

$P(v, t | v_0, t_0) dv$  : probability finding the Brownian particles have velocity  $[v, v+dv]$  given that the particle is at  $v_0$  at time  $t_0$

Consider stationary process, then

$$P(v, t | v_0, t_0) = P(v, t - t_0 | v_0, 0)$$

i.e. We consider that  $v_0$  is the value at time  $t=0$  and write  $P(v, t | v_0)$

$$\int_{-\infty}^{\infty} P(v, t | v_0) dv = 1$$

$$\lim_{t \rightarrow 0} P(v, t | v_0) = \delta(v - v_0) \quad (\text{initial condition})$$

for  $t \rightarrow \infty$  system forget its history  $v_0$

velocity should follow Maxwell distribution

$$\lim_{t \rightarrow \infty} P(v, t | v_0) \propto e^{-\beta(\frac{1}{2}mv^2)}$$

$$\text{with proper normalization} \quad = \left( \frac{m\beta}{2\pi} \right)^{\frac{1}{2}} e^{-\beta(\frac{1}{2}mv^2)}$$

Associated Langevin Eq is

$$m \frac{dv}{dt} = -m\gamma v + R(t)$$

F. Reif Chap 15  
R. Zwanzig Chap 14.2

Kramers-Moyal expansion

master Eq.

$\exists$  small  
infinitesimally

moving away from current  $v$

237

$$\frac{\partial P(v, t | v_0)}{\partial t} dv \cdot \tau = - \int_{v'} P(v, t | v_0) P(v', \tau | v) dv' +$$

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rate of

increase in prob  
finding particle  
in  $[v, v + dv]$

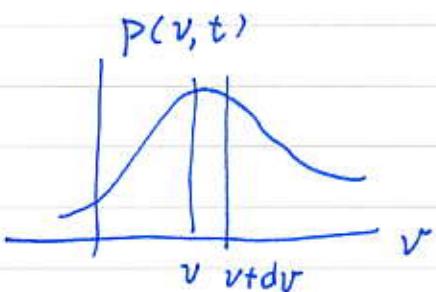
$$\approx [P(v, t + \tau | v_0) - P(v, t | v_0)] dv$$

after time elapsed by  $\tau$   
the prob. that particle has  
velocity  $v'$  is  $P(v', \tau | v) dv'$

$$P(A) P(B|A) = P(A \cap B)$$

$$+ \int_{v'} P(v', t | v_0) dv' P(v, \tau | v') dv$$

another velocity  $v'$  can be come the  
current one.



$$\text{but } \int_{v'} p(v', \tau | v) dv' = 1$$

$$v' = v - \xi \leftarrow \text{small change}$$

(see derivation  
by Reif)

$$\frac{\partial P(v, t | v_0)}{\partial t} \tau = - P(v, t | v_0) +$$

$$\int_{-\infty}^{\infty} p(v - \xi, t | v_0) P(v, \tau | v - \xi) d\xi$$

$\tau \rightarrow 0$ ,  $\xi$  small.  $P$  change slowly with respect to  $v$   $x_0 = v$

$$P(v - \xi, t | v_0) P(v, \tau | v - \xi)$$

$$x = v - \xi = x_0 - \xi$$

$$= P(v - \xi, t | v_0) P(v - \xi + \xi, \tau | v - \xi) = P(x, t | v_0) P(x + \xi, \tau | x)$$

$$= P(x_0 + \xi | v_0) P(x_0 + \xi, \tau | x_0) + \frac{\partial}{\partial x} P(x, t | v_0) P(x + \xi, \tau | x) / (x - x_0)$$

$$x = v$$

$$= p(v, t | v_0) p(v + \xi, \tau | v) + (-\gamma) \frac{\partial}{\partial v} \left( p(v, t | v_0) P_{v+3, \tau}^{(239)} \right) \\ + \frac{1}{2} (-\gamma)^2 \frac{\partial^2}{\partial v^2} p(v, t | v_0) p(v + \xi, \tau | v) + \dots$$

$$\frac{\partial p(v, t | v_0)}{\partial t} = - p(v, t | v_0) + \int_{-\infty}^{\infty} p(v, t | v_0) p(v + \xi, \tau | v) d\xi \\ + \frac{\partial}{\partial v} p(v, t | v_0) \int_{-\infty}^{\infty} (-\gamma) p(v + \xi, \tau | v) d\xi \\ \frac{1}{2} \frac{\partial^2}{\partial v^2} p(v, t | v_0) \int_{-\infty}^{\infty} \xi^2 p(v + \xi, \tau | v) d\xi + \dots$$

$v + \xi = v' \Rightarrow v(\tau)$

$$M_n = \frac{1}{\tau} \int_{-\infty}^{\infty} \xi^n p(v + \xi, \tau | v) d\xi = \frac{1}{\tau} \langle [v(\tau) - v]^n \rangle$$

change of  
velocity after  
time  $\tau$

$$\frac{\partial P}{\partial t} = - \frac{\partial}{\partial v} (M_1 P) + \frac{1}{2} \frac{\partial^2}{\partial v^2} (M_2 P) \leftarrow \text{Fokker-Planck Eq.}$$

$$M_1 = \frac{1}{\tau} \langle (v(\tau) - v) \rangle = \frac{1}{\tau} [\langle v(\tau) \rangle - v] \quad v(\tau=0) = v$$

average velocity

$$\langle v(\tau) \rangle = v e^{-\gamma \tau} = v [1 - \gamma \tau + O(\tau^2)] \\ = v - \gamma v \tau + \dots \\ = -\gamma v$$

$$M_2 = \frac{1}{\tau} \langle (v(\tau) - v)^2 \rangle = \frac{2 k_B T}{m} \gamma = 2 D \gamma^2$$

$M_n = 0$  for  $n > 3$  for gaussian process!

$$v(t) = v(0) e^{-\gamma t} + \int_0^t \frac{R(\tau)}{m} e^{-\gamma(t-\tau)} d\tau$$

Date \_\_\_\_\_

$$\lim_{t \rightarrow 0} \frac{1}{t} \langle (v(t) - v(0))^2 \rangle = \left\langle \left[ v(0) (e^{-\gamma t} - 1) + \int_0^t \frac{R(\tau)}{m} e^{-\gamma(t-\tau)} d\tau \right]^2 \right\rangle$$

$$= \frac{1}{t} \left[ \langle (v(0) [-\gamma t + \dots])^2 \rangle + \langle R(\tau) R(\tau') \rangle \frac{1}{m^2} \right]$$

$$= \frac{1}{t} \frac{C \cdot \frac{1}{m^2}}{m^2} \quad C = 2m\gamma k_B T \quad \int_0^t \int_0^t$$

→ with spectra  $M_1, M_2$   
we have

$$\frac{\partial P}{\partial t} = \gamma \frac{\partial}{\partial v} (vP) + \underbrace{\gamma \frac{k_B T}{m} \frac{\partial^2 P}{\partial v^2}}_{\gamma^2 D \uparrow}$$

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

solution of Fokker-Planck equation

Let  $\frac{\partial^2 P}{\partial v^2} = 0$  first

$\gamma \downarrow$

solution F.R.C.f

$$\frac{\partial P}{\partial t} - \gamma v \frac{\partial P}{\partial v} = \gamma P$$

multiply by  $\lambda(v, t)$  so that

$$\lambda \frac{\partial P}{\partial t} - \lambda \gamma v \frac{\partial P}{\partial v} = \lambda \gamma P \quad \text{is a total differential}$$

$$\frac{\partial P}{\partial t} dt + \frac{\partial P}{\partial v} dv = dP$$

we identify

$$\left. \begin{array}{l} dt = \lambda \\ dv = -\lambda \gamma v \\ dP = \lambda \gamma P \end{array} \right\}$$

$$\left. \begin{array}{l} \frac{dv}{dt} = -\gamma v \\ \frac{dP}{dt} = \gamma P \end{array} \right.$$

$$V = ue^{-\gamma t}, \quad P = Q e^{\gamma t}$$

Now add in the diff's terms

Date

$$\text{Let } P(r, t) = Q(u, t)e^{rt} \quad u = r e^{rt}$$

$$\frac{\partial P}{\partial V} = e^{r_t} \frac{\partial Q}{\partial u} \frac{\partial u}{\partial V} = e^{2r_t} \frac{\partial Q}{\partial u}$$

$$\frac{\partial^2 P}{\partial V^2} = e^{2\alpha t} \frac{\partial^2 Q}{\partial u^2} \frac{\partial^2 u}{\partial y} = e^{3\gamma t} \frac{\partial^2 Q}{\partial u^2}.$$

$$\frac{\partial P}{\partial t} - \gamma_V \frac{\partial P}{\partial V} - \gamma P = \frac{\partial^2 P}{\partial V^2} \left( \gamma \frac{k_B T}{m} \right)$$

$$\frac{\partial Q}{\partial t} e^{\gamma t} + \cancel{Q \gamma e^{\gamma t}} - \cancel{\gamma v e^{2\gamma t} \frac{\partial Q}{\partial u}} - \cancel{\gamma Q e^{\gamma t}} = e^{3\gamma t} \frac{\partial^2 Q}{\partial u^2} \left( \frac{v k T}{m} \right)$$

$\uparrow$

$e^{\gamma t} \frac{\partial Q}{\partial u} \Big|_t \underset{\sim}{\approx} v \gamma e^{\gamma t}$

$\tilde{D} = \frac{\gamma k_b T}{m}$

$$\frac{\partial Q}{\partial t} = e^{2\alpha t} \frac{\partial^2 Q}{\partial u^2} \left( \alpha \frac{k_b T}{m} \right) \rightarrow \frac{\partial Q}{e^{2\alpha t} \partial t} = \left( \alpha \frac{k_b T}{m} \right) \frac{\partial^2 Q}{\partial u^2}$$

$$\text{Let } d\theta = e^{2rt} dt \Rightarrow \theta = \frac{1}{2r} (e^{2rt} - 1)$$

$$\frac{\partial Q}{\partial \theta} = \tilde{D} \frac{\partial^2 Q}{\partial U^2} \rightarrow \text{standard Jitter eq.}$$

$$Q = \frac{1}{\sqrt{4\pi\beta\theta}} e^{-\frac{(u-u_0)^2}{4\beta\theta}} \quad (Q \rightarrow \delta(u-u_0) \text{ as } \theta \rightarrow 0)$$

$$P(v, t | v_0) = e^{\gamma t} \frac{1}{\sqrt{4\pi \tilde{\rho}_{2\gamma}^{\perp} (e^{2\gamma t} - 1)}} \exp \left[ -\frac{(v e^{\gamma t} - v_0)^2}{4\tilde{\rho}_{2\gamma}^{\perp} (e^{2\gamma t} - 1)} \right]$$

$$= \left[ \frac{m}{2\pi k_B T (1 - e^{-2\beta t})} \right]^{\frac{1}{2}} \exp \left[ - \frac{m(v - v_0 e^{-\beta t})^2}{2k_B T (1 - e^{-2\beta t})} \right]$$

$t \rightarrow \infty$  reduce to Maxwell distribution

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial v} (vP) + \frac{k_B T}{m} \frac{\partial^2 P}{\partial v^2}$$

equilibrium distribution is  $t \rightarrow \infty$

$$\frac{\partial}{\partial v} (vP) + \frac{k_B T}{m} \frac{\partial^2 P}{\partial v^2} = 0$$

$$\text{or } vP + \frac{k_B T}{m} \frac{\partial P}{\partial v} = \text{const.}$$

const must equal 0. b/c  $\int_{-\infty}^{+\infty} P dv = 1$

integrate on both sides

$$\left| \int_{-\infty}^{+\infty} vP dv \right| < M \text{ bounded}$$

$$\int_{-\infty}^{+\infty} \text{const} dv \text{ must be finite}$$

$$-\frac{m v c v}{k_B T} = \frac{\delta P}{P}$$

$$\Rightarrow P = P_0 e^{-\beta \left( \frac{1}{2} m v^2 \right)} \quad \beta = \frac{1}{k_B T}$$

From Langevin to Fokker-Planck, general setting

$$\dot{\vec{x}} = G(\vec{x}) + g(\vec{x}) \xi \quad \langle \xi \xi^T \rangle = 2D \delta(t-t') \quad D \text{ is const}$$

$$\frac{\partial P}{\partial t} = - \frac{\partial}{\partial \vec{x}} G P + \left( \frac{\partial}{\partial \vec{x}} \right)^T g D \left[ g^T \frac{\partial}{\partial \vec{x}} P \right]$$

$$\vec{x} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{pmatrix} \text{ is arbitrary vector}$$

when gas can be treated classically

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

$$\frac{\lambda}{(\frac{V}{N})^{\frac{1}{3}}} = \frac{\lambda}{b} \leftarrow \text{av. size of particle}$$

