left(\frac{V}{N}\right) \frac{(2\pi m k_B T)^{3/2}}{h^3} \zeta(3/2)$$

$$\frac{N_0}{N} = 1 - \left(T/T_c\right)^{3/2}$$



$$T_c = \frac{h^2}{2\pi m k_B} \left(\frac{N}{V} \frac{1}{\zeta(3/2)}\right)^{2/3}$$

$$T_c^{3/2} = \left(\frac{h^2}{2\pi m k_B}\right)^{3/2} \left(\frac{N}{V}\right) \frac{1}{\zeta(3/2)}$$

[R.K. Pathria Statistical Mechanics]

Biman Bagchi
SM for Chemists
. . . . .

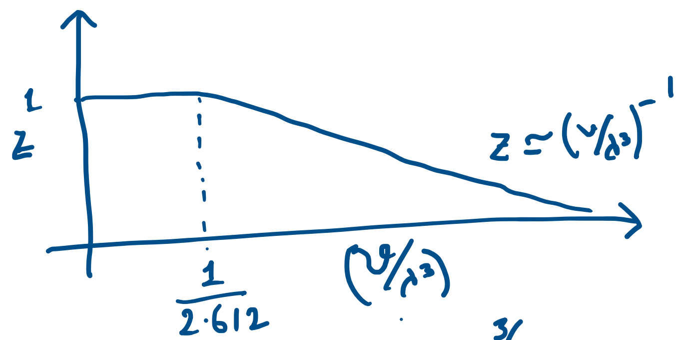
$$\frac{PV}{Nk_BT} = \sum_{l=1}^{\infty} a_l \left(\lambda^3/v\right)^{l-1}$$

"Virial Coefficients"

$v \equiv \frac{1}{n}$ → "vol^m/particle"

$z \rightsquigarrow$ can be expanded in powers of $n\lambda^3$

$\zeta(3/2) = 2.612$



$\rightsquigarrow T^{3/2}$

$$\frac{P}{k_B T} = \frac{1}{\lambda^3} g_{5/2}(z)$$

for unit fugacity

at the critical temperature? T_c

$$P(T) = \frac{k_B T}{\lambda^3} \zeta(5/2)$$

$$P(T_c) = k_B T_c \, \zeta(5/2) \left(\frac{2\pi m k_B T_c}{h^3}\right)^{3/2}$$

$$= k_B T_c \, \zeta(5/2) \frac{(2\pi m k_B)^{3/2}}{\cancel{h^3}} \cdot \cancel{\left(\frac{h^2}{2\pi m k_B}\right)^{3/2}} \left(\frac{N}{V} \frac{1}{\zeta(3/2)}\right)^{1}$$

$$P(T_c) = k_B T_c \left(\frac{N}{V}\right) \frac{\zeta(5/2)}{\zeta(3/2)}$$

$$P_{(T_c)} = k_B T_c \left(\frac{N}{V}\right) 0.5134$$

$$\approx \frac{1}{2} k_B T_c (N/V)$$

$$P = k_B T (N/V)$$

ideal gas
classical

Ideal Boson gas at $T = T_c$
exerts pressure $\frac{1}{2}$ of
that of a classical (Boltzmannian) ideal gas

Internal Energy:

$$\frac{PV}{k_B T} = \ln \Xi \leftarrow \text{grand canonical partition function}$$

$$E = k_B T^2 \frac{\partial}{\partial T}\left(\left(\frac{PV}{k_B T}\right)\right)_{z,V}$$

$$= k_B T^2 V g_{5/2}(z) \left[\frac{\partial}{\partial T}\left(\frac{1}{\lambda^3}\right)\right]$$

$$= k_B T^{\cancel{2}} V g_{5/2}(z) \frac{3}{2\cancel{T}} \frac{1}{\lambda^3}$$

$$E = \frac{3}{2} k_B T V g_{5/2}(z) \frac{1}{\lambda^3}$$

$$P = \frac{k_B T}{\lambda^3} g_{5/2}(z)$$

$$\boxed{E = \frac{3}{2} PV} \longrightarrow \text{familiar}$$

→ It satisfies the relationship for the ideal gas !!

$$\frac{PV}{k_B T} = \frac{V}{\lambda^3} g_{5/2}(z)$$

$$\frac{\partial}{\partial T}\left[\frac{(2\pi m k_B T)^{3/2}}{h^3}\right]$$

$$= \frac{(2\pi m k_B)^{3/2}}{h^3} \frac{3}{2} T^{1/2}$$

$$= \frac{(2\pi m k_B T)^{3/2}}{h^3} \frac{3}{2} \frac{T^{1/2}}{T^{3/2}}$$

$$= \frac{1}{\lambda^3} \frac{3}{2} \frac{1}{T}$$

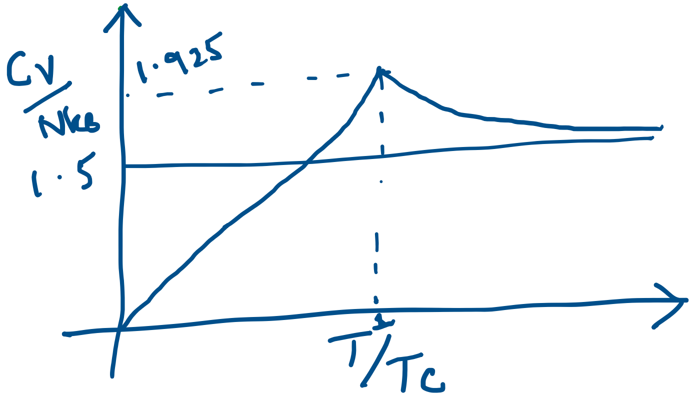
$E = \frac{3}{2} PV$ (ideal gas)

$$PV = N k_B T$$

$$E = 3/2 \, N k_B$$

Specific Heat of an ideal Bose gas :

For unit fugacity ($T \sim T_c$)



$$\frac{C_V}{Nk_B} = \frac{1}{Nk_B}\left(\frac{\partial E}{\partial T}\right)_{V,z}$$

$$= \frac{1}{N\cancel{k_B}}\,\frac{3}{2}\cancel{k_B}\,V\,\zeta(5/2)\left\{\frac{d}{dT}\left(\frac{T}{\lambda^3}\right)\right\}$$

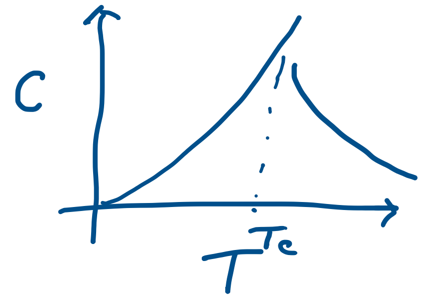
$$\frac{T}{\lambda^3} = \frac{(2\pi m k_B)^{3/2}}{h^3}T^{5/2}$$

$$= \frac{3V}{2N}\zeta(5/2)\frac{(2\pi m k_B)^{3/2}}{h^3}\,\frac{5}{2}T^{5/2-1}$$

$$= \frac{15}{4}\frac{V}{N}\zeta(5/2)\frac{(2\pi m k_B)^{3/2}}{h^3}T^{3/2}$$

He-I and He-II

He-4 (Boson).



$$\frac{C_V(T=T_c)}{Nk_B} = \frac{15}{4}\frac{\cancel{V}}{\cancel{N}}\zeta(5/2)\frac{\cancel{(2\pi m k_B)^{3/2}}}{\cancel{h^3}}\frac{\cancel{h^3}}{\cancel{(2\pi m k_B)^{3/2}}}\left(\frac{\cancel{N}}{\cancel{V}}\frac{1}{\zeta(3/2)}\right)^1 = \frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)} \simeq 1.925$$

$T \gg T_c$ (High temperature limit) $\Rightarrow \dfrac{C_V}{Nk_B} = \dfrac{3}{2}$

Fermi (ideal) gas

$$\langle n_k \rangle = \frac{1}{1+e^{\alpha+\beta\varepsilon_k}} = \frac{1}{1+e^{\beta(\varepsilon_k-\mu)}}$$

$\langle n_k \rangle$

β is positive

$(\varepsilon_k-\mu)$ is real

$e^{\beta(\varepsilon_k-\mu)}$ is always ≥ 0

$\langle n_k \rangle$ will vary bet^n 0 and 1

(Pauli-Exclusion principle)

Let us define a f^n (Fermi function)

$$F(\varepsilon) = \frac{1}{1+e^{\beta(\varepsilon-\mu)}} = \frac{1}{1+e^{\beta\varepsilon}e^{-\beta\mu}}$$

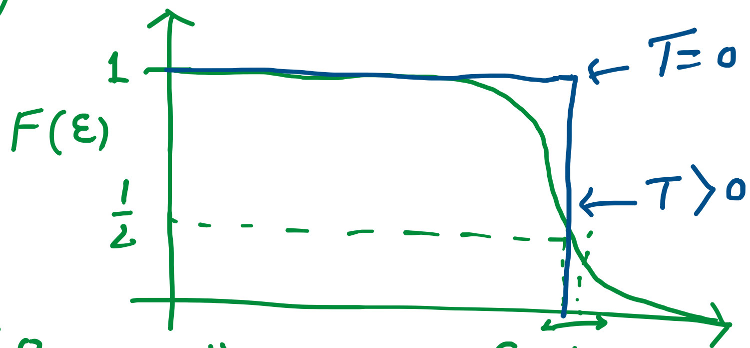
$\beta\mu \ll 0$ (condition)

$e^{\beta(\varepsilon-\mu)} \gg 1$

$\sim e^{-\beta(\varepsilon-\mu)}$

(Boltzmann)

$\{\mu \to -ve\}$



"at finite temperature"

Let us consider

i) $\beta\mu \gg 1$

ii) $\varepsilon \ll \mu$; $\beta(\varepsilon-\mu) \ll 0$

$F(\varepsilon) \sim 1$

$\varepsilon = \mu \qquad F(\varepsilon) = \frac{1}{1+1} = \frac{1}{2}$.

"Fermi Energy" (chemical pot).

DEPARTMENT OF CHEMISTRY

Indian Institute of Technology Bombay

Statistical Mechanics (Code: CH 576)

Assignment 1
Due date: February 12, 2021

1. The ensemble average of a function $B(p, q)$ is given by

$$\langle B \rangle = \int d\Gamma\, \rho(p, q, t)\, B(p, q)$$

Show

$$\frac{d}{dt}\langle B \rangle = \langle \{B, H\} \rangle,$$

where p and q represent momenta and position in $6N$ dimensional phase space, integration is over the phase space co-ordinates (momenta and positions) and H is the Hamiltonian of the classical system.

Answer: $d\Gamma = \prod_{i=1}^{N} d^3q_i d^3p_i$.

The ensemble average of a function $B(p, q)$ can be expressed as

$$\langle B \rangle = \int d\Gamma\, \rho(p, q, t)\, B(p, q).$$

Therefore,

$$\frac{d}{dt}\langle B \rangle = \int d\Gamma\, B(p, q)\, \frac{\partial}{\partial t}\rho(p, q, t), \tag{1}$$

as $\frac{\partial}{\partial t}B(p, q) = 0$. Using the Liouville equation,

$$\frac{\partial}{\partial t}\rho(p, q, t) + \{\rho, H\} = 0,$$

where

$$\{, H\} = \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i} \right),$$

one can explicitly write Eq. (1) as

$$\frac{d}{dt}\langle B \rangle = -\int d\Gamma\, B(p, q) \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} \right). \tag{2}$$

Doing the integration by parts in Eq. (2) and then taking boundary terms as zero, one can arrive at

$$\begin{aligned} \frac{d}{dt}\langle B \rangle &= \int d\Gamma\, \rho(p, q) \sum_{i=1}^{3N} \left(\frac{\partial H}{\partial p_i}\frac{\partial B}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial B}{\partial p_i} \right) + \cancelto{0}{\int d\Gamma\, \rho(p, q) \sum_{i=1}^{3N} B \left(\frac{\partial}{\partial p_i}\frac{\partial H}{\partial q_i} - \frac{\partial}{\partial q_i}\frac{\partial H}{\partial p_i} \right)} \\ &= \langle \{B, H\} \rangle. \end{aligned} \tag{3}$$

Please go on to the next page. . .

2. For a classical "N" particle system, let other than the Hamiltonian the angular momentum (l_n) is also conserved. Then show mathematically that $\frac{dl_n}{dt} = 0$.

   Answer: As both the Hamiltonian (H) and the angular momentum (l_n) are conserved, $\{H, l_n\} = 0$. We know, $l_n = l_n(\{p_i\}, \{q_i\})$. Therefore,

$$\frac{dl_n}{dt} = \sum_{i=1}^{3N} \left(\frac{\partial l_n}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial l_n}{\partial p_i} \frac{dp_i}{dt} \right)$$

   Using relations, $\frac{dq_i}{dt} = \dot{q}_i = \frac{\partial H}{\partial p_i}$ and $\frac{dp_i}{dt} = \dot{p}_i = -\frac{\partial H}{\partial q_i}$, one can rewrite the above equation as

$$\frac{dl_n}{dt} = \sum_{i=1}^{3N} \left(\frac{\partial l_n}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial l_n}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = \{l_n, H\} = 0. \tag{4}$$

3. For a single particle subjected to a potential $V(q)$, write down the action, $A[q(t)]$, where $A[q(t)] = \int_{t_a}^{t_b} dt\, L(q, \dot{q}))$, and $L(q, \dot{q})$ is the Lagrangian of the system. Show that the extremization of this action results the Newton's equation of motion.

   Answer: The action is given by

$$A[q(t)] = \int_{t_a}^{t_b} dt\, L(q, \dot{q})).$$

   The extremization of action, *i.e.*, $\delta A = 0$ leads to the Euler–Lagrange equation,

$$\frac{\partial L}{\partial q} - \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) = 0. \tag{5}$$

   For a single particle of mass m subjected to a potential $V(q)$, the action is given by

$$L(q, \dot{q}) = \frac{m}{2}\dot{q}^2 - V(q).$$

   So using Eq. (5), one gets

$$m\ddot{q} = -V'(q),$$

   which is the Newton's equation of motion.

4. For a free particle, the Lagrangian, $L = \frac{m}{2}\dot{q}^2$. Show that the action A_q corresponding to the classical motion of a free particle is

$$A_q = \frac{m}{2}\frac{(q_b - q_a)^2}{(t_b - t_a)},$$

   where end points are q_a and q_b at time t_a and t_b, respectively.

   Answer: For a free particle, the Lagrangian is $L = \frac{m}{2}\dot{q}^2$. So the action is given by $A[q(t)] = \frac{m}{2}\int_{t_a}^{t_b} dt\, \dot{q}^2$. Using the Euler–Lagrange equation given in Eq. (5), one finds $m\ddot{q}_{cl} = 0$, which is the equation for classical motion followed by the particle. From this, we have $\dot{q}_{cl} = constant = (q_b - q_a)/(t_b - t_a)$. Putting the value of $\dot{q}_{cl}$ in the expression of action, one gets

$$A_q = A[q(t)]_{q(t)=q_{cl}} = \frac{m}{2}\frac{(q_b - q_a)^2}{(t_b - t_a)}.$$

5. For a harmonic oscillator, the Lagrangian, $L = \frac{m}{2}(\dot{q}^2 - \omega^2 q^2)$. Show that the classical action is

$$A_q = \frac{m\,\omega}{2\,sin\omega T}\left[(q_b^2 + q_a^2)\,cos\omega T - 2q_a q_b\right],$$

where $T = t_b - t_a$.

Answer: The Lagrangian for a harmonic oscillator is given by $L = \frac{m}{2}(\dot{q}^2 - \omega^2 q^2)$. So by virtue of Eq. (5), one can find the equation of motion for the classical trajectory, which is given as

$$\ddot{q}_{cl} + \omega^2 q_{cl} = 0.$$

The general solution of the above equation is: $q_{cl}(t) = c_1 \mathrm{sin}\omega t + c_2 \mathrm{cos}\omega t$. The boundary conditions are: $q_{cl}(t)|_{t=t_b} = q_b$ and $q_{cl}(t)|_{t=t_a} = q_a$. Using them, one can get the following matrix equation for c_1, c_2:

$$\begin{bmatrix}\mathrm{sin}\omega t_b & \mathrm{cos}\omega t_b\\ \mathrm{sin}\omega t_a & \mathrm{cos}\omega t_a\end{bmatrix}\begin{bmatrix}c_1\\ c_2\end{bmatrix} = \begin{bmatrix}q_b\\ q_a\end{bmatrix} \implies \begin{bmatrix}c_1\\ c_2\end{bmatrix} = \begin{bmatrix}\mathrm{sin}\omega t_b & \mathrm{cos}\omega t_b\\ \mathrm{sin}\omega t_a & \mathrm{cos}\omega t_b\end{bmatrix}^{-1}\begin{bmatrix}q_b\\ q_a\end{bmatrix}. \tag{6}$$

Doing the matrix calculation, one obtains, $c_1 = -q_a\frac{\mathrm{cos}\omega t_b}{\mathrm{sin}\omega T} + q_b\frac{\mathrm{cos}\omega t_a}{\mathrm{sin}\omega T}$ and $c_2 = q_a\frac{\mathrm{sin}\omega t_b}{\mathrm{sin}\omega T} - q_b\frac{\mathrm{sin}\omega t_a}{\mathrm{sin}\omega T}$, where $T = t_b - t_a$. Therefore the classical action can be calculated as

$$A_q = \frac{m}{2}\int_{t_a}^{t_b} dt\,\left(\dot{q}_{cl}^2 - \omega^2 q_{cl}^2\right) = \frac{m\,\omega}{2\,\mathrm{sin}\omega T}\left[(q_b^2 + q_a^2)\,\mathrm{cos}\omega T - 2q_a q_b\right]$$

Detailed mathematical Steps:

$$\begin{aligned}\frac{m}{2}\int_{t_a}^{t_b} dt\dot{q}_{cl}^2 &= \frac{m}{2}[q(t)_{cl}\dot{q}_{cl}(t)]_{t=t_a}^{t=t_b} - \frac{m}{2}\int_{t_a}^{t_b} dt q_{cl}(t)\ddot{q}_{cl}(t)\\ &= \frac{m}{2}[q_{cl}(t)\dot{q}_{cl}(t)]_{t=t_a}^{t=t_b} - \frac{m\omega^2}{2}\int_{t_a}^{t_b} dt q_{cl}(t) q_{cl}(t)\end{aligned} \tag{7}$$

Therefore,

$$\begin{aligned}&\frac{m}{2}\int_{t_a}^{t_b} dt\,\left(\dot{q}_{cl}^2 - \omega^2 q_{cl}^2\right)\\ &= \frac{m}{2}[q_{cl}(t)\dot{q}_{cl}(t)]_{t=t_a}^{t=t_b}\\ &= \frac{m}{2}\left[q_b(c_1\omega\,\mathrm{cos}\omega t_b - c_2\omega\,\mathrm{sin}\omega t_b) - q_a(c_1\omega\,\mathrm{cos}\omega t_a - c_2\omega\,\mathrm{sin}\omega t_a)\right]\\ &= \frac{m\,\omega}{2}\left[q_b^2\left(\frac{\mathrm{cos}\omega t_b \mathrm{cos}\omega t_a}{\mathrm{sin}\omega T} + \frac{\mathrm{sin}\omega t_b \mathrm{sin}\omega t_a}{\mathrm{sin}\omega T}\right) + q_a^2\left(\frac{\mathrm{cos}\omega t_b \mathrm{cos}\omega t_a}{\mathrm{sin}\omega T} + \frac{\mathrm{sin}\omega t_b \mathrm{sin}\omega t_a}{\mathrm{sin}\omega T}\right)\right]\\ &\qquad - \frac{m\,\omega}{2}\frac{q_b q_a}{\mathrm{sin}\omega T}\left[\mathrm{cos}^2\omega t_b + \mathrm{sin}^2\omega t_b + \mathrm{cos}^2\omega t_a + \mathrm{sin}^2\omega t_a\right]\\ &= \frac{m\,\omega}{2\,\mathrm{sin}\omega T}\left[(q_b^2 + q_a^2)\,\mathrm{cos}\omega T - 2q_a q_b\right]\end{aligned} \tag{8}$$

6. The energy levels of a rigid rotor of moment of inertia I are given by

$$E_j = \frac{\hbar^2}{2I} j(j+1),$$

where $j = 0, 1, 2, \cdots$;

(i) Using the Boltzmann statistics (with proper degeneracy factor), find an expression for the thermodynamic internal energy of the system.

(ii) Under what conditions can the sum in the part (i) be *approximated* by an integral? In this case evaluate the specific heat C_v of the system.

Answer: For a rigid rotor, the energy of $j-$th state is

$$E_j = \frac{\hbar^2}{2I} j(j+1),$$

with degeneracy $2j+1$, where $j = 0, 1, 2, \cdots$. Therefore the partition function is given by

$$q(T) = \sum_{j=0}^{\infty} (2j+1)\, e^{-\frac{\beta\hbar^2}{2I} j(j+1)}, \tag{9}$$

where $\beta = 1/k_B T$.

The internal energy can be expressed in terms of partition function as $\bar{E} = k_B T^2 \left(\frac{\partial \ln q(T)}{\partial T}\right)$. So using Eq. (9), one has

$$\begin{aligned}
\bar{E} =& k_B T^2 \left(\frac{\partial \ln q(T)}{\partial T}\right) = k_B T^2 \sum_{j=0}^{\infty} \frac{(2j+1)}{q(T)} \frac{\hbar^2}{2k_B T^2 I} j(j+1)\, e^{-\frac{\hbar^2}{2k_B T I} j(j+1)} \\
=& \sum_{j=0}^{\infty} E_j \frac{1}{q(T)} (2j+1) e^{-\frac{\hbar^2}{2k_B T I} j(j+1)}.
\end{aligned} \tag{10}$$

For heavy molecules or at high temperature, *i.e.*, if $k_B T \gg B$, where $B = \frac{\hbar^2}{2I}$, then the sum can be replaced by an integral, and the partition function takes the following form:

$$\begin{aligned}
\lim_{k_B T/B \gg 1} q(T) &\approx \int_0^{\infty} dj\, (2j+1) e^{-\beta B j(j+1)} \\
&= -\frac{1}{\beta B} \int_0^{\infty} d\left(e^{-\beta B j(j+1)}\right) = k_B T/B.
\end{aligned} \tag{11}$$

So, $\bar{E} = k_B T^2 \left(\frac{\partial \ln q(T)}{\partial T}\right) = k_B T$, and molar average internal energy is $\bar{E}_{molar} = N_A k_B T = RT$. Therefore, $C_v = \frac{\partial \bar{E}}{\partial T} = R$.

7. The partition function of a crystal can be approximated by

$$Q = \left(\frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/2k_BT}}\right)^{3N} e^{\frac{U_0}{k_BT}},$$

where $h\nu/k_B = \Theta_E$ is a constant characteristic of the crystal, and U_0 is the sublimation energy of the crystal. Calculate the heat capacity from this simple partition function and show that at high temperatures, one obtains the law of Dulong and Petit, namely $C_v = 3Nk_B$ as $T \to \infty$. There is a typo in the question.

Answer: The partition function of a crystal can be approximated by

$$Q = \left(\frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}}\right)^{3N} e^{\frac{U_0}{k_BT}}.$$

Taking $h\nu/k_B = \Theta_E$, the above can be rewritten as

$$Q = \left(\frac{e^{-\Theta_E/2T}}{1-e^{-\Theta_E/T}}\right)^{3N} e^{\frac{U_0}{k_BT}}, \tag{12}$$

or, $\ln Q = -3N\Theta_E/2T - 3N\ln(1-e^{-\Theta_E/T}) + \frac{U_0}{k_BT}$. So the average internal energy is calculated using $\bar{E} = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)$, as

$$\begin{aligned}\bar{E} &= 3Nk_BT^2\frac{\Theta_E}{2T^2} + 3Nk_BT^2\frac{\frac{\Theta_E}{T^2}e^{-\Theta_E/T}}{(1-e^{-\Theta_E/T})} - k_BT^2\frac{U_0}{k_BT^2} \\ &= \frac{3}{2}Nh\nu + \frac{3Nh\nu e^{-\Theta_E/T}}{(1-e^{-\Theta_E/T})} - U_0. \end{aligned} \tag{13}$$

Therefore the heat capacity is given by

$$C_v = \frac{\partial \bar{E}}{\partial T} = 3Nk_B\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{-\Theta_E/T}}{(1-e^{-\Theta_E/T})^2}. \tag{14}$$

At high temperature, *i.e.*, for $T \to \infty$, the exponential can be well approximated as $e^{-\Theta_E/T} \approx 1 - \Theta_E/T + \mathcal{O}(1/T^2)$. Applying this, one obtains, $C_v \approx 3Nk_B\left(\frac{\Theta_E}{T}\right)^2 \frac{1}{(\Theta_E/T)^2} = 3Nk_B$, which is the mathematical form of the law of Dulong and Petit.

8. Consider a system of N non-interacting harmonic oscillators in three dimension with total energy E. Show that the microcanonical partition function is given by

$$Q(N,E) = \left(\frac{2\pi E}{3Nh}\right)^{3N} e^{3N} \prod_{i=1}^{N} \frac{1}{\omega_i^3},$$

where ω_i is the angular frequency of the $i-$th harmonic oscillator. Then show that the above partition function is consistent with the relation: $E = 3Nk_BT$. (Here, you can use: $\Gamma(3N) \approx (3N)! \approx (3N)^{3N}e^{-3N}$.)

