1 Random walks, diffusion and polymers

statistical mechanics: bridge between microscopic and macroscopic descriptions

set-up: fluid composed of a large number of identical particles
at any temp $T>0$: particles subject to thermal motion
we're interested in a test particle (larger than fluid part)
we want to describe the dynamics of this test particle at sufficiently long time scales so that an average large number of collisions with fluid particles has occurred
→ displacement test particle: distance a, randomly

Jump size distribution

random walk = path in space generated by series of steps each selected independently from a given probability distribution $p(\vec{r})$
↳ start walk @ origin @ $t=0$, then at times $\Delta t, 2\Delta t, 3\Delta t \ldots$ → random steps $\vec{r}_1, \vec{r}_2, \vec{r}_3 \ldots$ selected from $p(\vec{r})$

probability distribution $p(\vec{r})$ ⇒ $p(\vec{r})dxdydz$ is the prob that $\vec{r}=(x,y,z)$ is selected from interval $[x, x+dx], [y, y+dy], [z, z+dz]$

properties: $p(\vec{r}) \geq 0$, $\int p(\vec{r})d\vec{r} = 1$ (normalization)
$\langle\vec{r}\rangle = \int p(\vec{r})\vec{r}\, d\vec{r} = 0$, $\langle\vec{r}^2\rangle = \int p(\vec{r})\vec{r}^2 d\vec{r} = a^2$
(unbiased) (finite value mean squared jump)
↳ $p(\vec{r})$ has to decay fast @ infinity

examples:
1) $p(x) = \frac{1}{2}[\delta(x-a) + \delta(x+a)]$ → RW in a 1D lattice
2) $p(x) = \frac{1}{\sqrt{2\pi a}} e^{-x^2/2a^2}$ → RW w gaussian distr. steps
3) $p(x) = \begin{cases} \frac{1}{2\sqrt{3}a} & |x| \leq \sqrt{3}a \\ 0 & \text{else} \end{cases}$ → uniform distribution
4) $p(\vec{r}) = \frac{1}{4\pi a^2}\delta(|\vec{r}|-a)$ → freely jointed chain (FJC)

End-to-end vector

end-to-end vect. measures the distance of the walk from the origin
→ after N steps: $\langle\vec{R}_e\rangle = \langle\sum_{i=1}^N \vec{r}_i\rangle$
$= \sum_{i=1}^N\langle\vec{r}_i\rangle = \sum_{i=1}^N \int d\vec{r}_i\, \vec{r}_i\, p(\vec{r}_i) = 0$
average displacement is 0 by symmetry (unbiased prop.)
→ squared end-to-end distance:
$\langle\vec{R}_e^{\,2}\rangle = \langle\sum_{i,j=1}^N \vec{r}_i\cdot\vec{r}_j\rangle = \sum_{i=1}^N\langle\vec{r}_i^{\,2}\rangle + \sum_{i\neq j}\langle\vec{r}_i\cdot\vec{r}_j\rangle = \sum_{i=1}^N\langle\vec{r}_i^{\,2}\rangle = a^2N$
since jumps are selected independently and thus $\langle\vec{r}_i\cdot\vec{r}_j\rangle = \langle\vec{r}_i\rangle\cdot\langle\vec{r}_j\rangle = 0$ if $i\neq j$
↳ universal equation (indep. of spec. distr.)

Diffusion equation

end-to-end vector prob. distr.: $P(\vec{R},t)$ = prob that the walk which started @ origin @ $t=0$ arrives @ $\vec{R}$ @ time t , $t = N\Delta t$

→ $P(\vec{R},t)$ is a solution of $\frac{\partial P(\vec{R},t)}{\partial t} = D\nabla^2 P(\vec{R},t)$ the diffusion equation

$P(\vec{R}, t+\Delta t) = \int d\vec{r}\, P(\vec{R}-\vec{r}, t)\, p(\vec{r})$ [RW in a d-dim. space]

integrate over all possible values of $\vec{r}$

= prob of being in $\vec{R}-\vec{r}$ @ t multiplied by the prob. of making a jump of $\vec{r}$

→ prod. of prob since each new jump is indep from the previous ones

$$\approx \int d\vec{r} \left\{ P(\vec{R},t) - \vec{r}\cdot\nabla P(\vec{R},t) + \frac{1}{2}\sum_{k,l} r_k r_l \frac{\partial^2 P(\vec{R},t)}{\partial R_k \partial R_l} \right\} p(\vec{r})$$

at long times $P(\vec{R},t)$ varies slowly compared to typical jump size a

→ (expansion in $\vec{r}$ & considered lower order terms)

$\int d\vec{r}\, p(\vec{r}) = 1$

$\int d\vec{r}\, \vec{r}\, p(\vec{r}) = \langle \vec{r} \rangle = 0$

$P(\vec{R},t)$ a smooth function at long t

$$= P(\vec{R},t) + \frac{a^2}{2d}\nabla^2 P(\vec{R},t)$$

(used isotropy property for d-dim walks: $\langle r_k r_l \rangle = \delta_{kl}\frac{a^2}{d}$)

→ for small Δt:

→ for N part syst: $D = \frac{a^2 N}{2d\,\Delta t}$

$$\frac{\partial P(\vec{R},t)}{\partial t} = \frac{a^2}{2d\Delta t}\nabla^2 P(\vec{R},t)$$

→ diffusion eq. with $D = \frac{a^2}{2d\Delta t}$

↳ describes the behaviour of the collective motion of the fluid particles resulting from the random walk movements of each particle → diffusion of particles

- a RW describing the traj. of a part in time
  → zig-zag motion = Brownian motion → the presumably random moving of particles suspended in a fluid resulting from their bombardment by the fast-moving particles (atm/mol.) in the fluid
- the diffusion eq. describes the time evolution of the concentration of particles spreading on some medium, each indiv. part performing a Brownian motion

  → M non-interacting Brownian part concentration $c(\vec{R},t) = M P(\vec{R},t)$

- rewrite diff. eq: $\frac{\partial c(\vec{R},t)}{\partial t} = -\vec{\nabla}\cdot\vec{j}(R,t)$ with current $\vec{j}(\vec{R},t) = -D\nabla c(\vec{R},t)$

  → continuity eq.: describes time evolution conserved quantity, here: $\int d\vec{R}\, P(\vec{R},t)$ is cts in time (conservation of particles)

- reaction - diff equation

$$\frac{\partial c(\vec{R},t)}{\partial t} = D\nabla^2 c(\vec{R},t) + \underbrace{f(c(\vec{R},t))}_{\text{describes chemical reactions}}$$

general → total concentration not conserved
→ $f(c)$ a non-linear function

- general form diff eq

$$\frac{\partial c(\vec{R},t)}{\partial t} = \vec{\nabla}\left\{ D(c(\vec{R},t))\, \vec{\nabla} c(\vec{R},t) \right\}$$

→ diff coeff D can depend on concentration and position

Solving the diffusion equation

- gaussians

$(\vec{R},t)$ for $t \gg 1$

$$G_{\vec{R}_0}(\vec{R},t) = \left(\frac{1}{4\pi D t}\right)^{d/2} e^{-\frac{(\vec{R}-\vec{R}_0)^2}{4Dt}}$$

(d: dimension)

$g(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$ (for 1D)

$\lim_{t\to 0} G_{\vec{R}_0}(\vec{R},t) = \delta(\vec{R}-\vec{R}_0)$ and $\mathrm{var} = 2Dt$ $(\sigma = \sqrt{2Dt})$ } start from localized δ at $t=0$ (peak), spread out later in time $\sim\sqrt{t}$

↳ linear combinations $G_{\vec{R}_0}$ also solutions since diff eq is linear

most general solution: $c(x,t) = \int dy\, c(y)\, G_y(x,t)$

with right BC: $\lim_{t\to 0} c(x,t) = c(x) = \int dy\, c(y)\, \delta(y-x)$

Drift-diffusion equation

- external force acting on diff part → additional current j_F

$$j_F = v_d(x)\, c(x,t) = \frac{1}{\gamma} c(x,t) F(x) = -\frac{1}{\gamma} c(x,t)\frac{dV}{dx}$$

friction/viscous forces dominate, neglect initial acceleration

with v_d = drift velocity, γ = friction coeff, $V(x)$ the potential, since $F = \gamma v$

→ drift-diff eq: $\frac{\partial c(x,t)}{\partial t} = -\frac{\partial j_{tot}}{\partial x} = D\frac{\partial^2 c(x,t)}{\partial x^2} + \frac{1}{\gamma}\frac{\partial}{\partial x}\left\{ c(x,t)\frac{dV}{dx} \right\}$

$D\frac{\partial}{\partial x}\left\{ e^{-\beta V(x)} \left(\beta e^{\beta V(x)} \frac{dV}{dx} c(x,t) + e^{\beta V(x)} \frac{\partial c(x,t)}{\partial x} \right) \right\}$

$= D\frac{\partial^2 c}{\partial x^2} + D\beta\frac{\partial}{\partial x}\left(c(x,t)\frac{dV}{dx} \right)$

- in total equilibrium: net total current vanishes

$$j_{tot} = j_D + j_F = -D\frac{dc_{eq}(x)}{dx} - \frac{1}{\gamma} c_{eq}(x)\frac{dV}{dx} = 0$$

$-D A \exp(-)\frac{1}{k_B T}\frac{dV}{dx} + A\exp(-)\frac{dV}{dx} = 0$

with $c_{eq}(x) = A\exp\left(\frac{-V(x)}{k_B T}\right)$ * form solution T temp, k_B Boltzmann, A norm.

↳ distr expected for non-interacting part in eq. @ temp T

$\Rightarrow D = \frac{k_B T}{\gamma}$

Einstein relation → drift-diff → $\frac{\partial c(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left\{ e^{-\beta V(x)} \frac{\partial}{\partial x}\left(e^{\beta V(x)} c(x,t) \right) \right\}$

2 Ensembles in classical statistical mechanics

system of N particles for which position and momenta are given (microscopic)

Introduction

microscopic state of a syst. defined by a 6N-dim vector $\Gamma \equiv (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N, \vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$
→ Γ-space = 6N dim vector space

Hamiltonian $\mathcal{H}$ governs time-evolution

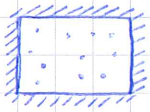
$$\mathcal{H}(\Gamma) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \Phi(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$$

observables $A(\Gamma)$ (functions in Γ-space)
- ex kin. energy $A(\Gamma) = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m$
- tot. energy $A(\Gamma) = \mathcal{H}(\Gamma)$
- part. density $A(\Gamma, \vec{r}) = \sum_{i=1}^{N} \delta(\vec{q}_i - \vec{r})$ part @ a given pos.; for a homogeneous syst $\langle \rho(\vec{r}) \rangle$ a constant indep. on $\vec{r}$

→ average values

* pure $\langle A \rangle_{pure} \equiv \frac{1}{\tau} \int_{t_0}^{t_0+\tau} A(\Gamma(t))\, dt$ (time average; with $\Gamma(t)$ a path in Γ-space, solution to eq. of motion)
  ~ experiments: → if in equil.: $\langle A \rangle$ indep on t_0 and τ
  t_0 = time @ which measurement started, τ = duration → $\langle A \rangle$ = average measured value observable
* SM $\langle A \rangle = \int d\Gamma\, \rho(\Gamma)\, A(\Gamma)$
  ensemble average, using prob distr funct $\rho(\Gamma)$ which represents the prob of finding a system in a microstate characterized by Γ
  3 different types of $\rho(\Gamma)$ ⇝ microcanonical ensemble
  canonical ensemble
  grandcanonical ensemble
  in the limit of $N \to \infty$ ⇒ all $\rho(\Gamma)$ lead to the same value of thermal averages
  ↳ in principle we can use any of the 3 ensembles to calc. thermal av., in practice canonical more convenient

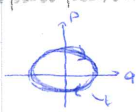
Microcanonical ensemble



E,V,N

isolated syst with fixed volume V, fixed # part N and NO energy exchange
→ total mechanical energy E conserved
→ part trajectories found in manifolds of constant tot. energy, ex (HO)

for a fixed energy, ρ_{mc} is constant along a part path in Γ



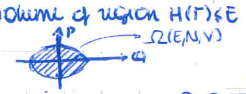
* PRINCIPLE OF EQUAL A PRIORI PROBABILITY (ESM, general)
  All the microstates with a constant E are equally probable

→ prob. dens $\rho_{mc}(\Gamma) = \dfrac{\delta(E - \mathcal{H}(\Gamma))}{\omega(E,N,V)\, N!\, h^{3N}}$ N = # part, h = Planck's constant

$$= \underbrace{\frac{1}{N!\,h^{3N}}}_{\text{QM: principle of indistinguishability of identical particles}} \; \underbrace{\frac{\delta(E-\mathcal{H}(\Gamma))}{\int \frac{d\Gamma}{N!\,h^{3N}} \delta(E-\mathcal{H}(\Gamma))}}_{\text{"norm."}}$$

QM → necessary for extensiveness thermodyn. quantities

? $\omega(E) = \int \frac{d\Gamma}{N!\,h^{3N}} \delta(E - \mathcal{H}(\Gamma))$
↳ microcanonical dens. of states
~ 6N-1 dim "volume" of manifold E = cte in Γ-space
→ $\Omega(E,N,V) = \int \frac{d\Gamma}{N!\,h^{3N}} \theta(E - \mathcal{H}(\Gamma))$
↳ step function $\theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases}$
~ volume of region $H(\Gamma) \leq E$



- connecting microscopic to macroscopic

BOLTZMANN $S(E,N,V) = k_B \log \omega(E,N,V)$
entropy $\approx k_B \log \Omega(E,N,V)$

with $\omega(E,N,V) = \dfrac{\partial \Omega(E,N,V)}{\partial E}$
$\approx \dfrac{\Omega(E) - \Omega(E - \Delta E)}{\Delta E}$ for $N \gg 1$, $N \approx 10^{23}$ negligible
→ $\Omega(E,N,V) \approx \omega(E,N,V)\, \Delta E$

example: Ideal gas

$\mathcal{H}(\Gamma) = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \sum_i \varphi_{wall}(\vec{q}_i)$

with $\varphi_{wall}(\vec{q}_i) = \begin{cases} 0 & \text{if } \vec{q}_i \in V \\ +\infty & \text{else} \end{cases}$ → confinement (fixed volume microcan.)

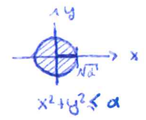
$\rightarrow \Omega(E,N,V) = \int \frac{d\Gamma}{N!\,h^{3N}} \Theta\left(E - \sum_i \frac{\vec{p}_i^{\,2}}{2m} - \sum_i \varphi_{wall}(\vec{q}_i)\right)$

$= \frac{1}{N!\,h^{3N}} \int_V d\vec{q}_1 \int_V d\vec{q}_2 \cdots \int_V d\vec{q}_N \int d\vec{p}_1 \dots d\vec{p}_N \, \Theta\left(E - \sum_i \frac{\vec{p}_i^{\,2}}{2m}\right)$

$= \frac{1}{N!\,h^{3N}} V^N \int d\vec{p}_1 \dots d\vec{p}_N \, \Theta\left(E - \sum_i \frac{\vec{p}_i^{\,2}}{2m}\right)$

$= \frac{V^N}{N!\,h^{3N}} \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} (2mE)^{3N/2}$

$\int dx\,dy\, \Theta(\alpha - (x^2+y^2)) = \pi\alpha$



for d-dim $V_d(R) = \frac{\pi^{d/2}}{(d/2)!} R^d$ and $\frac{1}{2}! = \frac{\sqrt{\pi}}{2} \rightarrow \frac{3}{2}! = \frac{3\sqrt{\pi}}{2 \cdot 2}$

3N-dim. with $R = \sqrt{2mE}$

(Boltzmann) $\rightarrow S \approx k_B \log \Omega(E,N,V)$

$P = T \frac{\partial S}{\partial V}\Big|_E = T \frac{\partial}{\partial V} k_B (\log V^N + \dots)\Big|_E$

$= T k_B \frac{N}{V}$ → ideal gas law

$S \approx k_B \log\left[\frac{V^N}{N^N e^{-N}} \left(\frac{2\pi m E}{\frac{3N}{2} h^2}\right)^{3N/2} \frac{1}{e^{-3N/2}}\right]$ using Stirling: $N! \approx N^N e^{-N}$

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

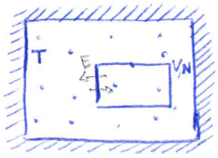
$= N k_B \log\left[\frac{V}{N}\left(\frac{4\pi m E}{3 N h^2}\right)^{3/2}\right] + \frac{5N}{2} k_B$ ← $e^{-N} e^{-3N/2} = e^{-5N/2}$

→ extensivity shows that $S(\alpha E, \alpha V, \alpha N) = \alpha S(E,V,N)$

origin extensivity → $N!$ → QM origin (indistinguishability particles)

does not depend on size or amount syst. intensive	extensive
$P \longleftrightarrow$	V applied P adjusts V $\left[\frac{1}{V}\right]$
$\mu \longleftrightarrow$	N
$T \longleftrightarrow$	S
…	E …

canonical ensemble



system in contact with a thermal bath fixed at temp T

N, V also fixed

system and bath can exchange energy E → no longer fixed

→ prob. dens: $\rho_c(\Gamma) = \frac{e^{-\beta\mathcal{H}(\Gamma)}}{N!\,h^{3N} \int \frac{d\Gamma}{N!\,h^{3N}} e^{-\beta\mathcal{H}(\Gamma)}} = \frac{e^{-\beta\mathcal{H}(\Gamma)}}{N!\,h^{3N} Z(N,V,T)}$ $\beta = \frac{1}{k_B T}$

$F(s) = \int_0^\infty f(t)\, e^{-st}\, dt$ → laplace transfo of $f(t)$

with $Z(N,V,T) = \int \frac{d\Gamma}{N!\,h^{3N}} e^{-\beta\mathcal{H}(\Gamma)}$ the canonical partition function