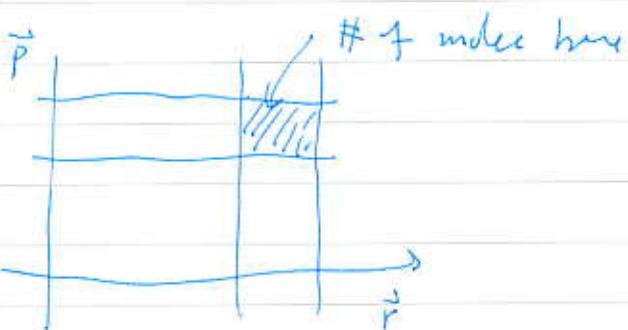
$$\lambda_{O_2} = \sqrt{\frac{10^{-34}}{10^{-26} \cdot 1.38 \times 10^{-23} \times 300 K}}$$

$$= 1.5 \times 10^{-11} \text{ m} = 0.15 \text{ Å}$$

$$b \approx 10 - 30 \text{ Å}$$

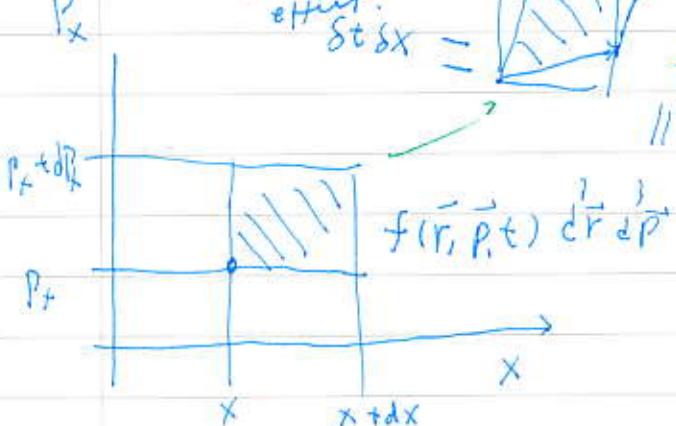
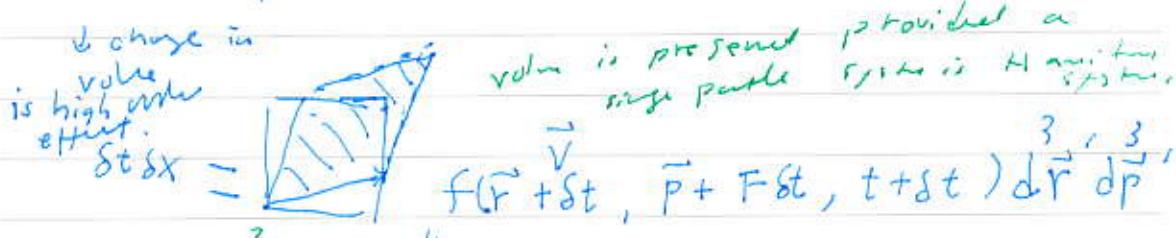
Applying to TD

$$f(\vec{r}, \vec{p}, t) d\vec{r} d\vec{p} = \# \text{ of molecules having position } \vec{r} \text{ in volume } d\vec{r} \\ \text{ & momentum } \vec{p} \text{ in } d\vec{p}$$



Joint distribution makes sense only in classical regime

$$\int f(\vec{r}, \vec{p}, t) d\vec{r} d\vec{p} = N$$



$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \vec{p} \cdot \vec{\nabla}_r f + \vec{F} \cdot \vec{\nabla}_p f = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}}$$

$$f(\vec{r}, \vec{p}) = N \int p(\vec{r}, \vec{p}; \vec{r}_1, \vec{p}_1, \dots) d\vec{r}_1 d\vec{p}_1 \dots d\vec{r}_N d\vec{p}_N$$

$$\sum_i SPC \dots$$

Sum of 1st part in  $d\vec{r} d\vec{p}$ , 2nd in  $d\vec{r} d\vec{p} \dots$  etc.

$$\frac{Df}{Dt} = \left( \frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla}_r + \vec{F} \cdot \vec{\nabla}_p \right) f = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}}$$

*screaming*

$\vec{R} - \vec{R}'$  = no. of collisions occurring per unit time in which one of the initial molecules

$R St \int d\vec{r} d\vec{p}$  = no. of collisions occurring during the time between  $t$  and  $t+St$  in which one of the initial molecules is in  $d\vec{r} d\vec{p}$  at  $(\vec{r}, \vec{p})$

$\bar{R} St \int d\vec{r} d\vec{p}$  = no. of collisions occurring during the time between  $t$  and  $t+St$  in which one of the final molecules is in  $d\vec{r} d\vec{p}$  at  $(\vec{r}, \vec{p})$ .

$$\vec{p} + \vec{p}_1 = \vec{p}' + \vec{p}'_1$$

$$\epsilon(\vec{p}) + \epsilon(\vec{p}_1) = \epsilon(\vec{p}') + \epsilon(\vec{p}'_1)$$

$$\epsilon = \frac{p^2}{2m}$$

in relative motion frame

given  $\vec{p}, \vec{p}_1$

$$b, \phi \text{ or } (\theta, \phi)$$

can still vary.

target (corr. molec. with  $\vec{p}$  is now target)

$$(p, p_1 | \sigma) p'_1, p'_1 \propto \delta(p+p_1 - p'_1 - p'_1) \delta[\epsilon(\phi) + \epsilon(\phi_1) - \epsilon(p') - \epsilon(p'_1)]$$

differential cross-section

target fixed, incoming flux is  $I$

$$I \sigma(\theta, \phi) d\Omega = \# \text{ of incident molecules scattered per second into solid angle } d\Omega \text{ in dirct } (\theta, \phi)$$

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = - \int d\vec{p}_1 \int d\vec{p}'_1 \int d\vec{p}' \sigma(p, p_1 | p'_1 p') (f f_1 - f' f'_1)$$

$$f_1 = f(r, p_1, t)$$

$$f' = f(r, p'_1, t)$$

$$f'_1 = f(r, p'_1, t)$$

another form

$$= - \int d\vec{p}_1 d\Omega |\mathbf{v}_1 - \mathbf{v}| \sigma(\theta, \phi) (f f_1 - f' f'_1)$$

$$= 4 \times 3$$

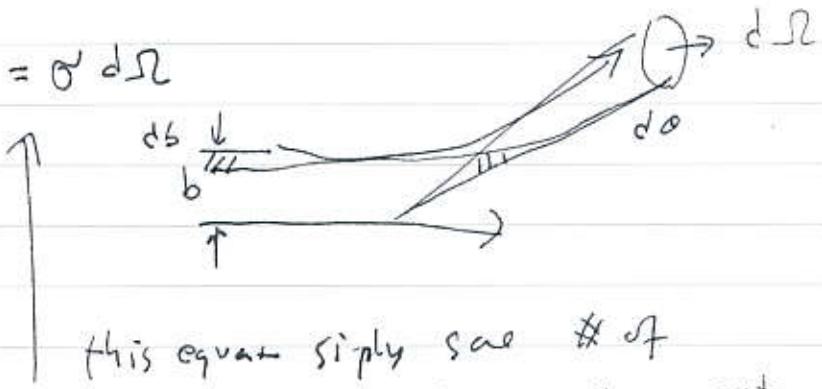
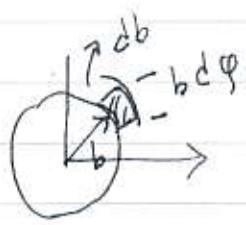
$\vec{p}, \vec{p}'$ ,  $\vec{p}_1, \vec{p}'_1$  have 12 degrees of freedom  
conservation law for  $p$  &  $\epsilon$  take away 4 degrees of

still left with 8 degrees of freedom which is  
 $\vec{p}, \vec{p}_1, d\Omega$   $\leftarrow$  out going angles in relative  
frame frame.

Boltzmann b: Impact parameter: we can think of  
this as precisely define  $\sigma$ .

Important relation between  $\sigma$  and impact parameter  $b$

$$d\sigma = b db d\phi = \sigma d\Omega$$



this equation simply says # of  
particles come from the area  $db \cdot b d\phi$  must go out  
to solid angle  $d\Omega$ , which is  $6d\Omega$  by definition

Date \_\_\_\_\_

## Two-body scattering problem

$$\mathcal{H}(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) = \frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} + V(|\vec{r}_1 - \vec{r}_2|)$$

reduce to one-body problem

momentum of the center of mass

$$\left\{ \begin{array}{l} \vec{r} = \vec{r}_2 - \vec{r}_1 \quad \text{relative position} \\ \vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \quad \text{center of mass} \end{array} \right.$$

$$\vec{P} = M \dot{\vec{R}} = (m_1 + m_2) \dot{\vec{R}}$$

$$M = \frac{m_1 m_2}{m_1 + m_2}, \quad \mu = \frac{1}{m_1} + \frac{1}{m_2}$$

solve  $\vec{r}_1$  &  $\vec{r}_2$  in terms  $\vec{r}$  &  $\vec{R}$ 

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 (\vec{r} + \vec{r}_1)}{m_1 + m_2} \quad (m_1 + m_2) \dot{\vec{R}} = (m_1 + m_2) \dot{\vec{r}}_1 + m_2 \dot{\vec{r}}$$

$$\vec{r}_1 = \vec{R} - \frac{m_2}{m_1 + m_2} \vec{r}, \quad \vec{r}_2 = \vec{r} + \vec{r}_1 = \vec{R} + \frac{m_1}{m_1 + m_2} \vec{r}$$

$$\vec{p}_1 = m_1 \dot{\vec{r}}_1 = m_1 \dot{\vec{R}} - \frac{m_1 m_2}{m_1 + m_2} \dot{\vec{r}} = m_1 \dot{\vec{R}} - \mu \dot{\vec{r}}$$

$$\vec{p}_2 = m_2 \dot{\vec{r}}_2 = m_2 \dot{\vec{R}} + \frac{m_1 m_2}{m_1 + m_2} \dot{\vec{r}} = m_2 \dot{\vec{R}} + \mu \dot{\vec{r}}$$

$$\vec{p}_1 + \vec{p}_2 = \vec{P} = \text{const.} \quad \dot{\vec{r}} = v$$

$$\frac{\vec{p}_1^2}{2m_1} = \frac{1}{2m_1} \left( m_1^2 \dot{\vec{R}}^2 + \mu^2 \dot{\vec{r}}^2 - 2m_1 \mu \dot{\vec{R}} \cdot \dot{\vec{r}} \right)$$

$$\frac{\vec{p}_2^2}{2m_2} = \frac{1}{2m_2} \left( m_2^2 \dot{\vec{R}}^2 + \mu^2 \dot{\vec{r}}^2 + 2m_2 \mu \dot{\vec{R}} \cdot \dot{\vec{r}} \right)$$

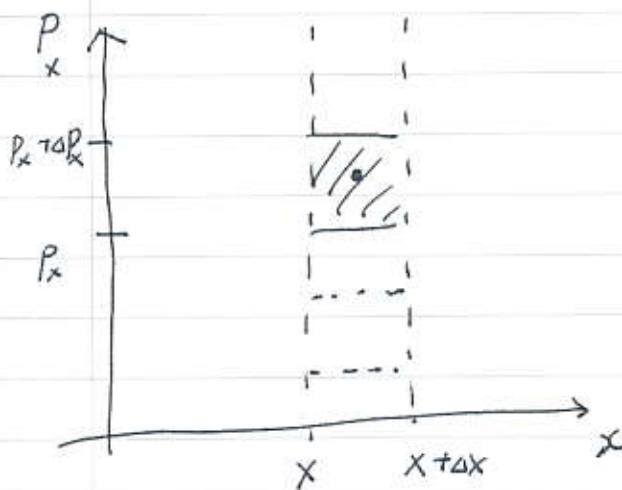
$$= \frac{1}{2} \left( \underbrace{m_1 + m_2}_{M} \right) \dot{\vec{R}}^2 + \frac{\mu^2}{2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) v^2$$

$$= \frac{1}{2M} \dot{\vec{R}}^2 + \frac{1}{2} [M] \dot{\vec{r}}^2$$

shown.

The collision term in Boltzmann Eq.