Question 8 continues on the next page…

Answer: The Hamiltonian for a system of N non-interacting harmonic oscillators in three-dimensional space is given by

$$\mathcal{H} = \sum_{i=1}^{N}\left(\frac{\boldsymbol{p}_i^2}{2m_i} + \frac{k_i}{2}\boldsymbol{r}_i^2\right), \tag{15}$$

where the mass m_i and the spring constant k_i of the $i-$th harmonic oscillator are related to the angular frequency ω_i, as $\omega_i = \sqrt{k_i/m_i}$. So the microcanonical partition function can expressed as

$$Q(N,E) = \frac{E_0}{h^{3N}}\int d^N\boldsymbol{p}\int d^N\boldsymbol{q}\,\delta\left(\sum_{i=1}^{N}\left(\frac{\boldsymbol{p}_i^2}{2m_i} + \frac{k_i}{2}\boldsymbol{r}_i^2\right) - E\right) \tag{16}$$

The above equation can be rescaled by taking $\boldsymbol{J}_i = \boldsymbol{p}_i/\sqrt{2m_i}$ and $\boldsymbol{W}_i = \sqrt{k_i/2}\,\boldsymbol{r}_i$, which makes

$$\mathcal{H} = \sum_{i=1}^{N}\left(\boldsymbol{J}_i^2 + \boldsymbol{W}_i^2\right), \tag{17}$$

and subsequently, Eq. (16) becomes

$$Q(N,E) = E_0\frac{2^{3N}}{h^{3N}}\sum_{i=1}^{N}\frac{1}{\omega_i^3}\int d^N\boldsymbol{J}\int d^N\boldsymbol{W}\,\delta\left(\sum_{i=1}^{N}\left(\boldsymbol{J}_i^2 + \boldsymbol{W}_i^2\right) - E\right). \tag{18}$$

Now defining $R^2 = \sum_{i=1}^{N}\left(\boldsymbol{J}_i^2 + \boldsymbol{W}_i^2\right)$, one can introduce a $6N-$dimensional spherical coordinates consisting of one polar coordinate R and $(6N-1)$ number of angular coordinates, Ω. Here the volume element is $R^{6N-1}dR\,d^{6N-1}\Omega$. Therefore Eq. (18) becomes

$$Q(N,E) = E_0\frac{2^{3N}}{h^{3N}}\sum_{i=1}^{N}\frac{1}{\omega_i^3}\int d^{6N-1}\Omega\int dR\,R^{6N-1}\,\delta\left(R^2 - E\right). \tag{19}$$

Using the formula, $\int d^n\omega = \frac{2\pi^{\frac{n+1}{2}}}{\Gamma(\frac{n+1}{2})}$ along with the relation, $\delta(R^2-E) = \frac{1}{2\sqrt{E}}[\delta(R-\sqrt{E}) + \delta(R+\sqrt{E})]$ in Eq. (19), one can arrive at

$$Q(N,E) = \frac{E_0}{E}\frac{2^{3N}\pi^{3N}}{h^{3N}\Gamma(3N)}E^{3N}\sum_{i=1}^{N}\frac{1}{\omega_i^3}. \tag{20}$$

For large N, using the relation, $\Gamma(3N) \approx (3N)! \approx (3N)^{3N}e^{-3N}$, the above can approximated as

$$Q(N,E) \approx \frac{E_0}{E}\frac{2^{3N}\pi^{3N}}{h^{3N}(3N)^{3N}}E^{3N}e^{3N}\sum_{i=1}^{N}\frac{1}{\omega_i^3}. \tag{21}$$

Ignoring the prefactor E_0/E and rearranging the terms, we obtain

$$Q(N,E) = \left(\frac{2\pi E}{3Nh}\right)^{3N} e^{3N}\prod_{i=1}^{N}\frac{1}{\omega_i^3}.$$

From the Boltzmann's equation, $S = k_B \ln Q$, and the definition of temperature, $\frac{1}{T} = \frac{\partial S}{\partial E}$, one can get

$$\frac{1}{T} = k_B \frac{3N}{E} \implies E = 3Nk_BT, \tag{22}$$

which is consistent with the equipartition theorem.

9. Consider a system consisting of N "indistinguishable", non-interacting point particles (each of mass m) with total energy E and volume V. Show that the microcanonical partition function of this system is

$$Q(N,V,E) = \frac{1}{N!}\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right]^N e^{3N/2}.$$

Then derive the equation of state for this system.

Answer: The Hamiltonian for N particles (each of mass m) is

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

For a system consisting of N particles with total energy E and volume V, the microcanonical partition function is given by

$$Q(N,V,E) = \frac{E_0}{N!h^{3N}} \int d\mathbf{p}_1 \int d\mathbf{p}_2 \cdots \int d\mathbf{p}_N \int d\mathbf{q}_1 \int d\mathbf{q}_2 \cdots \int d\mathbf{q}_N \, \delta\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - E\right), \tag{23}$$

where $\int d\mathbf{q}_i = \int dx_i \int dy_i \int dz_i$. The integration over q_i is straightforward and can be done easily as $\int d\mathbf{q}_i = V$. So Eq. (23) simplifies to

$$Q(N,V,E) = \frac{E_0\, V^N}{N!h^{3N}} \int d\mathbf{p}_1 \int d\mathbf{p}_2 \cdots \int d\mathbf{p}_N \, \delta\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} - E\right). \tag{24}$$

Taking $\mathbf{\Phi}_i^2 = \mathbf{p}_i^2/2m$, the above can be rewritten as

$$Q(N,V,E) = \frac{E_0\,(2m)^{3N/2}\, V^N}{N!h^{3N}} \int d\mathbf{\Phi}_1 \int d\mathbf{\Phi}_2 \cdots \int d\mathbf{\Phi}_N \, \delta\left(\sum_{i=1}^{N} \mathbf{\Phi}_i^2 - E\right). \tag{25}$$

Eq. (25) can calculated in an easier way if it is to be done in the polar coordinate. For that, we take, $r^2 = \sum_{i=1}^{N} \mathbf{\Phi}_i^2$, where r is the radial coordinate of a $3N-$dimensional spherical coordinates with $(3N-1)$ number of angular coordinates (ω). So the volume element is $r^{3N-1} dr\, d^{3N-1}\omega$. Now we can express Eq. (25) as

$$Q(N,V,E) = \frac{E_0\,(2m)^{3N/2}\, V^N}{N!h^{3N}} \int d^{3N-1}\omega \int_0^{\infty} dr\, r^{3N-1} \delta\left(r^2 - E\right). \tag{26}$$

Using the formula, $\int d^n\omega = \frac{2\pi^{\frac{n+1}{2}}}{\Gamma(\frac{n+1}{2})}$, where $\Gamma(n) = \int_0^\infty dy\, y^{n-1}e^{-y}$, one can perform the integration over ω, which transforms Eq. (26) to

$$\begin{aligned}
Q(N,V,E) &= \frac{E_0\,(2m)^{3N/2}\,2\pi^{3N/2}\,V^N}{N!h^{3N}\Gamma(3N/2)}\int_0^\infty dr\, r^{3N-1}\delta\left(r^2-E\right) \\
&= \frac{E_0\,(2m)^{3N/2}\,2\pi^{3N/2}\,V^N}{N!h^{3N}\Gamma(3N/2)}\int_0^\infty dr\, r^{3N-1}\frac{1}{2\sqrt{E}}[\delta(r-\sqrt{E})+\delta(r+\sqrt{E})] \\
&= \frac{E_0\,(2m)^{3N/2}\,\pi^{3N/2}\,V^N}{E\,N!h^{3N}\Gamma(3N/2)}E^{3N/2} = \frac{1}{N!}\frac{E_0}{E}\frac{1}{\Gamma(3N/2)}\left[V\left(\frac{2\pi mE}{h^2}\right)^{3/2}\right]^N. \qquad (27)
\end{aligned}$$

For the above calculation, we used the fact that $r \in (0,\infty)$, and $E > 0$, so the second term in the integrand has no contribution in the second step. In the large N limit, one can use the Sterling's approximation, $\Gamma(n+1) = e^{-n}n^n$. Applying this, one obtains, $\Gamma(3N/2) = e^{-3N/2+1}(3N/2-1)^{3N/2-1} \approx e^{-3N/2}\,(3N/2)^{3N/2}$. Also the prefactor E_0/E can be neglected. Taking all these results into account, we get

$$Q(N,V,E) = \frac{1}{N!}\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right]^N e^{3N/2}. \qquad (28)$$

The pressure is calculated from the partition function, using the formula

$$P = k_BT\left(\frac{\partial \ln Q(N,V,E)}{\partial V}\right)_{N,E}.$$

Since $Q(N,V,E) \sim V^N$, one gets $P = k_BTN/V$, or

$$PV = nRT,$$

where $n = N/N_A$. This is the equation of state of the system.

10. The canonical partition function of a monoatomic ideal gas is

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}V^N.$$

Derive expressions for the pressure and the energy from this partition function. Also show that the ideal gas equation of state is obtained if Q is of the form: $f(T)V^N$, where $f(T)$ is any function of temperature.

Answer: The canonical partition function of a monoatomic ideal gas is

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}V^N. \qquad (29)$$

The pressure P is given by $P = k_BT\left(\frac{\partial \ln Q(N,V,T)}{\partial V}\right)_{N,T}$. So using Eq. (29), one gets

$$\begin{aligned}
P &= k_BT\,N/V + k_BT\,\cancelto{0}{\frac{\partial}{\partial V}\ln\left(\frac{1}{N!}\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}\right)} \\
PV &= nRT. \qquad (30)
\end{aligned}$$

The average energy can be calculated using the formula, $\bar{E} = k_B T^2 \left(\frac{\partial \ln Q(N,V,T)}{\partial T}\right)_{N,V}$. So from Eq. (29), one has

$$\bar{E} = k_B T^2 \frac{\partial}{\partial T}\left(\ln\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}\right) + \cancelto{0}{k_B T^2 \frac{\partial}{\partial T}\left(\ln\left(\frac{V^N}{N!}\right)\right)}$$

$$\bar{E} = \frac{3}{2} N k_B T = \frac{3}{2} nRT. \tag{31}$$

If the partition function is of the form: $Q(T,V) = f(T)V^N$, the pressure can be calculated as $P = k_B T \left(\frac{\partial \ln Q(N,V,T)}{\partial V}\right)_{N,T} = k_B T N/V$, which leads to ideal gas equation of state, $PV = nRT$.

11. The partition function of an ideal gas of diatomic molecules in an external electric field ξ is

$$Q(N,V,T,\xi) = \frac{[q(V,T,\xi)]^N}{N!}$$

where

$$q(V,T,\xi) = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\left(\frac{8\pi^2 I k_B T}{h^2}\right)\left(\frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/2k_B T}}\right)\left(\frac{k_B T}{\mu\xi}\right) sinh\left(\frac{\mu\xi}{k_B T}\right).$$

Here I is the moment of inertia of the molecule; ν is its fundamental vibrational frequency, and μ is its dipole moment. Using this partition function along with the thermodynamic relation,

$$dA = -SdT - pdV - Md\xi,$$

where $M = N\bar{\mu}$, $\bar{\mu}$ is the average dipole moment of a molecule in the direction of the external field ξ, show that

$$\bar{\mu} = \mu\left[coth\left(\frac{\mu\xi}{k_B T}\right) - \left(\frac{k_B T}{\mu\xi}\right)\right].$$

Sketch this result versus ξ from $\xi = 0$ to $\xi = \infty$, and interpret it.

There is a typo in the question.

Answer: From the thermodynamic relation, $dA = -SdT - pdV - Md\xi$, one can find the magnetization M as

$$M = -\left(\frac{\partial A}{\partial \xi}\right)_{V,T}.$$

Here A is the Helmholtz free energy, and it is related to partition function via the formula: $A = -k_B T \ln Q(N,V,T,\xi)$. With the given partition function, one can see

$$\ln Q(N,V,T,\xi) = N\ln\left(\frac{k_B T}{\mu\xi}\right) + N\ln\left[\sinh\left(\frac{\mu\xi}{k_B T}\right)\right] + g(T,V,N),$$

where $g[T,V,N] = N\ln\left[V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\left(\frac{8\pi^2 I k_B T}{h^2}\right)\left(\frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}}\right)\right] - \ln N!$. So we get

$$
\begin{aligned}
M &= -Nk_BT\frac{\left(\frac{k_BT}{\mu\xi^2}\right)}{\left(\frac{k_BT}{\mu\xi}\right)} + Nk_BT\left(\frac{\mu}{k_BT}\right)\frac{\cosh\left(\frac{\mu\xi}{k_BT}\right)}{\sinh\left(\frac{\mu\xi}{k_BT}\right)} \\
&= N\mu\left[\coth\left(\frac{\mu\xi}{k_BT}\right) - \left(\frac{k_BT}{\mu\xi}\right)\right]. \qquad (32)
\end{aligned}
$$

Therefore,

$$\bar{\mu} = \frac{M}{N} = \mu\left[\coth\left(\frac{\mu\xi}{k_BT}\right) - \left(\frac{k_BT}{\mu\xi}\right)\right].$$

Interpretation: At low electric field, $\bar{\mu} = 0$, as spins are randomly oriented. With the

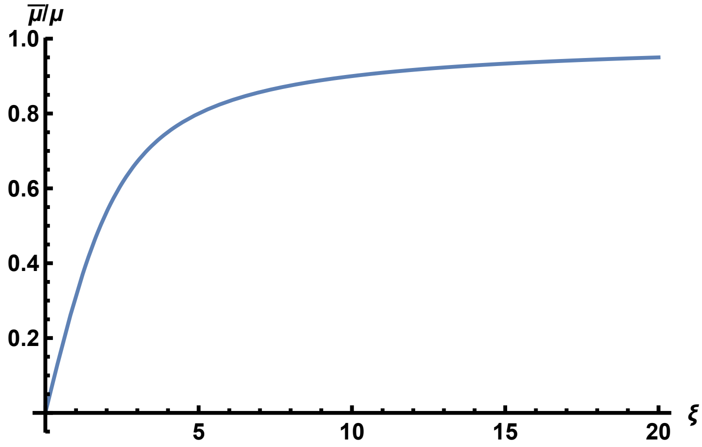


Figure 1: Plot of average dipole moment, $\bar{\mu}$ (rescaled by μ) as a function of electric field, ξ. In the given plot, we have taken $k_BT/\mu = 1$.

application of electric field, spins are continuously aligned in the field, thereby showing positive moment. At some point, all spins get aligned with the field, and the average moment saturates to μ.

12. An *approximate* partition function for a dense gas is

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}(V-Nb)^N e^{aN^2/Vk_BT},$$

where a and b are constants that are given in terms of molecular parameters. Calculate the equation of state from this partition function. What equation of state is this? Calculate the thermodynamic energy and the heat capacity.

Answer: The pressure of a gas can be calculated by using the formula, $P = k_BT\left(\frac{\partial \ln Q(N,V,T)}{\partial V}\right)_{N,T}$. The given partition function is of the form of

$$Q(N,V,T) = f(N,T)\,(V-Nb)^N e^{aN^2/Vk_BT},$$

where $f(N,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}$. Therefore,

$$P = k_B T\left(\frac{\partial \ln Q(N,V,T)}{\partial V}\right)_{N,T} = \frac{Nk_BT}{V-Nb} - k_BT\frac{aN^2}{V^2k_BT}. \tag{33}$$

Rearranging the terms, we have

$$\left(P + \frac{aN^2}{V^2}\right)(V-Nb) = Nk_BT,$$

which is the equation state for Van der Waals gas.

The average energy can be computed as

$$\begin{aligned}\bar{E} &= k_BT^2\left(\frac{\partial \ln Q(N,V,T)}{\partial T}\right)_{N,V} \\ &= k_BT^2\frac{3N}{2}\left(\frac{\partial \ln T}{\partial T}\right)_{N,V} + k_BT^2\left(\frac{\partial}{\partial T}\right)_{N,V}\left(\frac{aN^2}{Vk_BT}\right) \\ &= \frac{3}{2}Nk_BT - \frac{aN^2}{V}. \end{aligned} \tag{34}$$

The heat capacity is given by

$$C_v = \left(\frac{\partial \bar{E}}{\partial T}\right)_{N,V} = \frac{3}{2}Nk_B. \tag{35}$$

13. A Material consists of n independent particles and is in a weak external field H. Each particle can have a magnetic moment $m\mu$ along the magnetic field, where $m = j, j-1, \cdots, -j+1, -j$, j being an integer, and μ is a constant. The system is at temperature T.

    (i) Find the partition function for this system.

    (ii) Calculate the average magnetization, $\bar{M}$, of the material.

    (iii) For large values of T, find an asymptotic expression for $\bar{M}$.

    Answer: The interaction energy of $j-$th moment with the field H is $\epsilon_j = -j\mu H$. So the partition function of a particle can be given as

$$\begin{aligned} q(T,H) = \sum_{m=-j}^{+j} e^{\frac{m\mu H}{k_BT}} &= \frac{e^{-\frac{j\mu H}{k_BT}}\left(1 - e^{\frac{(2j+1)\mu H}{k_BT}}\right)}{1 - e^{\frac{\mu H}{k_BT}}} \\ &= \frac{e^{-\frac{j\mu H}{k_BT} - \frac{\mu H}{2k_BT}} - e^{\frac{j\mu H}{k_BT} + \frac{\mu H}{2k_BT}}}{e^{-\frac{\mu H}{2k_BT}} - e^{\frac{\mu H}{2k_BT}}} \\ &= \frac{\sinh\left((j+\frac{1}{2})\frac{\mu H}{k_BT}\right)}{\sinh\left(\frac{1}{2}\frac{\mu H}{k_BT}\right)} \end{aligned} \tag{36}$$

For the system of n independent particles, the partition function is

$$Q(n,T,H) = q^n(T,H) = \left[\frac{\sinh\left((j+\frac{1}{2})\frac{\mu H}{k_BT}\right)}{\sinh\left(\frac{1}{2}\frac{\mu H}{k_BT}\right)}\right]^n . \tag{37}$$

The average magnetization, $\bar{M}$ can be expressed as

$$\bar{M} = -\left(\frac{\partial A}{\partial H}\right)_{n,T}, \tag{38}$$

where $A = -k_BT\ln Q(n,T,H)$ is the free energy. Thus,

$$\begin{aligned}
\bar{M} &= nk_BT\left(\frac{\partial}{\partial H}\right)_{n,T}\left[\ln\left(\sinh\left((j+\frac{1}{2})\frac{\mu H}{k_BT}\right)\right) - \ln\left(\sinh\left(\frac{\mu H}{2k_BT}\right)\right)\right] \\
&= nk_BT\frac{\mu}{k_BT}\left[(j+\frac{1}{2})\frac{\cosh\left((j+\frac{1}{2})\frac{\mu H}{k_BT}\right)}{\sinh\left((j+\frac{1}{2})\frac{\mu H}{k_BT}\right)} - \frac{1}{2}\frac{\cosh\left(\frac{\mu H}{2k_BT}\right)}{\sinh\left(\frac{\mu H}{2k_BT}\right)}\right] \\
&= \frac{n\mu}{2}\left[(2j+1)\coth\left((2j+1)\frac{\mu H}{2k_BT}\right) - \coth\left(\frac{\mu H}{2k_BT}\right)\right].
\end{aligned} \tag{39}$$

For large values of T, *i.e.*, in the limit $k_BT \gg \mu H$, one can approximate the hyperbolic function as $\coth\left(\frac{\mu H}{k_BT}\right) \approx \frac{1}{\frac{\mu H}{k_BT}} + \frac{1}{3}\frac{\mu H}{k_BT}$. Using this, Eq. (39) becomes

$$\bar{M} \approx \frac{n\mu}{2}\frac{1}{6}\frac{\mu H}{k_BT}[(2j+1)^2 - 1] = \frac{n}{3}j(j+1)\frac{\mu^2 H}{k_BT}. \tag{40}$$

14. The entropy of an ideal paramagnet in a magnetic field is given *approximately* by

$$S = S_0 - CU^2,$$

where U is the energy of the spin system and C is a constant with fixed mechanical parameters of the system.

(i) Using fundamental definition of the temperature, determine the energy U of the spin system as a function of T.

(ii) Sketch s graph of U versus T for all values of T ($-\infty < T < \infty$).

(iii) Briefly tell what physical sense you can make of the negative temperature part of your result.

Answer: From the definition of temperature, $\frac{1}{T} = \frac{\partial S}{\partial U}$, one gets

$$\frac{1}{T} = -2CU \implies U = -\frac{1}{2CT},$$

where $C > 0$.

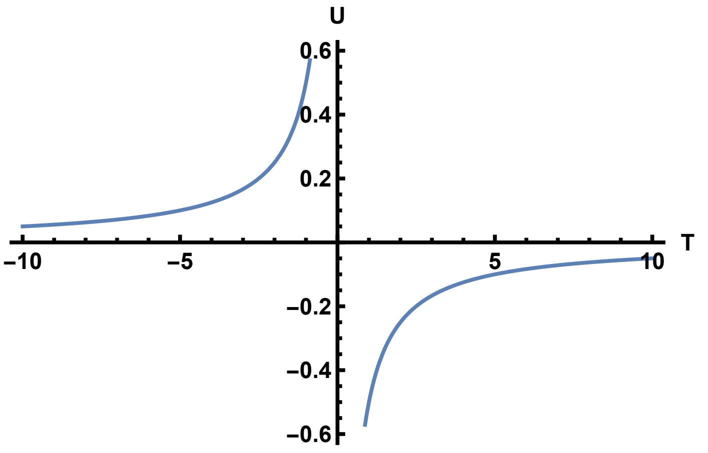


Figure 2: Plot of U versus T. Here, $C = 1$.

Interpretation: The negative temperature signifies that there are more number of particles in an excited state than the ground state (population inversion). For a spin system, one may have a situation where most of the spins are aligned anti-parallel to the applied field, thereby resulting negative temperature.

15. A one-dimensional quantum harmonic oscillator (whose ground state energy is $\hbar\omega/2$) is in thermal equilibrium with a heat bath at temperature T.

(i) What is the mean value of the oscillator's energy, $\langle E\rangle$, as a function of T?

(ii) What is the value of ΔE, the root mean square fluctuation in energy about $\langle E\rangle$?

(iii) How do $\langle E\rangle$ and ΔE behave in the limits $k_BT \leq \hbar\omega$ and $k_BT \gg \hbar\omega$?

Answer: The energy of $\nu-$th state of a harmonic oscillator with angular frequency ω is given by $\epsilon_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega$. Therefore the partition function can be expressed as

$$q(T) = \sum_{\nu=0}^{\infty} e^{-\frac{\hbar\omega}{k_BT}\left(\nu+\frac{1}{2}\right)} = \frac{e^{-\frac{\hbar\omega}{2k_BT}}}{1-e^{-\frac{\hbar\omega}{k_BT}}} = \frac{2}{\sinh\left(\frac{\hbar\omega}{2k_BT}\right)} \tag{41}$$

So the mean value of energy is

$$\bar{E} = k_BT^2\left(\frac{\partial \mathrm{ln}q(T)}{\partial T}\right) = +k_BT^2\frac{\cosh\left(\frac{\hbar\omega}{2k_BT}\right)}{\sinh\left(\frac{\hbar\omega}{2k_BT}\right)}\left(\frac{\hbar\omega}{2k_BT^2}\right) = \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2k_BT}\right). \tag{42}$$

The root mean square fluctuation in energy, ΔE is computed as

$$\Delta E = \sqrt{k_BT^2\frac{\partial\bar{E}}{\partial T}} = \sqrt{k_BT^2\frac{\hbar\omega}{2}\left(\frac{\hbar\omega}{2k_BT^2}\right)\mathrm{csch}^2\left(\frac{\hbar\omega}{2k_BT}\right)} = \frac{\hbar\omega}{2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)}. \tag{43}$$

Question 15 continues on the next page...

In the limit $k_BT \ll \hbar\omega$, $\coth\left(\frac{\hbar\omega}{2k_BT}\right) = \frac{e^{\frac{\hbar\omega}{2k_BT}}+e^{-\frac{\hbar\omega}{2k_BT}}}{e^{\frac{\hbar\omega}{2k_BT}}-e^{-\frac{\hbar\omega}{2k_BT}}} \approx \frac{e^{\frac{\hbar\omega}{2k_BT}}}{e^{\frac{\hbar\omega}{2k_BT}}} \approx 1$, and $\sinh\left(\frac{\hbar\omega}{2k_BT}\right) = \frac{e^{\frac{\hbar\omega}{2k_BT}}-e^{-\frac{\hbar\omega}{2k_BT}}}{2} \approx \frac{1}{2}e^{\frac{\hbar\omega}{2k_BT}}$. So in this limit, $\bar{E} \approx \frac{1}{2}\hbar\omega$ and $\Delta E \approx \hbar\omega e^{-\frac{\hbar\omega}{2k_BT}}$.

In the limit $k_BT \gg \hbar\omega$, $\coth\left(\frac{\hbar\omega}{2k_BT}\right) = \frac{\cosh\left(\frac{\hbar\omega}{2k_BT}\right)}{\sinh\left(\frac{\hbar\omega}{2k_BT}\right)} \approx \frac{1+\mathcal{O}(1/T^2)}{\left(\frac{\hbar\omega}{2k_BT}\right)+\mathcal{O}(1/T^3)} \approx \frac{2k_BT}{\hbar\omega}$, and $\sinh\left(\frac{\hbar\omega}{2k_BT}\right) \approx \frac{\hbar\omega}{2k_BT}$. Therefore, $\bar{E} \approx k_BT$ and $\Delta E \approx k_BT$.

Class 16: (04.03.2021)

Systems of interacting particles

Lattice vibrations and normal modes:

Solid → made of N atoms

Each atom can be described by its mass and position co-ordinates

ith atom

↳ m_i $\quad$ r_i ↓

$$\underbrace{(x_{i1}, x_{i2}, x_{i3})}_{\text{Like } (x_i, y_i, z_i)}$$

$\dot{x}_{i\alpha}$ → α component of vel. of i^{th} atom

To describe/measure the displacements from the equilibrium we introduce the variable

$$\xi_{i\alpha} \equiv x_{i\alpha} - x_{i\alpha}^{(0)} \ ; \qquad \alpha = 1, 2, 3$$

$x_{i\alpha}^{(0)}$ ← Eq^m

The kinetic energy of vibration of the solid

$$K = \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3} m_i \dot{x}_{i\alpha}^2 = \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3} m_i \dot{\xi}_{i\alpha}^2$$

"Potential energy" $V(x_{11}, x_{12}, \ldots x_{N3})$

Can be expressed as a Taylor series (since the displacements are small)

$$V = \underset{\substack{\text{Potential energy in eq}^{m} \\ \text{position}}}{V_0} + \sum_{i\alpha} \underbrace{\left(\frac{\partial V}{\partial x_{i\alpha}}\right)_0}_{\text{"0"}} \xi_{i\alpha} + \frac{1}{2} \sum_{i,j\alpha\gamma} \underbrace{\left(\frac{\partial^2 V}{\partial x_{i\alpha} \partial x_{j\gamma}}\right)_0}_{A_{i\alpha, j\gamma}} \xi_{i\alpha} \xi_{j\gamma} + \cdots\cdots$$

i or j from 1 to N

α or γ from 1 to 3

Evaluated at the equilibrium positions $x_{i\alpha} = x_{i\alpha}^{(0)}$

$$V = V_0 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} \xi_{i\alpha} \xi_{j\gamma}$$

$$H = \frac{1}{2} \sum_{i\alpha} m_i \dot{\xi}_{i\alpha}^2 + V_0 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} \xi_{i\alpha} \xi_{j\gamma}$$

Hamiltonian

interacting

"Complicated Hamiltonian"

Change of variables → eliminates the cross terms in the potential energy "Classical Mechanics"

$\xi_{i\alpha}^{(3N)} \rightarrow q_r^{(3N)}$ (generalized co-ordinate)

$$\xi_{i\alpha} = \sum_{r=1}^{3N} B_{i\alpha,r}\, q_r$$

→ A proper choice of coefficients gives the following Hamiltonian

$$H = V_0 + \frac{1}{2}\sum_{r=1}^{3N} \dot{q}_r^2 + \frac{1}{2}\sum_{r=1}^{3N} \omega_r^2 q_r^2$$

$\omega_r^2 \rightarrow$ positive constants

$$H_r = \frac{1}{2}\left(\dot{q}_r^2 + \omega_r^2 q_r^2\right) \xrightarrow{QM} \varepsilon_r = \left(n_r + \frac{1}{2}\right)\hbar\omega_r$$

$q_r \rightarrow$ normal co-ordinates

$$E_{n_1, \dots n_{3N}} = V_0 + \sum_{r=1}^{3N}\left(n_r + \frac{1}{2}\right)\hbar\omega_r = -N\eta + \sum_{r=1}^{3N} n_r \hbar\omega_r$$

$-N\eta$: independent of quantum no.