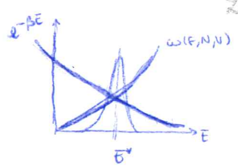
Laplace transfo ↳ $Z(\beta) = \int_0^\infty e^{-\beta E} g(E)\, dE$

$= \int dE\, e^{-\beta E}\, \omega(E,N,V)$

since $\int_{-\infty}^{+\infty} dE\, \delta(E - \mathcal{H}(\Gamma)) = 1$ (before $\int d\Gamma\, \delta(E - \mathcal{H}(\Gamma))$)

$\rightarrow Z = \int dE \int \frac{d\Gamma}{N!\,h^{3N}} e^{-\beta\mathcal{H}(\Gamma)} \delta(E - \mathcal{H}(\Gamma))$

$= \int dE\, e^{-\beta E} \underbrace{\int \frac{d\Gamma}{N!\,h^{3N}} \delta(E - \mathcal{H}(\Gamma))}_{\omega(E)}$



now for $N, V, T \rightarrow \infty$ (TD limit)

$\omega(E,N,V)$ fast growing function E

$e^{-\beta E}$ fast decreasing function E

→ peaked around char. value E^*

or use saddle point approx (see next page)

$\Rightarrow Z(N,V,T) \approx e^{-\beta E^*} \omega(E^*,N,V)$

$= e^{-\beta E^*} e^{S(E^*,N,V)/k_B}$ ← Boltzmann assumption

$= e^{-\beta[E^* - TS(E^*,N,V)]} = e^{-\beta F(E^*,N,V)}$

$\Rightarrow F = E - TS \approx -k_B T \log Z$ (Helmholtz free energy)

now for non-interacting particles

$\mathcal{H}(\Gamma) = \sum_{i=1}^N \mathcal{H}_1(\Gamma_i) = \sum_{i=1}^N \left(\frac{\vec{p}_i^{\,2}}{2m} + \varphi(\vec{q}_i)\right)$

$\Rightarrow Z(N,V,T) = \frac{\{Z_1(N,V,T)\}^N}{N!}$ with $Z_1 = \int d\vec{p}\, d\vec{q}\, e^{-\beta\mathcal{H}_1(\vec{p},\vec{q})}$

and in general, since the momenta integrals are gaussian integrals

gaussian integr. $\int_{-\infty}^{+\infty} e^{-a(x+b)^2} dx = \sqrt{\frac{\pi}{a}}$

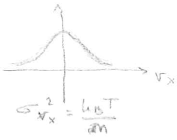
$\int_{-\infty}^{+\infty} e^{-\frac{1}{k_B T}\frac{p^2}{2m}} dp = \sqrt{2\pi m k_B T}$

$Z(N,V,T) = \frac{1}{N!\,\lambda_T^{3N}} \int d\vec{q}_1 \dots d\vec{q}_N\, e^{-\beta\varphi(\vec{q}_1,\dots,\vec{q}_N)} = \frac{Q(N,V,T)}{N!\,\lambda_T^{3N}}$

λ_T → kinetic energy

with $Q(N,V,T)$ the configurational partition function

and $\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$ the thermal wavelength



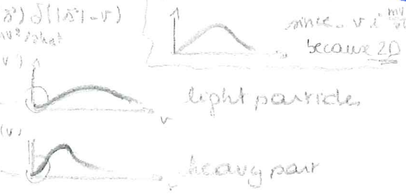
$\sigma_{v_x}^2 = \frac{k_B T}{m}$

$h(v) = \int d\vec{v}'\, p(\vec{v}')\, \delta(|\vec{v}'| - v)$

$= \dots v^2 e^{-mv^2/2k_BT}$

from Jacobian $dv_x dv_y dv_z = 4\pi v^2 dv$

in simulations: linear since $v\, e^{-\frac{mv^2}{2k_BT}}$ because 2D



light particle

heavy part

probability particle with speed v

momenta gaussian distr $\Rightarrow$ averages $\langle A(\vec{p})\rangle = \langle A(\vec{v})\rangle$ trivial

– distr. velocities follows a universal law indep. on type of interaction

$e^{\dots \frac{\vec{p}_i^2}{2m}} \int d\vec{p}_i\, e^{-\beta \sum_{i=1}^{N} \vec{p}_i^2} \int d\vec{q}_1 \dots d\vec{q}_N\, e^{-\beta\varphi}$

$= \dots e^{-\beta p^2/2m}$

* MAXWELL DISTRIBUTION OF VELOCITIES

$$p(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m\vec{v}^2/2k_BT} \quad \text{(prob distr.)}$$

$$\Rightarrow E = \langle \mathcal{H}(\Gamma)\rangle = -\frac{\partial \log Z(N,V,T)}{\partial \beta}$$

internal energy

or average energy

$\hookrightarrow \langle A\rangle = \int d\Gamma\, \rho(\Gamma)\, A(\Gamma)$

$= \dfrac{\int d\Gamma\, e^{-\beta\mathcal{H}(\Gamma)} A(\Gamma)}{\int d\Gamma\, e^{-\beta\mathcal{H}(\Gamma)}}$

with $\rho(\Gamma)$ norm.: $\int d\Gamma \rho(\Gamma) = 1$

$\rightarrow \langle \mathcal{H}\rangle = \dfrac{\int d\Gamma\, e^{-\beta\mathcal{H}(\Gamma)} \mathcal{H}(\Gamma)}{\int d\Gamma\, e^{-\beta\mathcal{H}(\Gamma)}} = -\dfrac{\partial}{\partial\beta} \log\left(\int d\Gamma\, e^{-\beta\mathcal{H}(\Gamma)}\right)$

since $\dfrac{\partial}{\partial\beta}\log\left(\int d\Gamma e^{-\beta\mathcal{H}(\Gamma)}\right) = \dfrac{1}{\int d\Gamma e^{-\beta\mathcal{H}(\Gamma)}} \int d\Gamma\, (-\mathcal{H})\, e^{-\beta\mathcal{H}(\Gamma)}$

and $Z(N,V,T) = \int \dfrac{d\Gamma}{N!\, h^{3N}}\, e^{-\beta\mathcal{H}(\Gamma)}$

thus $\langle \mathcal{H}\rangle = -\dfrac{\partial}{\partial\beta} \log Z$

· saddle point approx

to go from $Z(N,V,T) = \int dE\, e^{-\beta E}\, \omega(E,N,V)$ to $Z(N,V,T) \approx e^{-\beta E_*}\, \omega(E_*, N, V)$

approx as follows

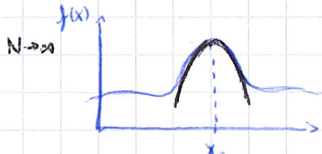
approx with a parabola

$$I = \int dx\, e^{Nf(x)} \underset{N\to\infty}{\approx} e^{Nf(x_0)} \int_{-\infty}^{+\infty} dx\, e^{\frac{N}{2} f''(x_0)(x-x_0)^2}$$

$f(x) \approx f(x_0) - \frac{1}{2}(x-x_0)^2 \dots$

$$= e^{Nf(x_0)} \sqrt{\frac{2\pi}{N|f''(x_0)|}}$$

dominant part



$N \to \infty$

dom. part is the maximum

$\rightarrow \log I = Nf(x_0) + O(\log N)$

$\Rightarrow$ taking $\log Z = \beta(E - TS)$ is a good approx.

· thermal wavelength

$p_T = \sqrt{\frac{2mE}{N}} = \sqrt{3mk_BT}$ = average mom per part

$\lambda_T = h/\sqrt{2\pi m k_B T}$ ~ average de Broglie wavelength gas part in ideal gas at specified T

$= h/p_T$ → the Broglie wavelength for a part. with average thermal energy

comparing the wavelength with the typical distance betw. part

$\Rightarrow$ if $\lambda_T \ll l \rightarrow$ classical regime

if $\lambda_T \gtrsim l \rightarrow$ quantum regime

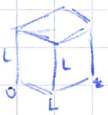
· non-interacting particles

$$Z(N,V,T) = \frac{1}{N!\,\lambda_T^{3N}} \int d\vec{q}_1 \dots d\vec{q}_N\, e^{-\beta\varphi(\vec{q}_1)}\, e^{-\beta\varphi(\vec{q}_2)} \dots e^{-\beta\varphi(\vec{q}_N)}$$

$$= \frac{1}{N!\,\lambda_T^{3N}} \int d\vec{q}_1\, e^{-\beta\varphi(\vec{q}_1)} \int d\vec{q}_2\, e^{-\beta\varphi(\vec{q}_2)} \dots$$

$$= \frac{1}{N!\,\lambda_T^{3N}} \left[\int d\vec{q}\, e^{-\beta\varphi(\vec{q})}\right]^N = \frac{[Q(1,V,T)]^N}{N!\,\lambda_T^{3N}}$$

→ in a gravitational field



$$Q(N,V,T) = \int d\vec{q}_1 \dots d\vec{q}_N\, e^{-\beta m g (z_1 + z_2 + \dots + z_N)}$$

$$= \int dx_1 dy_1 dz_1\, e^{-\beta m g z_1} \int dx_2 dy_2 dz_2\, e^{-\beta m g z_2} \dots$$

$$= \left[\int_0^L dx \int_0^L dy \int_0^L dz\, e^{-\beta m g z}\right]^N = \left[L^2 \frac{1}{\beta m g}\left(1 - e^{-\beta m g L}\right)\right]^N$$

example: Ideal gas

$$Z = \frac{1}{N!\,h^{3N}} \int d\Gamma\, e^{-\beta[\sum_i \vec{p}_i^2/2m + \sum_i \varphi_w(\vec{q}_i)]} = \frac{1}{N!\,h^{3N}} \left[\int d\vec{p}\, d\vec{q}\, e^{-\beta\left(\frac{\vec{p}^2}{2m} + \varphi_w(\vec{q})\right)}\right]^N$$

(same φ_{wall} as before)

$$= \frac{V^N}{N!\,h^{3N}} \left[\int d\vec{p}\, e^{-\beta\vec{p}^2/2m}\right]^N = \frac{V^N}{N!\,h^{3N}} \left[\int dp\, e^{-\beta p^2/2m}\right]^{3N} = \frac{V^N}{N!\,h^{3N}} (2m\pi/\beta)^{3N/2}$$

$$= \frac{V^N}{N!\,\lambda_T^{3N}}$$

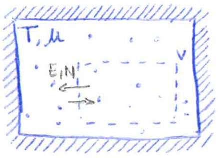
$Z = \frac{V^N}{N!\lambda_T^{3N}}$ $\rightarrow F = -k_B T \log Z = -k_B T [N \log V - 3N \log \lambda_T - \log N!]$

$P = -\frac{\partial F}{\partial V}\Big|_{N,T} = \frac{N k_B T}{V}$ $\rightarrow$ ideal gas law $\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} = A\,\beta^{1/2}$

and $E = \langle H \rangle = -\frac{\partial \log Z}{\partial \beta} = \frac{\partial\, 3N \log \beta^{1/2}}{\partial \beta} = \frac{3N}{2}\frac{\partial \log \beta}{\partial \beta} = \frac{3}{2} N k_B T$ OK!

= average kinetic energy of a system

Grandcanonical ensemble



V, T, μ (chemical potential) fixed

E, N can fluctuate

$\rightarrow$ prob dens $\rho_{GC}(\Gamma_N, N) = \frac{e^{-\beta \mathcal{H}_N(\Gamma_N)} e^{\beta \mu N}}{N!\, h^{3N}\, \Xi(\mu, V, T)}$ $\sum_N \int d\Gamma_N\, \rho_{GC}(\Gamma_N, N) = 1$

with $\Xi(\mu, V, T) = \sum_N e^{\beta\mu N} \underbrace{\int \frac{d\Gamma_N}{N!\, h^{3N}} e^{-\beta \mathcal{H}_N(\Gamma_N)}}_{Z(N,V,T)}$ Laplace transform

$= \sum_N e^{\beta \mu N} Z(N, V, T)$ $= \sum_N e^{\beta\mu N} \int dE\, e^{-\beta E}\, \omega(E, N, V)$

sum dominated by N_* the most probable value of the # of particles

$\approx e^{\beta\mu N_*} Z(N_*, V, T)$

$= e^{\beta \mu N_*} e^{-\beta F} = e^{-\beta[-\mu N_* + E - TS]} = e^{\beta P V}$

$\Rightarrow k_B T \log \Xi = PV$

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

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

(Euler relation)

we can also show that

$E = \langle \mathcal{H}(\Gamma) \rangle = -\frac{\partial \log \Xi(N,V,T)}{\partial \beta}\Big|_{\beta\mu = cts}$ $\langle \mathcal{H}(\Gamma) \rangle = \frac{\sum_N \mathcal{H}(\Gamma_N) e^{\beta\mu N} Z(N,V,T)}{\sum_N e^{\beta \mu N} Z(N,V,T)} = -\frac{\partial \log Z}{\partial \beta} = -\frac{\partial \log \Xi}{\partial \beta}\Big|_{\beta\mu = cts}$

$\langle N \rangle = \frac{\partial \log \Xi(N,V,T)}{\beta\, \partial \mu}$ $\langle N \rangle = \frac{\sum_N N e^{\beta\mu N} Z(N,V,T)}{\underbrace{\sum_N e^{\beta\mu N} Z(N,V,T)}_{\Xi}} = \frac{1}{\beta}\frac{\partial \log \Xi}{\partial \mu}$ $= \frac{1}{\beta \Xi}\frac{\partial \Xi}{\partial \mu}$ OK!

example: Ideal gas

$\Xi = \sum_N e^{\beta\mu N} Z(N,V,T) = \sum_N e^{\beta \mu N} \frac{V^N}{N!\lambda_T^{3N}} = \sum_N \left(\frac{e^{\beta\mu} V}{\lambda_T^3}\right)^N \frac{1}{N!}$

$= \exp\left(\frac{e^{\beta\mu} V}{\lambda_T^3}\right)$ $\lambda_T \sim \beta^{1/2}$ $\exp(x) = \sum_{k=0}^{\infty} \frac{x^k}{k!}$

$\Rightarrow \frac{PV}{k_B T} = \log \Xi = \frac{e^{\beta\mu} V}{\lambda_T^3}$ $\rightarrow$ how does this relate to the ideal gas law $PV = N k_B T$?

$\langle N \rangle = \frac{\partial \log \Xi}{\beta \partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\left(\frac{e^{\beta\mu} V}{\lambda_T^3}\right) = \frac{e^{\beta\mu} V}{\lambda_T^3}$ $\longrightarrow \frac{PV}{k_B T} = \langle N \rangle$ OK!

$E = -\frac{\partial \log \Xi}{\partial \beta} = -\frac{\partial}{\partial \beta}\left(\frac{e^{\beta\mu} V}{\lambda_T^3}\right)\Big|_{\beta\mu = cts} = -e^{\beta\mu} V \frac{\partial}{\partial \beta}\left(\sqrt{\frac{2\pi m}{\beta h^2}}^3\right) = \frac{3}{2} e^{\beta\mu} V \sqrt{\frac{2\pi m}{h^2}}^3 \sqrt{\beta}^{-5}$

$= \frac{3}{2}\frac{1}{\beta}\frac{e^{\beta\mu} V}{\lambda_T^3} = \frac{3}{2} k_B T \langle N \rangle$

$\rightarrow$ Ideal gas

syst with non-interacting particles: $\mathcal{H} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + \sum_{i=1}^N \varphi_W(\vec{q}_i)$

$\hookrightarrow$ with confining potential $\varphi_W(\vec{q}_i) = \begin{cases} 0 & \text{if } \vec{q}_i \in V \\ +\infty & \text{else} \end{cases}$

micro-canonical $\rightarrow \omega(E, N, V) = \frac{V^N}{N!\, h^{3N}} 2\pi m \frac{(2\pi m E)^{3N/2 - 1}}{(\frac{3N}{2} - 1)!}$

$\omega(E,N,V) = \frac{V^N}{N!\, h^{3N}} \int d\vec{p}_1 \ldots d\vec{p}_N\, \delta\left(E - \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}\right)$

Stirling $N! \approx e^{-N} N^N$

$\sim \left(\frac{V}{N}\right)^N \left(\frac{4\pi m E}{3h^2 N}\right)^{3N/2} e^{5N/2}$

$= \frac{V^N}{N!\, h^{3N}} \mu_{3N-1} \int_0^\infty dp\, p^{3N-1}\, \delta\left(E - \frac{p^2}{2m}\right)$

"polar" coord $d^d \vec{x} = \mu_{d-1} x^{d-1} dx$ with $\mu_{d-1} = \frac{2\pi^{d/2}}{\Gamma(d/2)}$

$= \frac{V^N}{N!\, h^{3N}}$ TODO

$\rightarrow P_{mc}(\vec{p}) = \langle \delta(\vec{p}_1 - \vec{p}) \rangle_{mc}$

$\sim \ldots \exp\left(-\frac{3N\vec{p}^2}{4mE}\right)$ || TODO $\rightarrow$ p41

canonical $\rightarrow Z(N, V, T) = \frac{V^N}{N!\, \lambda_T^{3N}}$

$\rightarrow P_c(\vec{p}) = \langle \delta(\vec{p} - \vec{p}_1) \rangle_c = \ldots e^{-\beta \frac{\vec{p}^2}{2m}}$ || TODO $\rightarrow$ p 42

$\Rightarrow$ you'll see that with the 3 ensembles, the ideal gas law $PV = N k_B T$ and the internal energy $E = \frac{3}{2} N k_B T$ can be calculated (see throughout summary)

if $N \rightarrow \infty$: mc, c and Gc all become the same

Equipartition theorem

- $\langle x_r \frac{\partial \mathcal{H}}{\partial x_s} \rangle = k_B T \delta_{rs}$, with x_r a comp. of pos. or mom. of the particle
  ↳ thermal average