Date \_\_\_\_\_



sizes of molecules are much smaller than  $\Delta x$   
each  $d\vec{r}$  still has a lot of molecules ( $\sigma_{tot} \ll \Delta x^2$ )

molecules inside  $d\vec{r} d\vec{p}$   
do not collide as they have the same velocity

consider one molecule in  $d\vec{r} d\vec{p}$ .  
and all the molecules in  $d\vec{r} d\vec{p}_1$ .

there is the flux of

$$I = f(\vec{r}, \vec{p}, t) |\vec{v}_1 - \vec{v}| \cdot d\vec{p}_1$$

the # of particles collided with the one (per second) is

$$I d\sigma = I \sigma(0, 0) d\Omega = f(\vec{r}, \vec{p}_1, t) \sigma(0, \varphi) d\Omega d\vec{p}_1$$

since there are  $f(\vec{r}, \vec{p}) d\vec{p}$  molecules there

The total collision per second is (in unit  $d\vec{r}$  and  $d\vec{p}_1$ )

$$I \sigma \cdot f(\vec{r}, \vec{p}_1) = f f_1 \sigma |\vec{v}_1 - \vec{v}| d\Omega d\vec{p}_1$$

sum over all possible  $\vec{p}_1$  and outcome  $d\Omega$ .

$$\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \# \text{ of collision per unit time}$$

in unit space and moment volumes.

## Assignment 5

Date \_\_\_\_\_

$$G = G_0 + a(T-T^*)M^2 - \frac{1}{3}cM^3 + \frac{1}{4}dM^4 \quad \leftarrow \text{cubic eq.}$$

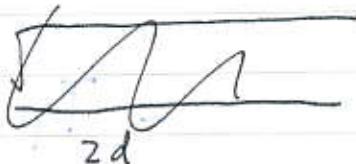
spontaneous  $M$

$$(a) h = \frac{\partial G}{\partial M} = 2a(T-T^*)M - cM^2 + dM^3 = 0 \quad \text{or } M=0$$

$$2a(T-T^*) - cM + dM^2 = 0$$

$$M = \frac{c \pm \sqrt{c^2 - 4d(T-T^*) \cdot 2a}}{2d} =$$

$$= \frac{c \pm \sqrt{c^2 - 8ad(T-T^*)}}{2d}$$

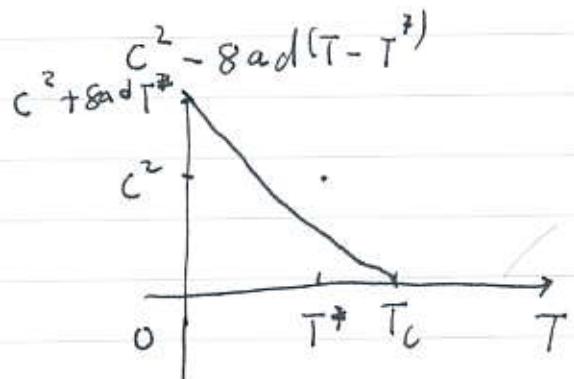


No real solutions if  $c^2 - 8ad(T-T^*) < 0$   
 or  $c^2 < 8ad(T-T^*)$

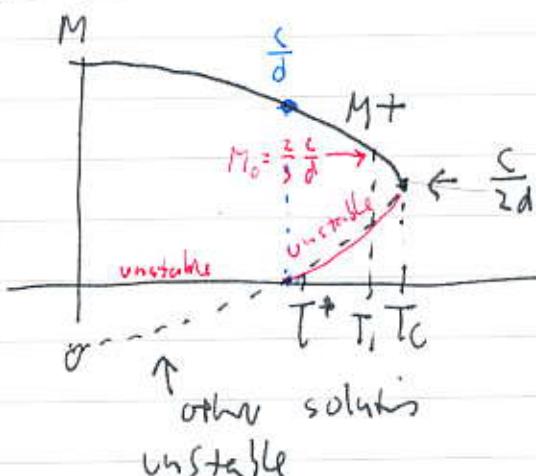
$$\text{or } \frac{c^2}{8ad} < T - T^*$$

$$\text{or } T_g = \frac{c^2}{8ad} + T^* \leq T$$

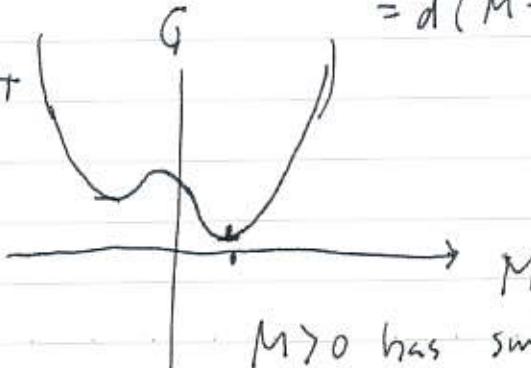
$$\text{so } T - T^* < \frac{c^2}{8ad}$$



There are two solutions for  $M$



need to be more clear  
 careful



$M > 0$  has smaller  $G$   
 thus more stable

$$T_1 = T^* + \frac{1}{9} \frac{c^2}{d^2 a}$$

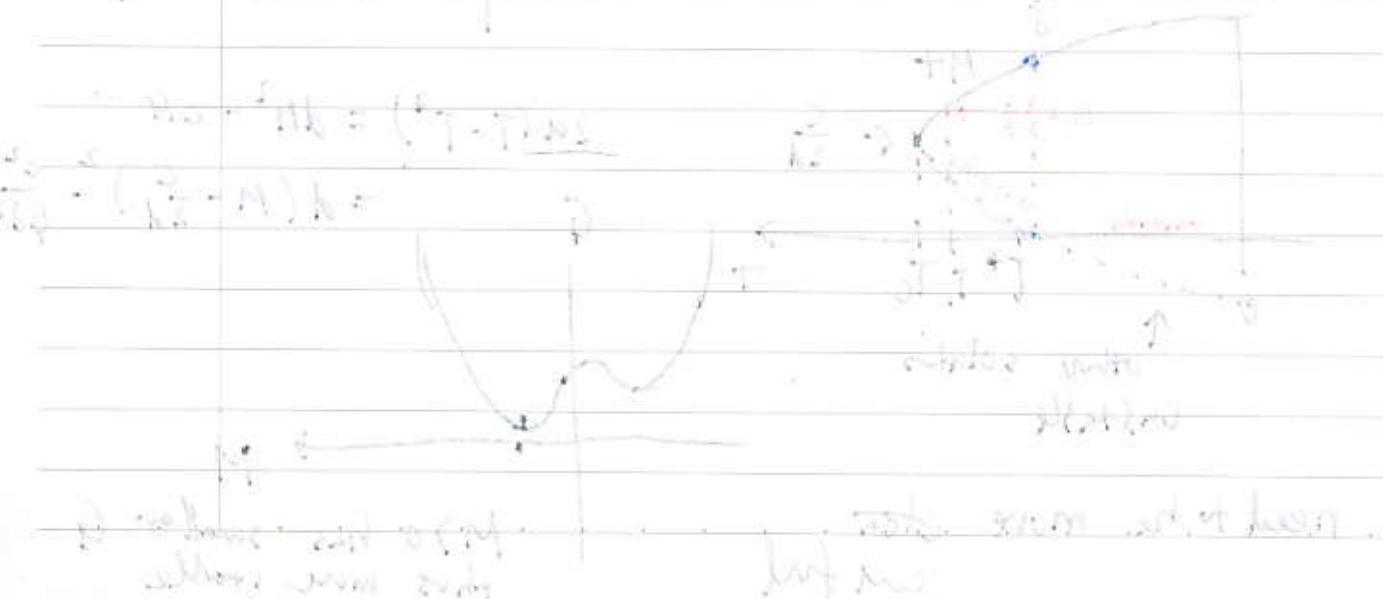
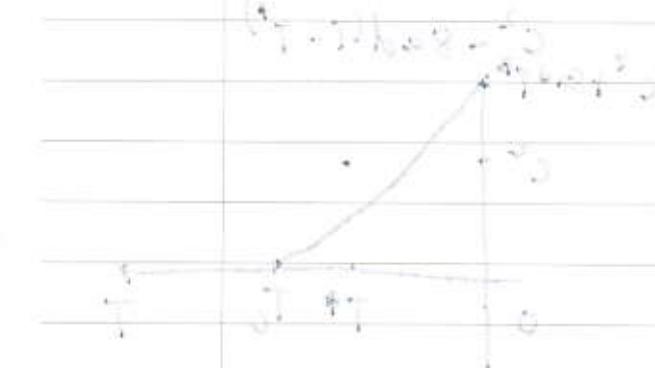
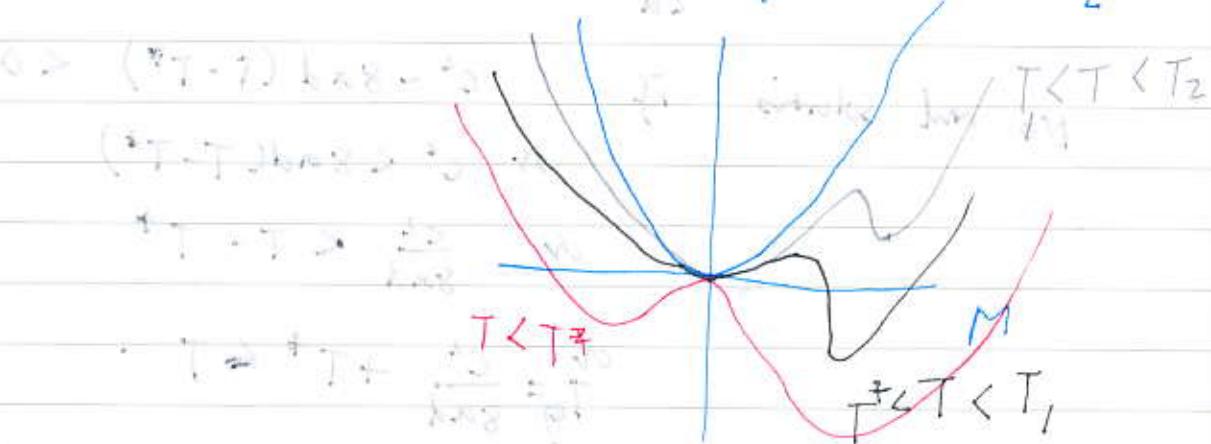
$$Q = T_1 \Delta S = T_1 (+0 \rightarrow a M_0^2)$$

$$= \left( T^* + \frac{1}{9} \frac{c^2}{d^2 a} \right) \left( a \cdot \left( \frac{2+c}{3d} \right)^2 \right)$$

$$= T_1 a \frac{c^2}{d^2} \left( \frac{4}{9} \right)$$

Date \_\_\_\_\_

$$T > T_2$$



latent heat

$$Q = T_c \Delta S = T_c \Delta S$$

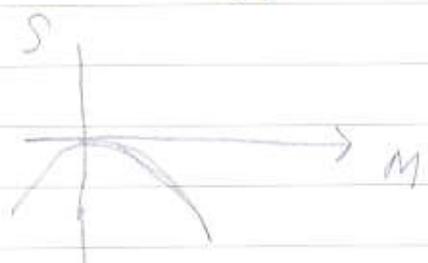
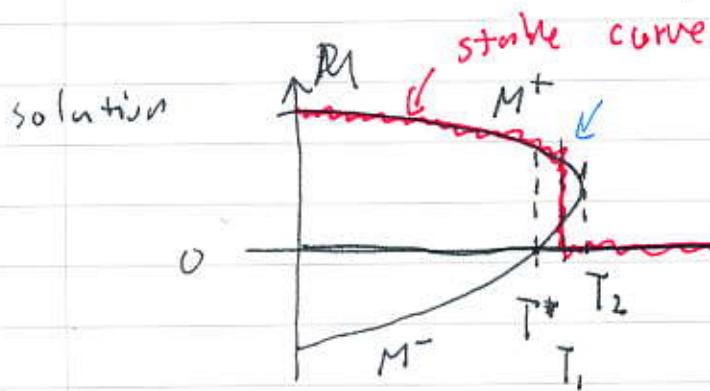
$$dQ = T dS$$

$$S = -\frac{\partial G}{\partial T} = -\alpha M^2$$

Date \_\_\_\_\_

$$\Delta S = S(T_c^+) - S(T_c^-) = 0 + \alpha M^2 = \alpha \left(\frac{c}{2d}\right)^2$$

$$Q = \left(\frac{c^2}{8ad} + T^*\right) \cdot \alpha \left(\frac{c}{2d}\right)^2$$



We have 3 solutions need to decide which one has global min.