$-N\eta = V_0 + \frac{1}{2}\sum_{r=1}^{3N} \hbar\omega_r$

$\frac{1}{2}\sum_{r=1}^{3N} \hbar\omega_r$ → zero point energy

$\eta \rightarrow$ binding energy per atom in the solid at absolute zero

Partition function:

$$Q = \sum_{n_1, n_2, \ldots n_{3N}} e^{-\beta\left[-N\eta + \sum_{r=1}^{3N} \hbar\omega_r\right]} \rightarrow E_{n_1, n_2 \ldots}$$

$$Q = e^{\beta N\eta} \sum_{n_1, n_2, \ldots n_{3N}} e^{-\hbar\beta(n_1\omega_1 + n_2\omega_2 + \cdots + n_{3N}\omega_{3N})}$$

$$= e^{\beta N\eta} \left(\sum_{n_1=0}^{\infty} e^{-\hbar\beta n_1\omega_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-\hbar\beta n_2\omega_2}\right) \cdots \left(\sum_{n_{3N}=0}^{\infty} e^{-\hbar\beta n_{3N}\omega_{3N}}\right)$$

$$Q = e^{\beta N\eta} \left(\frac{1}{1-e^{-\beta\hbar\omega_1}}\right)\left(\frac{1}{1-e^{-\beta\hbar\omega_2}}\right) \cdots \left(\frac{1}{1-e^{-\beta\hbar\omega_{3N}}}\right)$$

$$\ln Q = \beta N\eta - \sum_{r=1}^{3N} \ln\left(1-e^{-\beta\hbar\omega_r}\right)$$

If normal mode frequencies are closely space (ω_r)

$$\ln Q = \beta N\eta - \int_0^\infty \ln(1-e^{-\beta\hbar\omega})\,\underbrace{\sigma(\omega)\,d\omega}_{\text{the no. of normal modes with angular frequency in the range bet}^n\ \omega \text{ and } \omega+d\omega} \rightarrow \text{A knowledge is required}$$

$$\langle E\rangle = -\frac{\partial \ln Q}{\partial \beta} = -N\eta + \int_0^\infty \frac{(0+\hbar\omega e^{-\beta\hbar\omega})}{(1-e^{-\beta\hbar\omega})}\,\sigma(\omega)\,d\omega$$

$$\langle E\rangle = -N\eta + \int_0^\infty \frac{\hbar\omega}{(e^{\beta\hbar\omega}-1)}\,\sigma(\omega)\,d\omega$$

$$\boxed{\langle E\rangle = -N\eta + \int_0^\infty \frac{\hbar\omega}{(e^{\beta\hbar\omega}-1)}\,\sigma(\omega)\,d\omega}$$

$$\frac{d}{dx}\left(\frac{f(x)}{g(x)}\right) = \frac{f'(x)g(x) - g'(x)f(x)}{g(x)^2}$$

$$C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_V = -\frac{1}{k_B T^2}\left(\frac{\partial\langle E\rangle}{\partial\beta}\right)_V = -k_B\beta^2\left(\frac{\partial\langle E\rangle}{\partial\beta}\right)_V$$

$$= -k_B\beta^2\left[0 + \int_0^\infty \frac{(\hbar\omega)\left(0-\hbar\omega e^{\beta\hbar\omega}\right)}{(e^{\beta\hbar\omega}-1)^2}\,\sigma(\omega)\,d\omega\right]$$

$$\boxed{C_V = k_B\int_0^\infty \frac{(\beta\hbar\omega)^2\sigma(\omega)e^{\beta\hbar\omega}\,d\omega}{(e^{\beta\hbar\omega}-1)^2}}$$

if T is large
β is small

$$C_V = k_B\int_0^\infty \frac{(\beta\hbar\omega)^2\sigma(\omega)\,(1+\beta\hbar\omega+\cdots)}{(1+\beta\hbar\omega+\cdots-1)^2}\,d\omega$$

$$C_V = k_B\int_0^\infty \sigma(\omega)\,d\omega$$

$$C_V = k_B 3N = 3Nk_B$$

"Dulong-Petit's result"

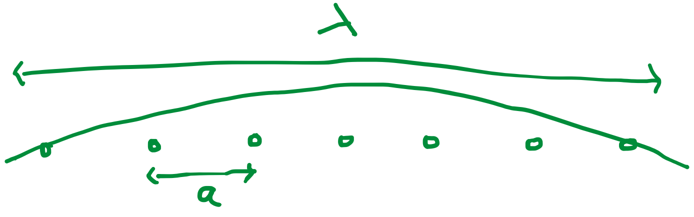
"Debye"

Solid $\equiv$ Neglecting the discreteness of the atoms and treating the latter as if it were a continuous isotropic elastic medium

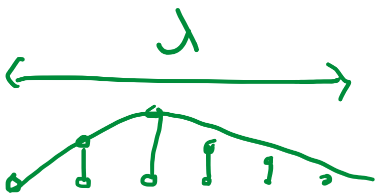
"a" $\rightarrow$ mean interatomic separation in solid ($\sim A^0$)

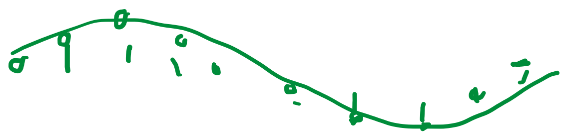
Elastic medium is characterised by a wavelength λ

$\lambda >> a$



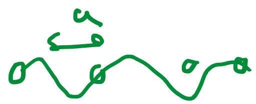
$U(r,t)$





$\lambda \approx a$

Discreteness becomes important



$\omega = c_s k$

velocity of sound

"wave vector"

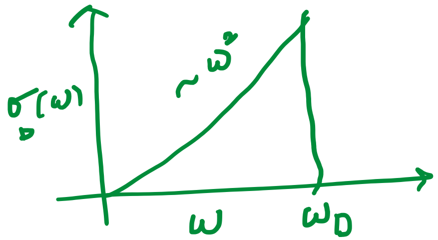
$$\sigma_c(\omega)\,d\omega = 3\,\frac{V}{(2\pi)^3}\left(4\pi k^2 dk\right) = 3\,\frac{V}{(2\pi^2 c_s^3)}\,\omega^2 d\omega = \sigma(\omega)\,d\omega$$

three possible polarizations
2 - transverse
1 - longitudinal

Debye approximation

$$\sigma_D(\omega) = \begin{cases} \sigma_c(\omega) & \omega < \omega_D \\ 0 & \omega > \omega_D \end{cases}$$

Debye frequency spectrum



$$\int_0^\infty \sigma_D(\omega)\,d\omega = \int_0^{\boxed{\infty}\;\omega_D} \sigma_c(\omega)\,d\omega = 3N$$

$$\left(\frac{3V}{2\pi^2 c_s^3}\right)\int_0^{\omega_D} \omega^2 d\omega = 3N$$

$$\Rightarrow \left(\frac{\cancel{3}V}{2\pi^2 c_s^3}\right)\frac{\omega_D^3}{\cancel{3}} = 3N$$

"Debye frequency"

$$\Rightarrow \omega_D = \left(6\pi^2 \frac{N}{V}\right)^{\frac{1}{3}} c_s$$

$c_s = 5\times10^5$ cm/s

$\left(\frac{V}{N}\right)^{\frac{1}{3}} = a = 10^{-8}$ cm

Different for different solids

$\omega_D \sim 10^{14}\ \text{sec}^{-1}$ "Infrared"

$$C_V = k_B \int_0^{\omega_D} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} (\beta\hbar\omega)^2 \left(\frac{3V}{2\pi^2 c_s^3}\right) \omega^2 d\omega$$

$x = \beta\hbar\omega$

$\omega = \frac{x}{\beta\hbar}$

$d\omega = \frac{dx}{\beta\hbar}$

$$= k_B \int_0^{\beta\hbar\omega_D} \frac{e^x \quad x^2}{(e^x-1)^2} \left(\frac{3V}{2\pi^2 c_s^3}\right) \frac{1}{(\beta\hbar)^3} x^2 dx$$

(F. Reif Fundamentals of Statistical and thermal physics)

$V = \frac{3N(2\pi^2 c_s^3)}{\omega_D^3}$

$V = 6\pi^2 N \left(\frac{c_s}{\omega_D}\right)^3$

$$C_V = k_B \frac{3V}{2\pi^2 (c_s\beta\hbar)^3} \int_0^{\beta\hbar\omega_D} \frac{e^x x^4}{(e^x-1)^2} dx$$

$T \to \infty$

$$\frac{3}{(\beta\hbar\omega_D)^3} \int_0^{\beta\hbar\omega_D} \frac{x^4(1+x+\cdot)}{(1+x+\cdots-1)^2} dx$$

$$= \frac{3}{(\beta\hbar\omega_D)^3} \int_0^{\beta\hbar\omega_D} x^2 dx = 1$$

$$C_V = k_B \frac{3 \cdot \cancel{6}^{3} \cancel{\pi^2} N \left(\frac{c_s}{\omega_D}\right)^3}{\cancel{2\pi^2} (c_s\beta\hbar)^3} \int_0^{\beta\hbar\omega_D} \frac{x^4 e^x}{(e^x-1)^2} dx = (3Nk_B) \frac{3}{(\beta\hbar\omega_D)^3} \int_0^{\beta\hbar\omega_D} \frac{x^4 e^x}{(e^x-1)^2} dx$$

$f_D(\beta\hbar\omega_D)$ Debye f^n

$x = \beta\hbar\omega$

Debye temperature

$$C_V = (3Nk_B) f_D\left(\frac{\Theta_D}{T}\right) \qquad \Theta_D = \frac{\hbar\omega_D}{k_B}$$

"Dulong-Petit" result

At high temperature ? $T \gg 1$

$\boxed{C_V = 3Nk_B}$

$f_D(y) \xrightarrow{y\to 0} 1$

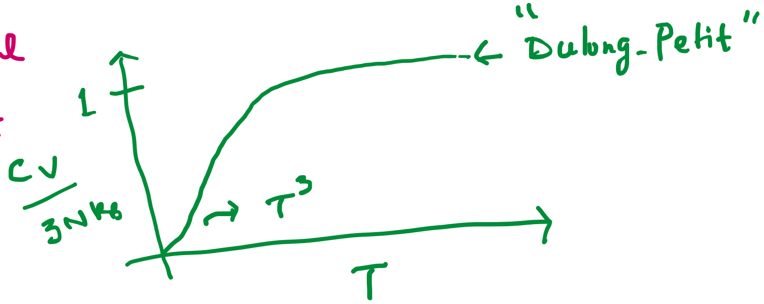
Low temperature $\qquad \beta\hbar\omega \gg 1 \qquad \frac{\hbar\omega}{k_B T} \gg 1 \qquad \omega < \omega_D \qquad \sigma(\omega) \neq 0$

$\omega \ll \omega_D$

$$\beta\hbar\omega_D \to \infty$$

$$C_V = \frac{k_B \times \text{constants}}{(\beta\hbar)^3} \underbrace{\left\{ \int_0^{\beta\hbar\omega_D} \frac{x^4 e^x}{(e^x-1)^2}\, dx \right\}}_{\text{Definite integral} = \text{constant}} \; \text{I} \to \; I = \frac{4\pi^4}{15} \; (\text{check})$$

$C_V \sim T^3$ at low temperature (Experimentally verified)



$C_V \sim 3Nk_B$ at high temperature

$$\int_0^{\infty} \frac{x^4 e^x}{(e^x-1)^2}\, dx = \int_0^{\infty} \frac{x^3}{(e^x-1)}\, dx = \frac{4\pi^4}{15}$$

$$C_V = \left(\frac{2\pi^2}{5}\right)(V k_B)\left(\frac{k_B T}{c_s \hbar}\right)^3$$

(F. Reif's book)

$\Theta_D(K) \to$ either from specific heat or elastic constants.

NaCl 308
KCl 230

Einstein's formulation

N no. of non-interacting independent harmonic oscillators
– each with frequency ω.

$$C_V = k_B \int_0^\infty \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} (\beta\hbar\omega)^2 \sigma(\omega)\, d\omega$$

"General" but in the normal mode picture

Einstein

$$C_V = 3Nk_B (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} = 3Nk_B (\theta_E/T)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}$$

$\theta_E = \frac{\hbar\omega}{k_B}$ "Einstein temp"

$T \to \infty$

$$C_V = 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{(1 + \underbrace{\theta_E/T}_{\to 0} + \dots)}{(1 + \theta_E/T + \dots - 1)^2}$$

$$\simeq 3Nk_B \left(\frac{\theta_E}{T}\right) \frac{1}{(\theta_E/T)^2} = 3Nk_B$$ (Dulong-Petit's result)

Low temperature

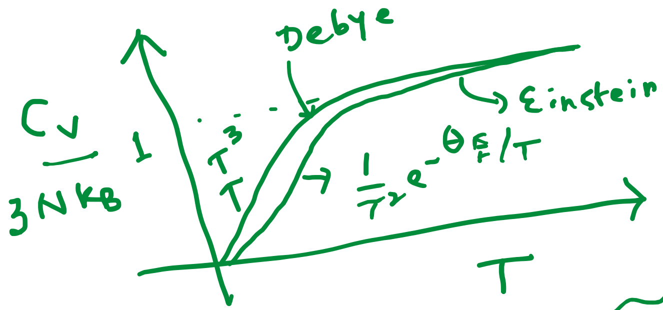
$T \to 0$ $\qquad \frac{\theta_E}{T} \gg 1$

$$C_V = 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{e^{2\theta_E/T}}$$

$$\left(e^{\theta_E/T}-1\right)^2 \approx \left(e^{\theta_E/T}\right)^2$$

$$C_V = 3Nk_B \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}$$

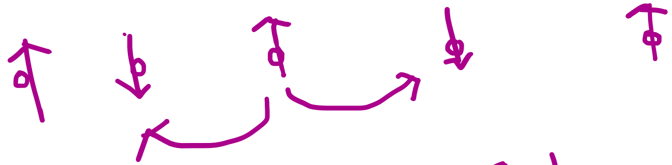
(Not T^3 !!!)



"Ising Model"

1925 (1-Dimension)

Linear Chain of N spin



Each of these spins could be in two states

$+ \to$ spin up

$- \to$ spin down

Only nearest neighbor interaction

$(i-1) \leftarrow$ "i" $\rightarrow (i+1)$

In addition we have an external magnetic field

Hamiltonian

Nearest neighbor interaction

External magnetic field

$$H = -J\sum_{i=1}^{N} \sigma_i \sigma_{i+1} - \sum_{i=1}^{N} B\sigma_i$$

Mag. moment

$B = h\mu$

$J > 0$ (interaction strength) $\qquad \sigma_i = \pm 1$

$\uparrow\uparrow \quad H = -J(1 \times 1) = -J$

$\downarrow\downarrow \quad H = -J(-1 \times -1) = -J$

Energy is lowered

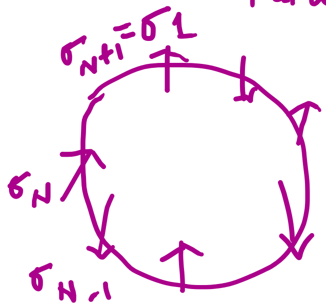
"ferromagnetic state"

All spins are up or all spins are down

Canonical partition function:

$$Q(N,B,T) = \sum_{\sigma_1 = \pm 1}\sum_{\sigma_2 = \pm 1} \cdots \sum_{\sigma_N = \pm 1} e^{+\beta\left(J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} + B\sum_{i=1}^{N}\sigma_i\right)}$$

"Put a Periodic boundary condition"



$$\sigma_{N+1} = \sigma_1$$

$$Q(B,T) = \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} \exp\left[\beta\left(J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} + \frac{B}{2}\sum_{i=1}^{N}(\sigma_i+\sigma_{i+1})\right)\right]$$

$$Q(B,T) = \sum_{\{\sigma_i\}}\prod_{i=1}^{N} \underbrace{\exp\left[\beta\left(J\sigma_i\sigma_{i+1} + \frac{B}{2}(\sigma_i+\sigma_{i+1})\right)\right]}_{M_{\sigma_i\sigma_{i+1}}}$$

$M_{\sigma_i\sigma_{i+1}}$ (Matrix elements)

$M \rightarrow 2\times 2$ Matrix
with matrix elements

$M_{++}\ \ M_{--}\ \ M_{+-}\ \ M_{-+}$

$$Q(B,T) = \sum_{\{\sigma_i\}}\prod_{i=1}^{N} M_{\sigma_i\sigma_{i+1}}$$

$$Q(B,T) = \sum_{\sigma_1}\sum_{\sigma_2}\sum_{\sigma_3}\cdots M_{\sigma_1\sigma_2}M_{\sigma_2\sigma_3}\cdots M_{\sigma_N\sigma_1}$$

$M_{\sigma_i\sigma_{i+1}} = \langle\sigma_i|M|\sigma_{i+1}\rangle$

Basis $\{\sigma_i\}$

Like quantum Mechanics

"Matrix Representation of operators"

$$\hat{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}$$

$A_{11} = \langle\psi_1|A|\psi_1\rangle$

$\vdots$

$A_{12} = \langle\psi_1|A|\psi_2\rangle$

$$Q(B,T) = \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} M_{\sigma_1\sigma_2} M_{\sigma_2\sigma_3}\cdots M_{\sigma_N\sigma_1}$$

$$Q(B,T) = \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N}\langle\sigma_1|M|\sigma_2\rangle\langle\sigma_2|M|\sigma_3\rangle\langle\sigma_3|\cdots\langle\sigma_{N-1}|M|\sigma_N\rangle\langle\sigma_N|M|\sigma_1\rangle$$

I $\quad$ I

$$\sum_i |\sigma_i\rangle\langle\sigma_i| = I$$

Resolution of identity

$$Q(B,T) = \sum_{\sigma_1}\langle\sigma_1|M^N|\sigma_1\rangle = Tr(M^N)$$

"trace"

$$M_{\sigma_i\sigma_{i+1}} = \exp\left[\beta\left(J\sigma_i\sigma_{i+1} + \frac{B}{2}(\sigma_i+\sigma_{i+1})\right)\right]$$

$$M = \begin{pmatrix} M_{++} & M_{+-} \\ M_{-+} & M_{--}\end{pmatrix} = \begin{pmatrix} \exp[\beta(J+B)] & e^{-\beta J} \\ e^{-\beta J} & \exp[\beta(J-B)]\end{pmatrix} = \begin{pmatrix} e^{x+y} & e^{-x} \\ e^{-x} & e^{x-y}\end{pmatrix}$$

Let us call $\beta J = x \quad \beta B = y$

$M^{\dagger} = M$ (check) $\quad$ M is Hermitian

↪ One should be able to diagonalize it + real eigenvalues

$$U^{-1} M U \equiv D \equiv \begin{bmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{bmatrix} \quad \lambda_\pm \rightarrow \text{eigen values}$$

$$U \underbrace{U^{-1} M U}_{D} U^{-1} = M = U D U^{-1}$$

$$Q = \mathrm{Tr}\{M^N\} = \mathrm{Tr}\{(U D U^{-1})^N\}$$

$$= \mathrm{Tr}\{U D \underbrace{U^{-1} U}_{I} D U^{-1} \cdots U D U^{-1} \cdots\}$$

$$= \mathrm{Tr}\{U D^N U^{-1}\}$$

$$= \mathrm{Tr}\{D^N U^{-1} U\} = \mathrm{Tr}\{D^N\} = \lambda_+^N + \lambda_-^N$$

$\mathrm{Tr}(A) = (\lambda_1 + \lambda_2 + \cdots\cdots)$ Sum of eigen values

$$\mathrm{Tr}(A^2) = (\lambda_1^2 + \lambda_2^2 + \cdots)$$

$$\mathrm{Tr}(A^N) = (\lambda_1^N + \lambda_2^N + \cdots)$$

$$A = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \rightarrow \mathrm{Tr}(A) = \lambda_1 + \lambda_2$$

$$A^2 = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} = \begin{pmatrix} \lambda_1^2 & 0 \\ 0 & \lambda_2^2 \end{pmatrix}$$

$$\mathrm{Tr}(A^2) = \lambda_1^2 + \lambda_2^2$$

Calculating eigen values:

$$|M-\lambda I| = 0 \qquad \begin{vmatrix} e^{x+y}-\lambda & e^{-x} \\ e^{-x} & e^{x-y}-\lambda \end{vmatrix} = 0$$

$$\cosh x = \frac{1}{2}(e^{x}+e^{-x})$$
$$\sinh x = \frac{1}{2}(e^{x}-e^{-x})$$

$$\Rightarrow (e^{x+y}-\lambda)(e^{x-y}-\lambda) - e^{-2x} = 0$$
$$\Rightarrow e^{x+\cancel{y}+x-\cancel{y}} - \lambda e^{x-y} - \lambda e^{x+y} + \lambda^2 - e^{-2x} = 0$$
$$\Rightarrow \lambda^2 - \lambda(e^{x-y}+e^{x+y}) + (e^{2x}-e^{-2x}) = 0$$
$$\Rightarrow \lambda^2 - \lambda e^{x}(e^{y}+e^{-y}) + (e^{2x}-e^{-2x}) = 0$$
$$\Rightarrow \lambda^2 - \lambda 2e^{x}\cosh y + 2\sinh(2x) = 0$$

$$ax^2+bx+c=0$$
$$x_\pm = \frac{-b\pm\sqrt{b^2-4ac}}{2a}$$

$$\lambda_\pm = \frac{2\cosh y\, e^{x} \pm \sqrt{4e^{2x}\cosh^2 y - 8\sinh(2x)}}{2}$$
$$\lambda_\pm = e^{x}\cosh y \pm \sqrt{e^{2x}\cosh^2 y - 2\sinh(2x)}$$
$$= e^{x}\cosh y \pm \sqrt{e^{2x}(1+\sinh^2 y) - \cancel{\tfrac{2}{2}}\, e^{2x} + e^{-2x}}$$

$$\boxed{\lambda_\pm = e^{x}\cosh y \pm \sqrt{e^{2x}\sinh^2 y + e^{-2x}}}$$

$$Q = (\lambda_+)^N + (\lambda_-)^N \qquad \lambda_+ \gg \lambda_-$$

$$= \lambda_+^N \qquad N \to \infty \text{ (thermodynamic limit)}$$

$$\frac{1}{N} \ln Q(B,T) = \ln \lambda_+ + \frac{1}{N} \ln \left(1 + \left(\frac{\lambda_+}{\lambda_{-1}} \right)^{-N} \right) \sim \ln \lambda_+$$

$$Q = (\lambda_+)^N = \left\{ e^{x} \cosh y + \sqrt{e^{2x} \sinh^2 y + e^{-2x}} \right\}^N$$

$$Q = \left\{ e^{\beta J} \cosh(\beta B) + \sqrt{e^{2\beta J} \sinh^2(\beta B) + e^{-2\beta J}} \right\}^N$$

$A = -k_B T \ln Q \to$ Helmholtz free energy

$$-k_B T \ln Q = A = -N k_B T \ln \left\{ e^{\beta J} \cosh(\beta B) + \sqrt{e^{2\beta J} \sinh^2(\beta B) + e^{-2\beta J}} \right\}.$$

Average Magnetization

$$\langle M(B,T)\rangle = \left\langle \sum_i \mu\sigma_i \right\rangle = -\left(\frac{\partial A}{\partial h}\right)_T = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial h}\right)_T = \frac{N}{\beta}\left(\frac{\partial \ln\lambda_+}{\partial h}\right)_T$$

$$= N\mu\left(\frac{\partial \ln\lambda_+}{\partial(\beta\mu h)}\right)$$

$$= N\mu\left(\frac{\partial \ln\lambda_+}{\partial y}\right)$$

Not Matrix M

Here, magnetization

$$\langle M(B,T)\rangle = N\mu\frac{\partial}{\partial y}\left\{ \ln\left(e^{x}\cosh y + \sqrt{e^{2x}\sinh^2 y + e^{-2x}}\right)\right\}$$

$$= N\mu\,\frac{\left(e^{x}\sinh y + \frac{1}{\cancel{2}}\frac{1}{\sqrt{e^{2x}\sinh^2 y + e^{-2x}}}\left(e^{2x}\cancel{2}\sinh y\cosh y + 0\right)\right)}{\left(e^{x}\cosh y + \sqrt{e^{2x}\sinh^2 y + e^{-2x}}\right)}$$

Average Magnetization

$$\langle M(B,T)\rangle = \left\langle \sum_i \mu\sigma_i \right\rangle = -\left(\frac{\partial A}{\partial h}\right)_T = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial h}\right)_T = \frac{N}{\beta}\left(\frac{\partial \ln \lambda_+}{\partial h}\right)_T$$

$$= N\mu\left(\frac{\partial \ln\lambda_+}{\partial(\beta\mu h)}\right)$$

$$= N\mu\left(\frac{\partial \ln\lambda_+}{\partial y}\right)$$

Not Matrix M

Here, magnetization

$$\langle M(B,T)\rangle = N\mu\frac{\partial}{\partial y}\left\{\ln\left(e^{x}\cosh y + \sqrt{e^{2x}\sinh^2 y + e^{-2x}}\right)\right\}$$

$$\frac{\partial}{\partial y}\cosh y = \sinh y$$

$$\frac{\partial}{\partial y}\sinh y = \cosh y$$

$$= N\mu\,\frac{\left(e^{x}\sinh y + \frac{1}{\cancel{2}}\frac{1}{\sqrt{e^{2x}\sinh^2 y + e^{-2x}}}\left(e^{2x}\cancel{2}\sinh y\cosh y + 0\right)\right)}{\left(e^{x}\cosh y + \sqrt{e^{2x}\sinh^2 y + e^{-2x}}\right)}$$

$$\langle M(B,T)\rangle = N\mu\,\frac{\left(e^{x}\sinh y\sqrt{e^{2x}\sinh^2 y + e^{-2x}} + e^{2x}\sinh y\cosh y\right)}{\sqrt{e^{2x}\sinh^2 y + e^{-2x}}\left(e^{x}\cosh y + \sqrt{e^{2x}\sinh^2 y + e^{-2x}}\right)}$$

$$\langle M(B,T)\rangle = N\mu \frac{\left(e^{x}\sinh y\sqrt{e^{2x}\sinh^2 y + e^{-2x}} + e^{2x}\sinh y\cosh y\right)}{\sqrt{e^{2x}\sinh^2 y + e^{-2x}}\left(e^{x}\cosh y + \sqrt{e^{2x}\sinh^2 y + e^{-2x}}\right)}$$

$$\langle M(B,T)\rangle = N\mu \frac{e^{x}\sinh y\,\cancel{\left(\sqrt{e^{2x}\sinh^2 y + e^{-2x}} + e^{x}\cosh y\right)}}{\sqrt{e^{2x}\sin^2 hy + e^{-2x}}\,\cancel{\left(e^{x}\cosh y + \sqrt{e^{2x}\sinh^2 y + e^{-2x}}\right)}}$$

$$\langle M(B,T)\rangle = N\mu \frac{e^{x}\sinh y}{\sqrt{e^{2x}\sinh^2 y + e^{-2x}}} = N\mu \frac{\cancel{e^{x}}\sinh y}{\cancel{e^{x}}\sqrt{\sinh^2 y + e^{-4x}}}$$

$$\langle M(B,T)\rangle = N\mu \frac{\sinh(B\beta)}{\sqrt{\sinh^2(B\beta) + e^{-4\beta J}}}$$