$\rightarrow \langle q_{i,x}\, \partial_{q_{i,y}} \mathcal{H} \rangle = \langle q_{i,x}\, \partial_{q_{j,x}} \mathcal{H} \rangle = \langle p_{i,x}\, \partial_{p_{j,x}} \mathcal{H} \rangle = 0$ for $i \neq j$

now

$$\langle \vec{p}_i \cdot \frac{\partial \mathcal{H}}{\partial \vec{p}_i} \rangle = \langle p_{i,x} \frac{\partial \mathcal{H}}{\partial p_{i,x}} \rangle + \langle p_{i,y} \frac{\partial \mathcal{H}}{\partial p_{i,y}} \rangle + \langle p_{i,z} \frac{\partial \mathcal{H}}{\partial p_{i,z}} \rangle = 3 k_B T$$

$\Rightarrow$ total kinetic energy (summing over all ^{N} part.): $E_{kin} = \frac{3 N k_B T}{2}$

since $\langle \vec{p} \cdot \frac{\partial \mathcal{H}}{\partial \vec{p}} \rangle = \langle \vec{p} \cdot \frac{\vec{p}}{m} \rangle = 2 \langle \frac{p^2}{2m} \rangle = 2 \langle \mathcal{H} \rangle$

↳ since $E_{kin} = E_{ideal\,gas}$ we can conclude that the only contribution comes from the kinetic energy

and

$$\langle \vec{q}_i \cdot \frac{\partial \mathcal{H}}{\partial \vec{q}_i} \rangle = \langle q_{i,x} \frac{\partial \mathcal{H}}{\partial q_{i,x}} \rangle + \langle q_{i,y} \frac{\partial \mathcal{H}}{\partial q_{i,y}} \rangle + \langle q_{i,z} \frac{\partial \mathcal{H}}{\partial q_{i,z}} \rangle = 3 k_B T$$

$$= \langle \vec{q}_i \cdot \frac{\partial \varphi}{\partial \vec{q}_i} \rangle = - \langle \vec{q}_i \cdot \vec{F}_i \rangle$$

$\Rightarrow \sum_{i=1}^{N} \langle \vec{q}_i \cdot \vec{F}_i \rangle = -3 N k_B T$ with $\vec{F}_i$ the total force applied to part. i

proof of the theorem

$$\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \frac{\int d\Gamma\, x_i \frac{\partial \mathcal{H}}{\partial x_j} e^{-\beta \mathcal{H}}}{\underbrace{\int d\Gamma\, e^{-\beta \mathcal{H}}}_{=Z}} = \frac{-1}{\beta Z} \int d\Gamma\, x_i \frac{\partial}{\partial x_j} \left(e^{-\beta \mathcal{H}} \right)$$

$\frac{\partial}{\partial x_j}(x_i e^{-\beta \mathcal{H}}) = \frac{\partial x_i}{\partial x_j} e^{-\beta \mathcal{H}} + x_i \frac{\partial e^{-\beta \mathcal{H}}}{\partial x_j}$

$$= \frac{-1}{\beta Z} \int d\Gamma \left[\underbrace{\frac{\partial}{\partial x_j} (x_i e^{-\beta \mathcal{H}})}_{=0} - e^{-\beta \mathcal{H}} \underbrace{\frac{\partial x_i}{\partial x_j}}_{=\delta_{ij}} \right]$$

$$= \frac{+1}{\beta Z} \int d\Gamma\, e^{-\beta \mathcal{H}} \delta_{ij}$$

$$= k_B T \delta_{ij} \quad \square$$

$\int d\Gamma \frac{\partial}{\partial x_j} (x_i e^{-\beta \mathcal{H}}) = \int d\Gamma_j\, (x_i e^{-\beta \mathcal{H}}) |^{x_j} = 0$

$\int dp_{1,x} dp_{1,y} \ldots dp_{k,y} \ldots dq_{1,x} \ldots dq_{N,z} \left[\frac{\partial}{\partial p_{k,y}} (x_i e^{-\beta \mathcal{H}}) \right]$

partial integration

$= \int dp_{1,x} dp_{1,y} \ldots dq_{1,x} \ldots dq_{N,z}^{\,6N-1} \left[x_i e^{-\beta \mathcal{H}} \Big|_{p_{k,y}=+\infty} - x_i e^{-\beta \mathcal{H}} \Big|_{p_{k,y}=-\infty} \right]$

with $e^{-\beta \mathcal{H}} \sim e^{-p_{k,y}^2/2m}$

$\Rightarrow 0$

for the potential: $\varphi \rightarrow +\infty$ at boundaries since there is a wall confining the part. within volume V

Diatomic molecules

$\underset{1}{\circ}\!\!-\!\!\underset{2}{\circ}$ $\quad \mathcal{H}_{mol} = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + \frac{k}{2} |\vec{q}_1 - \vec{q}_2|^2$

$$Z(N,V,T) = \frac{Z_{mol}(V,T)^N}{N!}$$

$$\rightarrow Z_{mol}(V,T) = \frac{1}{h^6} \int d\vec{p}_1 d\vec{p}_2 d\vec{q}_1 d\vec{q}_2\, e^{-\beta [\vec{p}_1^{\,2}/2m + \vec{p}_2^{\,2}/2m + k/2 |\vec{q}_1 - \vec{q}_2|^2]}$$

$$= \frac{1}{\lambda_T^6} \int d\vec{q}_1 d\vec{q}_2\, e^{-\beta k/2 |\vec{q}_1 - \vec{q}_2|^2}$$

$$= \frac{1}{\lambda_T^6} \int d\vec{Q}_{cm} d\vec{q}\, e^{-\beta k/2\, \vec{q}^{\,2}} \quad ; \quad \vec{q} = \vec{q}_1 - \vec{q}_2, \quad \vec{Q}_{cm} = \frac{\vec{q}_1 + \vec{q}_2}{2}$$

$$= \frac{V}{\lambda_T^6} \int d\vec{q}\, e^{-\beta k \vec{q}^{\,2}/2} = \frac{V}{\lambda_T^6} \left(\frac{2\pi}{\beta k} \right)^{3/2}$$

$$\rightarrow F = -k_B T \log Z = -k_B T \log \frac{Z_{mol}^N}{N!} \approx -N k_B T \log Z_{mol} + k_B T (N \log N - N)$$

$N! \approx e^{-N} N^N$

$\log N! \approx N \log N - N$

$$= -N k_B T \log \frac{V}{N \lambda_T^6} \left(\frac{2\pi}{\beta k} \right)^{3/2} - N k_B T$$

$\rightarrow C_V = \frac{\partial E}{\partial T}\Big|_{V,N}$, $E = \langle \mathcal{H} \rangle = -\frac{\partial \log Z}{\partial \beta}$

$$Z_{mol} \sim \frac{1}{\lambda_T^6} \frac{1}{\beta^{3/2}} \sim (\beta^{1/2})^{-6} \frac{1}{\beta^{3/2}} \sim \underbrace{\frac{1}{\beta^3}}_{\sim \text{momentum}} \underbrace{\frac{1}{\beta^{3/2}}}_{\sim \text{spring}} \sim \frac{1}{\beta^{9/2}} \rightarrow \log Z_{mol} = \ldots + \log \beta^{9/2}$$

$\rightarrow E_{mol} = \frac{9}{2} k_B T \quad \rightarrow \quad C_{V,mol} = \frac{9}{2} k_B$

$\rightarrow \langle |\vec{q}_1 - \vec{q}_2|^2 \rangle = \langle |\vec{q}^{\,2}| \rangle$

↳ $\mathcal{H}_{mol} = \ldots + \frac{\vec{q}^{\,2}}{2} k \rightarrow$ equip $\langle \vec{q} \cdot \frac{\partial \mathcal{H}}{\partial \vec{q}} \rangle = \langle \vec{q}^{\,2} k \rangle = 3 k_B T \rightarrow \langle \vec{q}^{\,2} \rangle = \frac{3 k_B T}{k}$

and $\langle \vec{q}^{\,2} \rangle = \frac{-2}{\beta} \frac{\partial}{\partial k} \log Z_{mol}$; $Z_{mol} \sim k^{-3/2}$

$$= \frac{2}{\beta} \frac{3}{2} \frac{1}{k} = \frac{3 k_B T}{k}$$

Energy fluctuations of ideal gases

Describing fluctuations: σ_a for quantity a

$\frac{\sigma_a^2}{N}$: how they change with N ; $\frac{\sigma_a}{\langle a \rangle}$: relative fluct.

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

proof $Z = \int d\Gamma\, e^{-\beta H(\Gamma)} = \sum e^{-\beta E}$

$$\rightarrow -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \left(-\frac{\partial \log Z}{\partial \beta} = \right) \langle E \rangle \qquad -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{Z}\int d\Gamma\,(-H(\Gamma))\,e^{-\beta H(\Gamma)} \ldots \langle H(\Gamma) \rangle$$

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} = \langle E^2 \rangle \qquad \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{Z}\int d\Gamma\,(-H(\Gamma))^2 e^{-\beta H(\Gamma)} = \langle (H(\Gamma))^2 \rangle$$

$$\frac{\partial^2 \log Z}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left[\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right] = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

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

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{\partial^2 \log \Xi}{\beta^2 \partial \mu^2}$$

proof $\Xi = \sum_N e^{\beta \mu N} Z(N,V,T)$

$$\rightarrow +\frac{\partial \log \Xi}{\beta \partial \mu} = \frac{1}{\beta \Xi}\frac{\partial \Xi}{\partial \mu} = \langle N \rangle \qquad \frac{1}{\beta \Xi}\frac{\partial \Xi}{\partial \mu} = \frac{1}{\beta \Xi}\sum_N \beta N e^{\mu \beta N} Z(N,V,T) = \langle N \rangle$$

$$\frac{1}{\beta^2 \Xi}\frac{\partial^2 \Xi}{\partial \mu^2} = \langle N^2 \rangle \qquad \frac{1}{\beta^2 \Xi}\frac{\partial^2 \Xi}{\partial \mu^2} = \langle N^2 \rangle$$

$$\frac{\partial^2 \log \Xi}{\beta^2 \partial \mu^2} = \frac{1}{\beta}\frac{\partial}{\partial \mu}\left[\frac{1}{\beta \Xi}\frac{\partial \Xi}{\partial \mu}\right] = \frac{1}{\beta^2 \Xi}\frac{\partial^2 \Xi}{\partial \mu^2} - \frac{1}{\beta^2 \Xi^2}\left(\frac{\partial \Xi}{\partial \mu}\right)^2 = \langle N^2 \rangle - \langle N \rangle^2$$

→ for an ideal gas

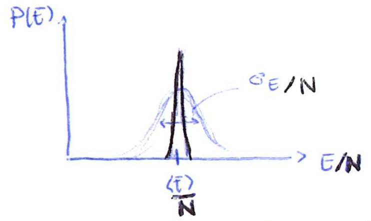
$$Z = \frac{V^N}{N!\,\lambda_T^3} \sim \beta^{-3N/2}$$

$$\Rightarrow \log Z = \ldots - \frac{3N}{2}\log \beta$$

$$\rightarrow \frac{\partial^2 \log Z}{\partial \beta^2} = \frac{3N}{2}\frac{1}{\beta^2} \Rightarrow \sigma_E^2 = \frac{3N}{2}(k_B T)^2$$

$$\rightarrow \frac{\sigma_E^2}{N} \sim \frac{1}{\sqrt{N}}$$

and $\langle E \rangle = \frac{3Nk_BT}{2}$



→ N larger ⇒ fluctuations smaller and smaller

$$N \rightarrow \infty : \frac{\sigma_E}{\langle E \rangle} \longrightarrow 0 \qquad \frac{\sqrt{\frac{3N}{2}}(k_BT)}{\frac{3N}{2}k_BT} = \frac{1}{\sqrt{3N/2}}$$

→ ensembles become equivalent, canonical → microcanonical

Harmonic oscillator in 1D

$$\varphi(\vec{q}) = \frac{k}{2}\vec{q}^2$$

$$\rightarrow Z = \ldots \int dq\, e^{-\frac{\beta k}{2}q^2}$$

$$= \ldots \frac{1}{\sqrt{\beta k}}\int = \ldots \frac{1}{\beta^{1/2}} \Rightarrow$$ only look at contribution oscillation

$$\rightarrow E = \frac{k_BT}{2}$$

for 2 oscillations $q_1 \overset{k_1}{\sim} q_2 \overset{k_2}{\sim} q_3$

$$Z = \ldots \frac{1}{\sqrt{\beta k_1}}\frac{1}{\sqrt{\beta k_2}}\int \ldots \quad \rightarrow \langle E \rangle = \frac{k_BT}{2} + \frac{k_BT}{2}$$

+ EQUIPARTITION THEOREM

every quadratic degree of freedom contributes as $\frac{k_BT}{2}$

$$\Rightarrow \text{for } H_{mol} = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + \frac{k}{2}|\vec{q}_1 - \vec{q}_2|^2$$

3 quadr dof, 3, 3

$$\Rightarrow \frac{9k_BT}{2}$$

careful for situations like these:

$\varphi(q) = \frac{k}{2}q^2 + \frac{k'}{4}q^4$ → can't apply equip.

but $\varphi(q) = \frac{k'}{4}q^4$ → equip: $E = \frac{k_BT}{4}$

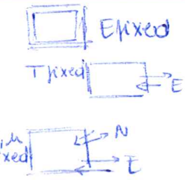
---

recap

$\rho_{mc}(\Gamma) = \ldots \delta(E - H(\Gamma))$, E, N, V

$\rho_c(\Gamma) = \ldots e^{-\beta H(\Gamma)}$, T, N, V

$\rho_{gc}(\Gamma) = \ldots e^{-\beta H(\Gamma)} e^{\beta \mu N}$, T, μ, V



– "preferred" ensemble in CSM

– used ensemble in QSM

3 Interacting Systems

so far we have used $Z(N,V,T) = \frac{1}{N!}[Z(1,V,T)]^N$
however this is NOT valid if we have interactions! (interactions $\rightsquigarrow$ potentials)

Pair potentials

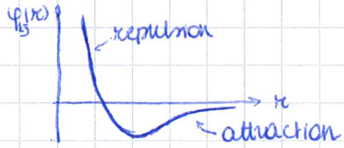
$H(\Gamma) = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m + \Phi(\vec{q}_1, \dots, \vec{q}_N)$

$\to$ pairwise interactions: $\Phi = \sum_{i<j} \varphi(|\vec{q}_i - \vec{q}_j|)$ $i \leftrightarrow j$

thus $Q(N,V,T) = \int d\vec{q}_1 \dots d\vec{q}_N\, e^{-\beta \sum_{i<j} \varphi_{ij}}$

$= \int d\vec{q}_1 \dots d\vec{q}_N\, e^{-\beta\varphi_{12}} e^{-\beta\varphi_{13}} \dots e^{-\beta\varphi_{23}} \dots e^{-\beta\varphi_{N-1,N}}$

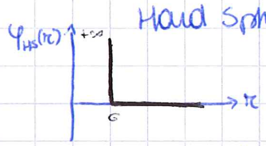
example Lennard-Jones potential



$\varphi_{LJ}(r) = \varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

repulsive at short distances ← strong repulsive energy against overlapping of e⁻ orbitals
attractive at longer distances ← van der Waals interactions between neutral atoms

Hard Spheres potential



$\varphi_{HS}(r) = \begin{cases} +\infty & 0 < r < \sigma \\ 0 & r \geq \sigma \end{cases}$ $\to$ short distance repulsion (only)

↳ since $Z(N,V,T) = \frac{1}{N!\lambda_T^{3N}} \int d\vec{q}_1 \dots d\vec{q}_N\, e^{-\beta\sum_{i<j}\varphi_{ij}}$ cannot be computed as Φ cannot be factorized

should include hard wall pot.