$$M=0 \text{ solut} \quad G = G_0 + \text{indep of } T$$

$$\text{for } M \neq 0 \quad G(M) = G(M=0)$$

$$G_0 + \alpha(T-T^*)M_0^2 - \frac{1}{3}cM_0^3 + \frac{1}{4}dM_0^4 = G_0$$

value of  $M$  at the transition  $T_1$  but

$$\begin{cases} \alpha(T-T^*) - \frac{1}{3}cM_0 + \frac{1}{4}dM_0^2 = 0 \\ 2\alpha(T-T^*) - cM_0 + dM_0^2 = 0 \end{cases}$$

then  $M_0$  is also on the  $M$  curve

$$\text{eliminate } T-T^* \quad \left(-\frac{2}{3} + 1\right)cM_0 + \left(\frac{1}{2} - 1\right)dM_0^2 = 0$$

$$\frac{1}{3}cM_0 + \frac{1}{2}dM_0^2 = 0$$

$$M_0 = \frac{2c}{3d}$$

$$\frac{1}{9} \frac{c^2}{d}$$

$$\alpha(T-T^*) = \frac{1}{3}c \frac{2c}{3d} - \frac{1}{4}d \left(\frac{2c}{3d}\right)^2 = \left(\frac{2}{9} - \frac{4}{4 \cdot 9}\right) =$$

low T expand

$M = \langle \sum_{i=1}^N \sigma_i \rangle =$	$\begin{matrix} + & + & + & + \\ + & + & + & + \\ + & + & + & + \\ + & + & + & + \\ + & + & + & + \end{matrix}$ <i>ground state</i>	$\begin{matrix} + & + & + & + \\ + & + & + & + \\ + & - & + & + \\ + & + & + & + \\ + & + & + & + \end{matrix}$ <i>1st excited</i>	$\begin{matrix} + & + & + & + \\ + & + & + & + \\ + & - & - & + \\ + & + & + & + \end{matrix}$ <i>Date</i>	261
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$\Sigma \sigma_i = N$        $\Sigma \sigma_i = N-2$        $\Sigma \sigma_i = N-4$

$\Delta E = E - E_0 = 0$        $\Delta E = 8J$        $\Delta E = 12J$

*genuine*      1      N       $2N$

$$M = \frac{N \cdot 1 \cdot 1 + (N-2) e^{-8K} \cdot N + (N-4) e^{-12K} \cdot 2N}{1 + e^{-8K} N + (N-4) e^{-12K} 2N} \quad x = e^{-2K}$$

$$= \frac{N + N(N-2) x^4 + (N-4) \cdot 2N x^6}{1 + N x^4 + 2N x^6 + \dots} \quad \frac{1}{1+x} = 1 - x + x^2 + \dots$$

$$= \frac{M}{N} = \left[ 1 + (N-2)x^4 + 2(N-4)x^6 \right] \left[ 1 - Nx^4 - 2Nx^6 + (Nx^4 + 2Nx^6)^2 + \dots \right]$$

$$= 1 + (N-2)x^4 + 2(N-4)x^6 - Nx^4 - 2Nx^6 + O(x^8)$$

$$= 1 - 2x^4 - 8x^6 + \dots \quad \theta \sinh(2K) = \frac{e^{2K} - e^{-2K}}{2}$$

$$\frac{M}{N} = \left( 1 - \frac{1}{\sinh^4(2K)} \right)^{\frac{1}{8}} \quad = \left( \frac{1}{x} - x \right)^{\frac{1}{2}}$$

$$\left( 1 - \frac{1}{\frac{1}{16}(x^{-2} - x^2)^4} \right)^{\frac{1}{8}}$$

$$= \left( 1 - \frac{16}{x^4(1-x^2)^4} \right)^{\frac{1}{8}} = \left( 1 - \frac{16x^4}{(1-x^2)^4} \right)^{\frac{1}{8}}$$

$$= \left( 1 - 16x^4(1+x^2+x^4+x^6+\dots)^4 \right)^{\frac{1}{8}}$$

$$\frac{M}{N} = \left( 1 - 16x^4(1 + 4x^2 + \dots) \right)^{\frac{1}{8}}$$

$$= \left( 1 - 16x^4 - 16 \cdot 4x^6 + \dots \right)^{\frac{1}{8}}$$

$$\chi = e^{-\gamma K}$$

Date \_\_\_\_\_

$$= 1 - \frac{1}{8} \cdot 16x^4 - \frac{16}{8} \cdot 4x^6 + \dots = 1 - 2x^4 - 8x^6 + \dots$$

$$-34x^8$$

2. (a)  $Z_\sigma = \sum_{\text{for}} e^{-\beta \sum_{i=1}^N (1-\varepsilon(-1)^i) \sigma_i \sigma_{i+1}}$

$$\begin{array}{cccccc} 1+\varepsilon & 1-\varepsilon & 1+\varepsilon & 1-\varepsilon & 1 \\ \hline 1 & 2 & 3 & 4 & 5 & 6 \end{array}$$

$$e^{\underbrace{P \sigma_1 \sigma_2}_{P} (1+\varepsilon)} e^{\underbrace{Q \sigma_2 \sigma_3}_{Q} (1-\varepsilon)} e^{\sigma_3 \sigma_4 (1+\varepsilon)} e^{\dots}$$

$$P = \begin{pmatrix} e^{\beta(1+\varepsilon)} & e^{-\beta(1+\varepsilon)} \\ e^{-\beta(1+\varepsilon)} & e^{\beta(1+\varepsilon)} \end{pmatrix} \quad Q = \begin{pmatrix} e^{\beta(1-\varepsilon)} & e^{-\beta(1-\varepsilon)} \\ e^{-\beta(1-\varepsilon)} & e^{\beta(1-\varepsilon)} \end{pmatrix}$$

(b)

$$\overline{F}_\sigma = -k_B T$$

$$Z_\sigma = \text{Tr}(PQ)^{\frac{N}{2}} = \cancel{\frac{N}{2}} \cancel{PQ} \lambda^{\frac{N}{2}}$$

$$Z_{\text{tot}} = \int_{-\infty}^{+\infty} d\varepsilon e^{-\beta N \omega \varepsilon^2 + \frac{N}{2} \ln \lambda}$$

$$= \int_{-\infty}^{\infty} d\varepsilon e^{-\beta N \left( \omega \varepsilon^2 + \frac{-1}{2\beta} \ln \lambda \right)}$$

$$g(\omega) = \omega \varepsilon^2 - \frac{1}{2} k_B T \ln \lambda$$

$$PQ = \begin{pmatrix} xy & \frac{1}{xy} \\ \frac{1}{xy} & x^2y^2 \end{pmatrix} \begin{pmatrix} x/y & y/x \\ y/x & x/y \end{pmatrix}$$

$$= \begin{pmatrix} x^2 + \frac{1}{x^2} & y^2 + \frac{1}{y^2} \\ \frac{1}{y^2} + y^2 & x^2 + \frac{1}{x^2} \end{pmatrix} = \begin{pmatrix} a & b \\ b & a \end{pmatrix}$$

$$\text{det} \begin{pmatrix} a-\lambda & b \\ b & a-\lambda \end{pmatrix} = 0 \quad (a-\lambda)^2 - b^2 = 0$$

$$a-\lambda = \pm b$$

$$\lambda = a \pm b = (e^{2\beta} + e^{-2\beta}) \pm (e^{2\beta\varepsilon} + e^{-2\beta\varepsilon})$$

$$= 2(\cosh(2\beta) \pm \sinh(2\beta\varepsilon))$$

+ is bigger than -

$$\text{So } \lambda(\varepsilon) = 2[\cosh(2\beta) + \cosh(2\beta\varepsilon)]$$

$$\begin{bmatrix} a & \frac{1}{a} \\ \frac{1}{a} & a \end{bmatrix} \quad \begin{bmatrix} b & \frac{1}{b} \\ \frac{1}{b} & b \end{bmatrix}$$

where  $a = \cosh(2\beta)$

$\lambda(\varepsilon) = 2[a + a\varepsilon \sinh(2\beta\varepsilon)]$

$\lambda(\varepsilon) = 2[a + a\varepsilon \sinh(2\beta\varepsilon)]$

Date \_\_\_\_\_

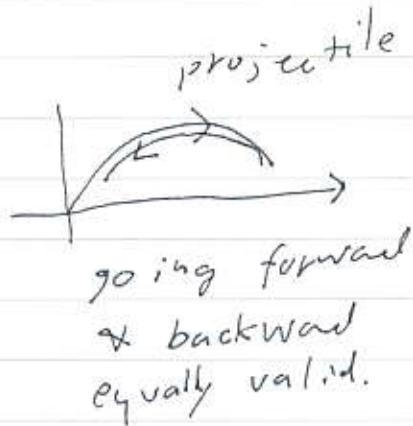
Microscopic laws are time-reversal symmetric!

Newton's law  $m \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$

if  $\vec{r}_i = \vec{r}_i(t)$  is a solution

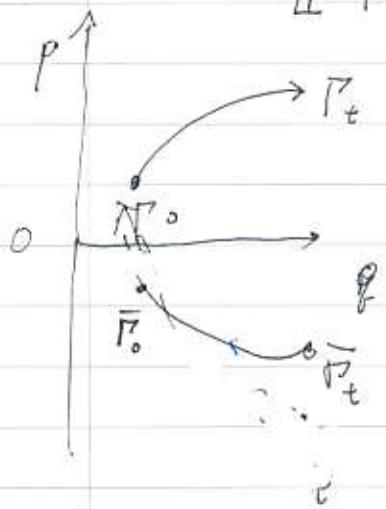
so is  $\vec{r}_i(-t)$

Newton's Eq. is invariant under  $t \rightarrow -t$



### Hamiltonian Dynamics

$P_0 = (q_0, p_0)$  starts in  $P_0$  we can move to  $P_t = (q_t, p_t) = e^{tL} P_0$   
after time  $t$ .  $L = [ \cdot, H ]$  Poisson bracket



in phase space

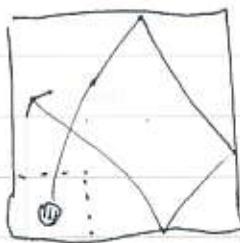
at  $P_t$  if we reverse the velocity.  $p_t \rightarrow -p_t$

when  $\bar{P}_0 = e^{tL} (q_0, -p_0) = (q_0, -p_0)$   
continuing running in time forward

### Quantum Mechanics

$\psi(t)$  is a solution of  $i\hbar \frac{\partial \psi}{\partial t} = H\psi$

then  $\psi^*(-t)$  is also a solution a solution moves back in time.  
Same is true for electromagnetic Equations of Maxwell.



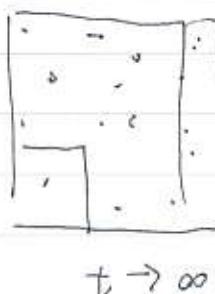
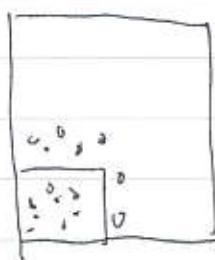
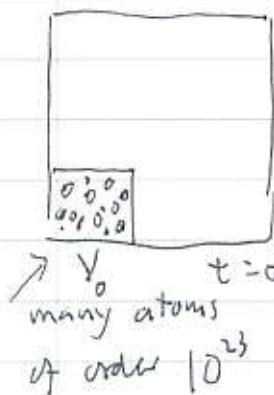
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one atom in a box at a box.  $\rightarrow$

you cannot see a difference  
if the motion of the atom  
is reversed

(a movie played forward or backward, there is no  
difference)

$$V > V_0$$



$$H = \frac{U}{\Omega} = \text{const}$$

energy is  
conserved.  
microcanonical

entropy (assuming ideal gas)

$$S = k \ln \Omega$$

\* of microscopic states

$$S = Nk_B \ln V + \underbrace{\text{terms dependent on } E}_{(\text{const if } U \text{ is fixed})}$$

[recall Sackur-Tetrode formula]

$$\text{entropy increases by } \Delta S = Nk_B \ln \frac{V}{V_0}$$

Reverse situation never happens no matter how long you wait. Why? (because  $N \rightarrow \infty$ ) <sup>first</sup>  
irreversibly due to the thermodynamics?

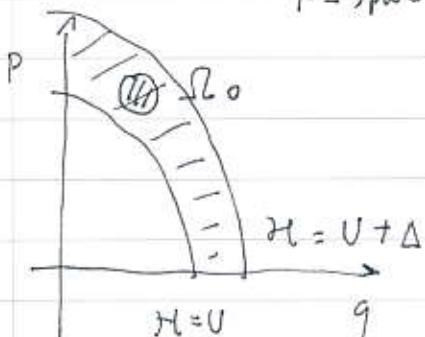
it is easy to see if there is one or two atoms, it is frequent that the atoms go back to small box  $V_0$  often!

$$TdS \geq dU + PdV = fQ$$

The equal sign holds only in reversible processes

Poincaré Recurrence

$\mathbb{P}$ -space



$S_n$  is the set

Theorem (1892):  
 (0) the phase flow is onto-one & onto  
 (1) phase space volume is finite

(2) starting in small regn  $S_0$  in  
 phase space, because Liouville thm  
 the hypervol does not change

(3)  $S_n = \hat{T}_t S_{n-1}$  for some  $t$   
 show on later  $S_n \cap S_0 \neq \emptyset$   
 (Consider  $S_0, S_1, \dots, S_n$ )

if they are all non intersect, then as  $n \rightarrow \infty$ , the  
 total phase vol goes to infinity

$\sum_{i=0}^n |S_i| = n |S_0| \rightarrow \infty$ . contradicts the  
 assumption that the phase space is finite. (remember  
 $S \approx k \ln S_0$ )

(in the sense of a set)

so the system returns to starting point arbitrarily close  
 after  $t_p$ .