Average magnetization

$$\frac{\langle M(B,T)\rangle}{N} \Rightarrow$$ Average magnetization per spin

$$\langle M(B,T)\rangle = N\mu \frac{\sinh(B\beta)}{\sqrt{\sinh^2(B\beta) + e^{-4\beta J}}}$$

If there is no external magnetic field $B = 0$

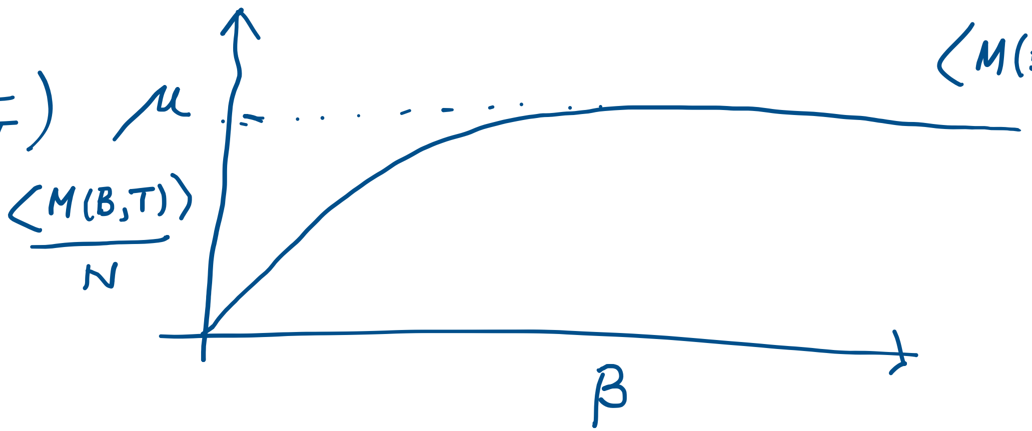
$$\frac{\langle M(B,T)\rangle}{N} = 0$$

(No, net magnetization ≡ No. ferromagnetic phase for Ising model in 1D.)

for finite β

spontaneous at $(B=0)$ finite temperature

$\dfrac{\langle M(B,T)\rangle}{N}$ vs β $\left(\equiv \dfrac{1}{k_B T}\right)$



$\langle M(B,T)\rangle = \mu N$ only $\beta \to \infty$

$(T_c = 0)$

"Absolute Zero"

$$\boxed{\langle M(B,T)\rangle = N\mu \frac{\sinh(B\beta)}{\sqrt{\sinh^2(B\beta)+e^{-4\beta J}}}}$$

$J=0$ (Non-interacting) but $B\neq 0$ (there is an external magnetic field)

$\sinh^2(B\beta)+1=\cosh^2(B\beta)$

$$\langle M(B,T)\rangle = N\mu\tanh(B\beta)$$

$$\frac{\langle M(B,T)\rangle}{N}=\mu\tanh(B\beta)$$

$J \to$ Completely aligned phase $\to$ Never wins in 1D $\downarrow$ No phase transition

k_BT (thermal energy) $\rightsquigarrow$ Disorder (maximizes entropy)

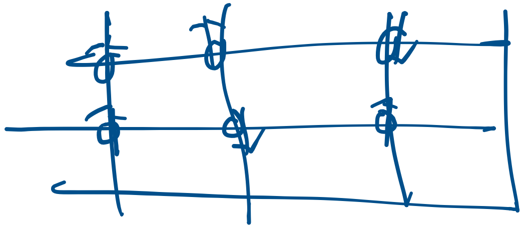
$\left.\begin{matrix}B=0\\ J=0\end{matrix}\right\}$ Non-interacting spins and no external magnetic field

$$\beta\to\infty \qquad \langle M(B,T)\rangle = N\mu\frac{\sinh(B\beta)}{\sqrt{\sinh^2(B\beta)+\underbrace{0}_{e^{-\infty}}}} = N\mu \quad \text{(independent of } B\text{) any finite } B$$

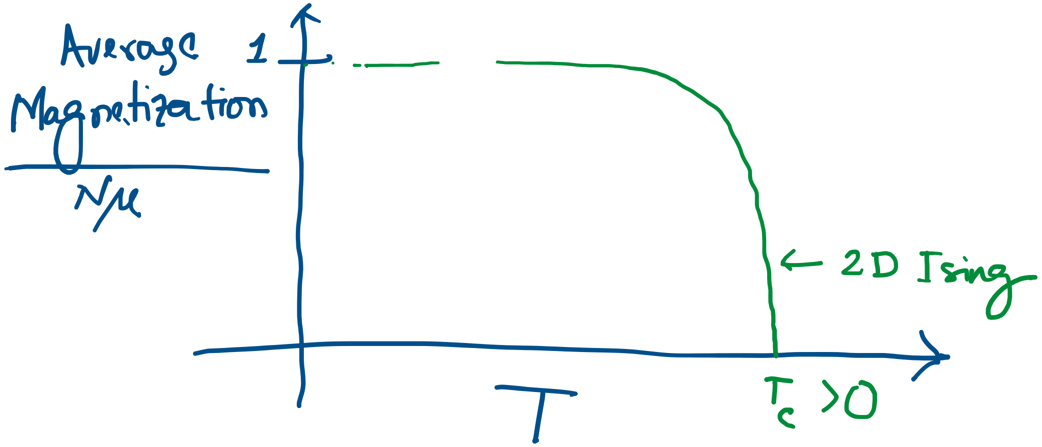
Lars Onsager 1944 $(B=0)$ (Analytically)

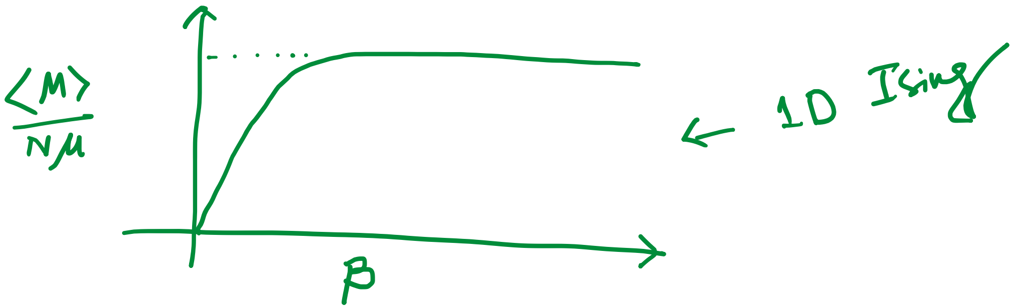
2D Ising Model $\rightsquigarrow$ Shows a phase transition!!

$(B \neq 0)$ $\rightsquigarrow$



↳ Transition to a ferromagnetic phase at finite temperature.





For 1D Ising model

T is $\gg 0$

$\langle M \rangle = 0$

$T \to \infty$

$\langle M \rangle \to 0$

Distribution function theory of liquids

Partition function $\quad Q = \sum_j e^{-\beta E_j}$ "Quantization" "Energy" QM

Purely classical system $\quad H[r^N; p^N] = K[p^N] + U[r^N]$

H: Hamiltonian of the system; K: K.E; U: P.E

$r^N \equiv 3N$ position co-ordinates

$p^N \equiv 3N$ momenta co-ordinates

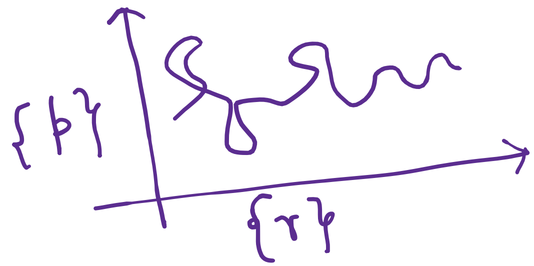
Canonical partition function for a purely classical system

$$Q = Q_{\text{classical}} = \frac{1}{N!\,h^{3N}} \int dr^N \int dp^N \exp\left[-\beta H(r^N, p^N)\right]$$

$N!$: if we assume the particles are indistinguishable

$\delta r^N \delta p^N \sim h^{3N}$

$f(r^N, p^N)$ = probability distribution for observing a system at phase space point (r^N, p^N).



$$f(r^N, p^N) = \frac{\exp[-\beta H(r^N, p^N)]}{\int dr^N \int dp^N \exp[-\beta H(r^N, p^N)]}$$

$$\int dr^N \equiv \int dr_1 \int dr_2 \cdots \int dr_N$$

$$\int dp^N \equiv \int dp_1 \int dp_2 \cdots \int dp_N$$

$$= \frac{\exp[-\beta(K(p^N) + U(r^N))]}{\int dr^N \int dp^N \exp[-\beta(K(p^N) + U(r^N))]}$$

$$\int dr \equiv \int dx \int dy \int dz$$

$$\int dp \equiv \int dp_x \int dp_y \int dp_z$$

$$= \underbrace{\frac{\exp[-\beta K(p^N)]}{\int dp^N \exp[-\beta K(p^N)]}}_{\to \phi(p^N)} \times \underbrace{\frac{\exp[-\beta U(r^N)]}{\int dr^N \exp[-\beta U(r^N)]}}_{\to P(r^N)}$$

$$f(r^N, p^N) = \phi(p^N)\, P(r^N)$$

$\phi(p^N) \equiv$ prob. distribution for observing System at momentum space point p^N

$P(r^N) \equiv$ prob. distribution for observing system at configuration space point r^N.

Reduced Configurational distribution functions:

$$P^{(2/N)}(r_1, r_2) = \int dr_3 \int dr_4 \cdots \int dr_N \, P(r^N)$$

$P(r^N) \to P(r_1, r_2, \ldots r_N)$

$P^{(2/N)}(r_1, r_2) \to$ joint probability distribution for finding particle 1 at r_1 and particle 2 at r_2 $\rightsquigarrow$ Specific probability distribution (Specifically requires particle 1 at r_1 and particle 2 at r_2).

generic reduced distribution functions:

$\rho^{(2/N)}(r_1, r_2) \equiv$ joint prob. distribution function for finding a particle (anyone) at position r_1 and any other particle at position r_2 (in the N particle system)

$$\rho^{(2/N)}(r_1, r_2) = \underbrace{N(N-1)}_{\frac{N!}{(N-2)!}} P^{(2/N)}(r_1, r_2)$$

$$\int dr^{N-n} \equiv \int dr_{n+1} \int dr_{n+2} \cdots \int dr_N$$

$$\rho^{(n/N)}(r_1, r_2, \ldots r_n) = \frac{N!}{(N-n)!} \frac{\int dr^{N-n} \exp[-\beta U(r^N)]}{\int dr^N \exp[-\beta U(r^N)]}$$

$\int dr^N \exp[-\beta U(r^N)] \rightarrow Z_N$ (configurational integral)

$\boxed{\int dr_1} \int dr_2 \cdots \int dr_N e^0$

$Z_N \equiv V^N$ (for ideal gas)

$$\rho^{(n/N)}(r_1, r_2, \ldots r_n) = \frac{N!}{(N-n)!}\frac{1}{Z_N}\int dr_{n+1}\int dr_{n+2}\cdots\int dr_N \exp\left(-\beta U(r^N)\right)$$

$$\{r_1, r_2, \ldots r_N\}$$

"Integrate"

$$\int\cdots\int \rho^{(n/N)}(r_1, r_2, \ldots r_n)\, dr_1 \ldots dr_n = \frac{N!}{(N-n)!}\frac{1}{\cancel{Z_N}}\underbrace{\int dr_1 \cdots \int dr_{n+1}\cdots\int dr_N \exp\left(-\beta U(r_1, r_2 \ldots r_N)\right)}_{\cancel{Z_N}}$$

$$\int \rho^{(n/N)}(r^n)\, dr^n = \frac{N!}{(N-n)!}$$

$$\int \rho^{(1/N)}(r_1)\, dr_1 = N$$ (number conservation)

$$\rho^{(1/N)}(r_1) = \frac{N!}{(N-1)!}\,\frac{1}{Z_N}\int dr_2 \int dr_3 \cdots \int dr_N \exp\left(-\beta U(r_1, r_2 \ldots r_N)\right)$$

For homogeneous liquid

$$Z_N = \left\{\int dr_1\right\}\int dr_2 \cdots\cdots dr_N \, e^{-\beta U(r_1, r_2, \ldots, r_N)}$$

$$Z_N = V \int dr_2 \int dr_3 \cdots dr_N \, e^{-\beta U(r^N)}$$

$$\rho^{(1/N)}(r) = \frac{N}{Z_N}\,\frac{Z_N}{V} = \frac{N}{V} = \rho \quad \text{(density)}$$

$$\rho^{(2/N)}(r_1, r_2) = \frac{N!}{(N-2)!} \frac{1}{Z_N} \int dr_3 \int dr_4 \ldots \int dr_N e^{-\beta U(r^N)}$$

$$= \frac{N(N-1)}{Z_N} \int dr_3 \int dr_4 \ldots\ldots \int dr_N e^{-\beta U(r^N)}$$

In case of ideal gas (fluid with interparticle interaction)

$$\rho^{(2/N)}(r_1, r_2) = \frac{N(N-1)}{Z_N} V^{N-2} = N(N-1)\frac{V^{N-2}}{V^N} = \frac{N(N-1)}{V^2} \simeq \frac{N^2}{V^2} = \rho^2$$

$Z_N \rightarrow V^N$

"N is very large"

$$= \rho^{(1/N)}(r_1)\, \rho^{(1/N)}(r_2) \qquad (U=0)$$

Let us define,

$$g(r_1, r_2) = \frac{\rho^{(2/N)}(r_1, r_2)}{\rho^2}$$

$g(r_1, r_2) = \rho^2/\rho^2 = 1$ (ideal gas)

Also,

$$h(r_1, r_2) = \frac{\left(\rho^{(2/N)}(r_1, r_2) - \rho^2\right)}{\rho^2} = g(r_1, r_2) - 1$$

$\rho \equiv$ Bulk density

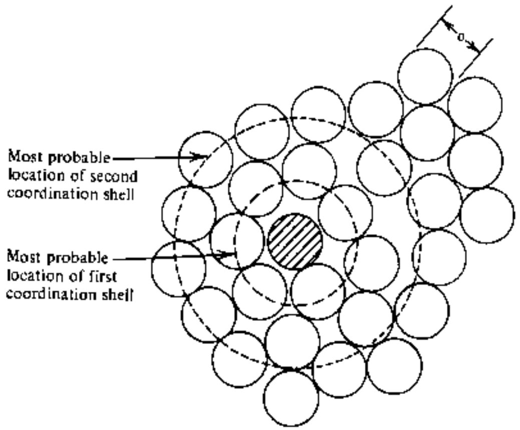
$g(r_1, r_2)$
↳ Pair-correlation f^n / radial distribution function

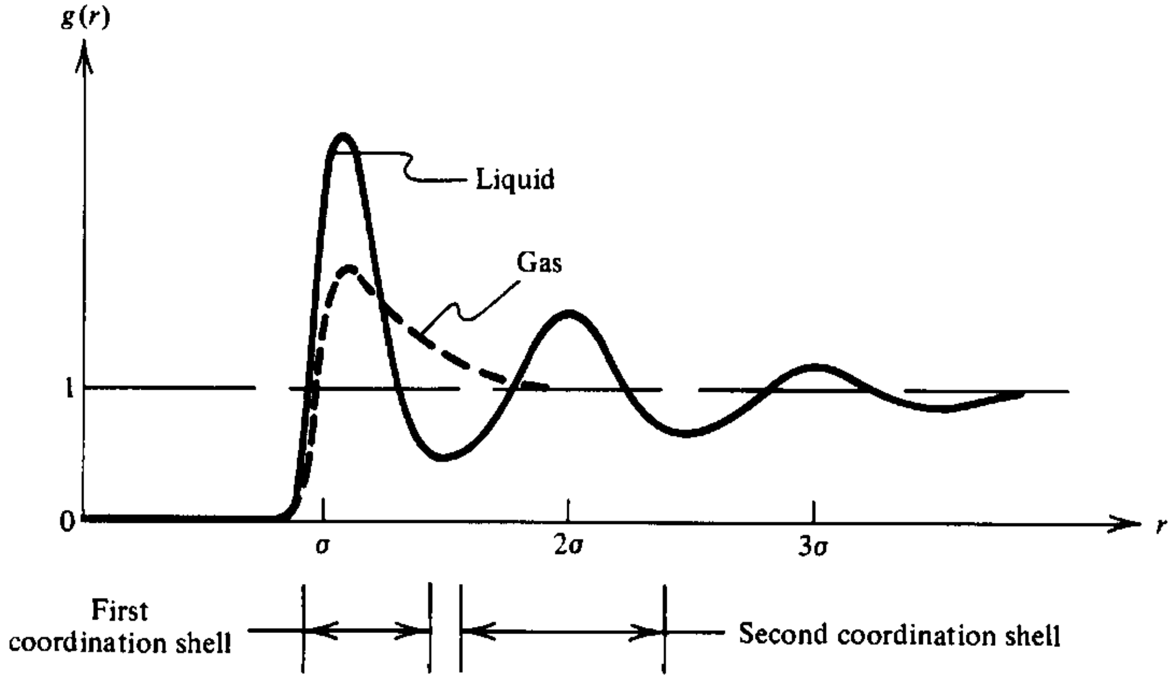
$$\rho^{(2/N)}(0, r) = \rho^2 g(r)$$

$$\frac{\rho^{(2/N)}(0, r)}{\rho} = \rho g(r) =$$ Conditional prob. that a particle will be found at r given that another is at the origin

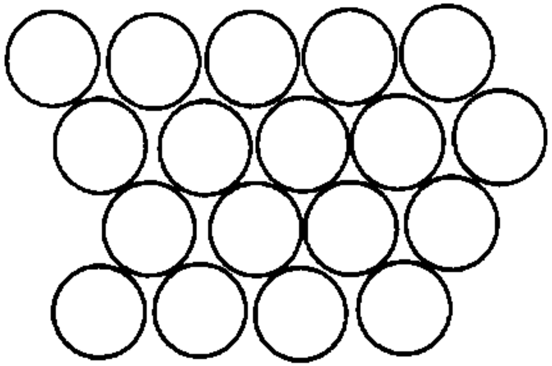
$\equiv$ average density of particles at r given that a tagged particle is at the origin

$\boxed{\text{Liquid Structure} \equiv g(r)}$

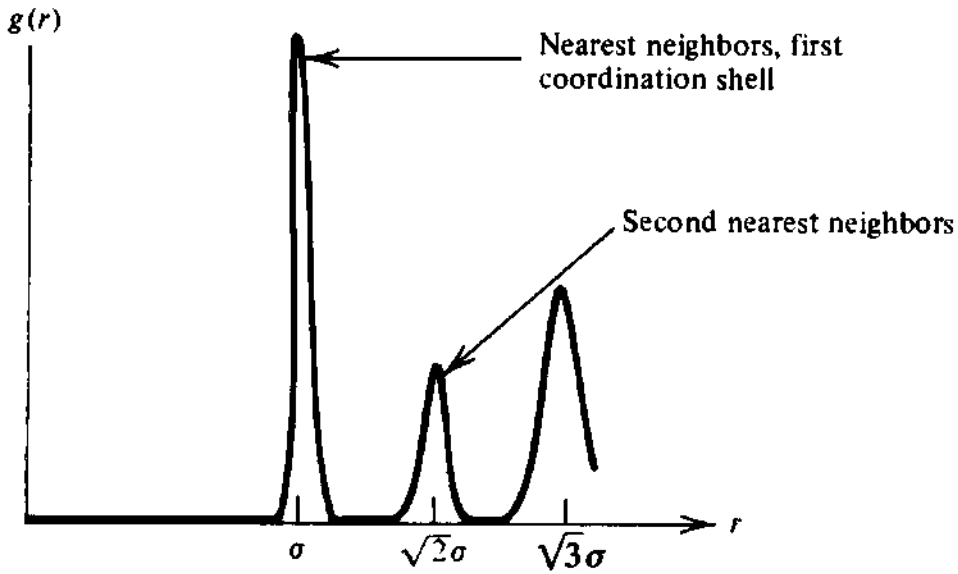




David Chandler → Introduction to SM



Crystalline order: solid



Highly ordered solid

$$\rho^{(2/N)}(r_1, r_2) = \frac{N!}{(N-2)!} \frac{1}{Z_N} \int dr_3 \int dr_4 \cdots \int dr_N \, e^{-\beta U(r^N)}$$

$\frac{N!}{(N-2)!} \to N(N-1)$

$$\langle X \rangle = \sum_{i=1}^{N} X_i P_i = \frac{\int P(x)\, x \, dx}{\int P(x)\, dx}$$

Using Dirac Delta f^n

$$\rho^{(1/N)}(r) = \left\langle \sum_{i=1}^{N} \delta(r - r_i) \right\rangle$$

Ensemble average of microscopic particle density

Let us consider

$$\langle \delta(r - r_1)\, \delta(r' - r_2) \rangle = \frac{1}{Z_N} \int \delta(r - r_1)\, \delta(r' - r_2)\, e^{-\beta U(r_1, r_2, \ldots r_N)}\, dr^N \quad \cdots\cdots \text{(A)}$$

$dr^N \to (dr_1 \cdots dr_N)$

$$Z_N = \int\!\!\int e^{-\beta U(r_1, r_2 \ldots r_N)}\, dr_1\, dr_2 \ldots dr_N$$

Prime means $i \neq j$

$$\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \delta(r - r_i)\, \delta(r' - r_j) \right\rangle = \rho^{(2/N)}(r_1, r_2)$$

$\downarrow$

$N(N-1) \times$ terms like (A)

$$\left\langle \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \delta(r - r_j + r_i) \right\rangle$$

$$= \left\langle \frac{1}{N} \int \underbrace{\sum_{i=1}^{N} \sum_{j=1}^{N}{}' \delta(r' + r - r_j)}_{\int f(r'+r-r_j)} \underbrace{\delta(r' - r_i)}_{\delta(r'-r_i)\,dr'} \, dr' \right\rangle$$

$$\| \qquad f(r_i + r - r_j) \equiv \delta(r_i + r - r_j)$$

$$= \frac{1}{N} \int \underbrace{\left\langle \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \delta(r' + r - r_j)\, \delta(r' - r_i) \right\rangle}\, dr'$$

$$= \frac{1}{N} \int \rho^{(2/N)}(r' + r, r')\, dr' = \frac{1}{N} \rho^2 \int g(r, r')\, dr'$$

$$= \frac{\rho^2}{N} \left(\frac{N}{\rho}\right) g(r) = \rho\, g(r)$$

$$\int dr'$$

$$\int \delta(r)\, dr = 1$$

$$\int \delta(r - r')\, dr' = 1$$

$$\int f(r)\, \delta(r - r')\, dr'$$

$$= f(r)$$

$$\int f(r' + r - r_j)\, \delta(r' - r_i)\, dr'$$

$$= f(r_i + r - r_j)$$

$$\rho = N/V$$

Homogeneous and isotropic liquid

$$S(k) = \frac{1}{N}\langle \rho(-k)\,\rho(k)\rangle$$

$\downarrow$ Structure factor (using X-ray or neutron scattering)

$$\rho(k) = \int dr\, e^{-ik.r}\rho(r)$$

$\hookrightarrow$ F.T of $\rho(r)$ "Fourier Transformation"

$$= \int dr\, e^{-ik.r}\sum_{i=1}^{N}\delta(r-r_i)$$

$$\rho(k) = \sum_{i=1}^{N} e^{-ik.r_i}$$

$$S(k) = \left\langle \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp(-ik.(r_i-r_j))\right\rangle$$

$$= \left\langle \frac{1}{N}N + \frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\exp\left(-ik.(r_i-r_j)\right)\right\rangle = 1 + \left\langle\frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\exp\left(-ik.(r_i-r_j)\right)\right\rangle$$

$$= 1 + \left\langle \frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\int\left(\exp\left(-ik.(r-r')\right)\delta(r-r_i)\,\delta(r'-r_j)\,dr\,dr'\right)\right\rangle$$

$\rightarrow \rho^{(2/N)}(r-r')$

$$S(k) = 1 + \frac{1}{N}\iint \exp\left(-ik\cdot(r-r')\right) \underbrace{\rho^{(2/N)}(r-r')}\, dr\, dr'$$

Since we have a homogeneous liquid (isotropic)

$$\Rightarrow \rho^2 g(r-r')$$

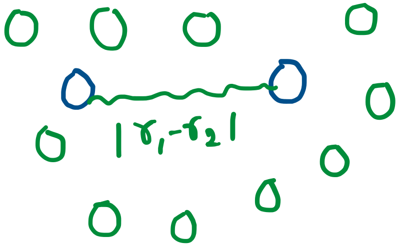
$$S(k) = 1 + \frac{1}{N}\rho^2 V \int g(r)\exp(-ik\cdot r)\, dr$$

$$S(k) = 1 + \rho \underbrace{\int g(r)\exp(-ik\cdot r)\, dr}$$

Structure factor in X-ray or neutron scattering

F.T of $g(r)$

Reversible work theorem:



Force acting on particle 1

↳ Due to all other particles

$$\left\langle -\frac{dU(r^N)}{dr_1} \right\rangle_{r_1, r_2 \text{ fixed}}$$

$$-\left\langle \frac{dU(r^N)}{dr_1} \right\rangle_{r_1, r_2 \text{ fixed}} = -\frac{\int dr_3 \ldots\ldots dr_N \left(\frac{dU}{dr_1}\right) e^{-\beta U(r^N)}}{\int dr_3 \ldots dr_N \, e^{-\beta U(r^N)}}$$

$$= (k_B T) \frac{\left[\frac{d}{dr_1} \int dr_3 \ldots dr_N e^{-\beta U(r^N)}\right]}{\int dr_3 \ldots dr_N \, e^{-\beta U(r^N)}}$$

$$\frac{d}{dr_1} e^{-\beta u} = -\beta e^{-\beta u} \left(\frac{dU}{dr_1}\right)$$

$$-\frac{1}{\beta} \frac{d}{dr_1} e^{-\beta u} = e^{-\beta U} \left(\frac{dU}{dr_1}\right)$$

$$-\left\langle \frac{d}{dr_1} U(r^N) \right\rangle_{r_1, r_2 \text{ fixed}} = \frac{k_B T \left[\frac{d}{dr_1} \int dr_3 \cdots dr_N \, e^{-\beta U(r^N)} \right]}{\int dr_3 \cdots dr_N \, e^{-\beta U(r^N)}}$$

$$= k_B T \frac{d}{dr_1} \left(\ln \int dr_3 \cdots dr_N \, e^{-\beta U(r^N)} \right)$$

$$= k_B T \frac{d}{dr_1} \ln \left[N(N-1) \int dr_3 \cdots dr_N \, e^{-\beta U(r^N)} \Big/ \int dr^N e^{-\beta U(r^N)} \right]$$

$$-\frac{dW(|r|)}{dr} = k_B T \frac{d}{dr_1} \ln g(r_1, r_2)$$

$W(r) = -k_B T \ln g(|r|)$ → Helmholtz free energy

Potential of mean force ⟶ Reversible work done

$r = r_1 - r_2$

(N, V, T)