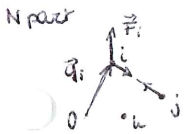
$\Rightarrow$ approximated techniques useful if SYSTEM IS DILUTED (n low)

$\to$ virial expansion: P as an expansion in powers of $n = N/V$

$P = nk_BT(1 + b_2 n + b_3 n^2 + \dots)$

ideal gas   mutual interactions between particles

Virial theorem



should always include hard wall potential in Z

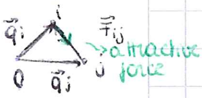
$\vec{F}_i = \vec{F}_i^{(w)} + \sum_{j\neq i} \vec{F}_{ij}$ $\to$ total force = force from collisions with the wall of the container + force from intermolecular interactions

$\frac{\partial\varphi_{ij}}{\partial q_{i\alpha}} = \frac{\partial\varphi_{ij}}{\partial q_{ij}} \frac{\partial q_{ij}}{\partial q_{i\alpha}} = \frac{\partial\varphi_{ij}}{\partial q_{ij}} \frac{q_{i\alpha} - q_{j\alpha}}{q_{ij}}$

$\vec{F}_{ij} \equiv -\frac{\partial\varphi(|\vec{q}_i - \vec{q}_j|)}{\partial\vec{q}_i} = -\frac{\partial\varphi(q_{ij})}{\partial q_{ij}} \frac{\vec{q}_i - \vec{q}_j}{q_{ij}}$ force that j exerts on i

$|\vec{q}_i - \vec{q}_j| = q_{ij}$
$\varphi_{ij} = \varphi(q_{ij})$

$\to$ equip: $\sum_{i=1}^{N} \langle \vec{q}_i \cdot \vec{F}_i^{(w)} \rangle + \sum_{i,j=1}^{N} \langle \vec{q}_i \cdot \vec{F}_{ij} \rangle = -3Nk_BT$ with $\vec{F}_{ii} = 0$



force perpendicular to wall, pointing inwards

$* \;\vec{F}^{(w)} = \frac{\Delta\vec{p}}{\Delta t} = \frac{-2\vec{p}_\perp}{\Delta t}$ particles collide elastically with the wall

now $\vec{p} = \vec{p}_{\parallel} + \vec{p}_\perp$ (∥ to wall, ⊥ to wall momentum)

$\vec{p}' = -\vec{p}_\perp + \vec{p}_{\parallel}$ after collision

contr. from specific location

$\to \sum_{i=1}^{N} \langle \vec{q}_i \cdot \vec{F}_i^{(w)} \rangle_{\vec{r},d\vec{s}}$ dS portion of wall @ point $\vec{r}$

$= \vec{r} \cdot \sum \langle \vec{F}_i^{(w)} \rangle_{\vec{r},d\vec{s}}$ only particles in $\vec{q}_i = \vec{r}$ contribute $\to \Delta\vec{p} = \vec{p}' - \vec{p} = \vec{p}_{\parallel} - \vec{p}_\perp - \vec{p}_\perp - \vec{p}_{\parallel} = -2\vec{p}_\perp$

$= -\vec{r} \cdot (P\, d\vec{S})$ P pressure = average force per unit area exerted on the wall by the particles

$\vec{F}^{(w)}$ points opposite to $\hat{n}$; $d\vec{S} = \hat{n}\, dS$ with $\hat{n}$ perpendicular in $\vec{x}$, pointing outwards

integr. over whole surface

$\to \sum_{i=1}^{N} \langle \vec{q}_i \cdot \vec{F}_i^{(w)} \rangle = -P \oint_S \vec{r} \cdot d\vec{S} = -P \int \vec{\nabla}\cdot\vec{r}\, dV = -3P\int_V dV = -3PV$

$\vec{\nabla}\cdot\vec{r} = dx/dx + dy/dy + dz/dz = 3$

$* \;\sum_{i,j=1}^{N} \langle \vec{q}_i \cdot \vec{F}_{ij} \rangle = \frac{1}{2}\sum_{i,j=1}^{N} \langle \vec{q}_i \cdot \vec{F}_{ij} + \vec{q}_j \cdot \vec{F}_{ji} \rangle = \frac{1}{2}\sum_{i,j=1}^{N} \langle (\vec{q}_i - \vec{q}_j) \cdot \vec{F}_{ij} \rangle$ ($\vec{F}_{ij} = -\vec{F}_{ji}$, NIII)

$= -\frac{1}{2}\sum_{i,j=1}^{N} \langle q_{ij} \frac{d\varphi(q_{ij})}{dq_{ij}} \rangle$ ↙ $\vec{F}_{ij} = -\frac{\partial\varphi_{ij}}{\partial q_{ij}} \frac{\vec{q}_i - \vec{q}_j}{q_{ij}}$

$\frac{|\vec{q}_i - \vec{q}_j|^2}{q_{ij}} = \frac{q_{ij}^2}{q_{ij}}$

(see back of this page)

$$\sum_{i,j=1}^{N} \langle \vec{q}_i \cdot \vec{F}_{ij} \rangle = -\frac{1}{2}\sum_{i,j=1}^{N} \langle q_{ij} \frac{d\varphi(q_{ij})}{dq_{ij}} \rangle$$

$$1 = \int d\vec{r}\, d\vec{r}'\, \delta(\vec{r}-\vec{q}_i)\,\delta(\vec{r}'-\vec{q}_j) = \int d\vec{r}\, d\vec{\rho}\, \delta(\vec{r}-\vec{q}_i)\,\delta(\vec{r}+\vec{\rho}-\vec{q}_j)$$

$$= -\frac{1}{2}\sum_{i,j=1}^{N} \langle q_{ij} \frac{d\varphi_{ij}}{dq_{ij}} \int d\vec{r}\, d\vec{\rho}\, \delta(\vec{r}-\vec{q}_i)\,\delta(\vec{r}+\vec{\rho}-q_j) \rangle$$

$$= -\frac{1}{2}\int d\vec{r}\, d\vec{\rho}\, \rho \frac{d\varphi(\rho)}{d\rho} \underbrace{\langle \sum_{i=1}^{N} \delta(\vec{r}-\vec{q}_i) \sum_{j\neq i}^{N} \delta(\vec{r}+\vec{\rho}-\vec{q}_j) \rangle}_{n^{(2)}}$$

$$= -\frac{1}{2}\int d\vec{r}\, d\vec{\rho}\, \rho \frac{d\varphi(\rho)}{d\rho}\, n^{(2)}(\vec{r},\vec{r}+\vec{\rho})$$

for ideal gas
$n^{(2)}(\vec{r},\vec{r}+\vec{\rho}) = n^2 = \frac{N^2}{V^2}$
$\rightarrow g(\rho) = 1$

for an ideal gas in a grav. field
$n^{(2)}(\vec{r},\vec{r}+\vec{\rho}) = \ldots e^{-\beta m g z} e^{-\beta m g (z+\rho_z)}$

with $n^{(2)}(\vec{r},\vec{r}+\vec{\rho})$ the pair correlation function
= prob of finding 2 particles in the volume elements $d\vec{r}$ and $d\vec{r}'$ around $\vec{r}$ and $\vec{r}'$ ($\vec{r}' = \vec{r}+\vec{\rho}$)
→ for a homogeneous system, far away from walls, with transl. & rot invariance:

for real system $n^{(2)}(\vec{r},\vec{r}+\vec{\rho}) = n^2 g(\rho)$ → no $\vec{r}$-dependence due to translational invar. + only $|\vec{\rho}| = \rho$ dep. due to isotropic

with $n = N/V$, $g(\rho)$ = radial correlation function

for $\rho \to \infty$ (large distances) → prob. of finding the 2 part. factorizes (no correlation)
$n^{(2)} \to n \Rightarrow g(\rho) \to 1$

$$= -\frac{N^2}{2V}\int \rho \frac{d\varphi(\rho)}{d\rho} g(\rho)\, d\vec{\rho}$$

$\int d\vec{r}\, n^{(2)}(\vec{r},\vec{\rho}) = V n^2 g(\vec{\rho})$

$$\Rightarrow -3Nk_BT = -3PV - \frac{N^2}{2V}\int \rho \frac{d\varphi(\rho)}{d\rho} g(\rho)\, d\vec{\rho}$$

$$\Rightarrow P = n k_B T - \frac{n^2}{6}\int r \frac{d\varphi(r)}{dr} g(r)\, d\vec{r}$$

→ for non-interacting particles $\varphi = cte$
⇒ reduces to ideal gas law

$n^2 g(\rho) = \sum_{i,j} \langle \delta(\vec{r}-\vec{q}_i)\,\delta(\vec{r}+\vec{\rho}-\vec{q}_j) \rangle$

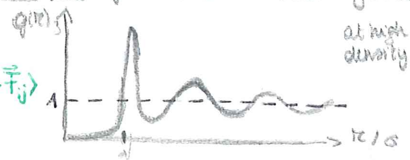
! EXACT EXPRESSION
↳ given by an integral over the positions of all particles
in general not solvable

$PV = Nk_BT + \frac{1}{6}\sum_{ij} \langle (\vec{q}_i - \vec{q}_j)\cdot\vec{F}_{ij} \rangle$

if attractive forces "win"
$\Sigma\langle\ldots\rangle < 0$
$\Rightarrow PV < Nk_BT$

if repulsive forces "win"
$\Sigma\langle\ldots\rangle > 0$
$\Rightarrow PV > Nk_BT$

example $g(r)$: Lennard-Jones



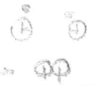
vanishes at short distances - due to repulsive part φ_{LJ}
at high ρ → damped oscillations
→ preference particles to be found @ specific distances from the origin
lower ρ → oscillations reduced
1st peak remains due to attraction, but $g(r) \to 1$ much more rapid

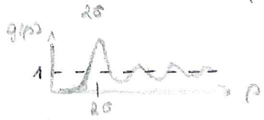
→ 1st layer prevents other particles on getting close to it
→ 1st min behind peak

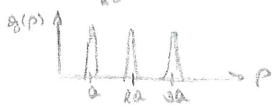
for ideal gas: $g(\vec{\rho}) = 1$ → goes to this value

other example

for hard spheres







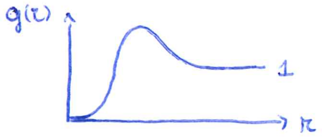
→ crystal structure

Virial expansion

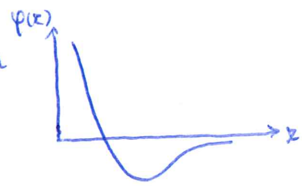
radial distribution function $g(r)$ describes how the probability of finding another particle varies with r (given a fixed ref. part at $r=0$)
→ prob of finding 2nd particle

! assume DILUTE system: very low density
→ assume only one particle in its surroundings
$\Rightarrow g(r) \approx e^{-\beta\varphi(r)}$

assume only 1 pair gets close



for



↳ for $r \to \infty$: $g(r) \to 1$ as $\varphi(r) \to 0$
neglect correlations between particles beyond pair interactions
oscillations φ_{LJ} not possible even though pair correlation since it manifests itself only at high densities

integration by parts
$\int_a^b u v' dx = [uv]_a^b - \int_a^b u' v dx$

low n

for $g(r) \approx e^{-\beta\varphi(r)}$, we get

$$P = nk_BT - \frac{n^2}{6}\int r \frac{d\varphi(r)}{dr} g(r)\, d\vec{r} = nk_BT - \underbrace{\frac{n^2}{6}\int r \frac{d\varphi(r)}{dr} e^{-\beta\varphi(r)} d\vec{r}}_{\text{correction } O(n^2)}$$

~~importance no effect and useful later~~ will avoid divergences at boundaries

$$= nk_BT + \frac{n^2}{6\beta}\int \vec{r} \cdot \frac{d}{d\vec{r}}\left(e^{-\beta\varphi(r)} - 1\right) d\vec{r}$$

$$= nk_BT - \frac{n^2 k_BT}{2}\int \left(e^{-\beta\varphi(r)} - 1\right) d\vec{r}$$

integration by parts with change of coord $d\vec{r} \to 4\pi r^2 dr$

$\Rightarrow -\frac{4\pi}{\beta}\int_0^{+\infty} r^3 \frac{d}{dr}\left(e^{-\beta\varphi(r)} - 1\right) dr$

$= -\frac{4\pi}{\beta}\left\{ \left[r^3 \left(e^{-\beta\varphi(r)} - 1\right)\right]_0^{+\infty} - \int_0^{+\infty} 3r^2 \left(e^{-\beta\varphi} - 1\right) dr \right.$

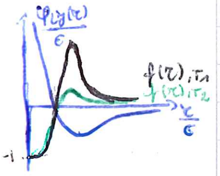
since if $\varphi(r) \sim \frac{A}{R^6}$ (LJ)

$\to R^3\left(e^{-\beta A/R^6} - 1\right) \underset{R\to\infty}{\sim} \frac{A}{R^3} \to 0$

$$= nk_BT\,(1 + b_2 n)$$

↳ 1st correction to ideal gas law

with $b_2 = \frac{1}{2}\int f(r)\, d\vec{r}$ 2nd virial coefficient



and $f(r) = e^{-\beta\varphi(r)} - 1$ the Mayer f-function
temp. dependent

@ low T: f has a strong peak
interpart. attraction dominates
$\Rightarrow b_2 < 0$, T_1
$\to P < P_{\text{ideal gas}}$

@ high T: attractive part interr. negligible
→ dominated by short dist. repulsion
$\Rightarrow b_2 > 0$, T_2
$\to P > P_{\text{ideal gas}}$

@ $T = T_{Boyle}$: $b_2 = 0$
→ behaviour very close to ideal gas - corrections of higher order in n

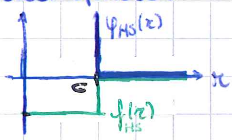
virial expansion:

$$P = nk_BT\,(1 + b_2 n + b_3 n^2 + \ldots)$$

with b_k the k^{th} virial coeff
and $b_3 = -\frac{1}{3}\int d\vec{r}\, d\vec{r}'\, f(\vec{r}) f(\vec{r}') f(\vec{r} - \vec{r}')$

examples:

Hard spheres



$\varphi_{HS} = \begin{cases} 0 & r \geq \sigma \\ +\infty & r < \sigma \end{cases}$

$\to b_2 = -\frac{1}{2}\int_0^{+\infty} dr\, 4\pi r^2 \left(e^{-\beta\varphi_{HS}} - 1\right) = \frac{2\pi\sigma^3}{3} > 0$, indep. on T

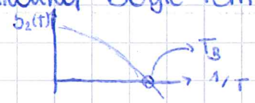
$= -2\pi\left[\int_0^{\sigma} r^2(-1)\, dr + \int_\sigma^{\infty} dr\, r^2 \cdot 0\right]$

→ hard spheres are athermal, $Z(N,V,T) = \frac{Q(N,V,\cancel{T})}{N!\,\lambda_T^{3N}}$

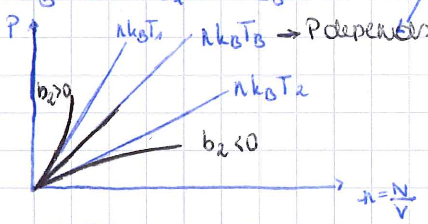
Lennard-Jones

if temp is high: $\beta\varphi \ll 1$, $\beta\epsilon \ll 1$
→ b_2 expected to be positive

finding Boyle temp.

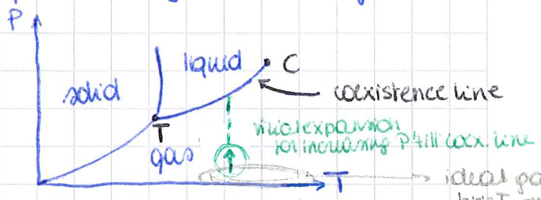


$P = nk_BT\,(1 + b_2 n + b_3 n^2 + \ldots)$



↳ look @ the virial exponents to see how a gas deviates from the ideal gas

phase diagram real system



with T triple and C critical point
two phase can coexist if
$P_A = P_B$ & $T_A = T_B$ & $\mu_A = \mu_B$
mechanical equilibrium   thermal equilibrium   chemical equilibrium

The van der Waals model

$$P = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2} \qquad a,b>0$$

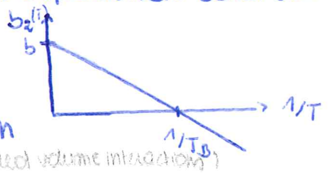
→ low density limit (n small)

$$P = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2} = \frac{Nk_BT}{V}(1 + nb + n^2b^2 + \dots) - an^2$$

$$= nk_BT\left[1 + n\left(b - \frac{a}{k_BT}\right) + \dots\right]$$

compare with virial expansion and we find

$$b_2 = b - \frac{a}{k_BT}$$



$$k_BT_B = \frac{a}{b} \qquad [b_2(T_B)=0]$$

where thus

repulsion $\to b_2>0$
attraction $\to b_2<0$

b should come from repulsion (excluded volume interaction)

a should come from attraction (intermolecular)

- Bogoliubov inequality

$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$ → interaction terms

$$\to Z = \sum e^{-\beta\mathcal{H}} = \sum e^{-\beta\mathcal{H}_0} e^{-\beta\mathcal{H}_1} = Z_0 \frac{\sum e^{-\beta\mathcal{H}_0} e^{-\beta\mathcal{H}_1}}{\sum e^{-\beta\mathcal{H}_0}} = Z_0 \langle e^{-\beta\mathcal{H}_1}\rangle_0$$

now $\langle e^{-\beta\mathcal{H}}\rangle_0 \geq e^{-\beta\langle\mathcal{H}\rangle_0}$

proof: for any $x \in \mathbb{R}$: $\exp(x) \geq 1 + x$

now x is a random variable distributed according to some distr. $p(x) \geq 0$

$\to \langle f \rangle = \int dx\, f(x)\, p(x)$

$\Rightarrow \langle e^{x-\langle x\rangle}\rangle \geq \langle 1 + (x - \langle x\rangle)\rangle = 1$

$\Rightarrow \langle e^x\rangle \geq e^{\langle x\rangle}$

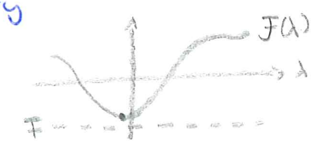
thus $Z \geq Z_0 e^{-\beta\langle\mathcal{H}_1\rangle_0}$

since $F = -k_BT \log Z$ (Helmholtz free energy)

$\leq -k_BT \log Z_0 + \langle\mathcal{H}_1\rangle_0$

$\Rightarrow F \leq F_0 + \langle\mathcal{H}_1\rangle_0$ Bogoliubov inequality

free energy full system



if $\mathcal{H}(\lambda) = \mathcal{H}_0(\lambda) + \mathcal{H}_1(\lambda)$

$\to F \leq \mathcal{F}(\lambda) = F_0(\lambda) + \langle\mathcal{H}_1(\lambda)\rangle_0$

Bogoliubov: $\hat{F} = \min_\lambda \mathcal{F}(\lambda)$ is best approx of free energy

- Derivation van der Waals

$$\mathcal{H} = \sum_{i=1}^N \left(\frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j}^N \varphi(q_{ij})\right) \qquad \text{with } \varphi(r) = \begin{cases} +\infty & r<\sigma \\ -r^{-6} & r>\sigma \end{cases}$$

→ hard sphere pot + attractive tail $\sim r^{-6}$

$$= \left(\sum_{i=1}^N \frac{\vec{p}_i^{\,2}}{2m} + N\lambda\right) + \left(\sum_{i=1}^N \sum_{i<j}^N \varphi(q_{ij}) - N\lambda\right) = \mathcal{H}_0(\lambda) + \mathcal{H}_1(\lambda)$$

ideal gas with a shifted constant potential

$Z(\lambda) = \int \frac{d\Gamma}{N!\,h^{3N}} e^{-\beta\mathcal{H}_0(\lambda)}$

$$\Rightarrow Z_0 = \frac{V^N}{N!\,\lambda_T^{3N}} e^{-\beta N\lambda} \quad \to F_0(\lambda) = -Nk_BT \log\left(\frac{V}{N\lambda_T^3}\right) - Nk_BT + N\lambda$$

$\to \log N! = N\log N - N$

$$\langle\mathcal{H}_1\rangle_0 = \frac{\int d\vec{q}_1 \dots d\vec{q}_N \left(\sum_{i=1}^N \sum_{i<j}^N \varphi(q_{ij}) - N\lambda\right) e^{-\beta N\lambda}}{\int d\vec{q}_1 \dots d\vec{q}_N\, e^{-\beta N\lambda}}$$