However  $t_p \propto V^N \rightarrow \infty$  as  $N \rightarrow \infty$ .

$t_p$  is too large (more than the age of Universe) <sup>to be</sup>  
 relevant.

If however, entropy is the fraction of  $\mathbb{P}$ , we have to  
 conclude then  $S$  can ~~increase~~ decrease as well as increase  
 due to Poincaré Recurrence!

Gibbs entropy

$$\int p(r) d\beta = 1$$

$$\bar{S} = -k_B \int p(r) \ln p(r) dr$$

Let assume we have a microscopic ensemble

$$p(r) = \begin{cases} C & U < H < U + \Delta \\ 0 & \text{otherwise} \end{cases}$$

$$G \int dr = C \Delta = 1$$

$$\text{then } \bar{S} = -k_B \int_C^C \ln C dr = -k_B \ln G = k_B \ln \Omega$$

consistent with Boltzmann entropy.  
in equil.

$\bar{S}$  do not increase even in nonequilibrium situation

$\bar{S} = \text{const}$  for any  $p(r, t)$

function  $\rightarrow$   $p(r, t) \propto e^{-\beta E_r}$

prove

$$\frac{d\bar{S}}{dt} = -k_B \int \frac{\partial}{\partial t} (\rho \ln \rho) dr$$

$$= -k_B \int \left[ \frac{\partial \rho}{\partial t} \ln \rho + \rho \frac{\partial \ln \rho}{\partial t} \right] dr$$

$$\frac{\partial \ln \rho}{\partial t} = \frac{1}{\rho} \frac{\partial \rho}{\partial t}$$

$$= -k_B \int \left( \frac{\partial \rho}{\partial t} \right) (\ln \rho + 1) dr$$

but  $\frac{\partial \rho}{\partial t} + \dot{E}(p, H) = 0$

point barw

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q} \frac{\partial H}{\partial p} - \frac{\partial \rho}{\partial q} \frac{\partial p}{\partial p} = 0$$

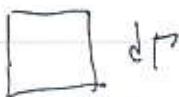
$$= -k_B \int \left[ -\frac{\partial \rho}{\partial q} \dot{q} + \frac{\partial \rho}{\partial p} \dot{p} \right] [\ln \rho + 1] dr$$

$$\frac{d\bar{S}}{dt} = -k_B \int \frac{\partial}{\partial t} (\rho \ln p) d\Gamma = -k_B \int \frac{D}{Dt} (\rho \ln p) d\Gamma = 0$$

because  $\frac{Dp}{Dt} = 0$

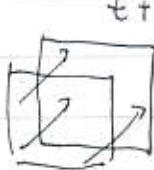
$$\int \frac{\partial g}{\partial t} d\Gamma = \int \frac{Dg}{Dt} d\Gamma$$

show this more carefully.



fixed  
volume element

now # of  
systems  
intrinsic



t

$d\Gamma_t$

$g$  does not change  
follow the flow  
into an all v.  
so  $\int g d\Gamma$  will not

how  $g$  change  
flowing the motion  
of particle.

however  $d\Gamma_t = d\Gamma$

by Liouville theorem

$$\int \bar{S} d\Gamma \text{ would not change for our gas experiment!}$$

Same is true if we use Q over  $\hat{\rho}$  density matrix

$$\bar{S} = \text{Tr}(\hat{\rho} \ln \hat{\rho})$$

$$\frac{d\bar{S}}{dt} = 0$$

This appear to say entropy  
is only meaningful for Equilibrium macroscopic system!!

proof of

H-theorem  $\swarrow$  one particle distribution valid only  
for dilute gas

$$\rightarrow S_B = -k_B \int f \ln f d\vec{r} d\vec{p}$$

Boltzmann's view  
for reduced variance f

$$\approx -k_B H$$

$$f(\vec{r}) N \int p(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_N) d\vec{r}_1 \dots d\vec{r}_N$$

$$H = \int f \ln f d\vec{r} d\vec{p}$$

$$\frac{dH}{dt} = \int \left[ \frac{\partial}{\partial t} [f \ln f] \right] d\vec{r} d\vec{p} = \int \left( \frac{\partial f}{\partial t} \ln f + f \frac{\partial \ln f}{\partial t} \right) d\vec{r} d\vec{p}$$

Date \_\_\_\_\_  
NO contribution from  $\vec{v}$

$$= \int \frac{\partial f}{\partial t} (1 + \ln f) d\vec{r} d\vec{p}$$

$\vec{v}$  and  $\vec{r}$   
are invariable  $\vec{v} = \vec{P}$

consider

$$\int \frac{\partial f}{\partial p} \int \frac{\partial (f v_x)}{\partial x} ((1 + \ln f)) d\vec{r} d\vec{p}$$

$$= \int \frac{\partial}{\partial x} (v_x f \ln f) d\vec{r} d\vec{p} = \int_{x=-\infty}^{\infty} dx \frac{\partial v_x f \ln f}{\partial x} dy dz d\vec{p}$$

$$- \left. \int dy dz d\vec{p} [v_x f \ln f] \right|_{x=\infty} = 0$$

since  $f = 0$   
at one well

$$\begin{aligned} \frac{\partial}{\partial x} (1 \ln f) &= \frac{\partial f}{\partial x} \ln f + f \frac{1}{f} \frac{\partial f}{\partial x} \\ &= \frac{\partial f}{\partial x} (1 + \ln f) \end{aligned}$$

assume  $f \rightarrow 0$   
when  $|x| \rightarrow \infty$   
or  $(R_L) \rightarrow \infty$

Same trick works for  $\frac{\partial F_x f}{\partial p_x}$  as long as  $F$  is a  
function of  $\vec{r}$  only  
(i.e. conservative force)

→ so

$$\frac{dH}{dt} = \int (1 + \ln f) \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} d\vec{r} d\vec{p}$$

$\vec{p} = p$  save writing

$$\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d\vec{p}_i \int d\vec{p}'_i d\vec{p}_j' \sigma(\vec{p}_i, \vec{p}_j | \vec{p}'_i, \vec{p}'_j) (f'_i - f_i)$$

$$\frac{dH}{dt} = \int d\vec{r} d\vec{p} d\vec{p}_i \int d\vec{p}'_i d\vec{p}_j' \sigma(\vec{p}_i, \vec{p}_j | \vec{p}'_i, \vec{p}'_j) \frac{\cancel{1 + f_i}}{\cancel{1 + f_j}} \cancel{1 + f_j} (1 + \ln f) (f'_i - f_i)$$

$$\frac{dH}{dt} = \int d\vec{r} \int dp dp_1 \underbrace{\int dp' dp'_1 \sigma(pp_1 | p'p'_1)}_{\substack{\text{symmetric due to permutations of} \\ \text{prime}}} (1 + \frac{1}{f}) (f'' - f_f)$$

all  $p$ 's are  
dummy integration variables

$$\int dp dp_1 dp' dp'_1 \sigma(pp_1 | p'p'_1) f(p') f(p'_1) \xleftarrow{\substack{\text{interchange} \\ p \leftrightarrow p'}} \sigma(p'p_1 | pp_1) f_f$$

this becomes identical to the second "term."  
need time-reversal plus  
space inversion

so

$$\frac{dH}{dt} = \int d\vec{r} dp dp_1 dp' dp'_1 \sigma(pp_1 | p'p'_1) \ln f (f'' - f_f)$$

$$\textcircled{1} \quad \sigma(pp_1 | p'p'_1) \ln f (f'' - f_f) \parallel = \phi_1 = \phi$$

$$\text{interchange } p \leftrightarrow p_1, \text{ } p' \leftrightarrow p'_1 \quad \textcircled{2} \quad \sigma(p_1 p | p' p') \ln f_1 (f_f' - f_f) = \phi_2 = \phi$$

$$\text{intensity } \textcircled{3} \quad \sigma(p'p_1 | pp_1) \ln f' (f_f - f_f') = \phi_3 = \phi$$

$$\text{prime & non-prime of } \textcircled{4} \quad \sigma(p'_p | p_1 p) \ln f'_1 (f_f - f_f') = \phi_4 = \phi$$

$$\text{above } \left\{ \begin{array}{l} p \leftrightarrow p', \sigma(\dots) \text{ all the same by symmetry} \\ p \leftrightarrow p_1, \sigma(\dots) \text{ all the same by symmetry} \end{array} \right. \ln \phi = 0$$

$$\frac{dH}{dt} = \int d\vec{r} dp dp_1 dp' dp'_1 \sigma(pp_1 | p'p'_1) \left[ \ln \left( \frac{f_f}{f_f'} \right) \cdot (f'' - f_f) \right]$$

$$= \int d\vec{r} dp dp_1 dp' dp'_1 \sigma(\dots) (B-A) \ln \frac{A}{B}$$

$$\sigma > 0, A > 0, B > 0 \quad \text{if } A < B, B-A > 0, \ln \frac{A}{B} < 0 \quad (B-A) \ln \frac{A}{B} < 0$$

$$\text{so } \frac{dH}{dt} \leq 0 \quad S_B > 0$$

$$H - theorem \quad \frac{dH}{dt} \leq 0$$

i.e.  $\int f \ln f d\vec{p}$  is constant or decrease but never increase with time.

Entropy then always non-decreasing. Entropy increases.

"Entropy cannot be a microscopic quantity".

Entropy concept appears (in the sense  $S > 0$ )

only at coarse-grain level. (macroscopic level)

Boltzmann Eq. describes irreversible process

For Maxwell distribution

$$f = A e^{-\beta \frac{P^2}{2m}}$$

1) from thermodynamic point of view entropy is unique & physical (because it is heat)

$$\Delta S = \frac{\delta Q}{T} \text{ in real process}$$

Ans:

due to energy conservation

$$\frac{\int f_1}{\int f'_1} = e^{-\beta \left( \frac{P^2}{2m} + \frac{P_1^2}{2m} - \frac{P'^2}{2m} - \frac{P_1'^2}{2m} \right)} = 1$$

2) Then is statistical entropy depends on the level of coarsening?

$$\text{so } \frac{dH}{dt} = 0 \text{ i.e. coarse-grain Gibbs formula}$$

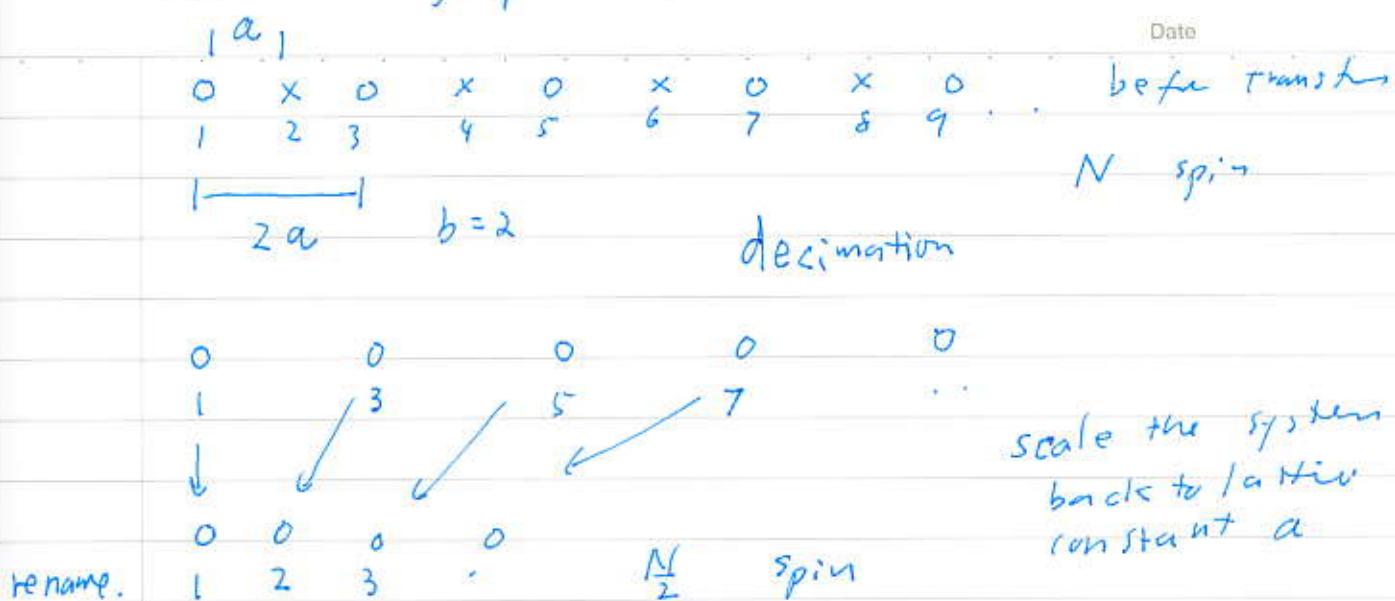
i.e. Maxwell distribution is stationary.

$$\text{equation state } \frac{dH}{dt} = 0 \quad f_1 f_1' - f'_1 f_1' = 0 \rightarrow \text{Maxwell distribution is a solution}$$

if  $f$  is Maxwell distribution then  $\frac{dH}{dt} = 0$

3) what level of coarsening is good enough?