How to model pair potential

$$U(r^N) \equiv U(r_1, r_2, \cdots r_N) \leftarrow \text{N-body potential.}$$

$$= \sum_{i>j=1}^{N} u(|r_i - r_j|) \quad \text{"Sum of pair potentials"}$$

A good example of this pair potential

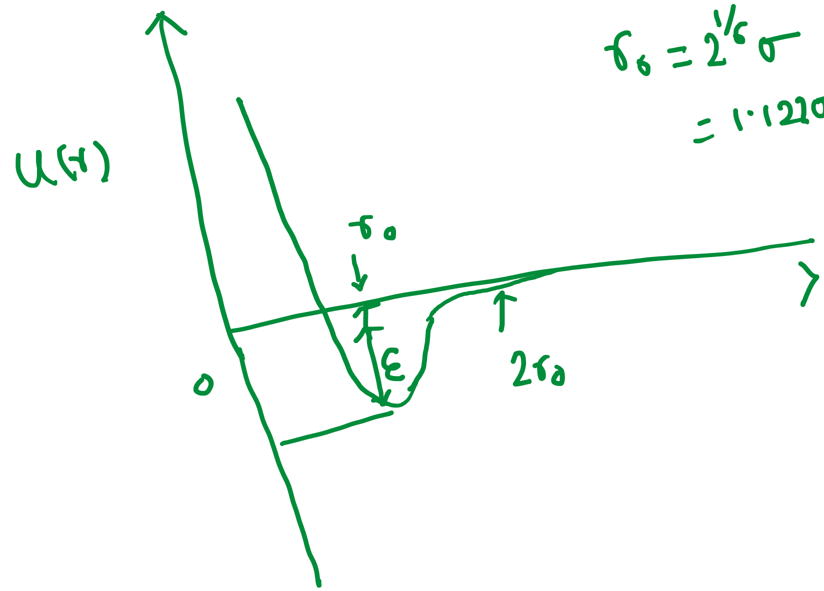
$\rightsquigarrow$ Lennard-Jones potential (not charged system)

$$u(r) = 4\varepsilon\left[\underbrace{\left(\sigma/r\right)^{12}}_{\text{Repulsion}} - \underbrace{\left(\sigma/r\right)^{6}}_{\text{attraction}}\right]$$

at $r = r_0$ $\quad u(r_0) = -\varepsilon$

$r_0 = 2^{1/6}\sigma$

$= 1.122\sigma$



Average internal energy

$$\langle E \rangle = \langle K(p^N) \rangle + \langle U(r^N) \rangle$$

$\langle K(p^N)\rangle \to$ K.E $\qquad \langle U(r^N)\rangle \leftarrow$ P.E

$$= N \left\langle \frac{p^2}{2m} \right\rangle + \left\langle \sum_{i>j=1}^{N} u(|r_i - r_j|) \right\rangle$$

$$= N \frac{3k_BT}{2} + \quad \cdots$$

How many distinct pairs

$$\frac{N(N-1)}{2}$$

$\leftarrow$ for not to have double counting

$$\left\langle \sum_{i>j=1}^{N} u(r_{ij}) \right\rangle = \frac{N(N-1)}{2} \langle u(r_{12}) \rangle$$

$$= \frac{N(N-1)}{2} \frac{\int dr^N u(r_{12}) e^{-\beta U(r^N)}}{\int dr^N e^{-\beta U(r^N)}}$$

$$= \frac{1}{2} \frac{\int dr_1 \int dr_2\, u(r_{12}) N(N-1) \int dr^{N-2} e^{-\beta U(r^N)}}{Z_N} = \frac{1}{2} \int dr_1 \int dr_2\, \rho^{(2/N)}(r_1, r_2)\, u(r_{12})$$

$$\frac{N(N-1) \int dr^{N-2} e^{-\beta U(r^N)}}{Z_N} \to \rho^{(2/N)}(r_1, r_2)$$

$$\left\langle \sum_{i>j=1}^{N} u(r_{ij}) \right\rangle = \frac{1}{2} \int dr_1 \int dr_2\, \rho^{(2/N)}(r_1, r_2)\, U(r_{12})$$

$$= \frac{1}{2} \int dr_1 \int dr_2\, \rho^2 g(r_{12})\, U(r_{12}) = \frac{V}{2}\left(\frac{N}{V}\right)^2 \int dr_{12}\, g(r_{12})\, U(r_{12})$$

$$\left[\int dr_1 \int dr_2 \equiv \underbrace{\int dr_1}_{V} \int dr_{12} \right]$$

$$\left\langle \sum_{i>j=1}^{N} u(r_{ij}) \right\rangle = \frac{N}{2} \int \rho\, g(r)\, u(r)\, dr$$

There are $4\pi r^2 \rho g(r)\, dr$ neighbors in a shell of radius r and thickness dr and the energy of interaction betn the central particles and these neighbors is $u(r)$.

$$\boxed{\frac{\langle E \rangle}{N} = \frac{3}{2} k_B T + \rho/2 \int dr\, g(r)\, u(r)}$$

Note that $\frac{\Delta E}{N} = \frac{\partial}{\partial \beta}\left(\beta \Delta A / N\right)$

$-\beta \Delta A = \ln\left(Q / Q_{ideal}\right)$

$\frac{\Delta E}{N} = \rho/2 \int dr\, g(r)\, u(r)$

low density case $g(r) \simeq e^{-\beta u(r)}$

$W(r) = u(r) + \Delta W(r)$ ← due to surrounding particle

↓ pair potential

(~ 0 at low density)

$W(r) = u(r) = -k_B T \ln g(r)$

$\Delta F = F - F_{ideal}$

$= \frac{3}{2} N k_B T + \frac{N}{2} \rho \int g(r)\, u(r)\, dr$

$- \frac{3}{2} N k_B T$

$= \frac{N}{2} \rho \int g(r) u(r)\, dr$

$= \rho/2 \int dr\, e^{-\beta u(r)}\, u(r) \left[1 + \underbrace{O(\rho)}_{\text{very small } \approx 0}\right]$

$$\frac{\Delta E}{N} = \rho/2 \int dr\, e^{-\beta u(r)} u(r)$$

$$\frac{\partial}{\partial \beta}\left(\beta \Delta A/N\right) = \rho/2 \int dr\, e^{-\beta u(r)} u(r)$$

Integrating over β

$$\beta \frac{\Delta A}{N} = \rho/2 \int dr\, u(r) \int_0^\beta d\beta' e^{-\beta' u(r)} = \rho/2 \int dr\, u(r) \left.\frac{e^{-\beta' u(r)}}{-u(r)}\right|_0^\beta$$

$$-\beta \frac{\Delta A}{N} = \rho/2 \int dr\, f(r) + \cancel{O(\rho^2)}$$

$$f(r) = 1 - e^{-\beta u(r)}$$

$$p = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} \quad \text{(recall)} \qquad A = -k_B T \ln Q$$

$$= -\left(\frac{\partial A}{\partial V}\right)_{N,T} \qquad p_{ideal} = \rho k_B T$$

$$\rho = N/V$$

$$V = N/\rho$$

$$\frac{\partial}{\partial V} = -\rho^2/N \frac{\partial}{\partial \rho}$$

$$\rho^2 \frac{\partial}{\partial \rho}\left(\frac{\beta \Delta A}{N}\right) = \rho^2 \frac{\partial}{\partial \rho}\left(\beta/_N \left(A - A_{ideal}\right)\right)$$

$$= \rho^2 \beta/_N \frac{\partial}{\partial \rho}\left(A - A_{ideal}\right)$$

$$= \rho^2 \beta/_N \left(\left(\frac{\partial A}{\partial \rho}\right) - \left(\frac{\partial A_{ideal}}{\partial \rho}\right)\right)$$

$$= \rho^2 \beta/_N \left(\frac{Np}{\rho^2} - \frac{N}{\rho^2}\, \rho/_\beta\right)$$

$$\frac{\partial}{\partial \rho} A_{ideal}$$

$$p_{ideal} = -\left(\frac{\partial A_{ideal}}{\partial V}\right)_{N,T}$$

$$= +\rho^2/_N \left(\frac{\partial A_{ideal}}{\partial \rho}\right)_{N,T}$$

$$\left(\frac{\partial A}{\partial \rho}\right)_{N,T} = N/_{\rho^2}\, p$$

$$\left(\frac{\partial A_{ideal}}{\partial \rho}\right)_{N,T} = N/_{\rho^2}\, p_{ideal}$$

$$\Rightarrow \quad \rho^2 \frac{\partial}{\partial \rho}\left(\frac{\beta \Delta A}{N}\right) = \beta p - \rho$$

$$\beta p = \rho + \rho^2 B_2(T)$$

$$\beta p = \rho + \rho^2 \frac{\partial}{\partial \rho}\left(\frac{\beta \Delta A}{N}\right)$$

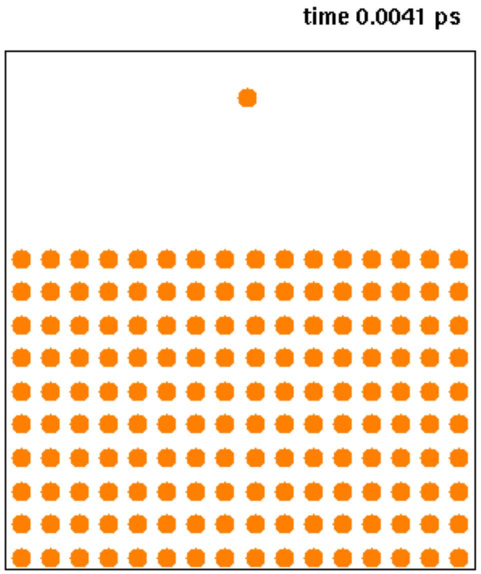
$$f(r) = e^{-\beta U(r)} - 1$$

$$\beta p = \rho + \rho^2 \frac{\partial}{\partial \rho}\left\{\left(-\rho/_2\right)\int dr\, f(r)\right\} = \rho + \rho^2 B_2(T)$$

$$B_2(T) = -\frac{1}{2}\int f(r)\, dr$$

$\longrightarrow$ second virial coefficient

Molecular dynamics simulation: Theory, Algorithm, and Applications



Source: Wikipedia

"If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the *atomic hypothesis* (or the atomic *fact*, or whatever you wish to call it) that *all things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another*. In that one sentence, you will see, there is an *enormous* amount of information about the world, if just a little imagination and thinking are applied."

Richard Feynman (1961)

- ❑ A method to capture the physical movements of atoms and molecules dynamically for a significant period of time
- ❑ Positions of a set of interacting particles over time are calculated by solving Newton's equation of motion
- ❑ The forces between the particles and their potential energies are calculated using molecular mechanics force field

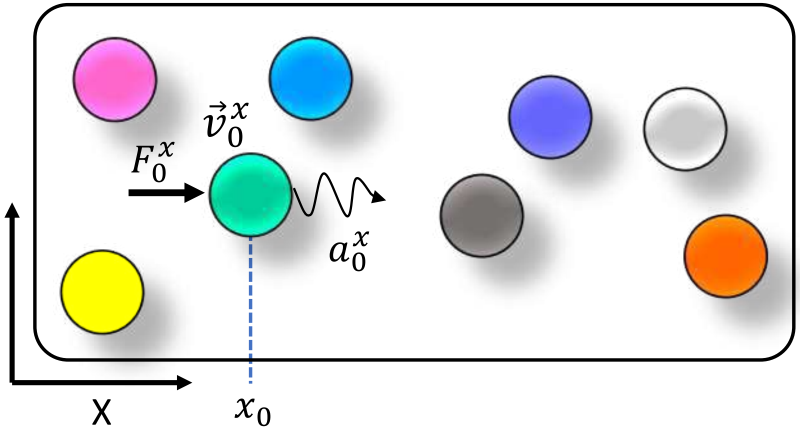
Classical Mechanics

$$F_i = m_i a_i = m_i \frac{d^2 r_i}{dt^2} = -\frac{dV}{dr_i} \qquad V = \text{Potential energy of the system}$$

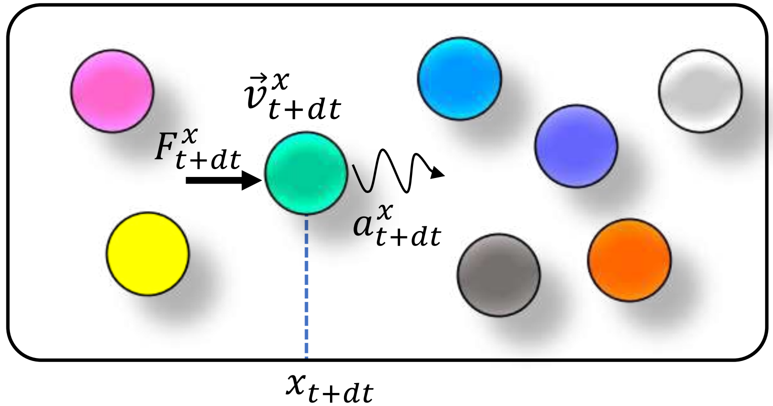
Time	Position (x_0)	Velocity (v_0^x)	Acceleration (a_0^x)
$t = 0$	x_0	v_0^x	$-\frac{1}{m_i}\frac{dV_0}{dx_i}$

Maxwell Boltzmann distribution

Molecular mechanics force field

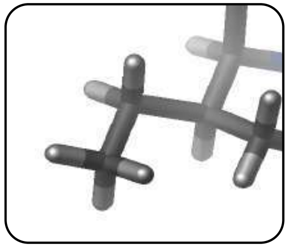


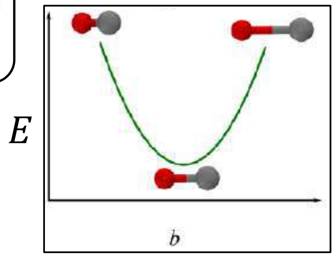
Time	Position (x_{t+dt})	Velocity (v_{t+dt}^x)	Acceleration (a_{t+dt}^x)
$t = t + dt$	$x_0 + v_0^x dt + \frac{1}{2} a_0^x dt^2$	$v_0^x + a_0^x dt$	$-\frac{1}{m_i}\frac{dV_{t+dt}}{dx_i}$



Force field

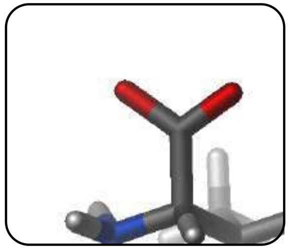
$$V = E_{bonded} + E_{non-bonded} \qquad E_{bonded} = E_{bond-stretching} + E_{angle-bending} + E_{dihedral-rotation}$$

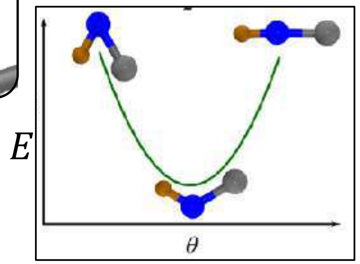




$$E_{bond-stretching} = \sum_{bonds} k_b (b - b_0)^2$$

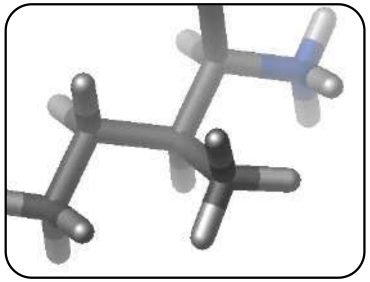
b = Bond length at any instance
b_0 = Equilibrium bond length
k_b = Force constant

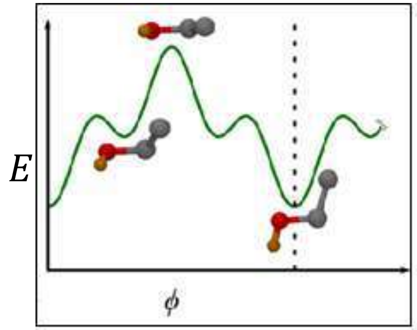




$$E_{angle-bending} = \sum_{angles} k_\theta (\theta - \theta_0)^2$$

θ = Bond angle at any instance
θ_0 = Equilibrium bond angle
k_θ = Force constant

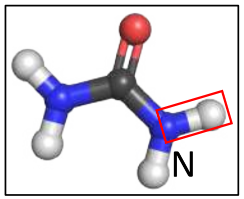




$$E_{dihedral-rotation} = \sum_{\substack{dihedral\\angles}} k_\varphi (1 - \cos(n\varphi - \delta))$$

φ = Bond angle at any instance
n = Dihedral multiplicity (number of local minima)
k_φ = Dihedral force constant
δ = Equilibrium dihedral angle

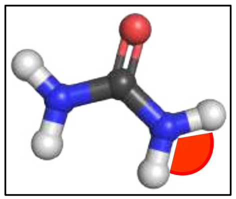
❑ Example: Force field parameters of urea (Charmm36 force field)



N---H

$b_0 = 1$ Å

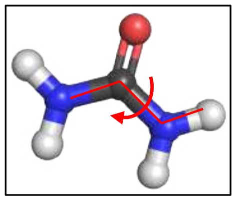
$k_b = 480\ kcal/mol$



H--N--H

$\theta_0 = 120°$

$k_\theta = 23\ kcal/mol$



H--N--C--N

$n = 2,\ k_\varphi = 1.5 \frac{kcal}{mol}$

$\delta = 180°$

Force field

$$E_{non-bonded} = E_{electrostatic} + E_{van\ der\ Waals}$$

$$E_{electrostatic} = \sum_{i,j} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

$$E_{van\ der\ Waals} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] = \epsilon_{ij}\left[\left(\frac{R_{min_{ij}}}{r_{ij}}\right)^{12} - 2\left(\frac{R_{min_{ij}}}{r_{ij}}\right)^{6}\right]$$

For n particles, the number of pair interaction terms = n(n-1)/2

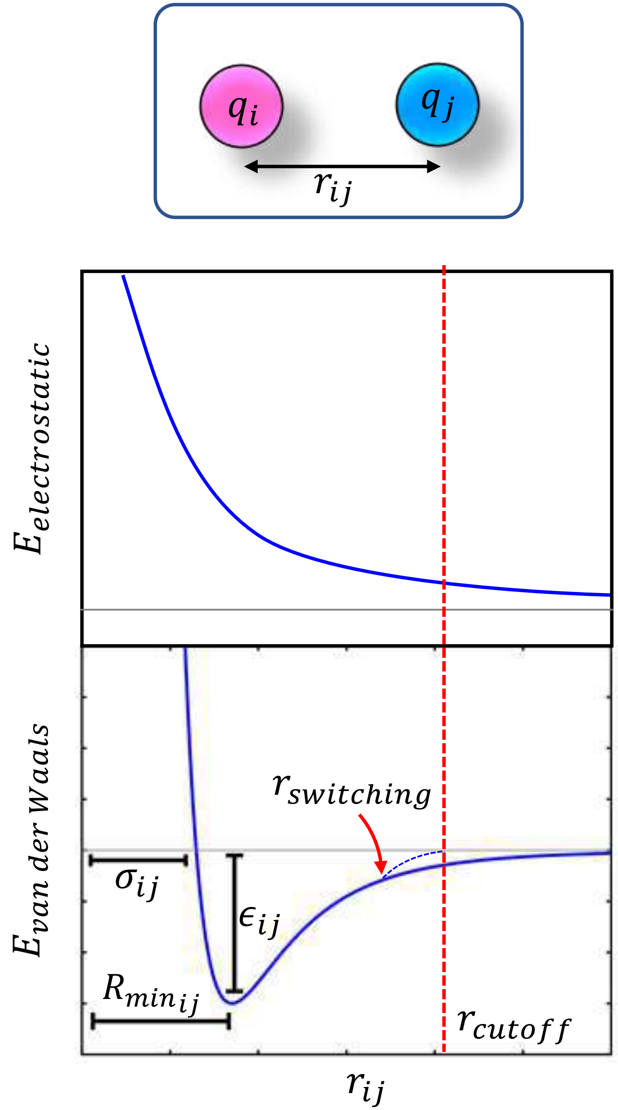
Truncation of interacting partner and cutoff distance

r_{cutoff} Distance at which the short-ranged interactions are turned off

Between $r_{switching}$ and r_{cutoff} the van der Waals interaction is switched to zero

Long-ranged electrostatic interactions are calculated using Particle Mesh Ewald (PME) summation method

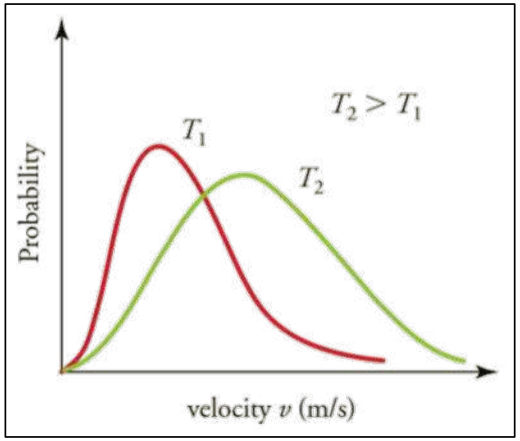
Reduces the computational time significantly



Velocity assignment

- Velocity is assigned randomly from Maxwell-Boltzmann distribution at a given temperature

$$p(v_i^x) = \left(\frac{m_i}{2\pi k_B T}\right)^{1/2} \exp\left[-\frac{1}{2}\frac{m_i (v_i^x)^2}{k_B T}\right]$$



- The *overall momentum is also ensured to be zero* $\sum_{i=1}^{N} m_i v_i = 0$

Integration algorithms

- Verlet Algorithm

$$r(t+\delta t) = r(t) + \frac{dr(t)}{dt}\delta t + \frac{1}{2!}\frac{d^2r(t)}{dt^2}\delta t^2 + \frac{1}{3!}\frac{d^3r(t)}{dt^3}\delta t^3 + \cdots$$

$$r(t-\delta t) = r(t) - \frac{dr(t)}{dt}\delta t + \frac{1}{2!}\frac{d^2r(t)}{dt^2}\delta t^2 - \frac{1}{3!}\frac{d^3r(t)}{dt^3}\delta t^3 + \cdots$$

Combining,

$$r(t+\delta t) + r(t-\delta t) = 2r(t) + \frac{d^2r(t)}{dt^2}\delta t^2$$

$$r(t+\delta t) = 2r(t) - r(t-\delta t) + a(t)\delta t^2$$

Faster since velocity need not to be calculated

Lower precision

Integration algorithms

- ❑ Leap-frog Algorithm

$$v\left(t+\frac{1}{2}\delta t\right)=\frac{r(t+\delta t)\ -\ r(t)}{\delta t} \quad \Longrightarrow r(t+\delta t)=r(t)+v(t+\frac{1}{2}\delta t)\delta t$$

$$v\left(t+\frac{1}{2}\delta t\right)=v\left(t-\frac{1}{2}\delta t\right)+a(t)\delta t$$

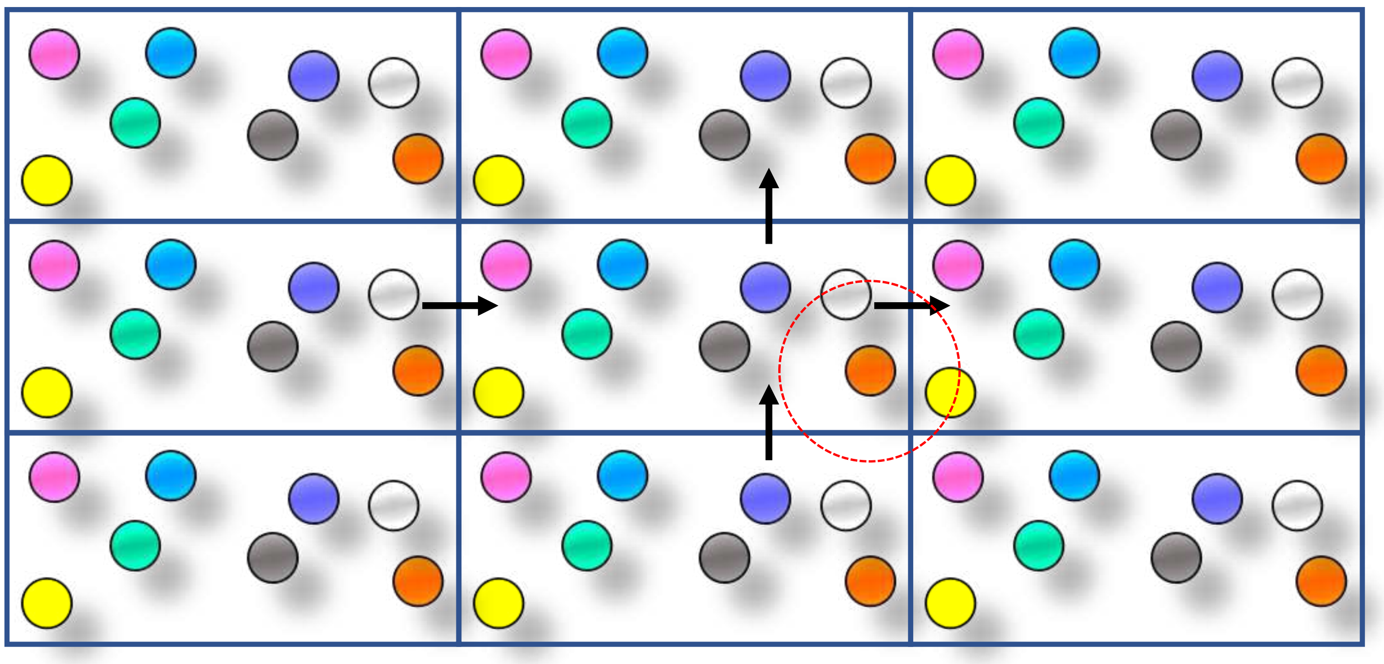
Velocities at time $t+\frac{1}{2}\delta t$ is used to calculate position at time t.
Velocity leaps over position and position leaps over velocity

velocities are calculated explicitly

Position and velocity are not calculated at the same time

Periodic boundary condition

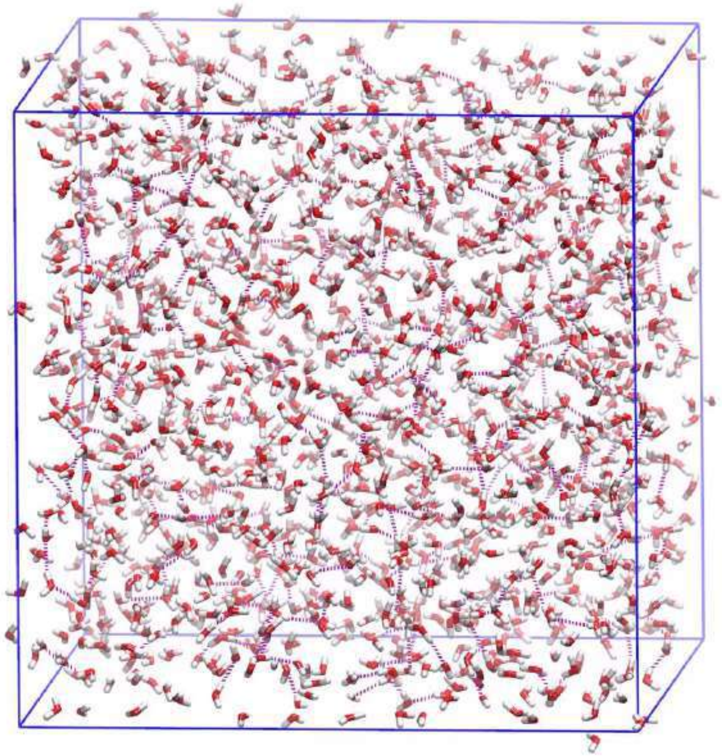
Periodic boundary conditions enable a simulation to be performed using a relatively small number of particles in such a way that the particles experience forces as if they are in a larger volume