$\sum_{i=1}^N \sum_{i<j}^N \to \frac{N(N-1)}{2}$

$$= \frac{1}{V^N}\left\{\frac{N(N-1)}{2}\int d\vec{q}_1 \dots d\vec{q}_N\, \varphi(q_{12}) - N\lambda V^N\right\}$$

$V^{N-2}\int d\vec{q}_1 d\vec{q}_2\, \varphi(q_{12})$
$= V^{N-1}\int d\vec{q}\, \varphi(\vec{q})$

$\vec{q} = \vec{q}_1 - \vec{q}_2$
$\vec{q}_{cm} = \frac{\vec{q}_1 + \vec{q}_2}{2}$

$$= \frac{N(N-1)}{2V}\int d\vec{q}\, \varphi(\vec{q}) - N\lambda \approx \frac{N^2}{2V}\int d\vec{q}\, \varphi(\vec{q}) - N\lambda$$

$\frac{N}{2}\int d\vec{q}\, \varphi(\vec{q})\, n$

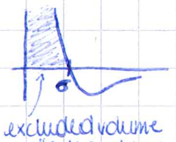
$$\to \mathcal{F}(\lambda) = F_0(\lambda) + \langle\mathcal{H}_1(\lambda)\rangle_0 = \underbrace{-Nk_BT \log\left(\frac{V}{N\lambda_T^3}\right) - Nk_BT}_{\text{ideal gas}} + \underbrace{\frac{N^2}{2V}\int d\vec{q}\, \varphi(\vec{q})}_{\text{corrections due to interactions}}$$

free energy approx. of interacting system

taken into account with a spatial average here F independent of λ, no minimization necessary

$\rightarrow$ pressure $P = -\frac{\partial F}{\partial V} \approx -\frac{\partial \mathcal{F}}{\partial V} = \frac{Nk_BT}{V} + \frac{N^2}{2V^2}\int d\vec{q}\,\varphi(\vec{q})$

note how the integral diverges : $\varphi = \begin{cases} +\infty & r<\sigma \quad (1) \\ -1/r^6 & r>\sigma \quad (2) \end{cases}$



$\Rightarrow$ split interaction pot. into 2 parts
(1) hard sphere repulsion
$\rightarrow$ correction ideal gas law : $V \rightarrow V-Nb$
(2) attractive tail

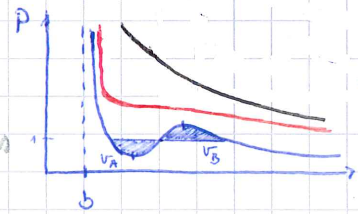
$\Rightarrow P \approx \frac{Nk_BT}{V-Nb} + \frac{N^2}{2V^2}\int_{r>\sigma} d\vec{r}\,\varphi(r)$

$= \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2}$ $\quad$) $a = -\frac{1}{2}\int_{|q|>\sigma} d\vec{q}\,\varphi(\vec{q})$

$\rightarrow$ van der Waals!

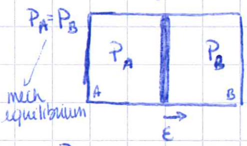
- Phase seperation

below critical point
$\Rightarrow$ seperation into 2 different phases



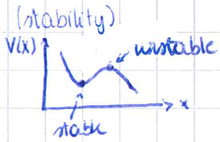
$T > T_c$ $\rightarrow \frac{aN^2}{V^2}$ neglected, pressure decreases monotonically with V
$T = T_c$
$T < T_c$ $\rightarrow$ for some values of V : $\frac{\partial P}{\partial V}\Big|_{N,T} > 0$ $\rightarrow$ thermodynamic instability

thermodyn instability $\frac{\partial P}{\partial V} > 0$:



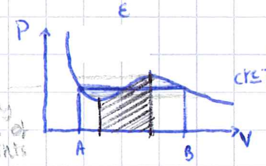
if $\frac{\partial P}{\partial V} < 0$: P_A decreases, P_B increases

(stability)



if $\frac{\partial P}{\partial V} > 0$: unstable equilibrium
$\rightarrow$ wall will move further until new stable equil. is reached

mech stability for each of these points $P_A = P_B$



$\rightarrow$ phase seperation : a dense (liquid) phase & a dilute (gas) phase

2 phase coexistence

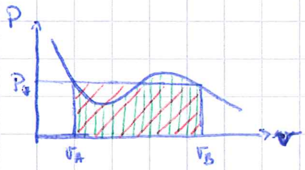
OK! $\begin{cases} \mu_A = \mu_B \\ P_A = P_B = P_* \\ T_A = T_B \end{cases}$ $\rightarrow$ $\mu N = E - TS + PV = F + PV = G$

thus $f_A + P_A v_A = f_B + P_B v_B$ $\qquad f = F/N,\ v = V/N$

$\Rightarrow f_A - f_B = P_*(v_B - v_A)$

$= -\int_{v_A}^{v_B} \frac{\partial f}{\partial v}\,dv$

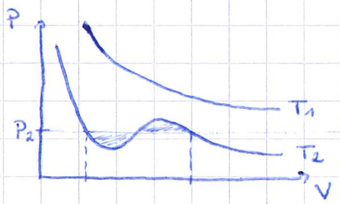
and since $P(v) = -\frac{\partial f}{\partial v}\Big|_{T,N} = \frac{\partial F}{\partial V}\Big|_{T,N}$



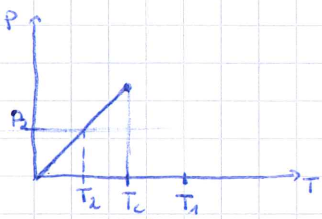
$\Rightarrow \int_{v_A}^{v_B} P(v)\,dv = P_*(v_B - v_A)$

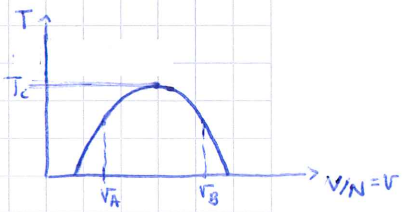
Maxwell construction (equal area law)

Some diagrams :



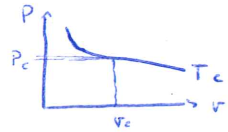
P(N,V,T)





critical point = endpoint phase coexistence

- Critical point and critical exponents



VDW $\quad P = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2} \quad (1)$

in vicinity critical point: $\left.\frac{\partial P}{\partial V}\right|_{N,T} = -\frac{Nk_BT}{(V-Nb)^2} + \frac{2aN^2}{V^3} = 0 \quad (2)$

$$\left.\frac{\partial^2 P}{\partial V^2}\right|_{N,T} = \frac{2Nk_BT}{(V-Nb)^3} - \frac{6aN^2}{V^4} = 0 \quad (3)$$

→ from these 3 eq, we find:

$$v_c = \frac{V_c}{N} = 3b \quad , \quad P_c = \frac{a}{27b^2} \quad , \quad k_BT_c = \frac{8a}{27b} \qquad (*)$$

→ rescaled thermodynamic variables

$$\tilde{p} = P/P_c \quad , \quad \tilde{T} = T/T_c \quad , \quad \tilde{v} = v/v_c \quad \xrightarrow{\text{VDW}} \quad \tilde{p}P_c = \frac{k_B\tilde{T}T_c}{\tilde{v}v_c - b} - a\frac{1}{\tilde{v}^2 v_c^2}$$

sub (*)

$$\Rightarrow \text{VDW} \quad \tilde{p} = \frac{8\tilde{T}}{3\tilde{v}-1} - \frac{3}{\tilde{v}^2}$$

now in the vicinity of the critical point (@ critical point: $\tilde{p}=1, \tilde{T}=1, \tilde{v}=1$)

$$\tilde{p} = 1+\delta p \quad , \quad \tilde{v} = 1+\delta v \quad \quad \tilde{T} = 1+\delta t \qquad \text{where } \delta p, \delta v, \delta t \ll 1$$

$$\rightarrow \text{VDW} \quad (1+\delta p) = \frac{8(1+\delta t)}{3(1+\delta v)-1} - \frac{3}{(1+\delta v)^2} = \frac{8(1+\delta t)}{2+3\delta v} - \frac{3}{(1+\delta v)^2}$$

expand

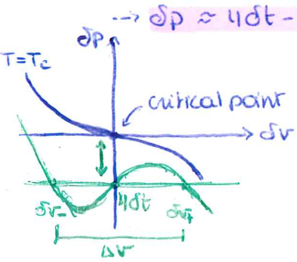
$\frac{1}{1-x} = (1+x+x^2+\dots)$

$$\approx 8(1+\delta t)\frac{1}{2}\left(1-\frac{3}{2}\delta v+\frac{9}{4}\delta v^2-\frac{27}{8}\delta v^3\right) - 3(1-2\delta v+3\delta v^2-4\delta v^3)$$

$$= 1 + 4\delta t - 6\delta t\delta v + 9\delta t(\delta v)^2 - \frac{3}{2}(\delta v)^3 + \dots$$

$4\left(1-\frac{3}{2}\delta v+\frac{9}{4}\delta v^2-\frac{27}{8}\delta v^3 + \delta t - \frac{3}{2}\delta t\delta v + \frac{9}{4}\delta t\delta v^2 - \frac{27}{8}\delta t\delta v^3\right)$
$-3+6\delta v-9\delta v^2+12\delta v^3$
$= 4+4\delta t-6\delta t\delta v+9\delta t\delta v^2$
$-\left[\frac{27}{2}-\frac{24}{2}\right]\delta v^3 - 3$
$-6\delta v+6\delta v+9\delta v^2-9\delta v^2+O(\delta v^4)$
$+O(\delta t^2)$

$$\rightarrow \delta p \approx 4\delta t - 6\delta t\delta v + 9\delta t(\delta v)^2 - \frac{3}{2}(\delta v)^3$$



1) for $T=T_c$ → $\delta t = 0$ along critical isotherm

$\delta p = -\frac{3}{2}(\delta v)^3$ → power law

2) for $T<T_c$ → $\delta t<0$ (approach T_c from below)

@ $\delta v = 0$: $\delta p = 4\delta t$

$$\rightarrow \cancel{4\delta t} \approx \cancel{4\delta t} - 6\delta t\delta v + 9\delta t(\delta v)^2 - \frac{3}{2}(\delta v)^3$$

$D = 6^2\delta t^2 - 16\delta t$ $\quad \Rightarrow \quad \delta v^2 - 6\delta t\delta v + 4\delta t = 0$

$\rightarrow \frac{\sqrt{D}}{2} = \sqrt{\frac{36}{4}\delta t^2 - \frac{16}{4}\delta t}$ $\quad \rightarrow \delta v_\pm = 3\delta t \pm \sqrt{9\delta t^2 - 4\delta t} \underset{\delta t\to 0}{\approx} \pm\sqrt{-4\delta t} = \pm 2\sqrt{-\delta t}$

→ $\sqrt{\delta t}$ largest order

how the difference Δv between the volumes of the 2 coex. phases vanishes as $\delta t \to 0$

maxwell construction $\quad \Delta v = \delta v_+ - \delta v_- = 4\sqrt{-\delta t} = 4(-\delta t)^{1/2}$ → power law

→ 2 coexisting phases with $\delta v_A = -\delta v_B$

2) alternative method:
neglect $9\delta t(\delta v)^2$ since of higher order than $\delta t\delta v$ and $(\delta v)^3$
→ $\delta p = 4\delta t - 6\delta t\delta v - \frac{3}{2}(\delta v)^3$
now maxwell construction $\delta v_A = -\delta v_B$
→ $\delta p(\delta v_A) = \delta p(-\delta v_A)$
$\Rightarrow 4\delta t - 6\delta t\delta v_A - \frac{3}{2}(\delta v_A)^3$
$= 4\delta t + 6\delta t\delta v_A + \frac{3}{2}(\delta v_A)^3$
$\Rightarrow -12\delta t\delta v_A = 3(\delta v_A)^3$
→ $\delta v = \delta v_A - \delta v_B = 2\delta v_A \sim \sqrt{|\delta t|}$

3) isothermal compressibility

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T$$

now $\frac{\partial \tilde{p}}{\partial \tilde{v}} = \frac{-24(1+\delta t)}{(3\tilde{v}-1)^2} + \frac{6}{\tilde{v}^3} = -6(1+\delta t) + 6 = -6\delta t$

$$= \frac{\partial p}{\partial v}\frac{v_c}{P_c} = \frac{v_c}{P_c}N\frac{\partial P}{\partial V} = \frac{V_c}{P_c}\frac{\partial P}{\partial V}$$

$\Rightarrow \kappa_T \sim \frac{1}{|\delta t|} = (\delta t)^{-1}$ → power

4) specific heat

$\lambda \sim \beta^{1/2}$

$$E = -\partial_\beta \log Z = \frac{\partial(\beta F)}{\partial \beta} = \frac{3}{2}Nk_BT - \frac{aN^2}{V}$$

$\beta F = -N\log\left(\frac{V}{N}\right) - N + N\log(\lambda^3) + \beta\frac{aN^2}{V}$

$$\Rightarrow c_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{3Nk_B}{2}$$

→ $c_V \sim$ const $(\delta t)^0$ → power

$$\Rightarrow \begin{cases} \delta p \sim (\delta v)^\delta \\ \delta v \sim (\delta t)^\beta \\ \kappa_T \sim |\delta t|^{-\gamma} \\ c_V \sim |\delta t|^{-\alpha} \end{cases}$$

	α	β	δ	γ
VDW	0	1/2	3	1
fluid exp	0.13	0.33	4.8	1.24

} critical exponents (universal: do not dep. on a or b)

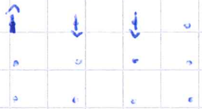
→ fluids @ liquid-vapor points (close to critical point)
→ performed in diff. fluids, all same value: universality

→ several quantities vanish or diverge as power laws in the vicinity of the critical point

Ising model

VdW fails to quantitatively predict the right exponents due to the used approx in the model – mean-field approx: interaction betw. part. accounted for in averaged way
↳ $\frac{N^2}{2V}\int d\vec{q}\,\varphi(\vec{q})$
⇒ model beyond mean field approx needed:
Ising model

lattice model with a spin at each lattice point ("magnetic model")

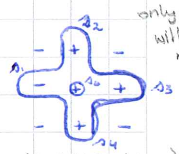


$s_i = \pm 1$ → for N spins: 2^N possible configurations

configuration:

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j - H \sum_i s_i$$

$\langle ij \rangle$: nearest-neighbours → favors alignment of neighbouring spins



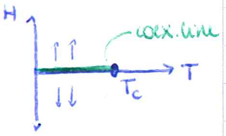
only coupling with nearest neighbours

with $J > 0$ (ferromagn. case) the coupling strength between spins (interaction)
$H \gtrless 0$ the magnetic field ($H=0$: minimal energy config, all spins "aligned")
↳ pos spin config have lower energies if $H>0$; neg spins if $H<0$
↳ spins want to follow H (lower energy state)

$$\rightarrow Z = \sum_{\{s_i\}} e^{-\beta \mathcal{H}(\{s_i\})}$$
↳ sum over 2^N states

→ average value of a spin: $\langle s_k \rangle = \frac{1}{Z} \sum_{\{s_i\}} e^{-\beta\mathcal{H}(\{s_i\})} s_k$

magnetization: $M = \sum_k \langle s_k \rangle$
↳ if $H \neq 0$ → spins predominantly aligned along direction H
→ $M \neq 0$



spontaneous magnetization: magn $M \neq 0$ in absence of magn field ($H=0$)
$= \lim_{H\to 0^\pm} m(T,H) = \pm m_0(T) \neq 0$ with $m = M/N$
⇒ phase transitions occur
@ coex. line: 2 diff. phases with opposite spontaneous magn

- *Absence of phase transition in one dimension*

1D: $Z = \sum_{s_1=\pm1} \sum_{s_2=\pm1} \cdots \sum_{s_N=\pm1} e^{\beta(J\sum_{i=1}^N s_i s_{i+1} + H \sum_{i=1}^N s_i)}$ $\quad s_{i-1}\ s_i\ s_{i+1}$

$= \mathrm{Tr}(T^N)$ → T is the transfer matrix with 2 eigenvalues $\lambda_\pm$: $T = \begin{pmatrix} e^{\beta J - \beta H} & e^{-\beta J - \beta H} \\ e^{-\beta J + \beta H} & e^{\beta J + \beta H} \end{pmatrix}$ → $\lambda^2 - 2e^{\beta J}\cosh(\beta H)\lambda + 2\sinh(\beta J) = 0$
→ $\lambda_\pm = e^{\beta J}\cosh(\beta H) \pm \sqrt{e^{2\beta J}\cosh^2(\beta H) - 2\sinh(\beta J)}$

$= \lambda_+^N + \lambda_-^N \approx \lambda_+^N$ in limit $N\to\infty$, largest λ dominates

⇒ $F = -N k_B T \log \lambda_+$

$\lambda_+ = e^{\beta J}\cosh(\beta H) + \sqrt{e^{2\beta J}\cosh^2(\beta H) - 2\sinh(\beta J)}$

$\frac{\partial \log(\lambda_+)}{\partial H} = \frac{2\beta e^{2\beta J}\sinh(\beta H)}{\sqrt{N e^{2\beta J}(2\cosh(2\beta H)+1) - 8\sinh(\beta J)}}\Big|_{H=0} = 0$

however no spontaneous magnetization at any finite temp
⇒ one-dim systems with short range interactions have no phase transitions at any finite temperature

$M = \sum_k \langle s_k \rangle$
$= \frac{\sum_{s_k} \sum_{\{s_i\}} e^{-\beta\mathcal{H}(\{s_i\})} s_k}{\sum_{\{s_i\}} e^{-\beta\mathcal{H}(\{s_i\})}}$
$= \frac{\partial \log Z}{\beta \partial H}$
$= -\frac{\partial(-k_B T \log Z)}{\partial H}$
$= -\frac{\partial F}{\partial H}$
↳ for spont. magn: $|_{H=0}$

however, at zero temp (TODO)
$\lim_{H\to\pm 0} \lim_{T\to 0^+} m(T,H) = \pm 1$ → spont. magn.