Renormalization group transformation in 1D



Real space RG

- ① find out the transform of  $H$
- ② find fixed pt and line and fixed pt to find critical exponents

$$\tilde{H} = -K \sum_{i=1}^N \sigma_i \sigma_{i+1} - h \sum_{i=1}^N \sigma_i - \sum_{i=1}^N c \quad \begin{matrix} \leftarrow \text{free energy} \\ \beta \text{ absorbed in} \\ \text{couplings} \end{matrix}$$

$$Z = \sum_{\{\sigma\}} e^{-\tilde{H}}$$

Aim: to change the scale by a factor of 2.

trace out the even-numbered spins.

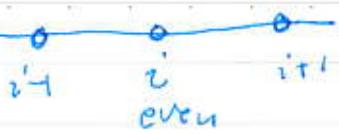
$$Z = \sum_{\{\sigma\}} e^{(K \sum_{i=1}^{\frac{N}{2}} \sigma_i \sigma_{i+1} + h \sum_{i=1}^{\frac{N}{2}} \sigma_i + \sum_{i=1}^{\frac{N}{2}} c)}$$

$$= \sum_{\{\sigma\}} e^{K \sigma_1 \sigma_2 + h \sigma_1 + c} e^{K \sigma_2 \sigma_3 + h \sigma_2 + c} e^{K \sigma_3 \sigma_4 + h \sigma_3 + c} \dots$$

$$Z = \sum_{\{\sigma_i\}} \prod_{i=2,4,6} e^{\{K\sigma_i(\bar{\sigma}_{i-1} + \bar{\sigma}_{i+1}) + h\sigma_i + \frac{h}{2}(\bar{\sigma}_{i-1} + \bar{\sigma}_{i+1}) + 2C\}}$$

sum over  $\sigma_i$  for  $i$  even

Date \_\_\_\_\_



$$= \sum_{\{\sigma_1 \dots \bar{\sigma}_{i-1}\}} \prod_{i=2,4,6} \left( e^{K(\bar{\sigma}_{i-1} + \bar{\sigma}_{i+1}) + h + \frac{h}{2}(\bar{\sigma}_{i-1} + \bar{\sigma}_{i+1}) + 2C} + e^{-K(\bar{\sigma}_{i-1} + \bar{\sigma}_{i+1}) - h + \frac{h}{2}(\bar{\sigma}_{i-1} + \bar{\sigma}_{i+1}) + 2C} \right)$$

Relabeling the spin

$$Z' = \sum_{\{\sigma_i\}} \prod_{i=1}^{N_2} \left( e^{(K + \frac{h}{2})(\sigma_i + \bar{\sigma}_{i+1}) + h + 2C} + e^{(-K + \frac{h}{2})(\sigma_i + \bar{\sigma}_{i+1}) - h + 2C} \right)$$

We demand the renormalized partition function can be cast in the same form as the original

$$\begin{aligned} &= \sum_{\{\sigma_i\}} \prod_i e^{(K'\sigma_i \bar{\sigma}_{i+1} + h'\sigma_i + C')} \\ &\quad \text{symmetric for } \sigma_1, \bar{\sigma}_2 + \frac{h'}{2}(\sigma_1 + \bar{\sigma}_2) + C' \\ &= e^{(K + \frac{h}{2})(\sigma_1 + \bar{\sigma}_2) + h + 2C} + e^{(-K + \frac{h}{2})(\sigma_1 + \bar{\sigma}_2) - h + 2C} \end{aligned}$$

$$\sigma_1 = \bar{\sigma}_2 = +1 \quad \left\{ \begin{array}{l} e^{K' + h' + C'} = e^{(2K + h + 2C)} + e^{(-2K + 2C)} \end{array} \right. \quad (1)$$

$$\sigma_1 = \bar{\sigma}_2 = -1 \quad \left\{ \begin{array}{l} e^{K' - h' + C'} = e^{(2K - 2h + 2C)} + e^{(-2K + 2C)} \end{array} \right. \quad (2)$$

$$\left. \begin{array}{l} \sigma_1 = -\bar{\sigma}_2 = +1 \\ \sigma_1 = -\bar{\sigma}_2 = -1 \end{array} \right\} \quad \left\{ \begin{array}{l} e^{-K' + C'} = e^{h + 2C} + e^{-h + 2C} \end{array} \right. \quad (3)$$

$$(1) \div (2) \quad e^{2h'} = \frac{e^{2h} e^{2K} + e^{-2K}}{e^{-2h} e^{2K} + e^{-2K}} = e^{2h} \frac{\cosh(2K + h)}{\cosh(2K - h)}$$

$$(1) \times (2) \div (3)^2 \quad e^{4K'} = \cosh(2K+h) \cosh(2K-h) / \cosh^2 h$$

 $\rightarrow$ 

$$(1) \times (2) \times (3)^2 \rightarrow e^{4C'} = e^{8C} \cosh(2K+h) \cosh(2K-h) \cosh^2 h$$

Date \_\_\_\_\_

Use new variables

$$\omega = e^{-4C}$$

$$x = e^{-4K}$$

$$y = e^{-2h}$$

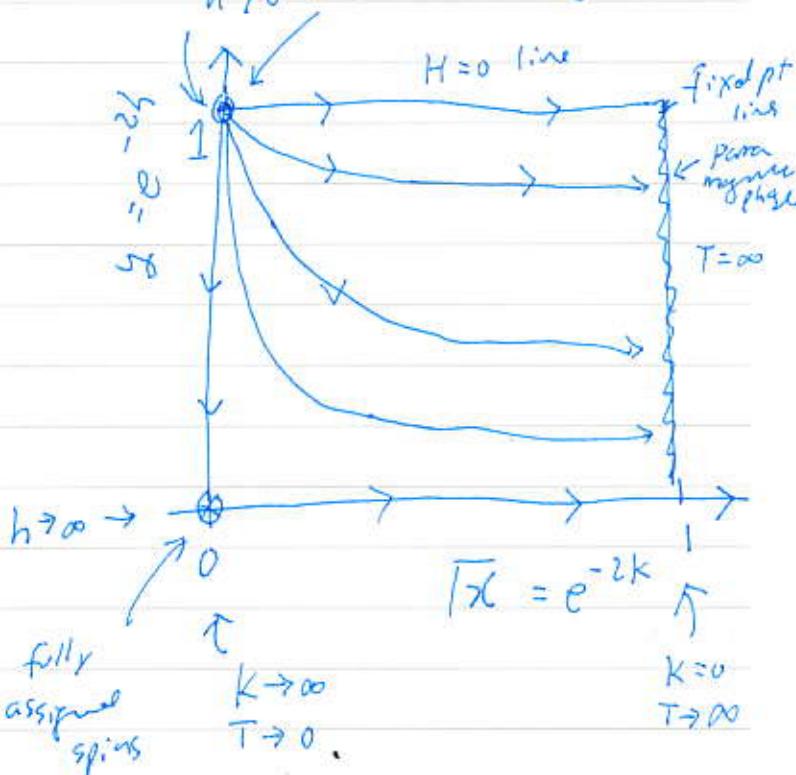
$h \rightarrow 0$  unstable fixed pt.  
 $h \rightarrow \infty$  critical fixed pt.

RG Transfer

$$\left\{ \begin{array}{l} \omega' = \omega^2 xy^2 (1+y)^2 \\ (x+y)(1+xy) \end{array} \right.$$

$$x' = \frac{x(1+y)^2}{(x+y)(1+xy)}$$

$$y' = \frac{y(x+y)}{(1+xy)}$$



$$\bar{x} = e^{-2K}$$

$$K=0$$

$$T \rightarrow \infty$$

linearized transformation at

unstable fixed point  $(x^*, y^*) = (0, 1)$ 
 $\epsilon$  small  
 $x$  and

$$\text{consider } x = x - x^* = x$$

$$y = 1 + \epsilon$$

$$\epsilon = y - y^* = y - 1$$

$$x' = \frac{x(1+1+\epsilon)^2}{(x+1+\epsilon)(1+x(1+\epsilon))}$$

$$\approx 4x = b^? x$$

$$= z^2 x$$

$$= b^2 x$$

$$\epsilon' = y' - 1 = \frac{(1+\epsilon)(x+1+\epsilon)}{1+x(1+\epsilon)} - 1 \approx$$

$$\frac{1+x+2\epsilon+\dots}{1+x+\dots} x 2\epsilon = b\epsilon$$

This means

$$\bar{f}_s(x, \epsilon) = b^{-1} \tilde{f}_s(b^2 x, b\epsilon)$$

The usual variable has to be replaced by  $x = e^{-4K}$  !

Date \_\_\_\_\_

$$\left. \begin{array}{l} m \frac{dV}{dt} = - \frac{dV}{dx} - m \int_{-\infty}^t \gamma(t-t') V(t') dt' + R(t) \\ \frac{dx}{dt} = v \end{array} \right\} \quad x, v$$

$$\begin{aligned} (a) \quad \frac{dE(t)}{dt} &= \frac{d}{dt} \left( \frac{1}{2} mv^2 + V \right) = \frac{1}{2} m v \frac{dV}{dt} + \frac{dV}{dx} \frac{dx}{dt} \\ &= \underline{m v \ddot{v}} + \frac{dV}{dx} v \\ &= v \left[ - \frac{dV}{dx} - m \int_{-\infty}^t \gamma(t-t') V(t') dt' + R(t) \right] + \frac{dV}{dx} v \\ &= V(t) \left[ - m \int_{-\infty}^t \gamma(t-t') V(t') dt' + R(t) \right] \end{aligned}$$

$$(b) \quad W_D = \int_0^T m \gamma(t) \int_{-\infty}^{\infty} \gamma(t-t') V(t') dt' dt$$

$$W_R = \int_0^T V(t) R(t) dt$$

$$\int_0^T m \frac{dV}{dt} \cdot v dt = - \int_0^T \frac{dV}{dx} \cdot v(t) dt \quad \oplus W_D + W_R$$

$$\int_0^T \left[ m v \ddot{v} + \frac{dV}{dx} \cdot v \right] dt = - W_D + W_R$$

$$= \int_0^T \frac{dE(t)}{dt} dt = \int_0^T dE(t) = E(T) - E(0) \quad \begin{matrix} \swarrow \text{some} \\ \text{bond value} \end{matrix}$$

$$W_R \propto T, \quad W_D \propto T,$$

More precisely  $\frac{1}{T} [E(T) - E(0)] = -\frac{W_p}{T} + \frac{W_R}{T} \rightarrow 0$  as  $T \rightarrow \infty$  291

power =  $\frac{\text{work}}{\text{time}}$   $\langle v \cdot R \rangle = \langle v(t) \int_{-\infty}^t \gamma(t-t') R(t') dt' \rangle$   
 $\langle \cdot \rangle = \frac{1}{T} \int_0^T \cdot dt$  ange ~~rate~~ of power-dissipation  
 problem 6.3)

consider  $\frac{d}{d\lambda} (e^{\lambda H} A e^{-\lambda H}) = e^{\lambda H} H A e^{-\lambda H} + e^{\lambda H} (A(-H)) e^{-\lambda H}$   
 $= e^{\lambda H} (H A - A H) e^{-\lambda H} = e^{\lambda H} [H, A] e^{-\lambda H} = \cancel{e^{\lambda H}}$   
 $= -i\hbar e^{\lambda H} \dot{A} e^{-\lambda H}$   $i\hbar \frac{dA}{dt} = [A, H]$   
 integrate both sides  $\int_0^\beta$   $= i\hbar \dot{A}$   
 Heisenberg eq