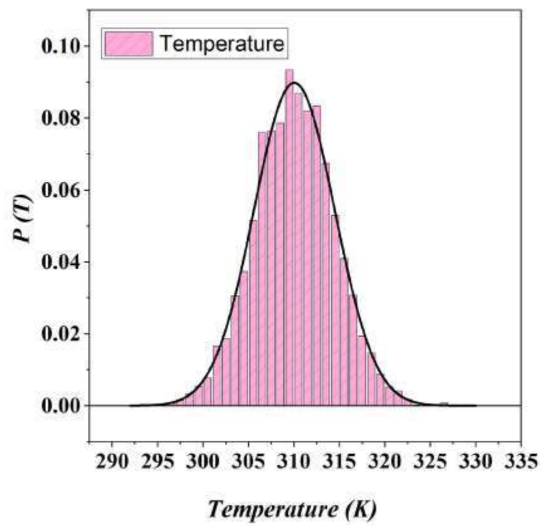
Ergodic hypothesis: Simulation of a water-box

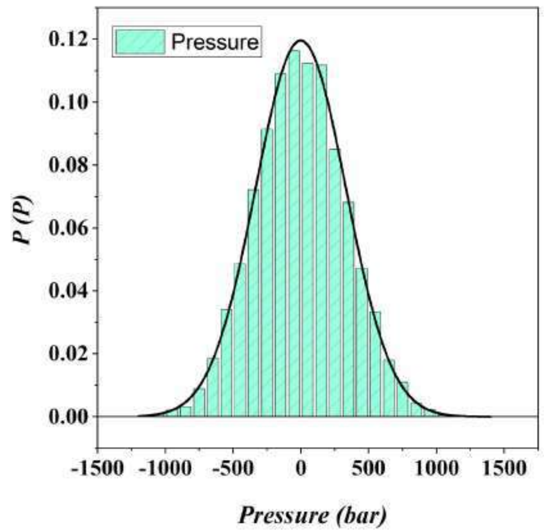
Initial conditions:

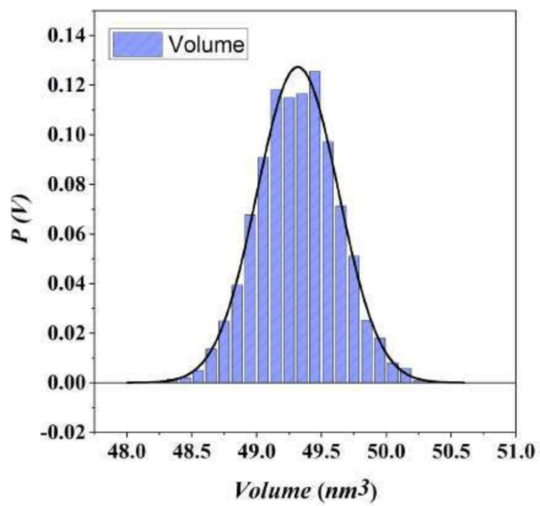
- 6136 water molecules
- Cubic box of edge length of 3.67 nm (Volume ~ 49 nm^3)
- Pressure: 1.01325 bar
- Temperature: 310 K
- Simulation time: 1ns
- Water model: TIP3P



Statistics of temperature, pressure and volume





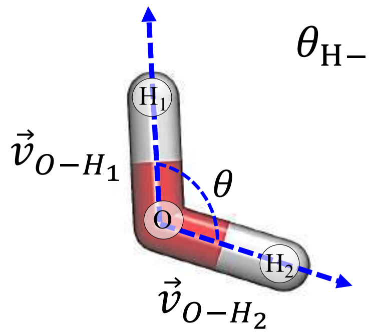


$$\langle T \rangle = 310.032\ K$$

$$\langle P \rangle = 1.13\ bar$$

$$\langle V \rangle = 49.32\ nm^3$$

Ergodic hypothesis: Distributions of H-O-H angle in water



$$\theta_{\mathrm{H-O-H}} = \cos^{-1}(\vec{v}_{O-H_1} \cdot \vec{v}_{O-H_2})$$

Time

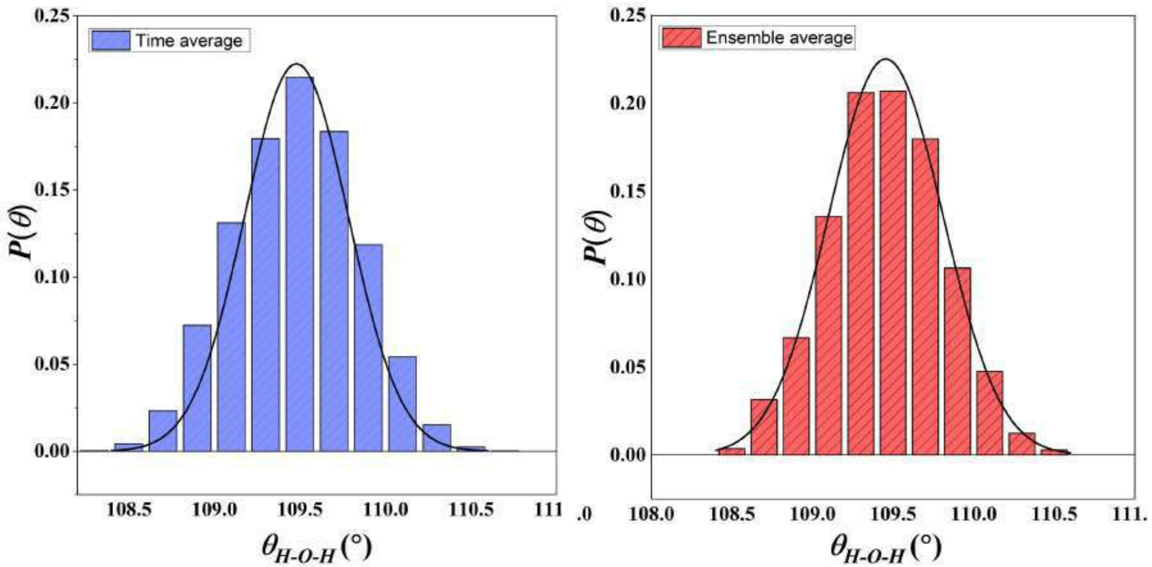
Ensemble

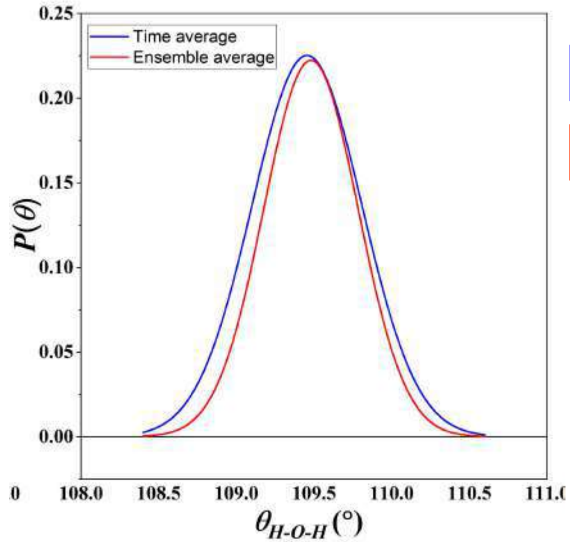
	t_1	t_2	t_3	t_4	.....	t_n
w_1	θ	θ	θ	θ	.....	θ
w_2	θ	θ	θ	θ	.....	θ
w_3	θ	θ	θ	θ	.....	θ
⋮	⋮	⋮	⋮	⋮	⋮	⋮
w_N	θ	θ	θ	θ	.....	θ

Time average

$$\langle\theta\rangle_t = \lim_{t\to\infty} \frac{1}{t_n}\int_0^{t_n} \theta(t)dt$$

Ensemble average $\langle\theta\rangle_N = \lim_{N\to\infty} \frac{1}{N}\sum_{i=1}^{N} \theta(i)$

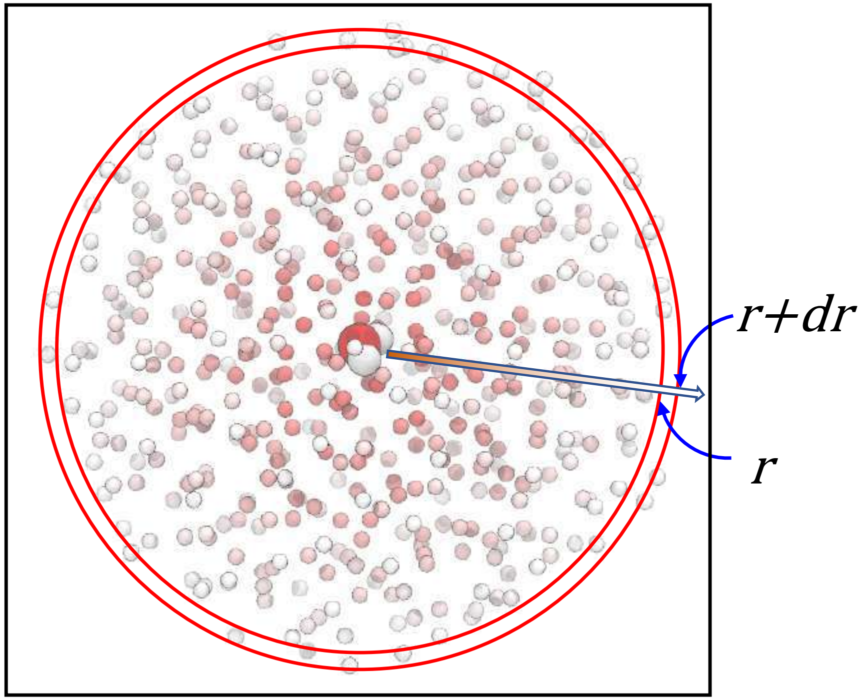




$\langle\boldsymbol{\theta}\rangle_t = \mathbf{109.47°}$

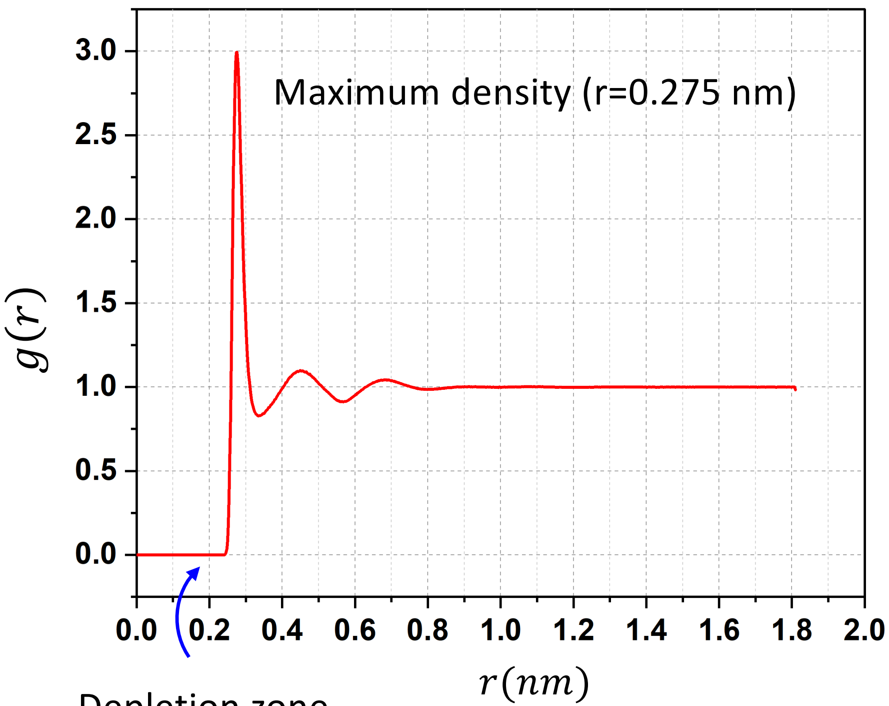
$\langle\boldsymbol{\theta}\rangle_N = \mathbf{109.45}$

Calculation of radial distribution function (g(r)):



$$g(r) = \frac{\rho_r}{\rho_{r_{Bulk}}} \qquad \rho_r = \frac{dN_r}{4\pi r^2 dr} = \frac{N_{r+dr} - N_r}{4\pi r^2 dr}$$

$N_r = No.\, of\ water\ oxygen\ atoms\ \ in\ the\ sphere\ of\ radius\ r$
$surrounding\ a\ central\ water\ oxygen\ atom$



$$4\pi r^2 g(r)\rho_{r_{Bulk}} dr = dN_r$$

$$4\pi\rho_{r_{Bulk}} \int g(r) r^2 dr = \int dN_r = N_r$$

Coordination number

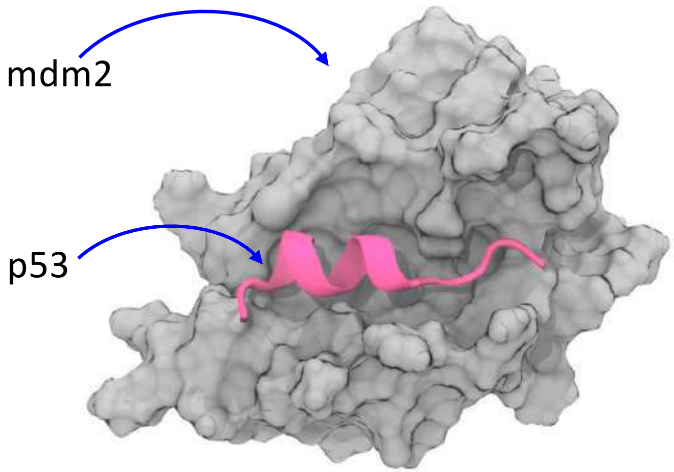
Depletion zone

$[> 2r_{O-H}\ (r_{O-H} = 0.095\ nm)]$

Simulation of protein-peptide complex

- p53 regulates the DNA repairing or apoptosis (removal of diseased cell) in response to different stresses
- mdm2 is overexpressed in cancerous cells to bind to p53 and inhibit its function to ensure tumor progression
- Cross-stitched peptides are designed to replace p53 and bind to mdm2
- For that, these must have higher binding affinity with mdm2 than the natural binding partner.

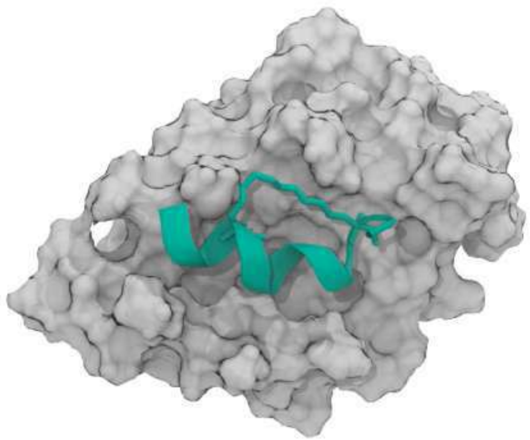
mdm2 + p53 (natural binding partner)



ΔH	-62.34
TΔS	- 53.88
ΔG	-8.46 ± 0.69

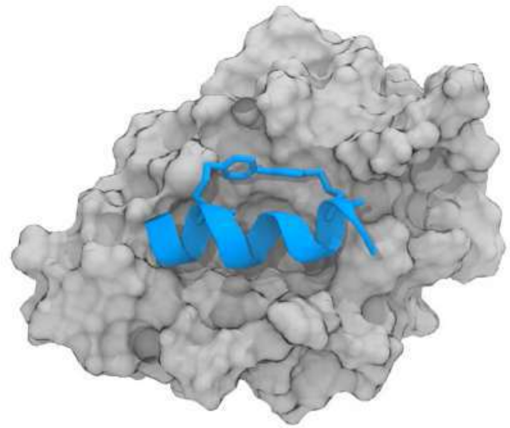
Unit: kcal/mol

mdm2 + **designed peptide inhibitor**

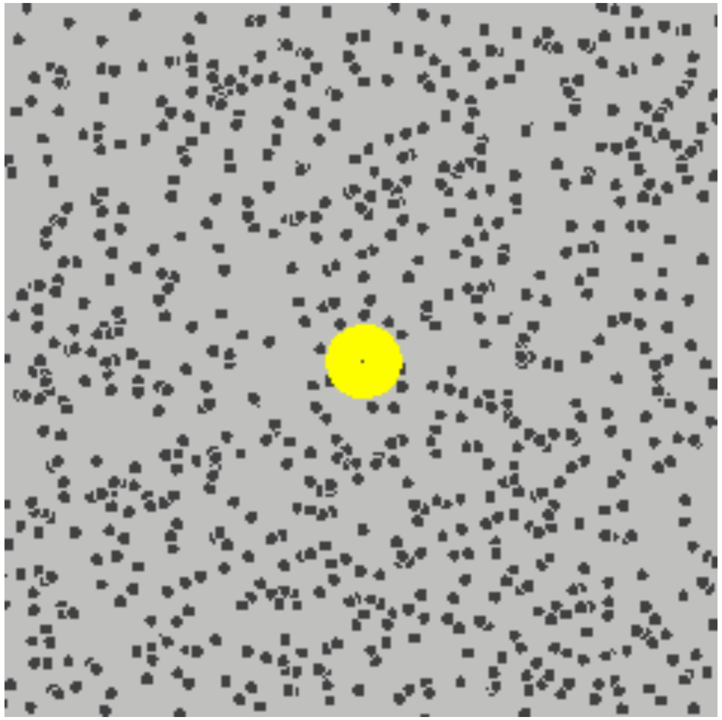


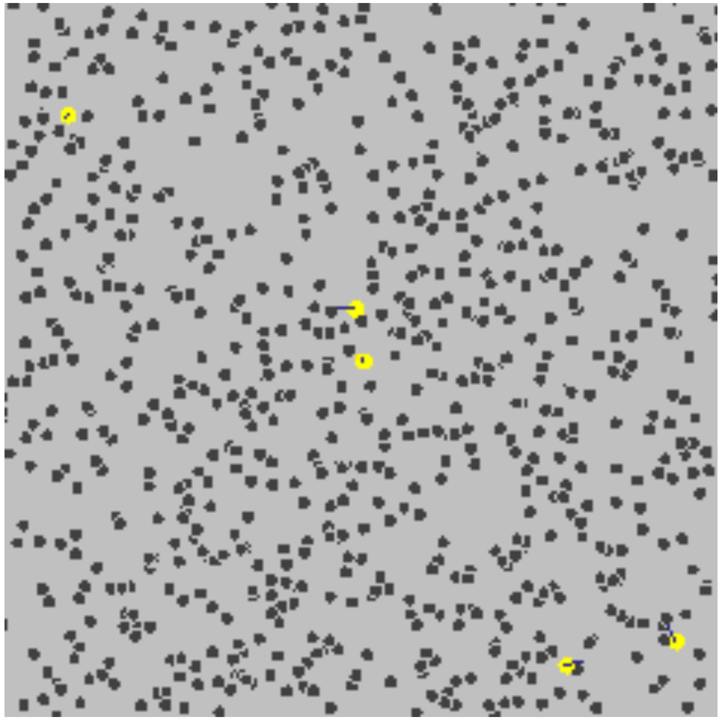
ΔH	-56.53
TΔS	- 26.41
ΔG	-30.12 ± 2.97

mdm2 + **designed peptide inhibitor**



ΔH	-54.65
TΔS	- 15.95
ΔG	-38.70 ± 2.46



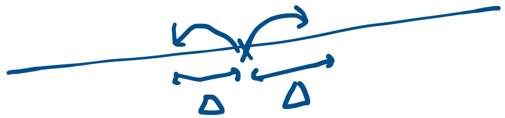


Einstein
1905

$n \to$ number of particles

$dn \to$ No. of particles which experience a displacement between Δ and $\Delta + d\Delta$ in time interval $\tau \longrightarrow$ is small compared to observation time but larger than any correlation time

For Simplicity take 1D motion



$x(t)$
$x(t+\tau)$ $\Big\}$ they are uncorrelated

$$\frac{dn}{n} = \phi(\Delta)\, d\Delta$$

$\rightsquigarrow$ probability of jump

$$\circledast \quad \int_{-\infty}^{+\infty} \phi(\Delta)\, d\Delta = 1$$

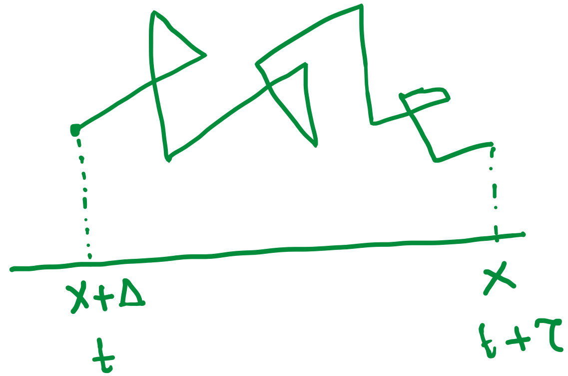
$$\circledast \quad \phi(-\Delta) = \phi(\Delta)$$

"Even" function

$\nu = f(x,t)$

$\hookrightarrow$ No. of particles per unit vol^m at time "t"

$$f(x,t+\tau) = \int_{-\infty}^{+\infty} f(x+\Delta,t)\,\phi(\Delta)\,d\Delta$$



$\downarrow$

Taylor expansion

$$f(x,t) + \tau \frac{\partial f(x,t)}{\partial t} = \int_{-\infty}^{+\infty} \left\{ f(x,t) + \Delta \frac{\partial f}{\partial x} + \frac{\Delta^2}{2!}\frac{\partial^2 f}{\partial x^2} + \cdots \right\} \phi(\Delta)\,d\Delta$$

$$= \int_{-\infty}^{+\infty} f(x,t)\,\phi(\Delta)\,d\Delta + \underbrace{\int_{-\infty}^{+\infty} \left(\frac{\partial f}{\partial x}\right) \Delta\,\phi(\Delta)\,d\Delta}_{0 \quad \langle\Delta\rangle} + \int_{-\infty}^{+\infty} \left(\frac{\partial^2 f}{\partial x^2}\right) \frac{\Delta^2}{2!}\,\phi(\Delta)\,d\Delta$$

$$\cancel{f(x,t)} + \tau \frac{\partial f}{\partial t} = \cancel{f(x,t)} + \int_{-\infty}^{+\infty} \frac{\Delta^2}{2!}\,\phi(\Delta)\,d\Delta \left(\frac{\partial^2 f}{\partial x^2}\right)$$

$$\frac{\partial f(x,t)}{\partial t} = \underbrace{\int_{-\infty}^{+\infty} \frac{\Delta^2}{2!\,\tau}\,\phi(\Delta)\,d\Delta}_{D \text{ (Diffusion coefficient)}}\ \frac{\partial^2 f}{\partial x^2}$$

$$\boxed{\frac{\partial f(x,t)}{\partial t} = D\,\frac{\partial^2 f}{\partial x^2}}$$

$\leftarrow$ "Einstein's Diffusion equation"

"Initial value problem"

$$i\hbar\,\frac{\partial \psi}{\partial t} = H\psi = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\psi \implies \boxed{\frac{\partial \psi}{\partial t} = +\frac{i\hbar}{2m}\,\frac{\partial^2 \psi}{\partial x^2}}$$

$\hookrightarrow$ Schrödinger eqⁿ for a free particle

"Boundary value problem"

$\hookrightarrow$ Solving it using separation in variables technique

$$f(x,0) = n\,\delta(x)$$

$\hookrightarrow$ "Dirac Delta function"

$f(x,0) = n\delta(x)$

$$\delta(x) = 0 \quad x \neq 0$$
$$= \infty \quad x = 0$$

$$f(x_0) = \int_{-\infty}^{+\infty} f(x)\,\delta(x - x_0)\,dx$$

Fourier representation of Delta function

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ikx}\,dk$$

$$f(x,t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \tilde{f}(k,t)\, e^{ikx}\,dk$$

representing this as the Fourier transform of $\tilde{f}(k,t)$

$$\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2}$$

$$\frac{\partial f(x,t)}{\partial t} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \frac{\partial \tilde{f}(k,t)}{\partial t}\, e^{ikx}\,dk \quad \cdots\cdots \text{(A)}$$

$$\|$$

$$D\frac{\partial^2 f}{\partial x^2} = \frac{1}{2\pi} D\int_{-\infty}^{+\infty} \tilde{f}(k,t)\,(ik)^2 e^{ikx}\,dk = \frac{+D}{2\pi}\int_{-\infty}^{+\infty} \tilde{f}(k,t)\,(-k^2)\, e^{ikx}\,dk \quad \cdots \text{(B)}$$

$\equiv$

$$\frac{\partial \tilde{f}(k,t)}{\partial t} = -Dk^2\tilde{f}(k,t)$$

$$\frac{\partial \tilde{f}(k,t)}{\partial t} = -Dk^2 \tilde{f}(k,t)$$

$$\tilde{f}(k,t) = \tilde{f}(k,0)\, e^{-Dk^2 t}$$

$f(x,0) = n\,\delta(x)$ (initial condition)

$$f(x,0) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ikx}\, \tilde{f}(k,0)\, dk$$

$$|||$$

$$f(x,0) = n\,\frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ikx}\, dk$$

$$\tilde{f}(k,0) = n$$

$$\tilde{f}(k,t) = n\, e^{-Dk^2 t}$$

$$f(x,t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \tilde{f}(k,t)\, e^{ikx}\, dk$$

$$f(x,t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} n\, e^{-Dk^2 t}\, e^{ikx}\, dk = \frac{n}{2\pi}\int_{-\infty}^{+\infty} e^{-Dk^2 t}\, e^{ikx}\, dk$$

$$f(x,t) = \frac{n}{2\pi}\int_{-\infty}^{+\infty} e^{-Dk^2t} e^{ikx}\, dk = \frac{n}{2\pi}\int_{-\infty}^{+\infty} e^{-\left\{(k\sqrt{Dt})^2 - 2k\sqrt{Dt}\,\frac{1}{2}\frac{ix}{\sqrt{Dt}} + \frac{x^2 i^2}{4Dt}\right\}} e^{-x^2/4Dt}\, dk$$

$$= \frac{n}{2\pi} e^{-x^2/4Dt}\int_{-\infty}^{+\infty} e^{-\left(k\sqrt{Dt} - \frac{ix}{2\sqrt{Dt}}\right)^2} dk$$

Let, $y = k\sqrt{Dt} - \frac{ix}{2\sqrt{Dt}}$

$dy = dk\sqrt{Dt}$

$$= \frac{n}{2\pi} e^{-x^2/4Dt}\int_{-\infty}^{+\infty} e^{-y^2} \frac{dy}{\sqrt{Dt}}$$

$$\left[\int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = (\pi/\alpha)^{\frac{1}{2}}\right]$$

$$= \frac{n}{2\pi} e^{-x^2/4Dt} \frac{1}{\sqrt{Dt}}\sqrt{\pi}$$

$$f(x,t) = \frac{n}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \rightarrow \text{"Probability density"}$$

$n=1$

$$f(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}$$

$$f(r,t) = \frac{1}{\sqrt{4\pi D t}} e^{-x^2/4Dt}$$

$\langle x \rangle = 0$, all the odd moments are zero and all the even moments are non-zero

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 \frac{1}{\sqrt{4\pi D t}} e^{-x^2/4Dt}\, dx$$

$$I = \int_{-\infty}^{+\infty} e^{-\alpha x^2} dx = \left(\pi/\alpha\right)^{\frac{1}{2}}$$

$$\frac{\partial I}{\partial \alpha} = -\int_{-\infty}^{+\infty} e^{-\alpha x^2} x^2\, dx$$

$$= \frac{1}{\sqrt{4\pi D t}} \int_{-\infty}^{+\infty} x^2 e^{-x^2/4Dt}\, dx \qquad \alpha \equiv \frac{1}{4Dt}$$

$$= -\frac{1}{2\alpha}\left(\pi/\alpha\right)^{\frac{1}{2}}$$

$$= \frac{1}{\sqrt{4\pi D t}} \frac{1}{2 \cdot \frac{1}{4Dt}} \left(\pi / \tfrac{1}{4Dt}\right)^{\frac{1}{2}}$$

$$\int_{-\infty}^{+\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha}\left(\pi/\alpha\right)^{\frac{1}{2}}$$

$$= \frac{1}{\cancel{\sqrt{4\pi D t}}} 2Dt \cancel{\sqrt{4\pi D t}}$$

$$\langle x^2 \rangle = 2Dt \rightarrow \text{Diffusive}$$

Mean Square displacement

$$\lambda_x = \sqrt{\langle x^2 \rangle} \sim \sqrt{2D}\, t^{1/2}$$

Mean displacement

For Newtonian particle moving with constant velocity $\lambda_x \sim v t$ $\qquad \lambda_x^2 \sim t^2$ (Ballistic)

Diffusion & Mobility (1-Dimension)

f = force of gravity

○ Spherical particle of radius r is moving under the force of gravity in a liquid.