⇒ $T_c = 0$ for 1D Ising

- *Two dimensional Ising model: exact solution*

(2D and 3D do have spont. magn, there is ferromagn)

spontaneous magn for $T<T_c$:
$$m_0(T) = \left[1 - \sinh^{-4}\left(\frac{2J}{k_B T}\right)\right]^{1/8}$$
with T_c derivable from
$$\sinh(2J/k_B T) = 1$$
in the vicinity of the critical point: $m_0(T) \sim (T_c - T)^{1/8}$
⇒ $\beta = 1/8$ since $m_0(T) \sim$ δv VdW

- *Mean-field approximation*

approximate solution Ising model using Bogoliubov

$\rightarrow \mathcal{H} = \mathcal{H}_0(\lambda) + \mathcal{H}_1(\lambda)$

$$= \underbrace{-\lambda \sum_i s_i}_{\text{non-int}} \underbrace{- J \sum_{\langle ij\rangle} s_i s_j - (H-\lambda)\sum_i s_i}_{\text{interacting}}$$

$$Z_0 = \sum_{\{s_i\}} e^{+\beta\lambda \sum_i s_i} = \sum_{s_1=\pm1}\sum_{s_2=\pm1}\dots\sum_{s_N=\pm1} e^{\beta\lambda s_1} e^{\beta\lambda s_2}\dots e^{\beta\lambda s_N}$$

$$= \Big(\sum_{s=\pm1} e^{\beta\lambda s}\Big)^N = \big(e^{\beta\lambda}+e^{-\beta\lambda}\big)^N = (2\cosh\beta\lambda)^N$$

$$\rightarrow F_0 = -k_B T \log Z_0 = -N k_B T \log(2\cosh\beta\lambda)$$

$$\langle \mathcal{H}_1(\lambda)\rangle_0 = \frac{1}{Z_0}\sum_{\{s_i\}}\Big\{-J\sum_{\langle ij\rangle} s_i s_j - (H-\lambda)\sum_i s_i\Big\} e^{-\beta \mathcal{H}_0}$$

they do not interact in $\mathcal{H}_0$

$$= -J\sum_{ij}\langle s_i s_j\rangle_0 - (H-\lambda)\sum_i \langle s_i\rangle_0 = -\frac{JNz}{2}\langle s\rangle_0^2 - (H-\lambda)N\langle s\rangle_0$$

z = # neighbours each spin has $= 2\cdot$dimension
N spins
do not consider each pair twice $\rightarrow \frac{1}{2}$

$$\rightarrow \mathcal{F}(\lambda) = F_0(\lambda) + \langle \mathcal{H}_1(\lambda)\rangle_0$$

$$= -Nk_BT\log(2\cosh\beta\lambda) - \frac{JzN}{2}\langle s\rangle_0^2 - (H-\lambda)N\langle s_*\rangle_0$$

$$= -Nk_BT\log(2\cosh\beta\lambda) - \frac{JzN}{2}\tanh^2(\beta\lambda) - (H-\lambda)N\tanh(\beta\lambda)$$

$$\langle s\rangle_0 = \frac{1}{N}\frac{\partial \log Z_0}{\beta\partial\lambda} = \frac{\partial\log(\cosh\beta\lambda)}{\beta\partial\lambda} = \tanh(\beta\lambda)$$

$$\rightarrow \tilde{F} = \lim_{\lambda} \mathcal{F}(\lambda)$$

$\frac{\partial}{\partial\lambda}$ $\qquad$ $\frac{\partial}{\partial\langle s\rangle_0}\frac{\partial\langle s\rangle_0}{\partial\lambda}$

$$\frac{\partial\mathcal{F}}{\partial\lambda}\Big|_{\lambda=\lambda_*} = 0 \Rightarrow \underbrace{-N\tanh\beta\lambda_* + N\langle s\rangle}_{0} - N\frac{\partial\langle s\rangle_0}{\partial\lambda}\big(Jz\langle s\rangle_0 + H - \lambda\big)\Big|_{\lambda_*} = 0$$

$$\Rightarrow N\frac{\partial\langle s\rangle_0}{\partial\lambda}\big(Jz\langle s\rangle_0 + H - \lambda_*\big) = 0 \Rightarrow Jz\langle s\rangle_0 + H - \lambda_* = 0$$

$$\Rightarrow \lambda_* = H + Jz\tanh(\beta\lambda_*)$$

$$\tilde{F} = \mathcal{F}(\lambda_*)$$

$$= -Nk_BT\log(2\cosh\lambda_*) - \frac{NJz}{2}\tanh^2(\beta\lambda_*) - N(H-\lambda_*)\tanh(\beta\lambda_*)$$

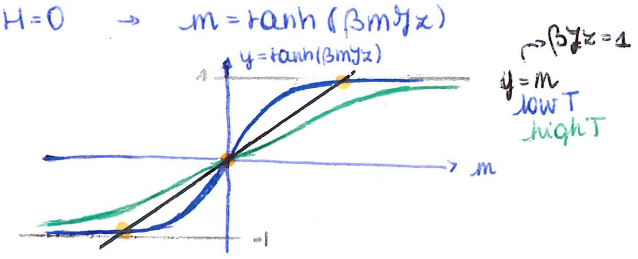
$$m = -\frac{\partial\tilde{F}}{N\partial H} = \frac{-1}{N}\Big[\underbrace{\frac{\partial\tilde{F}}{\partial\lambda_*}\frac{\partial\lambda_*}{\partial H}}_{0 \text{ since } \lambda_* \text{ minimizes } \tilde{F}} + \frac{\partial\tilde{F}}{\partial H}\Big|_{\lambda_*}\Big]_T$$

$$= \tanh(\beta\lambda_*) = \tanh[\beta(mJz + H)]$$

$m = \tanh(\beta\lambda_*)$
$\Rightarrow \tanh(\beta[H + Jz\tanh(\beta\lambda_*)])$
$= \tanh(\beta[H + Jzm])$

now spontaneous magnetization?

$H=0 \rightarrow m = \tanh(\beta m J z)$



at "high" T, low β ($\beta Jz < 1$)
only 1 solution: $m=0$

at sufficiently low T, high β ($\beta Jz > 1$)
spont. magn is possible:
$m = \tanh(\beta m J z)$ also has
2 additional solutions: $m = \pm m_0 \neq 0$

critical point

$$\frac{d\tanh(\beta mJz)}{dm}\Big|_{m=0} = 1$$

$$\tanh(\beta mJz) \approx \beta mJz - \frac{1}{3}(\beta mJz)^3$$

$$\beta Jz - (\beta mJz)^2\big|_{m=0} = \beta_c Jz = 1$$

$$\Rightarrow k_B T_c = Jz$$

approximation becomes better at higher dimensions

we've approx. the effect of spin-spin interactions with an average field λ

a given spin s_j appears in the Hamiltonian with a term of type

$$\Big(\sum_i' s_i + H\Big)s_j$$

where the sum is over all its neighbours

if each spin has many neighbours, the approx $\sum_i' s_i \approx$ cte becomes more and more accurate

Critical exponents

several quantities vanish with power-laws in the vicinity of the critical point
→ critical exponents

spontaneous magn.
$$m_0(T) \sim (T_c - T)^{\beta} \quad \text{along coex line } H=0$$
$$c \sim |T - T_c|^{\alpha}$$
$$\chi = \frac{\partial M}{\partial H} \sim |T - T_c|^{-\gamma}$$
↳ magn. susceptibility
$$H \sim |M|^{\delta} \quad @\, T = T_c$$

Ising	α	β	γ	δ
2d	0	1/8	7/4	15
3d	0.13	0.33	1.24	4,8
Bragg-Williams mean field	0	1/2	1	3

→ identical to experim values for fluids

→ $m = \tanh[\dots]$
↳ same as mean field VDW
✓ BMF exponents do not dep on dim
dim ~ z

correspondance VDW ⟷ Ising model: $P \leftrightarrow H$, $V \leftrightarrow M$

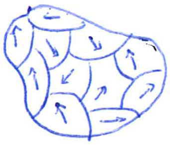
* $H \sim m^3$ @ $T = T_c$
  $k_B T_c = Jz \;\to\; m = \tanh(m + \beta_c H)$
  $\Rightarrow \cancel{m} \approx \cancel{m} + \beta_c H - \frac{1}{3}(m + \beta_c H)^3$
  $\Rightarrow m^3 \sim H$
* correlation length ξ = char. distance at which two spins are correlated
  = measure of the char. length scale of fluctuations of the syst.
  @ $T = T_c$: $\xi \sim |T_c - T|^{-\nu}$ → no longer a char lengthscale, system is scale invariant, fluctuations occur at all length scales
  $G^{(2)} \sim \frac{1}{r^{d-2+\eta}}$ the correlation function

correlation function $G^{(2)}$
for $T > T_c$, $H = 0$ (absence spont. magn):
$$G^{(2)}(\vec{x}, \vec{y}) = \langle s_{\vec{x}}\, s_{\vec{y}} \rangle$$
spins close by → aligned (more likely)
far away spins → weakly interacting → more likely uncorrelated
for $T < T_c$: $m_0 \neq 0$, $\langle s \rangle \neq 0$
$$G^{(2)}(\vec{x}, \vec{y}) = \langle (s_{\vec{x}} - \langle s \rangle)(s_{\vec{y}} - \langle s \rangle) \rangle \quad \text{(subtr. spin average)}$$
for large distances both decay exponentially
$$G^{(2)}(\vec{x}, \vec{y}) \sim e^{-\frac{|\vec{x}-\vec{y}|}{\xi}}$$

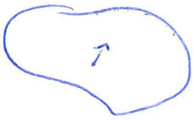
critical opalescence in fluids:
in vicinity of critical points fluctuations become of a size comparable to the wavelength of light → light is scattered
⇒ normally transparent liquid appears cloudy

↳ correlation length ξ diverges at critical point
→ critical behavior indep on local properties of the Hamiltonian
only determined by global properties (dim & symm)
⇒ many different systems share the same critical behaviour

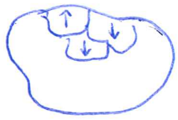
Magnetism



paramagnet   all points magnetized



ferromagnet
all points same magnetization



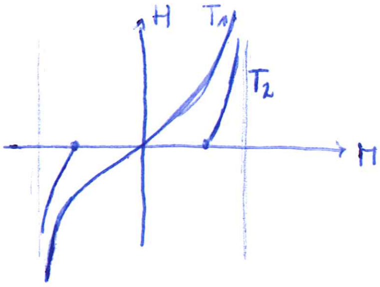
uniaxial ferromagnet

with thermodynamical variables

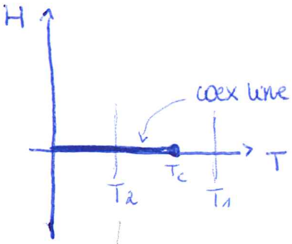
$M = \sum_i \mu_i$ (magn. moments)   magnetization

H magnetic field (external)

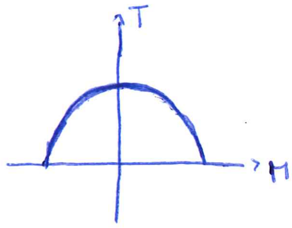
T temperature



at very large H
magnetization → asymptotes



coexistence
between 2 phases



4 Quantum Statistical Mechanics

Before: $\rho(\Gamma) = \rho(P, Q)$ the prob. distribution for 6N-dim config.

Now: + Heisenberg's uncertainty principle
$\Delta p_x \Delta x \geq \hbar/2$ (no simultaneous info about mom & pos)
→ $\rho(P,Q)$ (prob. dens) can't be

cannot specify state with Γ

+ Built-in probabilities
QM state given by $|\Psi_\alpha\rangle$; 1 part. w/ mass m ~ $\Psi(\vec{r}, t)$
→ SE: $i\hbar \partial_t \Psi(\vec{r},t) = \hat{H}\Psi(\vec{r},t)$
with $\hat{H} = -\hbar^2/2\mu \, \vec{\nabla}^2 + V(\vec{r},t)$
↳ $|\Psi_\alpha\rangle$ eigenstates $\hat{H}$ with energy E_α
→ $|\Psi(\vec{q},t)|^2$: prob. to find particle at time t, position $\vec{q}$

⇒ QM states & probabilities for system in state $|\Psi_\alpha\rangle$

* QM probability
for operator $\hat{A}$ (physical observable):
$$\langle \hat{A} \rangle_{pure} = \int \Psi_\alpha^*(q)\, \hat{A}\, \Psi_\alpha(q)\, d^{3N}q = \langle \Psi_\alpha | \hat{A} | \Psi_\alpha \rangle$$

* Quantum statist. mech. prob
$$\langle \hat{A} \rangle = \sum_\alpha c_\alpha \langle \Psi_\alpha | \hat{A} | \Psi_\alpha \rangle_{pure}$$
with c_α the prob to find the syst. in state $|\Psi_\alpha\rangle$
norm.: $\sum_\alpha c_\alpha = 1$

Using $\sum_n |n\rangle\langle n| = \mathbb{1}$ [complete set of orthonorm. states]
→ $\langle \hat{A} \rangle = \mathrm{Tr}_H(\hat{A}\hat{\rho})$ where $\hat{\rho} \equiv \sum_\alpha c_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha|$ the density matrix
$= \sum_n \langle n | \hat{A}\hat{\rho} | n \rangle$

classical equivalent: $\langle A \rangle = \int d\Gamma \rho(\Gamma) A(\Gamma)$; classical equivalent: prob. distr. function $\rho(\Gamma)$

special case: pure state := $\rho = |\phi\rangle\langle\phi|$ (no summ)

→ Quantum canonical ensemble
since $\hat{H}|\Psi_\alpha\rangle = E_\alpha |\Psi_\alpha\rangle$
and $c_\alpha = 1/Z \; e^{-\beta E_\alpha}$ specifies prob distr of states
with $\beta = 1/k_B T$
$Z = \sum_\alpha e^{-\beta E_\alpha}$ [norm factor] = PARTITION FUNCTION

→ $\hat{\rho}_{can} = \exp(-\beta\hat{H}) / \mathrm{Tr}(\exp(-\beta\hat{H}))$

↳ $f(\Pi) = \begin{pmatrix} f(\Pi_{11}) & & \\ & f(\Pi_{22}) & \\ & & f(\Pi_{nn}) \end{pmatrix}$ for Π diag.
⇒ $e^{\hat{\Pi}} = \mathbb{1} + \hat{\Pi} + \frac{1}{2}\hat{\Pi}\hat{\Pi} + \frac{1}{3!}\hat{\Pi}\cdot\hat{\Pi}\cdot\hat{\Pi} + \dots$

example: Quantum Harm. Osc
$\hat{H} = -\hbar^2/2\, \partial_x + \omega^2/2\, x^2$
→ $H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2} = (2x - \frac{d}{dx})^n \cdot 1$
with hermite polynomials as Ψ_α, and ω the frequency
⇒ $E_n = \hbar\omega(n + 1/2)$ $n \in \mathbb{N}$ $\{0,1,2,\dots\}$ (non-degenerate energy spectr.)
→ $Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}$

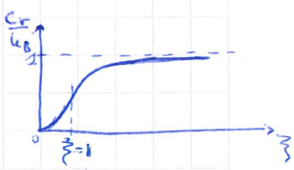
$\sum_n e^{-\beta E_n} = \sum_n e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2}\sum_n e^{-\beta\hbar\omega n} = e^{-\beta\hbar\omega/2}\frac{1}{1-e^{-\beta\hbar\omega}}$

using $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$

→ $\langle E \rangle = -\partial_\beta \log Z = \partial_\beta \left[\frac{\beta\hbar\omega}{2} + \log(1 - e^{-\beta\hbar\omega}) \right]$
$= \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right]$

dimensionful $C_V = \partial E/\partial T = k_B (\hbar\omega/k_B T)^2 \; e^{\beta\hbar\omega}/(1 - e^{\beta\hbar\omega})^2$

dimensionless $\xi = k_B T/\hbar\omega$ → $\frac{C_V}{k_B} = \frac{1}{\xi^2} \cdot \frac{e^{-1/\xi}}{(1 - e^{-1/\xi})^2}$ → equipart. $1 - 1/12\xi^2$ $\xi \gg 1$ high T
→ 0 purely quantum effect which peaks at some point $\xi \ll 1$ low T



⇒ $\xi \approx 1$ → $T_* \approx \hbar\omega/k_B$ crossover from QM → CM
↳ charact. temp
$T \gg T_*$ CM
$T \ll T_*$ QM

Fermions & Bosons

QM: particles indistinguishable $\Rightarrow |\Psi(\vec{q}_1,\dots,\vec{q}_i,\dots,\vec{q}_j,\dots,\vec{q}_N)|^2 = |\Psi(\vec{q}_1,\dots,\vec{q}_j,\dots,\vec{q}_i,\dots,\vec{q}_N)|^2$ for $i\neq j$ → symm under the exchange of coord of any pair of part.