$$\int_0^\beta \frac{d}{d\lambda} (e^{\lambda H} A e^{-\lambda H}) = -i\hbar \int_0^\beta d\lambda e^{\lambda H} \dot{A} e^{-\lambda H}$$
 $e^{\rho H} A e^{-\rho H} - A = -i\hbar \int_0^\beta d\lambda e^{\lambda \rho} \dot{A} e^{-\lambda H}$ 

from left  $\rho$  from right  $B$  take trace

 $\beta \langle \dot{A}; B \rangle = \cancel{\rho} \frac{1}{i\hbar} \int_0^\beta d\lambda \text{Tr} (\rho e^{\lambda H} \dot{A} e^{-\lambda H} B)$

$$\rho = \frac{e^{\rho H}}{Z} = \left(\frac{-1}{i\hbar}\right) \text{Tr} [\rho e^{\rho H} A e^{-\rho H} - \rho A B]$$
 $= \frac{-1}{i\hbar} \text{Tr} \left[ \frac{1}{Z} A \overbrace{e^{-\rho H} B}^{\rho B A} - \rho A B \right]$

$$= \frac{-1}{i\hbar} \text{Tr} [\rho B A - \rho A B] = \frac{1}{i\hbar} \text{Tr} [\rho (AB - BA)]$$
 $= \frac{1}{i\hbar} \langle [A, B] \rangle$

problem 1

left      right  
 $\rightarrow \quad \leftarrow \quad \leftarrow \quad \leftarrow$

$$P = \begin{pmatrix} 1 & e^{-\beta\varepsilon} & e^{-\beta\varepsilon} & 0 \\ e^{\beta\varepsilon} & 1 & 1 & e^{-\beta\varepsilon} \\ e^{-\beta\varepsilon} & 1 & 1 & e^{-\beta\varepsilon} \\ 0 & e^{-\beta\varepsilon} & e^{-\beta\varepsilon} & 1 \end{pmatrix}$$

Date \_\_\_\_\_

or

$$P = \begin{pmatrix} 1 & x & x & 0 \\ x & 1 & 1 & x \\ x & 1 & 1 & x \\ 0 & x & x & 1 \end{pmatrix} \quad x = e^{-\beta\varepsilon}$$

$$|P - \lambda I| = 0$$

$$\lambda = 1, 0, \frac{1}{2}(3 \pm \sqrt{1+16x^2})$$

$$\lambda_{\max} = \frac{1}{2}(3 + \sqrt{1+16x^2})$$

$$\begin{aligned} |P - \lambda I| &= \lambda^4 - 4\lambda^3 + 4x^2\lambda^2 + 5\lambda^2 + 4x^2\lambda - 2\lambda \\ &= (\lambda - 1)\lambda(2 - 4x^2 - 3\lambda + \lambda^2) \end{aligned}$$

$$F = -k_B T \ln Z$$

$$= -k_B T N \ln \lambda_{\max}$$

prob 2.

(a)

$$\xi(t, 0) = b \xi(b^Y t, 0)$$

$$= t^{-\frac{Y}{Y}} \dots$$

$$\text{compare with } \xi \propto t^{-\nu} \rightarrow \nu = \frac{1}{Y}$$

$$\text{Let } b^Y t = 1$$

$$b = \frac{1}{t^{\frac{1}{Y}}}$$

Date

(b)

$$M = \langle \sum_i \sigma_i \rangle = \frac{1}{Z} \sum_{\{s\}} \sum_i \sigma_i e^{-\beta(E(s) - h \sum_i \sigma_i)}$$

$$\chi = \left. \frac{\partial M}{\partial h} \right|_h = \frac{1}{Z} \sum_{\{s\}} (\sum_i \sigma_i) (\beta \sum_j \sigma_j) e^{-\beta E(s)} - \frac{\langle \sum_i \sigma_i \rangle \langle \beta \sum_i \sigma_i \rangle}{Z^2}$$

$$= \beta \sum_{ij} \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle$$

$$= \beta \sum_{ij} G(|i-j|) = \beta \sum_i \sum_j G(j-i)$$

$$= \beta N \int d\vec{r} G(\vec{r})$$

(c)

$$\chi = \beta N \int d^d r G(r)$$

$$\text{let } b = \frac{r}{\ell}$$

$$= \beta N \int r^{d-1} dr b^d G(r/b, \frac{r}{b})$$

$$= \beta N \int_{-\infty}^{\ell} r^{d-1} dr G\left(\frac{r}{b}, 1\right)$$

$$= \beta N \int_{-\infty}^{\ell} r^{d-1} dr \int_0^\infty \left(\frac{r}{b}\right)^{d-1} d\left(\frac{r}{b}\right) G\left(\frac{r}{b}, 1\right)$$

$$\approx \ell^{2-n} = t^{-\nu(2-n)}$$

$$\text{compare with defn. } \chi \approx t^{-\gamma}$$

$$\text{we find } \gamma = \nu(2-n) !$$

$$3. m \frac{dV}{dt} = -m\gamma V + f + R(t)$$

Date \_\_\_\_\_

$$(a) m \frac{d\langle V \rangle}{dt} = -m\gamma \langle V \rangle + f$$

$$\frac{d\langle V \rangle}{dt} = -\gamma \langle V \rangle + f/m$$

$$\frac{d\langle V \rangle}{-\gamma \langle V \rangle + f/m} = dt$$

$$-\frac{1}{\gamma} d(\ln(-\gamma \langle V \rangle + \frac{f}{m})) = dt$$

$$\ln(-\gamma \langle V \rangle + \frac{f}{m}) = -\gamma t + c$$

$$-\gamma \langle V \rangle + \frac{f}{m} = A e^{-\gamma t}$$

$$\langle V \rangle = \frac{f}{\gamma m} + A' e^{-\gamma t}$$

$$\langle V \rangle_0 = \frac{f}{\gamma m} + A'$$

$$\langle V \rangle = \frac{f}{\gamma m} + [\langle V_0 \rangle - \frac{f}{\gamma m}] e^{-\gamma t}$$

if  $R(t) \neq 0$

$$V(t) = \frac{f}{\gamma m} + [\langle V_0 \rangle - \frac{f}{\gamma m}] e^{-\gamma t} + e^{-\gamma t} \int_0^t \frac{R(\tau)}{m} e^{\gamma \tau} d\tau$$

$$m \frac{dV(t)}{dt} = f e^{-\gamma t} - \gamma e^{-\gamma t} \int_0^t \frac{R(\tau)}{m} e^{\gamma \tau} d\tau + R(t)$$

$$\left( \gamma \langle V_0 \rangle + \right) = -m\gamma(V - \frac{f}{m\gamma}) + R(t)$$

$$v(t) - \bar{v}(t) = e^{-\gamma t} \int_0^t \frac{R(\tau)}{m} e^{\gamma \tau} d\tau$$

$$\begin{aligned} \langle (v(t) - \bar{v}(t))^2 \rangle &= e^{2\gamma t} \int_0^t \int_0^t d\tau_1 d\tau_2 \frac{R(\tau_1) R(\tau_2)}{m^2} e^{\gamma(\tau_1 + \tau_2)} \\ &= e^{-2\gamma t} \int_0^t \int_0^t d\tau_1 d\tau_2 \frac{1}{m^2} C \delta(\tau_1 - \tau_2) e^{2\gamma \tau_1} \\ &= C e^{-2\gamma t} \int_0^t d\tau_1 e^{2\gamma \tau_1} \\ &= \frac{C}{2\gamma m^2} e^{-2\gamma t} \left[ \frac{1}{2\gamma} e^{2\gamma t} \right]_0^t \\ &= \frac{C}{2\gamma m^2} e^{-2\gamma t} [e^{2\gamma t} - 1] \\ &= \frac{C}{2\gamma m^2} [1 - e^{-2\gamma t}] \end{aligned}$$

$C = \frac{m}{2\pi k_B T}$

(3) Fokker-Planck equation

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial v} (M_1 P) + \frac{1}{2} \frac{\partial^2}{\partial v^2} (M_2 P)$$

$$\begin{aligned} M_1 &= \frac{1}{\tau} \langle v(\tau) - v_{(0)} \rangle & \tau \rightarrow 0 \\ &= \frac{1}{\tau} \left[ \frac{f}{\gamma m} + (v_{(0)} - \frac{f}{\gamma m})(1 - e^{-\gamma \tau}) - v(\tau) \right] \end{aligned}$$

$$\begin{aligned} M_2 &= \frac{1}{\tau} \langle (v(\tau) - v_{(0)})^2 \rangle \\ &= \frac{1}{\tau} \frac{C}{2\gamma m^2} [2\gamma \tau + \cdot] \\ &= \frac{1}{\tau} \left[ \frac{f}{\gamma m} + v - \frac{f}{\gamma m} \downarrow v - (v - \frac{f}{\gamma m}) \gamma \tau \right] \end{aligned}$$

$$= -\left(v - \frac{f}{\gamma m}\right) \gamma$$

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial v} \left[ \left(v - \frac{f}{\gamma m}\right) P \right] + \frac{1}{2} \frac{C}{m^2} \frac{\partial^2}{\partial v^2} P$$

$$Z = \sum_{n_1 n_2 \dots n_N} e^{-\beta(\sum \epsilon n_i - \mu n_i)}$$

Date \_\_\_\_\_

$$= \sum_{n_1} e^{-\beta(\epsilon - \mu) n_1} \sum_{n_2} e^{-\beta(\epsilon - \mu) n_2} \dots$$

$$= \left[ \sum_{n=0}^{\infty} e^{-\beta(\epsilon - \mu) n} \right]^N = \left[ \frac{1}{1 - e^{-\beta(\epsilon - \mu)}} \right]^N$$

$$S = \frac{\partial}{\partial T} (k_B T \ln Z) = \frac{\partial}{\partial T} f k_B T N \ln (1 - e^{-\beta(\epsilon - \mu)})$$

$$\cancel{-k_B N} = -N k_B \ln (1 - e^{-\beta(\epsilon - \mu)})$$

$$= k_B T N \frac{e^{-\beta(\epsilon - \mu)}}{1 - e^{-\beta(\epsilon - \mu)}} \left[ \frac{\epsilon - \mu}{k_B T^2} \right]$$

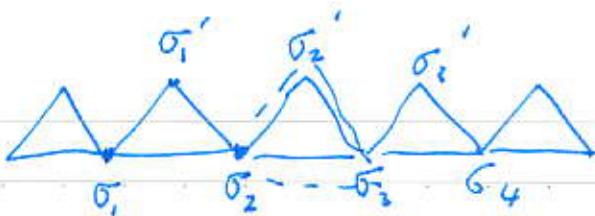
$$= -N k_B \ln (1 - e^{-\beta(\epsilon - \mu)}) - N \frac{\epsilon - \mu}{T} \frac{1}{e^{\beta(\epsilon - \mu)}} - 1$$

$$\langle N \rangle = \frac{\partial}{\partial \mu} (k_B T \ln Z) = k_B T \cancel{f}$$

$$= \frac{\partial}{\partial \mu} \left[ N k_B T \ln (1 - e^{-\beta(\epsilon - \mu)}) \right]$$

$$= -N k_B \cancel{T} \frac{-e^{-\beta(\epsilon - \mu)}}{1 - e^{-\beta(\epsilon - \mu)}} \cdot \cancel{\beta}$$

3.