↓

Coefficient of viscosity "η"

Viscous drag

$$= 6\pi\eta r v_0 \leftarrow \text{"Stokes law"}$$

When this external force 'f' balances the viscous drag, then the particle moves with the constant velocity v_0

$$f = 6\pi\eta r v_0$$

$$v_0 = \frac{f}{6\pi\eta r}$$

If ν is the number of particles per unit volume, then $\nu v_0 \rightarrow$ no. of particles passing through a unit area per unit time $\Rightarrow \dfrac{\nu f}{6\pi\eta r}$

$-D\frac{\partial \nu}{\partial x}$ → Fick's law (first law)

↳ "Diffusion flux"

→ no. of particles per unit area per unit time

D → "Diffusion coefficient"

f → force due to gravity

Boltzmann distribution of ν (Density)

$$\boxed{\nu = \nu_0 \exp\left[-\frac{f(x-x_0)N_A}{RT}\right]} \quad \cdots \text{I}$$

$$-D\frac{\partial \nu}{\partial x} = \frac{\nu f}{6\pi\eta r}$$

$$-\int_{\nu_0}^{\nu}\frac{d\nu'}{\nu'} = \frac{f}{6\pi\eta r D}\int_{x_0}^{x} dx'$$

$$\Rightarrow \quad \ln(\nu/\nu_0) = -\frac{f}{6\pi\eta r D}(x-x_0)$$

$$\Rightarrow \quad \boxed{\nu = \nu_0 \exp\left[-\frac{f(x-x_0)}{6\pi\eta r D}\right]} \quad \cdots \text{II}$$

Comparing I & II

$$\boxed{\frac{N_A}{RT} = \frac{1}{6\pi\eta r D}}$$

$$\boxed{D = \frac{RT}{N_A}\cdot B}$$

$$B = \frac{1}{6\pi\eta r}$$

↳ Mobility

$$\boxed{D = k_B T B}$$

$$\boxed{D = \frac{k_B T}{6\pi\eta r}}$$

Stokes-Einstein relation

Determination of Avagadro's number:

$$D = \frac{RT}{N_A} \frac{1}{6\pi\eta r}$$

$$\lambda_x = \sqrt{2Dt}$$

$$\langle x^2 \rangle = 2Dt$$

$$\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$$

$$\downarrow$$

$$\lambda_x$$

$$\lambda_x = \sqrt{2t}\left(\frac{RT}{N_A}\right)^{\frac{1}{2}} \left(\frac{1}{6\pi\eta r}\right)^{\frac{1}{2}}$$

↳ to find N_A

Experimentally can be measured

$\eta \rightarrow$ known for liquids

At the single particle level

Force (Newton's equation)

$$m\frac{dv}{dt} = -6\pi\eta r v$$

$$v = v_0 \exp\left(-\frac{6\pi\eta r}{m}t\right)$$

$$\ln\left(v/v_0\right) = -\frac{6\pi\eta r}{m}t$$

$$t_{1/10} \equiv v/v_0 = \frac{1}{10}$$

$$\ln 10 = \frac{6\pi\eta r}{m}t_{1/10}$$

$$\Rightarrow t_{1/10} = 3.3\times 10^{-7}\text{ sec}$$

$$\sim 10^{-7}\text{ sec}$$

Plantinum particles

$r = 2.5\times 10^{-6}$ cm

$\eta = 0.01$ poise (water)

$m = 2.5\times 10^{-15}$ g

Within very short time the particle nearly completely losses its original velocity $\rightarrow$ In reality it does not happen!!

$$m\frac{dv}{dt} = -6\pi\eta r v + F(t)$$ → random kicks

↳ random function of time ≡ Noise

1908

Langevin eqn

"Paul Langevin"

$$\langle F(t)\rangle = 0 \qquad \langle F(t)F(t')\rangle = 2C'\delta(t-t')$$

$$m\ddot{x} = -6\pi\eta r\dot{x} + F(t)$$

$$\dot{x} = v$$

$$\ddot{x} = \dot{v} = \frac{dv}{dt}$$

Multiplying both sides by x

$$m x\ddot{x} = -6\pi\eta r\, x\dot{x} + xF(t)$$

$$\Rightarrow \quad x\ddot{x} = -\underbrace{\frac{6\pi\eta r}{m}}_{\Gamma} x\dot{x} + \frac{1}{m}xF(t)$$

$$x\ddot{x} = -\Gamma x\dot{x} + \frac{1}{m} x F(t)$$

$$\frac{1}{2}\ddot{x^2} - (\dot{x})^2 = -\Gamma x\dot{x} + \frac{1}{m} x F(t)$$

$$\Rightarrow \ddot{x^2} - 2(\dot{x})^2 = -2\Gamma x\dot{x} + \frac{2}{m} x F(t)$$

$$\Rightarrow \ddot{x^2} - 2(\dot{x})^2 = -\Gamma \dot{x^2} + \frac{2}{m} x F(t) \Rightarrow \frac{d^2}{dt^2}(x^2) - 2\left(\frac{dx}{dt}\right)^2 = \cdots\cdots$$

Taking the averages on both sides

$$\frac{d^2}{dt^2}\langle x^2\rangle - 2\langle \dot{x}^2\rangle = -\Gamma \frac{d}{dt}\langle x^2\rangle + \frac{2}{m}\langle x F(t)\rangle$$

$-2\langle v^2\rangle \rightarrow \frac{2k_BT}{m}$

Zero (position and the random force are uncorrelated)

$$\dot{x^2} = \frac{d}{dt}(x^2)$$

$$= 2x\dot{x}$$

$$\ddot{x^2} = \frac{d^2}{dt^2}(x^2)$$

$$= \frac{d}{dt}(2x\dot{x})$$

$$\ddot{x^2} = 2(\dot{x})^2 + 2x\ddot{x}$$

$$\Rightarrow x\ddot{x} = \frac{1}{2}\ddot{x^2} - (\dot{x})^2$$

$$\frac{d^2}{dt^2}\langle x^2\rangle + \Gamma \frac{d}{dt}\langle x^2\rangle - \frac{2k_BT}{m} = 0$$

Let, $\frac{d}{dt}\langle x^2\rangle = y$

$\frac{2k_BT}{m} = c$

$$\dot{y} + \Gamma y - c = 0$$

Let, $\Gamma y - c = y'$ (not derivative)

$$\dot{y} = -y' \implies \dot{y} = \frac{1}{\Gamma}\dot{y}'$$

$$\dot{y}' = \Gamma\dot{y} + 0$$

$$\dot{y}' = \Gamma\dot{y}$$

$$\dot{y}' = -\Gamma y' \quad (\text{as } \dot{y} = -y')$$

$$\implies \frac{dy'}{dt} = -\Gamma y'$$

$\dot{x} = -\Gamma x$

$$\implies \int_{y'(t=0)}^{y'} \frac{dy'}{y'} = -\Gamma\int_0^t dt' \implies$$

$$y' = Ae^{-\Gamma t} \qquad A = y'(t=0)$$

$$y = \frac{d}{dt}\langle x^2 \rangle$$

$$\Gamma y - C = y' = A e^{-\Gamma t}$$

$$\Rightarrow y = \frac{C}{\Gamma} + \frac{A}{\Gamma} e^{-\Gamma t}$$

$$\frac{d}{dt}\langle x^2 \rangle = \frac{C}{\Gamma} + \frac{A}{\Gamma} e^{-\Gamma t}$$

Integrating

$$\langle x^2 \rangle = \frac{C}{\Gamma} t + \frac{A}{\Gamma} \int_0^t e^{-\Gamma t'} dt'$$

$$\langle x^2 \rangle = \frac{C}{\Gamma} t + A/\Gamma \left. \frac{e^{-\Gamma t'}}{-\Gamma} \right|_0^t = \frac{C}{\Gamma} t + \frac{A}{\Gamma^2}\left(1 - e^{-\Gamma t}\right)$$

$$\langle x^2 \rangle = \frac{C}{\Gamma} t + \frac{A}{\Gamma^2}\left(1 - e^{-\Gamma t}\right)$$

$$y'(0) = A$$

$$\Gamma y(0) - C = A$$

$$y(0) = \left(\frac{d}{dt}\langle x^2 \rangle\right)_{t=0}$$

$$= 0$$

$$A = -C$$

$$\langle x^2\rangle = \frac{c}{\Gamma}t + \frac{(-c)}{\Gamma^2}\left(1-e^{-\Gamma t}\right) \qquad c = \frac{2k_BT}{m}$$

$$\langle x^2\rangle = \frac{2k_BT}{m\Gamma}t - \frac{2k_BT}{m\Gamma^2}\left(1-e^{-\Gamma t}\right)$$ → general expression for the mean square displacement of a Brownian particle suspended in a fluid (no external force)

When $t \to \infty$ (long time limit)

$$\langle x^2\rangle = \frac{2k_BT}{m\Gamma}t - \frac{2k_BT}{m\Gamma^2}(1-0)$$

$$\langle x^2\rangle \simeq \frac{2k_BT}{m\Gamma}t = \frac{2k_BT}{m\frac{6\pi\eta r}{m}}t = 2\left(\frac{k_BT}{6\pi\eta r}\right)t$$

$$\langle x^2\rangle = 2Dt$$

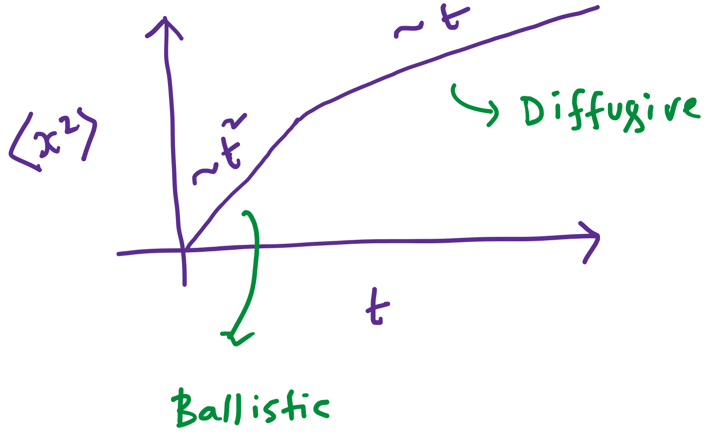
$$\langle x^2\rangle = \frac{2k_BT}{m\Gamma}t - \frac{2k_BT}{m\Gamma^2}\left(1-\left(1-\Gamma t+\frac{\Gamma^2t^2}{2!}+\cdots\right)\right)$$

$t \to 0$ (short time limit)

$$\langle x^2\rangle = \frac{2k_BT}{m\Gamma} t - \frac{2k_BT}{m\Gamma^2}\left(\cancel{1} - \cancel{1} + \Gamma t - \frac{\Gamma^2 t^2}{2} \cdots\cdots\right)$$

$$= \cancel{\frac{2k_BT}{m\Gamma}} t - \frac{2k_B\cancel{T}}{\cancel{m}\Gamma} t + \frac{k_BT}{m} t^2 \cdots\cdots$$

$$\langle x^2\rangle = \frac{k_BT}{m} t^2 \rightarrow$$ Ballistic → inertia driven



A Langevin description without inertia (large viscosity limit).

$$6\pi\eta r \dot{x} = F(t) \rightarrow \langle x^2\rangle \sim t$$

"no ballistic"

Relation between the random and the viscous force: The fluctuation-dissipation theorem (FDT)

Langevin equation

$$\frac{dv}{dt} = -\frac{6\pi\eta r v}{m} + \frac{F(t)}{m}$$

$$\Gamma = \frac{6\pi\eta r}{m}$$

$$\frac{dv}{dt} = -\Gamma v + \frac{F(t)}{m}$$

Multiplying both sides by v

$$\frac{d}{dt}v^2 = 2v\frac{dv}{dt}$$

$$v\frac{dv}{dt} = -\Gamma v^2 + \frac{1}{m}vF(t)$$

$$\Downarrow$$

$$\frac{d}{dt}v^2 = -2\Gamma v^2 + \frac{2}{m}vF(t)$$

Taking ensemble average

$$\frac{d}{dt}\langle v^2\rangle = -2\Gamma\langle v^2\rangle + \underbrace{\frac{2}{m}\langle v F(t)\rangle}_{\text{How to evaluate ??}}$$

Now $$\int_{t-\Delta t}^{t} \dot{v}(t')\,dt' = v(t) - v(t-\Delta t) \Rightarrow v(t) = v(t-\Delta t) + \int_{t-\Delta t}^{t} \dot{v}(t')\,dt'$$

Multiplying both sides by $F(t)$ and taking average

$$\langle F(t)\,v(t)\rangle = \underbrace{\langle F(t)\,v(t-\Delta t)\rangle}_{=0} + \int_{t-\Delta t}^{t} \langle F(t)\,\dot{v}(t')\rangle\,dt'$$

$= 0$ [as the velocity at earlier instant, $v(t-\Delta t)$ $t-\Delta t < t$, has no dependence on the future fluctuating force]

$$\langle F(t)\,v(t)\rangle = \int_{t-\Delta t}^{t} \langle F(t)\,\dot{v}(t')\rangle\,dt'$$

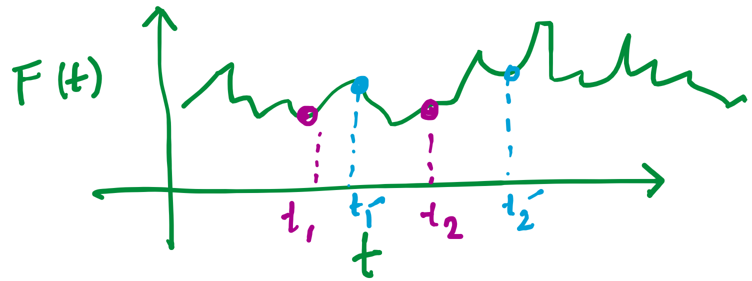
$$\langle F(t)\, v(t)\rangle = \int_{t-\Delta t}^{t} \langle \dot{v}(t')\, F(t)\rangle\, dt'$$

$$= \int_{t-\Delta t}^{t} \left\langle \left(-\Gamma v(t') + \frac{F(t')}{m}\right) F(t)\right\rangle dt'$$

$$= -\Gamma \int_{t-\Delta t}^{t} \underbrace{\langle v(t')\, F(t)\rangle\, dt'}_{?} + \frac{1}{m}\int_{t-\Delta t}^{t} \langle F(t')\, F(t)\rangle\, dt'$$

Since t' is the earlier time $(<t)$
and the fluctuating force is
at a later time t has no dependence
on velocity at earlier time t', except
at $t=t'$, for which the integral is 0.

$$\langle v(t)F(t)\rangle = \frac{1}{m}\int_{t-\Delta t}^{t}\langle F(t)F(t')\rangle dt'$$



$\Delta t = t_2 - t_1 = t_2' - t_1'$

(time translation invariance)

We assume that F(t) is stationary in time. This means the value of the integral depends on the difference $t - t'$ but not on t and t' individually.

$$\langle v(t)F(t)\rangle = \frac{1}{2m}\int_{t-\Delta t}^{t+\Delta t}\langle F(t)F(t')\rangle dt'$$

$$= \frac{1}{2m}\int_{t-\Delta t}^{t+\Delta t}\langle F(t)F(t+s)\rangle ds \quad ; \; t = t'+s$$

$$= \frac{1}{2m}\int_{-\infty}^{+\infty}\langle F(0)F(s)\rangle ds$$

(I) Since $\Delta t \gg (t'-t=s)$ we put $\Delta t \sim \infty$

(II) Without any loss of generality we put $t=0$

We had

$$\frac{d}{dt}\langle v^2\rangle = -2\Gamma\langle v^2\rangle + \frac{2}{m}\langle v(t)\,F(t)\rangle$$

$\langle v^2\rangle = \frac{k_BT}{m}$

$$0 = -2\Gamma\langle v^2\rangle + \frac{2}{m}\,\frac{1}{2m}\int_{-\infty}^{+\infty}\langle F(0)F(s)\rangle\,ds$$

$$= -2\Gamma\,\frac{k_BT}{m}$$

$$\boxed{\Gamma = \frac{1}{2k_BTm}\int_{-\infty}^{+\infty}\langle F(0)\,F(s)\rangle\,ds}$$

Dissipation

Correlation betn the random forces

FDT

(Fluctuation Dissipation theorem)

Recall

$\langle F \quad \Gamma \quad = 2c'L$

Balance betn Dissipation & fluctuation

$$\langle F(0)F(s)\rangle = 2C'\delta(s)$$

$$\int \delta(s)\,ds = 1$$

$$\Gamma = \frac{1}{2k_BTm}\int_{-\infty}^{+\infty} 2C'\delta(s)\,ds = \frac{C'}{k_BTm}$$

$$C' = \Gamma k_B T m = \frac{6\pi\eta r}{m} k_B T m$$

$$C' = 6\pi\eta r k_B T \rightarrow \text{Special form of FDT}$$

$$\langle F(t)F(t')\rangle = 2\gamma k_B T \delta(t-t') \quad ; \quad \gamma = 6\pi\eta r$$

friction coefficient

Brownian Motion in velocity space:

Recall, in the co-ordinate space

$\Delta \to$ jump in coordinate space

$$f(x, t+\tau) = \int_{-\infty}^{+\infty} f(x+\Delta, t)\, \phi(\Delta)\, d\Delta$$

$$\Rightarrow \frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}$$

"Einstein's Diffusion equation"

Velocity space

$$f(v, t+\tau) = \int_{-\infty}^{+\infty} f(v-\Delta, t)\, \underbrace{\phi(v-\Delta, \Delta)}_{\text{jump probabity}}\, d\Delta$$

L.H.S.

$$f(v,t)+\tau\frac{\partial f}{\partial t}+\frac{\tau^2}{2}\frac{\partial^2 f}{\partial t^2}+\cdots$$

$\Delta \equiv$ has the dimension of velocity

$$\int_{-\infty}^{+\infty} d\Delta\, \phi(v,\Delta)=1$$

R.H.S (integrand)

$$\left(f(v,t)-\Delta\frac{\partial f}{\partial v}+\frac{\Delta^2}{2}\frac{\partial^2 f}{\partial v^2}\right)\left(\phi(v,\Delta)-\Delta\frac{\partial\phi}{\partial v}+\frac{\Delta^2}{2}\frac{\partial^2\phi}{\partial v^2}\cdots\right)$$

$$=\Big(f(v,t)\phi(v,\Delta)-\Delta\frac{\partial f}{\partial v}\phi(v,\Delta)+\frac{\Delta^2}{2}\frac{\partial^2 f}{\partial v^2}\phi(v,\Delta)\ \cdots$$

$$=f(v,t)\phi(v,\Delta)-\Delta\frac{\partial f}{\partial v}\phi(v,\Delta)$$

$$\text{R.H.S}=f(v,t)\underbrace{\int_{-\infty}^{+\infty}\phi(v,\Delta)\,d\Delta}_{=1}-\frac{\partial}{\partial v}\left[f(v,t)\int_{-\infty}^{+\infty}\Delta\,\phi(v,\Delta)\,d\Delta\right]+\frac{\partial^2}{\partial v^2}\left[f(v,t)\int_{-\infty}^{+\infty}\frac{\Delta^2}{2}\phi(v,\Delta)\,d\Delta\right]$$

$$\frac{\partial f}{\partial t}=-\frac{\partial}{\partial v}\left[f(v,t)\underbrace{\frac{1}{\tau}\int_{-\infty}^{+\infty}\Delta\,\phi(v,\Delta)\,d\Delta}_{M_1(v)\,\equiv\,\frac{\langle\Delta\rangle}{\tau}}\right]+\frac{\partial^2}{\partial v^2}\left[f(v,t)\underbrace{\int_{-\infty}^{+\infty}\frac{\Delta^2}{2\tau}\phi(v,\Delta)\,d\Delta}_{M_2(v)}\right]$$

$$\frac{\partial f(v,t)}{\partial t} = -\frac{\partial}{\partial v} \underbrace{M_1(v)}_{\text{Drift term}} f(v,t) + \frac{\partial^2}{\partial v^2} \underbrace{M_2(v)}_{\text{Diffusion term}} f(v,t)$$

(in velocity) → Fokker-Planck equation.