→ In $D\neq 2+1$ (2 pos + 1 time) 2 options

1) Ψ is symmetric $i\leftrightarrow j$ → bosons: $s=0,1,2,\dots$ (integer spin) (phase 0)

2) Ψ is antisymmetric $i\leftrightarrow j$ → fermions: $s=1/2, 3/2, \dots$ (half-integer spin) (phase 1/2)

D=2+1 → anyons

example 2 non-interacting particles

- $\mathcal{H} = \mathcal{H}_1(\vec{p}_1,\vec{q}_1) + \mathcal{H}_1(\vec{p}_2,\vec{q}_2)$

  with $\mathcal{H}_1 = -\hbar^2/2m\,\vec{\nabla}_1^2 + V(\vec{q}_1)$ and $\hat{\mathcal{H}}_1|\phi_k\rangle = \varepsilon_k|\phi_k\rangle$ w k a quantum number

- quantum state:

  $\Psi(\vec{q}_1,\vec{q}_2) = \phi_k(\vec{q}_1)\phi_l(\vec{q}_2)$ with $k\neq l$

→ $\mathcal{H}\Psi = [\mathcal{H}_1(\vec{p}_1,\vec{q}_1)+\mathcal{H}_2(\vec{p}_2,\vec{q}_2)]\phi_k(\vec{q}_1)\phi_l(\vec{q}_2) = (\mathcal{H}_1(\vec{p}_1,\vec{q}_1)\phi_k(\vec{q}_1))\phi_l(\vec{q}_2) + \phi_k(\vec{q}_1)(\mathcal{H}_2(\vec{p}_2,\vec{q}_2)\phi_l(\vec{q}_2))$

$= (\varepsilon_k+\varepsilon_l)\Psi(\vec{q}_1,\vec{q}_2)$

However: no symm: $|\Psi(\vec{q}_1,\vec{q}_2)|^2 \neq |\Psi(\vec{q}_2,\vec{q}_1)|^2$ $k\neq l$ $\Psi(\vec{q}_2,\vec{q}_1) = \phi_k(\vec{q}_2)\phi_l(\vec{q}_1) \neq \phi_k(\vec{q}_1)\phi_l(\vec{q}_2)$

⇒ (anti)symmetrization

$$\Psi_\pm(\vec{q}_1,\vec{q}_2) = \frac{1}{\sqrt{2}}\left[\phi_k(\vec{q}_1)\phi_l(\vec{q}_2) \pm \phi_k(\vec{q}_2)\phi_l(\vec{q}_1)\right]$$

→ Ψ_+ : wavefunction for 2 ident. BOSONS (photons, phonons)

Ψ_- : " " 2 ident. FERMIONS (electrons, protons)

NOW: 2 particles in same quantum states

$\Psi(\vec{q}_1,\vec{q}_2) = \phi_k(\vec{q}_1)\phi_k(\vec{q}_2)$

→ $\Psi_+ = \sqrt{2}[\phi_k(\vec{q}_1)\phi_k(\vec{q}_2)]$ → Bosons ok

$\Psi_- = 0$ → Fermions: PAULI EXCLUSION PRINCIPLE "2 identical fermions cannot occupy the same quantum state"

N identical particles

n_γ = occupation # (# of particles) in state with ε_γ

↳ for example above (N=2): $n_k = n_l = 1$, $n_j = 0$ for $j\neq k,l$

general: * bosons: $n_\gamma \geq 0$

* fermions: $n_\gamma = 0,1$ (Pauli)

→ $N = \sum_\gamma n_\gamma$ (tot amount particles), $E = \sum_\gamma n_\gamma\varepsilon_\gamma$ (total energy)

→ canonical ensemble: partition function

$$Z(N,V,T) = \sum_{n_1}\sum_{n_2}\dots\sum_{n_\gamma}\dots e^{-\beta\sum n_\gamma\varepsilon_\gamma}\,\underbrace{\delta_{N,\sum_\gamma n_\gamma}}_{\text{restricts \# part to N}}$$

makes expr. complicated $\delta_{ij} = \begin{cases}0 & i\neq j\\ 1 & i=j\end{cases}$

→ grand canonical ensemble: part. function

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} Z(N,V,T)\,e^{\beta\mu N} = \sum_{\{n_\gamma\}} e^{-\beta\sum_\gamma n_\gamma\varepsilon_\gamma}\sum_{N=0}^{\infty} e^{\beta\mu N}\delta_{N,\sum_\gamma n_\gamma}$$

$$= \sum_{\{n_\gamma\}} e^{-\beta\sum_\gamma n_\gamma\varepsilon_\gamma}\,e^{\beta\mu\sum_\gamma n_\gamma}$$

$$= \prod_\gamma\sum_{n_\gamma} e^{-\beta n_\gamma(\varepsilon_\gamma-\mu)}$$

$e^{a+b} = e^a e^b$

$$\Xi(\mu,V,T) = \prod_\gamma \sum_{n_\gamma} e^{-\beta n_\gamma(\varepsilon_\gamma-\mu)}$$

→ Bosons
! convergent only for $e^{\beta(\mu-\varepsilon_\gamma)} < 1$ → $\mu < \min(\varepsilon_\gamma)$ upperbound μ
+ uses geom. series $\left(\sum_{n=0}^{\infty} a r^k = \frac{a}{1-r}\right)$

$$\Rightarrow \Xi_{BE} = \prod_\gamma \frac{1}{1-e^{\beta(\mu-\varepsilon_\gamma)}}$$

→ Fermions

$$\Xi_{FD} = \prod_\gamma \left[1 + e^{\beta(\mu-\varepsilon_\gamma)}\right]$$

$(n_\gamma = 0,1)$ no cond. on μ

$$\Rightarrow \log \Xi = \mp \sum_\gamma \log\left(1 \mp e^{\beta(\mu-\varepsilon_\gamma)}\right)$$

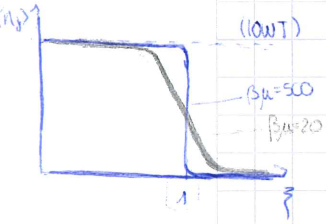
upper sign = bosons
lower sign = fermions

$$\rightarrow \langle n_\gamma \rangle = \frac{-\partial \log \Xi}{\beta \partial \varepsilon_\gamma} = \frac{1}{\left(e^{\beta(\varepsilon_\gamma-\mu)} \mp 1\right)}$$

↳ $\exp(\beta(\varepsilon_\gamma-\mu)) \geq 1$ bosons → $\langle n_\gamma \rangle > 0$
> 0 fermions → $\langle n_\gamma \rangle \leq 1$

$$E = \left.\frac{-\partial \log \Xi}{\partial \beta}\right|_{\beta\mu = \text{cst}} = \sum_\gamma \frac{\varepsilon_\gamma}{e^{\beta(\varepsilon_\gamma-\mu)} \mp 1} = \sum_\gamma \langle n_\gamma \rangle \varepsilon_\gamma$$

↳ comments



* FD: $\langle n_\gamma \rangle_{FD} = \dfrac{1}{\exp(\beta\mu(\xi-1))+1}$ $\xi \equiv \varepsilon_\gamma/\mu$ (dimless)

value to which all energy states are occupied

low T $(\beta \to \infty)$: $\langle n_\gamma \rangle = 1$ for $\varepsilon_\gamma < \mu$ $(\xi < 1$ → occupied)
~ step function $\langle n_\gamma \rangle = 0$ for $\varepsilon_\gamma > \mu$ $(\xi > 1$ → free)
→ zero temperature limit: $\lim_{T\to 0} \mu(T) = \varepsilon_F$ fermi-energy

* BEC: $\langle n_\gamma \rangle_{BE} \gg 1$ $(\to \infty)$
⇒ $\mu \to \varepsilon_\gamma$

* Bosons with $\mu = 0$: $\langle n_\gamma \rangle = 1/(e^{\beta\varepsilon_\gamma}-1)$ — same as QHO

bosons good approx. for photons & phonons
fermions good for electrons in metal

Quantum corrections to ideal gas law

(particles in a box)

system of non-interacting quantum particles in a cubic box of size L with single particle energy levels

$$\varepsilon_p = \vec{p}^2/2m$$

SE → $-\frac{\hbar^2}{2m}\nabla^2\phi_p = \varepsilon_p\phi_p$ ⇒ $\phi_{\vec{k}} = e^{i\vec{k}\cdot\vec{x}}$ (plane wave) w/ $\vec{p} = \hbar\vec{k}$

impose periodic boundary cond → quantization $\vec{p}$?
$e^{ik_x(x+L)} = e^{ik_x x}$ ⇒ $k_x = \frac{2\pi}{L} n_x$ ⇒ $\vec{p} = \frac{h}{L}(n_x, n_y, n_z)$ $\in \mathbb{Z}$

controls spacing between energy levels

now: $\log \Xi = \mp \sum_{\vec{p}} \log\left(1 \mp e^{\beta(\mu - \vec{p}^2/2m)}\right)$

$= \mp \frac{V}{h^3} \int d\vec{p} \log\left(1 \mp \exp(\beta(\mu - \vec{p}^2/2m))\right)$

↗ $\int_{x_a}^{x_b} f(x)dx \approx \sum f(x_i)\Delta x_i$ small
$\times \Delta p = h/L$ $\times L^3 = V$

$z = e^{\beta\mu}$ ↳

$\log(1 \mp x) = -\sum_{l=1}^{\infty} (\pm 1)^l \frac{x^l}{l}$

$= \pm \frac{V}{h^3} \int d\vec{p} \left[\sum_{l=1}^{\infty} (\pm 1)^l \frac{z^l}{l} e^{-\beta\vec{p}^2 l/2m}\right]$

$4\pi \int dp\, p^2 e^{-\beta p^2 l/2m} = 4\pi \left(\frac{\beta l}{2m}\right)^{-3/2} \frac{\sqrt{\pi}}{4}$

bosons: $\mu < \varepsilon_0 = 0$, $\beta > 0$ → $z < 1$

$= \pm \frac{V}{h^3} \pi^{3/2} (2m k_B T)^{3/2} \sum_{l=1}^{\infty} (\pm 1)^l z^l / l^{5/2}$

↗ $\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$

$$= \pm \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} (\pm 1)^l z^l / l^{5/2}$$

$$\log \Xi = \pm \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} (\pm 1)^l \frac{z^l}{l^{5/2}}$$

$$\rightarrow N = \frac{1}{\beta}\partial_\mu \log \Xi = \pm \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} (\pm 1)^l \frac{z^l}{l^{3/2}}$$

$z = e^{\beta\mu}$

$$\Rightarrow \begin{cases} \frac{PV}{k_B T} = \pm \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} (\pm 1)^l \frac{z^l}{l^{5/2}} \\ n\lambda_T^3 = \pm \sum_{l=1}^{\infty} (\pm 1)^l \frac{z^l}{l^{3/2}} \end{cases}$$

$n = \frac{N}{V}$

$\log \Xi = \frac{PV}{k_B T}$

$\rightarrow$ ~~lowest order~~ expand in z (small)

1st order $\begin{cases} \frac{PV}{k_B T} = \frac{V}{\lambda_T^3} z \\ n\lambda_T^3 = z \end{cases}$ $\Rightarrow p = n k_B T$ classical ideal gas

2nd order $\begin{cases} \frac{pV}{k_B T} \approx \frac{V}{\lambda_T^3}\left(z \pm \frac{z^2}{4\sqrt{2}}\right) \\ n\lambda_T^3 \approx z \pm \frac{z^2}{2\sqrt{2}} \end{cases}$

$p = n k_B T \frac{(z \pm z^2/4\sqrt{2})}{(z \pm z^2/2\sqrt{2})} \underset{z \ll 1}{\overset{*}{\approx}} n k_B T \left(1 \mp \frac{z}{4\sqrt{2}}\right)$

$\Rightarrow p \approx n k_B T \left(1 \mp \frac{n\lambda_T^3}{4\sqrt{2}}\right)$

classical

quantum correction

* using

$\frac{x + \alpha x^2}{x + \beta x^2} \approx \frac{1 + \alpha x}{1 + \beta x}$

$\approx (1 + \alpha x)(1 - \beta x)$

$\mapsto (1 \pm z/4\sqrt{2})(1 \mp z/2\sqrt{2})$

$\approx 1 \pm z/4\sqrt{2} \mp z/2\sqrt{2} + O(z^2)$

$\approx 1 \pm z/4\sqrt{2} \mp 2z/4\sqrt{2}$

3rd order $\begin{cases} \frac{PV}{k_B T} = \frac{V}{\lambda_T^3}\left(z \pm \frac{z^2}{4\sqrt{2}} + \frac{z^3}{9\sqrt{3}}\right) \\ n\lambda_T^3 = z \pm \frac{z^2}{2\sqrt{2}} + \frac{z^3}{3\sqrt{3}} \end{cases}$

$p = n k_B T \left[1 \mp \frac{z}{4\sqrt{2}} + \left(\frac{1}{16} - \frac{2}{9\sqrt{3}}\right) z^2\right]$

$\Rightarrow p \approx n k_B T \left(1 \mp \frac{n\lambda_T^3}{4\sqrt{2}} + \left(\frac{1}{8} - \frac{2}{9\sqrt{3}}\right) n^2 \lambda_T^6\right)$

Bose-Einstein condensation

For (free) bosons we considered

$$n\lambda_T^3 = \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}$$ inverting

with $z = e^{\beta\mu}$, $n = N/V$, from $\Xi = \prod_r \frac{1}{1 - \exp(\beta(\mu - \epsilon_r))}$

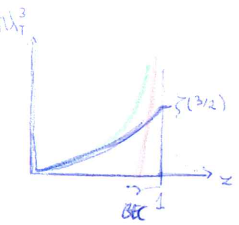
$\rightarrow z \leq 1$ since $\beta > 0$, $\mu \leq \epsilon_0 = 0$

$\rightarrow$ else series diverges (for $z > 1$)

Now $\mu = \beta^{-1} \log z \rightarrow \mu(N, V, T)$

Then $P(N, V, T)$ by replacing $z = e^{\beta\mu}$ by pressure since $\frac{PV}{k_B T} = \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}}$

$\rightarrow n\lambda_T^3 = \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}$ converges for $z \leq 1$, diverges for $z > 1$



for $z \to 1$, $\mu \to \epsilon_0$: $n\lambda_T^3 = \sum_{l=1}^{\infty} \frac{1}{l^{3/2}} = \zeta(3/2) \approx 2{,}612\ldots$

$\Rightarrow$ can only find a chem. potential for $n\lambda_T^3 \leq 2{,}612$
else unphysical result (no inversion possible)
(no μ)

with $\zeta(s)$ Riemann zeta

$\zeta(s) \equiv \sum_{l=1}^{\infty} \frac{1}{l^s}$

$\zeta = 0$ for $s = -2n$ or $s = \frac{1}{2} + iy$

$n \in \mathbb{N}_0$ $y \in \mathbb{R}$

$\mapsto$ Riemann Hypothesis

$\rightarrow$ reevaluate analysis:

$$N = \sum_{\vec{p}} \langle n_{\vec{p}} \rangle = \sum_{\vec{p}} \frac{1}{e^{\beta(p^2/2m - \mu)} - 1} = \underbrace{\frac{z}{1-z}}_{\substack{p = 0 \\ \text{or ground} \\ \text{state contribution}}} + \underbrace{\sum_{\vec{p} \neq 0} \frac{z}{e^{\beta p^2/2m} - z}}_{\substack{p \neq 0 \\ \text{excited states} \\ \text{contribution}}}$$

for $z \to 1^-$ the 1st term diverges

this isn't taken into account in the integral form (z.o.z.)

$N = \frac{z}{1-z} + \frac{4\pi V}{h^3} \sum_{l=1}^{\infty} z^l \int dp\, p^2 e^{-l\beta p^2/2m}$

$\sqrt{\pi}\left(\frac{2m}{l\beta}\right)^{3/2}$

$N = \frac{z}{1-z} + \frac{V}{\lambda_T^3} \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}$

"separating ground state contr. from exited states"

$$\rightarrow n\lambda_T^3 = \frac{\lambda_T^3}{V} \frac{z}{1-z} + \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}$$

* low n, high T ($n\lambda_T^3 < 2{,}612$):
"classical regime", can neglect 1st term $\sim O(1/V)$

* high n, low T ($n\lambda_T^3 > 2{,}612$):
take into account ground state $\sim O(1)$
since a macroscopic number of particles can occupy the ground state
$\rightarrow$ BEC

correction term for ground state contributions not taken into account for fermions
since only 1 fermion can occupy that state $\rightarrow$ minimal mistake

estimate

$n\lambda_T^3 \approx \zeta(3/2) \Rightarrow (N/V)^{2/3}\ h^2/2\pi m k_B T \approx (\zeta(3/2))^{2/3}$

$\Rightarrow k_B T_{BEC} \approx \frac{h^2}{2\pi m}\left(\frac{N}{V\zeta(3/2)}\right)^{2/3}$

$\to$ atoms/mol. superfluids at low T

general (also valid for non-interacting bosons subject to external pot.)

bosons w density of states $g(\varepsilon)$

$[\,g(\varepsilon)d\varepsilon = \#$ of states w energy $[\varepsilon, \varepsilon + d\varepsilon]\,]$

$\to N = \sum_\gamma \frac{1}{e^{\beta(\varepsilon_\gamma - \mu)} - 1}$

$\approx \int_{\varepsilon_{min}}^{+\infty} \frac{g(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon_0-\mu)}-1}$ convergent if $\mu < \varepsilon_{min}$

for $\mu \to \varepsilon_{min} \Rightarrow$ BEC — whether this happens ~ $g(\varepsilon)$ in vicinity ε_{min}

Photons and black body radiation

model: cubic cavity of side L

inside photons in thermal equilibrium at temp T

$\to$ Maxwell eq. $1/c^2\, \partial_t^2 \vec{E} = \nabla^2 \vec{E}$

solution: $\vec{E} = \vec{E}_0\, \mathrm{Re}\{\exp(i(\vec{k}\cdot\vec{x} - \omega t))\}$ (traveling wave with speed c in direction $\vec{k}$)

$\to$ dispersion relation: $\omega = c|\vec{k}|$

in a box $\Rightarrow$ boundary conditions: assume conducting walls

$\vec{E} = \vec{E}_0 \sin(\vec{k}\cdot\vec{x})\sin(\omega t)$

with $\vec{k} = \frac{\pi}{L}(n_x, n_y, n_z)$ $n_{x,y,z} \in \mathbb{N}_0$, $(x,y,z) \in (0,L)$

then # of allowed waves in a volume element: $2V/\pi^3\, d\vec{k}$

photons have 2 transversal polarizations ($\vec{\nabla}\cdot\vec{E} = 0 \Rightarrow \vec{k}\cdot\vec{E} = 0$)

$\Rightarrow$ density of state $g(\omega)d\omega = \frac{1}{8}\frac{2V}{\pi^3} 4\pi k^2 dk = \frac{V}{\pi^2 c^3}\omega^2 d\omega$

number of one. with freq $[\omega, \omega + d\omega]$ — only $(n_x, n_y, n_z) > 0$