Date \_\_\_\_\_

$$Z = \sum_{\{\sigma\}} e^{K(\sigma_2 \sigma_3 + \sigma_2 \sigma_2' + \sigma_3 \sigma_2')} e^{K(\sigma_3 \sigma_4 + \sigma_3 \sigma_3' + \sigma_4 \sigma_3')}$$

$$= \sum_{\sigma_2'} e^{K(\sigma_2 \sigma_3 + \sigma_2 \sigma_2' + \sigma_3 \sigma_2')} \\ = P(\sigma_2 \sigma_3)$$



$$P(\sigma_2 \sigma_3) = \sum_{\sigma_2'} e^{K(\sigma_2 \sigma_3 + \sigma_2 \sigma_2' + \sigma_3 \sigma_2')}$$

$$= e^{K(\sigma_2 \sigma_3 + \sigma_2 + \sigma_3)} + e^{K(\sigma_2 \sigma_3 - \sigma_2 - \sigma_3)}$$

$$P = + \begin{bmatrix} e^{\sigma_2} + & - \\ e^{3K} + e^{-K} & 2e^{-K} \end{bmatrix} \\ - \begin{bmatrix} 2e^{-K} & e^{-K} + e^{3K} \end{bmatrix}$$

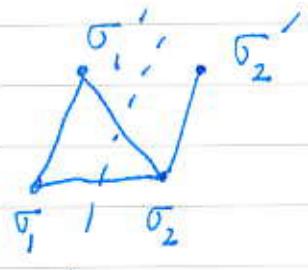
$$\begin{vmatrix} e^{3K} + e^{-K} - \lambda & 2e^{-K} \\ 2e^{-K} & e^{3K} + e^{-K} - \lambda \end{vmatrix} = 0$$

$$(e^{3K} + e^{-K} - \lambda)^2 - 4e^{-2K} = 0$$

$$\lambda = e^{3K} + e^{-K} \pm 2e^{-K} = \left\{ \begin{array}{l} e^{1K} + 3e^{-K} \\ e^{3K} - e^{-K} \end{array} \right.$$

$$F = -Nk_B T \ln Z = -Nk_B T \ln \lambda$$

$\lambda = e^{\beta k} + 3e^{-\beta k}$



$$P(\sigma_1 \sigma'_1; \sigma_2 \sigma'_2) = C \quad k \left( \frac{1}{2} \sigma_1 \sigma'_1 + \frac{1}{2} \sigma_2 \sigma'_2 + \sigma_1 \sigma_2 + \sigma'_1 \sigma'_2 \right)$$

$$= \begin{matrix} \sigma_1 \sigma'_1 \\ \sigma_2 \sigma'_2 \\ + + \\ + - \\ - + \\ - - \end{matrix} \begin{bmatrix} e^{3k} & e^{2k} & e^{-2k} & e^{-k} \\ 1 & e^{-k} & e^{-k} & 1 \\ 1 & e^{-k} & e^{-k} & 1 \\ e^{-k} & e^{-2k} & e^{2k} & e^{3k} \end{bmatrix}$$

$$\lambda_1 = 0, \lambda_2 = 0, \lambda_3 = e^{3k} + e^{-k}, \lambda_4 = e^{\beta k} + 3e^{-\beta k}$$

same as above

$$G = (T - T_c) \alpha M^2 + b M^4$$

$$h = \frac{\partial G}{\partial M} = (T - T_c) 2 \alpha M + 4b M^3$$

Date \_\_\_\_\_

$$\langle \frac{1}{2} m v^2 \rangle = \frac{k_B T}{2}$$

5. (a)  $P = \langle m \gamma v \cdot v \rangle = \sigma \langle m v^2 \rangle = \sigma k_B T$

(b)  $I = \langle R(t) V(t) \rangle$

$$V(t) = V(0) e^{-\gamma t} + \int_0^t \frac{R(\tau)}{m} e^{-\gamma(t-\tau)} d\tau$$

$\parallel$

$$t \rightarrow \infty$$

$$I = \int_0^t \underbrace{\langle R(t) R(\tau) \rangle}_{C \delta(t-\tau)} \frac{e^{-\gamma(t-\tau)}}{m} d\tau$$

or  $\delta(t-t)$



we have to think of  $\delta$  is  
an idealized of gaussian-like peaks

integrate to  $t$  take half of the value

$$= \frac{C}{m} \int_0^t \delta(t-\tau) e^{-\gamma(t-\tau)} d\tau = \frac{C}{2m}$$

(i)  $\int d\tau$  fluctuation-dissipation give  $C = 2m \gamma k_B T$   
 } This shows  $P = I$ .

alternatively  $V m \frac{dv}{dt} = -m \gamma v^2 + R(t) v$

neglect  $\frac{d}{dt} \left( \frac{1}{2} m v^2 \right) = \dots$

$$\frac{1}{T} \int_0^T (-m \gamma v^2) dt + \frac{1}{T} \int_0^T R(t) v dt$$

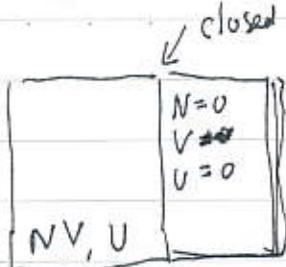
$$\frac{E(T) - E(0)}{T} = - \langle m \gamma v^2 \rangle + \langle R v \rangle = -P + \frac{1}{2} m v^2$$

$T \rightarrow \infty$

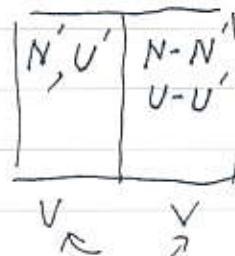
Entropy of ideal gas (monoatomic)

$$S = k_B N \ln(V U^{\frac{3}{2}}) + \text{const}$$

↑ depends on  $N$   
↓ not on  $V$



closed wall (adiabatic,  
immovable,  
nonperm  
impermeable) →  
compare



$S + 0$   
equal in volume

always fixed

what is  $N' U'$  if partition is removed (becomes permeable)?

$$-S_{\text{tot}} = k_B N' \ln(V U'^{\frac{3}{2}}) + k_B(N-N') \ln(V(U-U')^{\frac{3}{2}})$$

Need  $N$ -degree

$$S = k_B N \ln(V U^{\frac{3}{2}}) + \frac{5}{2} N k_B (1 \cancel{\ln N}) + \text{const}$$

$$S_{\text{tot}} = k_B N' \ln(V U'^{\frac{3}{2}}) + \frac{5}{2} N' k_B (1 - \ln N')$$

$$+ k_B(N-N') \underbrace{\ln(V(U-U')^{\frac{3}{2}})}_{k_B(N-N') \left[ \ln V + \ln(U-U')^{\frac{3}{2}} \right]} + \frac{5}{2} (N-N') k_B (1 - \ln(N-N'))$$

$$\cancel{k_B(N-N')} \left[ \ln V + \ln(U-U')^{\frac{3}{2}} \right]$$

$$= k_B N' \ln V + k_B N' \ln U'^{\frac{3}{2}} + k_B(N-N') \ln V + \cancel{(k_B N')} \ln(U-U')^{\frac{3}{2}}$$

$$+ \frac{5}{2} N' k_B + \frac{5}{2} (N-N') k_B - \frac{5}{2} N' \ln N' - \frac{5}{2} k_B (N-N') \ln(N-N')$$

$$= k_B N \ln V + \frac{5}{2} N k_B + k_B N' \ln \frac{U'^{\frac{3}{2}}}{(k_B N)^{\frac{1}{2}}} + k_B(N-N') \ln(U-U')$$

$$- \cancel{\frac{5}{2} k_B} \left[ N' \ln N' + (N-N') \ln(N-N') \right]$$

$$\frac{\partial S_{\text{tot}}}{\partial N'} = 0 = k_B \ln U'^{\frac{3}{2}} - k_B \ln(U-U')^{\frac{3}{2}}$$

$$- \frac{5}{2} k_B \left[ \ln N' + \cancel{N} \neq \ln(N-N') \right]$$

$$I_1 \frac{\frac{U'}{2} - \frac{(N-N')}{2}}{\frac{N}{2} - \frac{(U-U')}{2}} = 0 \quad \left( \frac{N-N'}{N} \right)^{\frac{1}{2}} \left( \frac{U'}{U-U'} \right)^{\frac{1}{2}} = 1$$

Date \_\_\_\_\_

$$\frac{\partial S_{tot}}{\partial U'} = \left[ k_b N' \left[ \frac{1}{U'^{\frac{3}{2}}} \right] + k_b (N-N') \frac{(-1)}{(U-U')^{\frac{1}{2}}} \right]^{\frac{1}{2}} = 0$$

$$\frac{N-N'}{N} = \frac{(U-U')^{\frac{1}{2}}}{U'^{\frac{3}{2}}} \rightarrow$$

$$\left( \frac{N-N'}{N} \right)^{\frac{1}{2}} \cdot \left( \frac{N-N'}{N} \right) = 1 \quad \left( \frac{N-N'}{N} \right)^{\frac{3}{2}} = 1$$

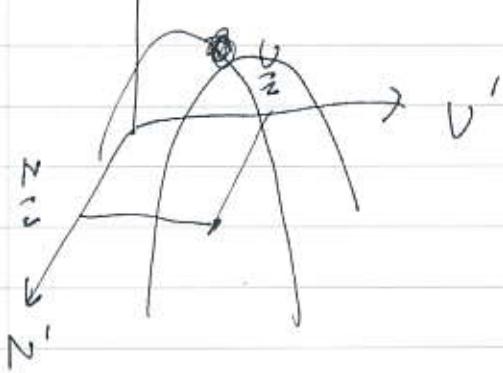
$$\frac{N-N'}{N} = 1 \quad N - N' = N' \quad N = 2N'$$

$$N' = \frac{N}{2} \quad \text{as expected.}$$

$$\left( \frac{U-U'}{U'} \right)^{\frac{1}{2}} = 1 \quad U-U' = U' \rightarrow U' = \frac{U}{2}$$

i.e., ~~parallel~~ particles distributed evenly has max.  $S_{tot}$

exactly a maximum at  $\left( \frac{N}{2}, \frac{U}{2} \right)$



$$dU = TdS - pdV + \mu dN$$

equilibrium statistical  
density operator

$$\hat{\rho}$$

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

Date

□ canonical  $\hat{\rho} \propto e^{-\beta \hat{H}}$   $\text{Tr}(\hat{\rho}) = 1$  fix the constant

$$dF = -SdT - pdV + \mu dN$$

$$\Xi = \text{Tr}(e^{-\beta \hat{H}}) \quad \xrightarrow{\text{Helmholtz free energy}} F = -k_B T \ln \Xi$$

$$\hat{\rho} = \frac{1}{\Xi} e^{-\beta \hat{H}}$$

$$\beta F = -\ln \Xi = \ln Z$$

$$e^{\beta F} = \Xi Z^{-1}$$

$$= e^{-\beta(\hat{H} - F)}$$

compare  $F = U - TS$

$$\text{Tr} \rightarrow \int \frac{dP_i d\mathbf{q}_i \dots}{h^{3n} N!}$$

$$\nexists \rightarrow e^{-\beta(U-F)} = e^{-\beta(TS)}$$

$$= e^{-\frac{S}{k_B}}$$

entropy

□ grand canonical

$$\hat{\rho} \propto e^{-\beta(\hat{H} - \mu \hat{N})}$$

$$\Xi = \sum_{\text{Fock space}} e^{-\beta(\hat{H} - \mu \hat{N})}$$

Fock space = 0 particle states  $\otimes$  1 particle states  $\otimes$  2 particle states ...

$$\hat{\rho} = \frac{1}{\Xi} e^{-\beta(\hat{H} - \mu \hat{N})}$$

$$= e^{-\beta(\hat{H} - \mu \hat{N} - 4)}$$

again

$$\text{Tr} \hat{\rho} = 1$$

$$e^{-\beta(U - \mu N - 4)}$$

$$\Psi = -k_B T \ln \Xi$$

$$= F - \mu N = U - TS - \mu N = -PV$$

$$= e^{-\beta(TS)} = e^{-\frac{S}{k_B}}$$

$$dU = -SdT - pdV - N d\mu$$

□ isothermal - isobaric ensemble (fix  $T, P, N$ )

$$G = F + PV = U - TS + PV = \mu_N \text{Gibbs free energy} \quad e^{-\beta(TS)} = e^{-\beta(U + PV - G)}$$

$$dG = -SdT + Vdp + \mu dN$$

$$\hat{\rho} = e^{-\beta(\hat{H} + \gamma \hat{V} - G)}$$

$$\text{Tr} \hat{\rho} = 1 \rightarrow G = -k_B T \ln \text{Tr}_{\hat{H}, \hat{V}} [e^{-\beta(\hat{H} + \gamma \hat{V})}]$$

→ closed  
solve  $e^{-\beta PV}$

□ microcanonical

$$\hat{\rho} = \begin{cases} \sum_{\varphi \in (\mathbb{V}, U + \Delta)} | \varphi \rangle \langle \varphi | & \leftarrow \text{sum over project} \\ 0 & \end{cases}$$

$$\text{Tr} | \varphi \rangle \langle \varphi | = 1$$

$$\text{Tr}(\hat{\rho}) = 1 = C \text{Tr} \sum_{\varphi} | \varphi \rangle \langle \varphi | = C \Omega$$

state of microstates

$$C = \Omega^{-1}$$

=

$$\hat{\rho} = \frac{1}{\Omega} \sum_{\varphi} | \varphi \rangle \langle \varphi |$$

$$k_B \ln \Omega = S$$

$$\ln \Omega = \frac{S}{k_B}$$

$$= e^{-S/k_B} \sum_{\varphi} | \varphi \rangle \langle \varphi |$$

$$\Omega = e^{S/k_B}$$

↑ also in this form if we take  $\sum_{\varphi} | \varphi \rangle \langle \varphi | \approx 1$