Calculation of $M_1(v)$

$$\frac{dv}{dt} = -\Gamma v + \frac{F(t)}{m}$$

$$dv = -\Gamma v\,dt + \frac{F(t)}{m}\,dt$$

$$\Rightarrow dv = -\Gamma v\,dt$$

Integrating betn t and $t+\tau$

$$\left(v(t+\tau) - v(t) \right) = -\Gamma v \tau + \frac{1}{m}\int_t^{t+\tau} F(t')\,dt'$$

$$\Delta = -\Gamma v \tau + \frac{1}{m}\int_t^{t+\tau} F(t')\,dt'$$

$\to 0$

Take average $\langle \Delta \rangle = -\Gamma v \tau$

$\langle F(t') \rangle = 0$

$$\langle \Delta \rangle = -\Gamma v \tau$$

$$\frac{\langle \Delta \rangle}{\tau} = -\Gamma v$$

↳ Drift term

Calculation of $M_2(v)$:

$$\Delta = -\Gamma v \tau + \frac{1}{m}\int_t^{t+\tau} F(t')\,dt'$$

$$\Delta^2 = +\Gamma^2 v^2 \tau^2 - \frac{2\Gamma v \tau}{m}\int_t^{t+\tau} F(t')\,dt' + G_t^2(\tau)$$

$$G_t(\tau) = \frac{1}{m}\int_t^{t+\tau} F(t')\,dt'$$

τ is small, hence the first term can be neglected, $\langle F(t')\rangle = 0$

$$\langle \Delta^2 \rangle = \frac{1}{m^2}\int_t^{t+\tau} dt' \int_t^{t+\tau} \langle F(t')F(t'')\rangle\,dt''$$

$$\langle \Delta^2 \rangle = \frac{1}{m^2} \int_t^{t+\tau} dt' \int_t^{t+\tau} dt'' \langle F(t') F(t'') \rangle$$

$$= \frac{1}{m^2} 2C' \int_t^{t+\tau} dt' \int_t^{t+\tau} dt'' \, \delta(t'-t'')$$

$$\langle \Delta^2 \rangle = \frac{2C'\tau}{m^2}$$

$$\frac{\langle \Delta^2 \rangle}{2\tau} = \frac{C'}{m^2} \longleftarrow$$

Diffusion coefficient in the velocity space

$$\frac{dv}{dt} = -\Gamma v + \frac{1}{m} F(t)$$

Integrate using integrating factor

$$v(t) = v(0) e^{-\Gamma t} + \frac{e^{-\Gamma t}}{m} \int_0^t e^{\Gamma t'} F(t') \, dt'$$

$$\left\langle \left(v(t) - v(0) e^{-\Gamma t} \right)^2 \right\rangle = \frac{e^{-2\Gamma t}}{m^2} \int_0^t dt' \int_0^t dt'' \, e^{\Gamma(t'+t'')} \left\langle F(t') F(t'') \right\rangle$$

$$= \frac{e^{-2\Gamma t}}{m^2} \int_0^t dt' \int_0^t dt'' \, e^{\Gamma(t'+t'')} \, 2c' \, \delta(t'-t'')$$

$$= \frac{2c'}{m^2} e^{-2\Gamma t} \int_0^t e^{2\Gamma t'} dt' = \frac{2c'}{m^2} e^{-2\Gamma t} \left. \frac{e^{2\Gamma t'}}{2\Gamma} \right|_0^t$$

$$= \frac{2c'}{2m^2\Gamma} e^{-2\Gamma t} \left(e^{2\Gamma t} - 1 \right) = \frac{c'}{m^2 \Gamma} \left(1 - e^{-2\Gamma t} \right)$$

$$\left\langle \left(v(t) - v(0) e^{-\Gamma t} \right)^2 \right\rangle$$

$$= \frac{c'}{\Gamma m^2} \left(1 - e^{-2\Gamma t} \right)$$

for $t \gg \frac{1}{\Gamma}$ (long time limit)

then $\langle v(t)^2 \rangle = \frac{c'}{\Gamma m^2}$

$$\frac{C'}{m^2} = \Gamma \langle v(t)^2 \rangle = \Gamma \frac{k_B T}{m}$$

$$\hookrightarrow \frac{\langle \Delta^2 \rangle}{2\tau} = M_2(v) = \frac{\Gamma k_B T}{m}$$

$$M_1(v) = -\Gamma v$$

Now, the Fokker-Planck equation reads

$$\frac{\partial f(v,t)}{\partial t} = \frac{\partial}{\partial v} [\Gamma v] f(v,t) + \frac{\partial^2}{\partial v^2} \left[\frac{\Gamma k_B T}{m} \right] f(v,t)$$

Brownian Motion in phase Space: Under a force field

$q \to$ position $\quad p \to$ momentum

$$q_1 = q + (p/m)\tau \; ; \qquad p_1 = p + K\tau$$

$$K = -\frac{\partial V}{dq} = V'(q)$$

$K \to$ force

$\frac{\partial V}{dq} \to$ Derivative of a potential energy

$$f(p+K\tau, q+p/m\,\tau, t+\tau)$$

$$= \int_{-\infty}^{+\infty} f(p-\Delta, q, t)\,\phi(p-\Delta, q, \Delta)\,d\Delta$$

$$\text{L.H.S} = f(p,q,t) + \frac{\partial f}{\partial p}(K\tau) + \frac{\partial f}{\partial q}(p/m)\tau + \cdots \frac{\partial f}{\partial t}\tau$$

$$\text{R.H.S} = \int_{-\infty}^{+\infty} \left(f(p,q,t) - \Delta \frac{\partial f}{\partial p} + \frac{\Delta^2}{2} \frac{\partial^2 f}{\partial p^2} \cdots \right) \left(\phi(p,q,\Delta) \cdots \right) d\Delta$$

R.H.S

$$= f(p,q,t)\underbrace{\int_{-\infty}^{+\infty}\phi(p,q,\Delta)\,d\Delta}_{1} - \frac{\partial}{\partial p}[f]\int_{-\infty}^{+\infty}\Delta\,\phi(p,q,\Delta)\,d\Delta + \frac{\partial^2}{\partial p^2}[f]\int_{-\infty}^{+\infty}\frac{\Delta^2}{2}\phi(p,q,\Delta)\,d\Delta$$

$$k = -\frac{dV}{dq} = -V'(q)$$

$$\cancel{f(p,q,t)} + \frac{\partial f}{\partial p}k\tau + \frac{\partial f}{\partial q}(p/m)\tau + \frac{\partial f}{\partial t}\tau = \cancel{f(p,q,t)} - \cdots\cdots$$

$$\frac{\partial f}{\partial p}k + \frac{\partial f}{\partial q}(p/m) + \frac{\partial f}{\partial t} = -\frac{\partial}{\partial p}[f]\underbrace{\frac{1}{\tau}\int_{-\infty}^{+\infty}\Delta\phi(p,q,\Delta)\,d\Delta}_{M_1(p,q)\,=\,-\gamma v} + \frac{\partial^2}{\partial p^2}[f]\underbrace{\frac{1}{\tau}\int_{-\infty}^{+\infty}\frac{\Delta^2}{2}\phi(p,q,\Delta)\,d\Delta}_{M_2(p,q)\,=\,\gamma\frac{k_BT}{m}}$$

$$m = 1, \quad q = x, \quad p = v$$

$$\frac{\partial f(x,v,t)}{\partial t} = -\frac{\partial f}{\partial x}v + \frac{\partial f}{\partial v}V'(x) - \frac{\partial}{\partial v}\left[\gamma v f(x,v,t)\right] + \gamma k_BT\frac{\partial^2 f}{\partial v^2}$$

Kramers' equation

$$\underbrace{\frac{\partial f(x,v,t)}{\partial t} = -\frac{\partial f}{\partial x} v + \frac{\partial f}{\partial v} V'(x)} - \frac{\partial}{\partial v}\left[\gamma v f(x,v,t)\right] + \gamma k_B T \frac{\partial^2 f(x,v,t)}{\partial v^2}$$

Corresponds to the Liouville's eqn

$\frac{\partial f}{\partial t} = 0 \rightarrow$ Equilibrium/Steady state

$$f(x,v) = \frac{1}{Z} e^{-\frac{\left(\frac{1}{2}v^2 + V(x)\right)}{k_B T}}$$

$\rightarrow$ one can check

Maxwell.

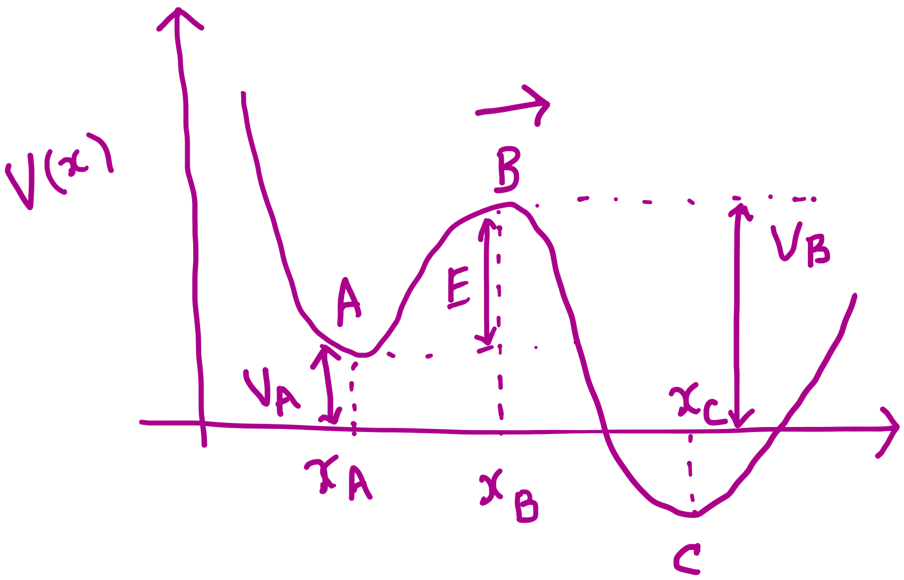
$H = \frac{v^2}{2} + V(x)$

$$= \frac{1}{Z} e^{-\beta H}$$

(Boltzmann Distribution)

Kramers' Theory of activated processes:

"Chemical Reaction"



x (Reaction Co-ordinate)

$E = V_B - V_A$

↓

Activation energy

$x_A \to$ Reactant State

$x_C \to$ Product State

$x_B \to$ Barrier top

We want to calculate the steady state rate from A to C

* Stationary situation → Steady state current at the barrier top

$f(x,v,t) \Rightarrow P(x,v,t)$

$$\frac{\partial P}{\partial t} = 0$$

$$\left[-\frac{\partial}{\partial x}v + \frac{\partial}{\partial x}\left\{V'(x) + \gamma v\right\} + \gamma k_B T \frac{\partial^2}{\partial v^2}\right] P(x, v) = 0$$

"inverted parabola"

At the Barrier top

$$V(x) = V(x_B) + \underbrace{\frac{\partial V}{\partial x}\bigg|_{x=x_B}}_{0} (x - x_B) + \frac{1}{2}\frac{\partial^2 V}{\partial x^2}\bigg|_{x=x_B} (x - x_B)^2 + \cdots$$

$$V(x) = V(x_B) - \frac{1}{2}\omega_B^2 (x - x_B)^2$$

$$V(x) = V(x_A) + \underbrace{\frac{\partial f}{\partial x}\bigg|_{x=x_A}}_{0} (x - x_A) + \frac{1}{2}\frac{\partial^2 f}{\partial x^2}\bigg|_{x=x_A} (x - x_A)^2$$

Near the bottom well, we have Equilibrium.

$$P(x, v) = \frac{1}{Z} e^{-\left(\frac{1}{2}v^2 + V(x)\right)/k_B T} \quad \text{at } x \approx x_A$$

$$V(x) = V(x_A) + \frac{1}{2}\omega_A^2 (x - x_A)^2$$

Population in the well A

$$n_a = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dv \, P(x,v)$$

Flux j over the barrier

$$j = \int_{-\infty}^{+\infty} v \, P(x,v) \, dv$$

The steady state Kramers' rate is given by $k_{A\to C} = j/n_a$

$$\frac{\text{flux}}{\text{populate}} = \text{Steady State rate}$$

Calculation of j:

We construct $P(x,v) = \xi(x,v) \exp\left[-\frac{\left(\frac{1}{2}v^2 + V(x)\right)}{k_B T}\right]$

After a little bit of algebra

$$\left[-v\frac{\partial}{\partial x}-\left\{\omega_B^2(x-x_B)+\gamma v\right\}\frac{\partial}{\partial v}+\gamma k_B T\frac{\partial^2}{\partial v^2}\right]\xi(x,v)=0$$

$\xi(x,v)=1$ inside the well $x \simeq x_A$

$\xi(x,v)=0$ beyond the barrier top B, $x > x_B$

We use the following linear transformation

$u = v + (x-x_B)a$ $\quad$ a is a constant to be determined later

$$\frac{\partial}{\partial x}=a\frac{\partial}{\partial u}\;;\;\frac{\partial}{\partial v}=\frac{\partial}{\partial u}$$

$$\left[-va\frac{\partial}{\partial u}-\left\{\omega_B^2(x-x_B)+\gamma v\right\}\frac{\partial}{\partial u}+\gamma k_B T\frac{\partial^2}{\partial u^2}\right]\xi(x,u)=0$$

$$\gamma k_B T \frac{\partial^2 \xi}{\partial u^2} - \left[\omega_B^2 (x - x_B) + \gamma v + a v\right] \frac{\partial \xi}{\partial u} = 0$$

Let $\quad \omega_B^2 (x - x_B) + v(\gamma + a) = -\lambda u \qquad \lambda =$ constant (to be determined)

Since, $\quad u = v + a(x - x_B)$

$$\omega_B^2 (x - x_B) + v(\gamma + a) = -\lambda v - \lambda a (x - x_B)$$

$$-\lambda a = \omega_B^2$$

$$a + \gamma = -\lambda$$

$$a^2 + \gamma a = -\lambda a$$

$$a^2 + \gamma a - \omega_B^2 = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$a = -\frac{\gamma \pm \sqrt{\gamma^2 + 4\omega_B^2}}{2}$$

$$= -\gamma/2 \pm \sqrt{(\gamma/2)^2 + \omega_B^2}$$

$$\gamma k_B T \frac{\partial^2 \xi}{\partial u^2} - \left[\omega_D^2 (x - x_B) + v(a+\gamma)\right] \frac{\partial \xi}{\partial u} = 0$$

$$\gamma k_B T \frac{\partial^2 \xi}{\partial u^2} + \lambda u \frac{\partial \xi}{\partial u} = 0$$

Let $\frac{\partial \xi}{\partial u} = y$

$$\gamma k_B T \frac{\partial y}{\partial u} = -\lambda u y$$

$$\Rightarrow \int \frac{dy}{y} = -\frac{\lambda}{\gamma k_B T} \int du\, u$$

$$\ln y = -\frac{\lambda}{2\gamma k_B T} u^2 + \ln F_2$$ ← constant of integration

$$y = F_2 \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right)$$

$$\xi(u) = F_2 \int_0^u \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) du + F_1$$

We look for a sol^n that vanishes as $x \to \infty$, but the above integral remain finite for all $|u| \to \infty$

This implies $\lambda > 0$

$\lambda = -\frac{\omega_B^2}{\alpha} \Rightarrow$ Negative root of α should be chosen

$$a = -\frac{\gamma}{2} - \sqrt{(\gamma/2)^2 + \omega_B^2}$$ (negative root)

Now when $x \to \infty$ $\quad u \to -\infty$ $\qquad u = v + a(x - x_B)$

$$\left[\int_{-\infty}^{+\infty} e^{-\alpha x^2} = \left(\pi/\alpha\right)^{\frac{1}{2}} \right]$$

$x \to \infty$ $\quad \xi(x, v) \to 0$

$$0 = F_1 + F_2 \int_0^{-\infty} \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) du$$

$$F_1 = F_2 \int_{-\infty}^{0} \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) du = \frac{F_2}{2} \int_{-\infty}^{+\infty} \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) du = \frac{F_2}{2} \left(\frac{2\pi \gamma k_B T}{\lambda}\right)^{1/2}$$

$$= F_2 \left(\frac{\pi \gamma k_B T}{2\lambda}\right)^{\frac{1}{2}}$$

$$\xi(u) = F_2 \left[\sqrt{\frac{\pi \gamma k_B T}{2\lambda}} + \int_0^u \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) du \right]$$

$$P(x,v) = F_2\left[\sqrt{\frac{\pi\gamma k_BT}{2\lambda}} + \int_0^u \exp\left(-\frac{\lambda u^2}{2\gamma k_BT}\right)du\right] \times \exp\left(-\frac{\left(\frac{1}{2}v^2 + V(x_B) - \frac{\omega_B^2}{2}(x-x_B)^2\right)}{k_BT}\right)$$

$$C = \sqrt{\frac{\pi\gamma k_BT}{2\lambda}}$$

then at $x \approx x_B$

$$= F_2 \exp\left(-\frac{V(x_B)}{k_BT}\right)\left[C\exp\left(-\frac{v^2}{2k_BT}\right) + F(x,v)\exp\left(-\frac{v^2}{2k_BT}\right)\right]$$

$$F(x,v) = \int_0^v \exp\left(-\frac{\lambda u^2}{2k_BT\gamma}\right)du$$

$$j = \int_{-\infty}^{+\infty} v\, P(x_B, v)\, dv$$

$$\int_{-\infty}^{+\infty} v\, e^{-v^2/2k_BT}\, dv = 0$$

$$\left[\ \int f\,dg = fg - \int g\, df\ \right]$$

$$j = F_2 \exp\left(-\frac{V(x_B)}{k_BT}\right)\left[\int_{-\infty}^{+\infty} v\, e^{-\frac{v^2}{2k_BT}}\, F(x_B, v)\, dv\right]$$

$$= F_2 \exp\left(-\frac{V(x_B)}{k_BT}\right)(-k_BT)\int_{-\infty}^{+\infty}\left(\frac{\partial}{\partial v} e^{-v^2/2k_BT}\right) F(x_B, v)\, dv$$

$$= F_2 \exp\left(-\frac{V(x_B)}{k_BT}\right)(-k_BT)\left[\cancelto{0}{F(x_B, v)\, e^{-v^2/2k_BT}\Big|_{-\infty}^{+\infty}} - \int_{-\infty}^{+\infty} e^{-v^2/2k_BT}\, \frac{\partial F(x_B, v)}{\partial v}\, dv\right]$$

$$j = F_2 \exp\left(-\frac{V(x_B)}{k_B T}\right)(k_B T) \int_{-\infty}^{+\infty} \left(\frac{\partial F}{\partial v}\right) e^{-v^2/2k_B T}\, dv$$

$$F(x,v) = \int_0^v \exp\left(-\frac{\lambda u^2}{2\gamma k_B T}\right) du$$

then $\dfrac{\partial F}{\partial v} = \exp\left(-\dfrac{\lambda v^2}{2\gamma k_B T}\right)$

$$j = F_2 \exp\left(-\frac{V(x_B)}{k_B T}\right)(k_B T) \int_{-\infty}^{+\infty} \exp\left[-\frac{v^2}{2k_B T}\left(\frac{\lambda}{\gamma}+1\right)\right] dv$$

$$j = F_2 \exp\left(-\frac{V(x_B)}{k_B T}\right)(k_B T)\, \frac{\pi^{1/2}}{\sqrt{\lambda/2k_B T\gamma + \frac{1}{2k_B T}}}$$

$$j = F_2 \exp\left(-\frac{V(x_B)}{k_B T}\right)(k_B T)\sqrt{2\pi k_B T}\left(\frac{\gamma}{\lambda+\gamma}\right)^{\frac{1}{2}}$$

Calculation of population n_a

$$n_a = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dv \, P(x,v)$$

$$P(x,v) = \xi(x,v) \exp\left[-\frac{\left(\frac{1}{2}v^2 + V(x)\right)}{k_B T}\right]$$

$$V(x) = V(x_A) + \frac{\omega_A^2}{2}(x - x_A)^2$$

$$\xi(x,v) = F_2\left[\left(\frac{\pi \gamma k_B T}{2\lambda}\right)^{\frac{1}{2}} + \int_0^{u \to \infty} e^{-\frac{du^2}{2\gamma k_B T}} du\right]$$

$$= F_2 \, 2 \cdot \left(\frac{\pi \gamma k_B T}{2\lambda}\right)^{\frac{1}{2}} = F_2 \left(\frac{2\pi \gamma k_B T}{\lambda}\right)^{1/2}$$

$$n_a = F_2 \left(\frac{2\pi \gamma k_B T}{\lambda}\right)^{\frac{1}{2}} \exp\left(-\frac{V(x_A)}{k_B T}\right) \int_{-\infty}^{+\infty} e^{-v^2/2k_B T} dv \int_{-\infty}^{+\infty} e^{-\frac{1}{2k_B T}\omega_A^2 (x - x_A)^2} dx$$

$$n_a = F_2 \left(\frac{2\pi\gamma k_B T}{\lambda}\right)^{\frac{1}{2}} \exp\left(-\frac{V(x_A)}{k_B T}\right) (2\pi k_B T)^{1/2} \left(\frac{2\pi k_B T}{\omega_A^2}\right)^{1/2}$$

$$n_a = F_2 \frac{(2\pi k_B T)^{3/2}}{\omega_A} \left(\frac{\gamma}{\lambda}\right)^{1/2} \exp\left(-\frac{V(x_A)}{k_B T}\right)$$

$$j = F_2\, e^{-V(x_B)/k_B T} (k_B T\, 2\pi)^{3/2} \left(\frac{\gamma}{\lambda+\gamma}\right)^{1/2} \frac{1}{2\pi}$$

$$k_{A\to c} = \frac{j}{n_a} = \left(\frac{\lambda}{\lambda+\gamma}\right)^{\frac{1}{2}} \left(\frac{\omega_A}{2\pi}\right) \exp^{-\frac{(V(x_B)-V(x_A))}{k_B T}}$$

$$n_a = F_2 \left(\frac{2\pi\gamma k_B T}{\lambda}\right)^{\frac{1}{2}} \exp\left(-\frac{V(x_A)}{k_B T}\right) (2\pi k_B T)^{1/2} \left(\frac{2\pi k_B T}{\omega_A^2}\right)^{1/2}$$

$$n_a = F_2 \frac{(2\pi k_B T)^{3/2}}{\omega_A} \left(\frac{\gamma}{\lambda}\right)^{1/2} \exp\left(-\frac{V(x_A)}{k_B T}\right)$$

$$j = F_2\, e^{-V(x_B)/k_B T} (k_B T\, 2\pi)^{3/2} \left(\frac{\gamma}{\lambda+\gamma}\right)^{1/2} \frac{1}{2\pi}$$

$$k_{A\to c} = \frac{j}{n_a} = \left(\frac{\lambda}{\lambda+\gamma}\right)^{\frac{1}{2}} \left(\frac{\omega_A}{2\pi}\right) \exp\left(-\frac{(V(x_B)-V(x_A))}{k_B T}\right)$$

$V(x_B) - V(x_A) = E$

Activation energy

$-\lambda = a + \gamma$

We should take the negative root a_-

$$\lambda = -a_- - \gamma$$

$$= -(a_- + \gamma)$$

$$\lambda = -\left[\gamma + \left\{-\frac{\gamma}{2} - \sqrt{\left(\gamma/2\right)^2 + \omega_B^2}\right\}\right] = -\frac{\gamma}{2} + \sqrt{\left(\gamma/2\right)^2 + \omega_B^2} = a_+$$

$$\frac{\lambda}{\lambda+\gamma} = \frac{a_+}{-a_-} = -\frac{a_+ a_+}{a_- a_+}$$

$$= -\frac{\left(-\gamma/2 + \sqrt{\left(\gamma/2\right)^2 + \omega_B^2}\right)^2}{\left\{\left(-\gamma/2\right)^2 - \left(\gamma/2\right)^2 - \omega_B^2\right\}} = \frac{1}{\omega_B^2}\left(-\gamma/2 + \sqrt{\left(\gamma/2\right)^2 + \omega_B^2}\right)^2$$

Thus the final expression for the Kramers rate is

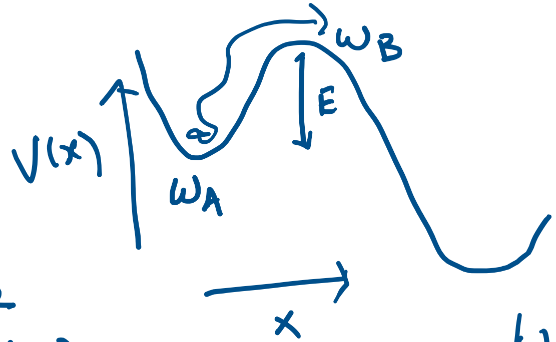
$$k = \left(\frac{\omega_A}{2\pi\omega_B}\right)\left(-\gamma/2 + \sqrt{\left(\gamma/2\right)^2 + \omega_B^2}\right)\exp\left[-E/k_BT\right]$$

We know for 1st order rate constant

$$k = Ae^{-E/k_BT} \leftarrow \text{Arrehenius relation}$$

One can compare $A \to (\omega_A, \omega_B, \gamma)$.

$$k = \left(\frac{\omega_A}{2\pi\omega_B}\right)\left(-\gamma/2 + \sqrt{(\gamma/2)^2+\omega_B^2}\right) e^{-E/k_BT}$$



Now, $\gamma \to 0$ (low friction/small viscosity)

$$\boxed{k = \left(\frac{\omega_A}{2\pi}\right) e^{-E/k_BT}} = k_{TST}$$ (Transition State theory rate)

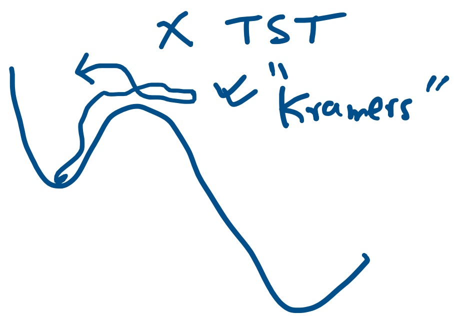
$$k_{TST} = \left(\frac{\omega_A}{2\pi}\right) e^{-E/k_BT}$$

"Upper bound to the rate"

Maximum possible rate

(No dissipation)

No-recrossing



Transmission coefficient

$$k = k_{TST}\,\kappa$$

$$\kappa = \frac{1}{\omega_B}\left(-\gamma/2 + \sqrt{(\gamma/2)^2+\omega_B^2}\right)$$

varies between 0 and 1

When $\gamma \to$ large

$\gamma \gg \omega_B$ (large viscosity limit)

$$k_{\gamma \to large} = \frac{\omega_A}{2\pi} e^{-E/k_BT} \frac{1}{\omega_B}\left[-\gamma/2 + \sqrt{(\gamma/2)^2 + \omega_B^2}\right]$$

$$\Big\downarrow$$

$$\frac{1}{\omega_B}\left[-\gamma/2 + (\gamma/2)\sqrt{1 + \omega_B^2 \cdot \frac{4}{\gamma^2}}\right]$$

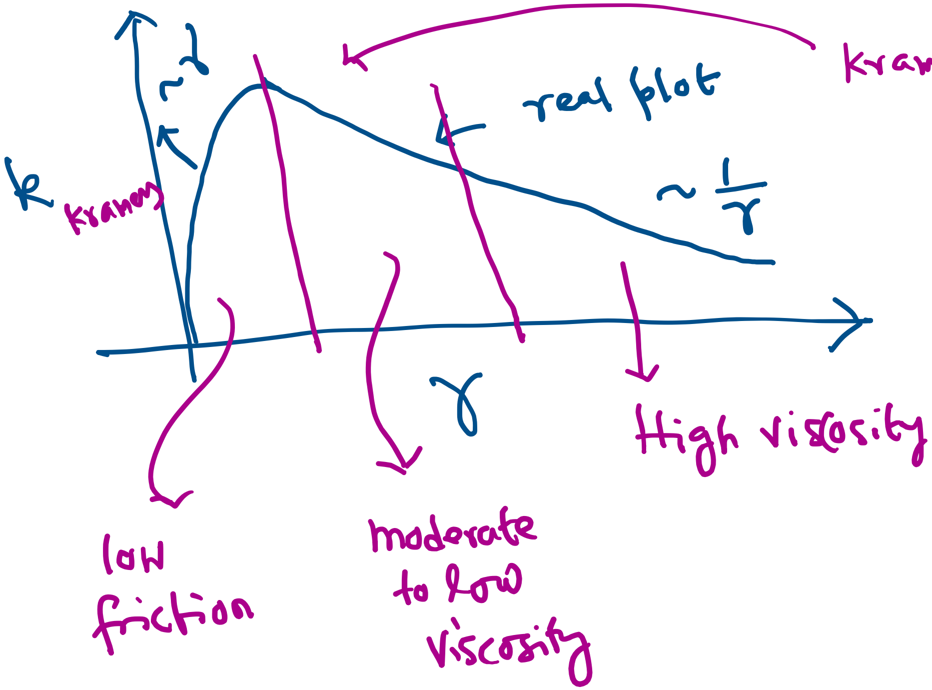
$$\Big\downarrow \ \gamma \to \text{large}$$

$$\frac{1}{\omega_B}\left[-\gamma/2 + \frac{\gamma}{2}\left(1 + \frac{1}{2}\omega_B^2 \frac{4}{\gamma^2}\right)\right]$$

$$\Big\downarrow$$

$$\frac{1}{\omega_B}\left[\cancel{-\gamma/2} + \cancel{\gamma/2} + \frac{\cancel{\gamma}}{\cancel{4}}\omega_B^2 \frac{\cancel{4}}{\gamma \cancel{\gamma}}\right) = \frac{1}{\omega_B}\frac{\omega_B^2}{\gamma} = \frac{\omega_B}{\gamma}$$

$$k_{\gamma \to large} = \frac{\omega_A \omega_B}{2\pi \gamma} e^{-E/k_BT} \rightsquigarrow \text{rate} \sim \frac{1}{\gamma} \sim \frac{1}{\text{viscosity}}$$



Kramers turn over

Peter Hanggi
50 years after Kramers
RMP 1990

Eli Pollack → see his papers.

Quantum Kramer's problem → D.S. Ray (IACS).