Planck: treating photons as particles with energy $h\nu = \hbar\omega$

Planck: $\varepsilon = \hbar\omega(n + \tfrac{1}{2})$ — $\tfrac12$: ignore here

$\to \Xi = \sum_{\{n_\gamma\}} e^{-\beta\hbar\omega_\gamma n_\gamma} = \prod_\gamma \frac{1}{1 - e^{-\beta\hbar\omega_\gamma}}$ $\to$ Bosons with $\mu = 0$

$\to \log \Xi = -\int_0^\infty d\omega\, g(\omega) \log(1 - e^{-\beta\hbar\omega})$

$V\omega^2/\pi^2 c^3$

$E = -\frac{\partial \log\Xi}{\partial\beta} = \int_0^\infty d\omega\, g(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$ $\leadsto x = \beta\hbar\omega$ (dimensionless)

$= \boxed{\frac{V\hbar}{\pi^2 c^3}\int_0^\infty d\omega \frac{\omega^3}{e^x - 1}} = \frac{V\hbar}{\pi^2 c^3}\frac{1}{\beta^4\hbar^4}\int_0^\infty dx \frac{x^3}{e^x - 1}$

$= \frac{V\hbar}{c^3}\left(\frac{k_B T}{\hbar}\right)^4\left(\frac{I}{\pi^2}\right) = \frac{V\pi^2\hbar}{15 c^3}\left(\frac{k_B T}{\hbar}\right)^4$

$\hookrightarrow$ Stefan-Boltzmann: $E \sim T^4$ ($E = \sigma T^4$)

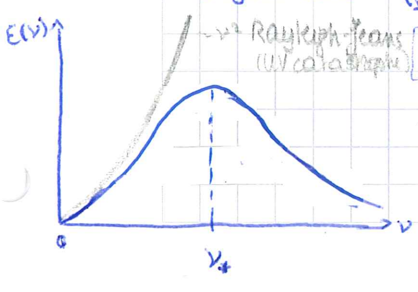
$I = \int_0^\infty dx\, x^3/e^x - 1 = \int dx\, x^3 \sum_{n=1}^\infty e^{-nx} = \sum_{n=1}^\infty \int_0^\infty dx\, x^3 e^{-nx}$ $\leftarrow$ 3 times integr. by parts

$= \sum_{n=1}^\infty \int_0^\infty \frac{6e^{-nx}}{n^3}dx = \sum_{n=1}^\infty \left(-\frac{6e^{-nx}}{n^4}\right)\Big|_0^\infty$

$= \sum_{n=1}^\infty \frac{6}{n^4} = 6\sum_{n=1}^\infty \frac{1}{n^4} = 6\zeta(4)$ $\pi^4/90$

$= \pi^4/15$

$E = \int d\omega\, \varepsilon(\omega)$



$\varepsilon(\omega) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}$ Planck's law

$\leadsto$ energy dens per unit volume

expand

$\omega \gg 1 \to \varepsilon \to 0$

$\omega \ll 1 \to x \to 0: \frac{x^3}{e^x - 1} \approx x^2 - \frac{x^3}{2}$

$\Rightarrow \varepsilon_p \underset{x \ll 1}{\approx} \frac{1}{\pi^2 c^3}\{\underbrace{\omega^2 k_B T}_{\text{equip.}} - \underbrace{\tfrac{1}{2}\hbar\omega^3}_{\text{quantum corr.}} + \dots\}$

Fermions

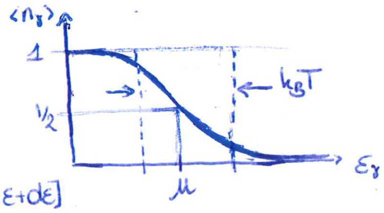
non-interacting fermions:

$$\log \Xi = \sum_\gamma \log\left(1 + e^{-\beta(\varepsilon_\gamma - \mu)}\right)$$

$$\rightarrow E = -\frac{\partial \log \Xi}{\partial \beta}\bigg|_{\beta\mu} = \sum_\gamma \frac{\varepsilon_\gamma}{e^{\beta(\varepsilon_\gamma - \mu)} + 1} = \sum_\gamma \langle n_\gamma \rangle \varepsilon_\gamma \approx \int_0^\infty \frac{\varepsilon g(\varepsilon) d\varepsilon}{1 + e^{\beta(\varepsilon_\gamma - \mu)}}$$

$$\langle n_\gamma \rangle = \frac{1}{1 + e^{\beta(\varepsilon_\gamma - \mu)}}$$

Fermi function



$g(\varepsilon)$ = dens. of states

$g(\varepsilon) d\varepsilon$ = # states in $[\varepsilon, \varepsilon + d\varepsilon]$

fermions → μ is not bounded, can take any possible value

* for $\varepsilon_0 = 0$: if $\mu < 0$ and $-\beta\mu \gg 1$ ⇒ $e^{-\beta\mu} \gg 1$

  → $\langle n_\gamma \rangle \approx e^{-\beta(\varepsilon_\gamma - \mu)}$ Fermi → classical

  if $\mu > 0$ and $\beta\mu \gg 1$ ⇒ distribution becomes sharper

* for $T = 0$: all states below Fermi energy ε_F occupied

  → degenerate Fermi system

  $$E_0 = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon \quad \text{and} \quad N = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon$$

= know its double ...

define Fermi temperature $T_F = \varepsilon_F / k_B$: $T \ll T_F$ → $\langle n_\gamma \rangle$ is very sharp and almost fully degenerate

for $T \to 0$

$$\langle n_\gamma \rangle = \begin{cases} 1 & \varepsilon_\gamma < \varepsilon_F \\ 1/2 & \varepsilon_\gamma = \varepsilon_F \\ 0 & \text{else} \end{cases} \qquad \text{with } \varepsilon_F \equiv \lim_{T\to 0} \mu$$

thus $\lim_{T \to 0} E \equiv E_0 = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon$

$\lim_{N \to 0} N = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon$

$$\frac{PV}{k_B T} = \log \Xi \approx \int_0^\infty d\varepsilon\, g(\varepsilon) \log\left(1 + e^{-\beta(\varepsilon_\gamma - \mu)}\right)$$

$$\lim_{T\to 0} \frac{1}{\beta} \log\left(1 + e^{-\beta(\varepsilon_\gamma - \mu)}\right) = \begin{cases} -(\varepsilon_\gamma - \varepsilon_F) & \varepsilon < \varepsilon_F \\ 0 & \varepsilon > \varepsilon_F \end{cases}$$

for e^{large}: $\log(1 + e^{-\beta\ldots}) \approx \log(e^{-\beta \ldots}) = -\beta \ldots$

$$\Leftrightarrow \lim_{T \to 0} p = \lim_{T \to 0} \frac{1}{V} \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)(\varepsilon_F - \varepsilon)$$

$$= \frac{1}{V} \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)(\varepsilon_F - \varepsilon) = p_0 > 0$$

→ pressure does NOT vanish

some fermions have non-zero momentum due to the exclusion principle

⇒ non-zero pressure

[in their ground state: occupy high mom. state → generate finite pressure]

low temperature behaviour

$$E = \int_0^{+\infty} d\varepsilon \frac{g(\varepsilon)\varepsilon}{e^{\beta(\varepsilon - \mu)} + 1} = \int_0^\mu d\varepsilon\, g(\varepsilon) \frac{1 + e^{\beta(\varepsilon - \mu)} - e^{\beta(\varepsilon - \mu)}}{1 + e^{\beta(\varepsilon - \mu)}} \varepsilon + \int_\mu^{+\infty} d\varepsilon \frac{g(\varepsilon)\varepsilon}{1 + e^{\beta(\varepsilon - \mu)}}$$

$$= \int_0^\mu d\varepsilon\, g(\varepsilon)\varepsilon - \int_0^\mu d\varepsilon \frac{g(\varepsilon)\varepsilon}{1 + e^{-\beta(\varepsilon - \mu)}} + \int_\mu^{+\infty} d\varepsilon \frac{g(\varepsilon)\varepsilon}{1 + e^{\beta(\varepsilon - \mu)}}$$

sub with $x \equiv \mp \beta(\varepsilon - \mu)$

$$= \int_0^\mu d\varepsilon\, g(\varepsilon)\varepsilon - \frac{1}{\beta}\int_0^{\beta\mu} dx \frac{(\mu - x/\beta) g(\mu - x/\beta)}{1 + e^x} + \frac{1}{\beta}\int_0^\infty dx \frac{(\mu + x/\beta) g(\mu + x/\beta)}{1 + e^x}$$

set $g(\varepsilon) = 0$ for $\varepsilon < 0$

assuming that $\varepsilon_0 = 0$

→ can extend 1st integr. without any problems

$$= \int_0^\mu d\varepsilon\, g(\varepsilon)\varepsilon + \frac{1}{\beta}\int_0^{+\infty} dx \frac{(\mu + x/\beta) g(\mu + x/\beta) - (\mu - x/\beta) g(\mu - x/\beta)}{1 + e^x}$$

$$E = \int_0^{\mu} d\varepsilon\, g(\varepsilon)\varepsilon + k_BT \int_0^{+\infty} dx\, \frac{(\mu + k_BTx)g(\mu+k_BTx) - (\mu - k_BTx)g(\mu - k_BTx)}{1+e^x}$$

low temp T: expansion

$$g(\mu \pm k_BTx) \approx g(\mu) \pm k_BTx\, g'(\mu)$$

$$\Leftrightarrow (\mu \pm k_BTx)g(\mu \pm k_BTx) \approx \mu g(\mu) \pm k_BTx(\mu g'(\mu) + g(\mu))$$

(only keep smallest order term in k_BT)

$$\Rightarrow E \approx \int_0^{\mu} d\varepsilon\, g(\varepsilon)\varepsilon + 2(k_BT)^2(\mu g'(\mu) + g(\mu)) \int_0^{\infty} \frac{x\,dx}{1+e^x}$$

$\int_0^{\infty} \frac{x\,dx}{1+e^x} = \frac{\pi^2}{12}$

as $T \to 0$
$\mu \to \varepsilon_F$

$$= \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)\varepsilon + \int_{\varepsilon_F}^{\mu} d\varepsilon\, g(\varepsilon)\varepsilon + \frac{\pi^2}{6}(k_BT)^2[\varepsilon_F g'(\varepsilon_F) + g(\varepsilon_F)]$$

$\int_x^{x+\Delta x} f(x)dx$
$= \int_x^{x+\Delta x}[f(x_0) + f'(x-x_0) + \dots]dx$
$= f(x_0)\Delta x + O(\Delta x^2)$

$$\approx \underbrace{\int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)\varepsilon}_{E_0} + g(\varepsilon)\varepsilon_F(\mu - \varepsilon_F) + (k_BT)^2[\varepsilon_F g'(\varepsilon_F) + g(\varepsilon_F)]\frac{\pi^2}{6}$$

similarly

$$N \approx \int_0^{+\infty} d\varepsilon \frac{g(\varepsilon)}{1+e^{\beta(\varepsilon-\mu)}} \approx \dots \approx \underbrace{\int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)}_{N_0} + g(\varepsilon_F)(\mu - \varepsilon_F) + \frac{\pi^2}{6}(k_BT)^2 g'(\varepsilon_F)$$

$$\Leftrightarrow (\mu - \varepsilon_F)g(\varepsilon_F) = -\frac{\pi^2}{6}g'(\varepsilon_F)(k_BT)^2 + O(N - N_0)$$

$$\Rightarrow E \approx E_0 - \varepsilon_F\frac{\pi^2}{6}g'(\varepsilon_F)(k_BT)^2 + \frac{\pi^2}{6}(k_BT)^2\varepsilon_F g'(\varepsilon_F) + \frac{\pi^2}{6}(k_BT)^2 g(\varepsilon_F)$$
$$= E_0 + \frac{\pi^2}{6}(k_BT)^2 g(\varepsilon_F)$$

$$\Rightarrow C_V = \left.\frac{\partial E}{\partial T}\right|_V \approx \frac{\pi^2}{3}g(\varepsilon_F)k_B^2T$$ which vanishes for low T

in good approx: conducting e^- in metal ~ gas of free Fermions
@T_{room}: c_V contribution e^- masked by that of lattice vibrations ($\sim T^3$)
@T_{low}: $c_V \sim T$ e^-, no longer affect lattice vibr. (phonons)

$g(\varepsilon)$ for free particles:
$\vec{p} = h\vec{n}/L$
$\Rightarrow$ # states with mom. in $[p, p+dp]$
$$2\frac{V}{h^3}4\pi p^2 dp = \frac{16\pi V}{h^3} m^{3/2}\sqrt{2\varepsilon}\, d\varepsilon \equiv g(\varepsilon)d\varepsilon$$

Oral exam questions

1] Show how the average number of particles $\langle N\rangle$ and the variance of N $\sigma_N = \langle N^2\rangle - \langle N\rangle^2$ can be calculated from the partition function Ξ.
Now consider a system of non-interacting particles and assume that the one-particle $Z_1(V,T)$ is known. Compute Ξ and show that the relative fluctuations of the number of particles is small.

2] Discuss (analyze) the formula $n\lambda_T^3 = \frac{\lambda_T^3}{V}\frac{z}{1-z} + \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}}$ where $z = e^{\beta\mu}$ (bosons)
in the 2 limits
- with low density and high temp ; $n\lambda_T^3 \gg 1$
- with high dens and low temp ; $n\lambda_T^3 \ll 1$.

Pay in particular attention to the ground state and discuss some physical ~~pro~~ syst where this analysis is applicable and important

3] In the mean field approx we have the equation $m = \tanh(\beta(mJz + H))$
Explain the meaning of every quantity in the formula. Show that there is a critical temperature so that there ~~dh~~ is spontaneous magn. for temp lower than T_c.
In the vicinity of the critical point, many things behave as a power law. Show this for one or two examples.

4] The equipartition theorem states that $\langle x_r \frac{\partial H}{\partial x_s}\rangle = k_B T \delta_{rs}$
Explain the meaning of this formula. Show the meaning of "Every quadratic degree of freedom contributes $k_BT/2$ to the system." Show ~~the~~ some applications to a few examples.

5] For bosons and fermions $\log \Xi = \mp \sum_r \log(1 \mp e^{\beta(\mu-\epsilon_r)})$
Derive this eq. and explain the + and − sign. Why would you want to use the grand canonical ensemble? Then derive from the result the average occupation number $\langle n_r\rangle$. Why is the QM important in your derivation and in your end result?

6] Prove the ideal gas law $PV = Nk_BT$ in the canonical and grand-canonical ensemble. In general the ensembles are equivalent to each other in the sense that relative fluctuations $\sigma_x^2/\langle x\rangle^2$ vanish. Give an example of this for an ideal gas in the canonical and grand-canonical ensemble

7] Sketch the derivation of Planck's law. $\epsilon(\omega) = \frac{\hbar}{\pi^2 c^3}\,\frac{\omega^3}{e^{\beta\hbar\omega}-1}$
What does this mean?
The density of states is the following $g(\omega) = \frac{V}{\pi^2 c^3}\omega^2$
How is your result dependent on the temp? How would you derive $\epsilon(\omega)$ classically?

8] The pressure ~~of~~ a quantum gas of non-interacting particles is given by
$$p = nk_BT\left(1 \pm \frac{n\lambda_T^3}{4\sqrt{2}}\right)$$
Why are there 2 different signs and what do they correspond to? The formula describes the effect of quantum corrections to the ideal gas law. These corrections are small if $n\lambda_T^3$ is small. Why? Which kind of dimensionless param. do you expect to control the quantum corrections for a gas in 2D

9] The virial expansion for an interacting system reads
$p = nk_BT(1 + b_2 n + b_3 n^2 + \ldots)$ where b_i are the virial coeff.
~~The~~ b_2 usually depends on temp and it can be either pos or neg. Discuss the temp. dep. and the sign of b_2. ~~Do~~ you know a system in which b_2 does not dep. on temp?

Written part

1] Consider particles in a potential $V(x) = -ax$ with diffusion coefficient D.
Show that $c(x,t) = \frac{N}{\sqrt{4Dt}} e^{-(x-vt)^2/4Dt}$ is a solution of the drift-diffusion eq.
and find v. Plot this solution for different times. Show that $F = \gamma v$ where F is the force on the particles and γ is the friction coeff

2] Consider a single 1D oscillator in the canonical ensemble and calculate the average energy $\langle E \rangle$ and the variance of E, $\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2$.
Do the same for N indep. HO.

3] Consider a 2D oscillator in polar coord $\mathcal{H} = \frac{1}{2m}\left(p_r^2 + \frac{p_\phi^2}{r^2}\right) + \frac{m\omega^2 r^2}{2}$
1. calculate the part. function in " "
2. calculate $\langle E \rangle$ and compare with the result in Cartesian coord
3. Do this calculation with the equip. theorem in polar coords.

4] We have N part in a volume V at temp T. Consider a part V_1 with N_1
1. Calculate $\langle N_1 \rangle$ and $\langle N_1^2 \rangle$
2. Calculate the variance and show that relative fluct. are small.

5] Consider N-1 coupled osc. such that $\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N-1} \frac{K}{2}(x_{i+1} - x_i)^2$
1. Calculate $\langle E \rangle$ and $\langle E^2 \rangle - \langle E \rangle^2$ and show that the relative fluct are small
2. Repeat for anharmonic osc $\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N-1} \frac{K}{2}(x_{i+1} - x_i)^4$

6] Consider a syst of N molecules in vol V and temp T. The molecules each consist of 3 atoms m_1, m_2, m_3. The atoms interact through a potential
$\varphi(\vec{x}_1, \vec{x}_2, \vec{x}_3) = \frac{K}{2}(\vec{x}_1 - \vec{x}_2) + \frac{\Gamma}{2}(\vec{x}_2 - \vec{x}_3)^2$
1. Calculate Z. Also calculate the internal energy and c_V
2. Calculate $\langle(\vec{x}_1 - \vec{x}_2)^2\rangle$, $\langle(\vec{x}_2 - \vec{x}_3)^2\rangle$, $\langle(\vec{x}_3 - \vec{x}_1)^2\rangle$
3. Calculate the pressure on the syst