

20<sup>th</sup> January 2025 (Monday) →

Often, we deal with integrals of the following kind,

$$I = \int dx \exp(N\phi(x))$$

↑ large, statistical #  
has some defined maxima.

Now,

$$\lim_{N \rightarrow \infty} I \approx \phi(x_{\max}) \rightarrow \text{Apparently, we also use this while doing steepest descent.}$$

□ Laplace method → (Same thing)

$$\int_a^b e^{mf(x)} dx, f(x) \text{ has unique global maxima at } x_0, m \gg 1$$

$$\text{Now, } g(x) = mf(x)$$

$$h(x) = \exp(mf(x))$$

Clearly, if  $g(x)$  has maxima at  $x_0$ ,  $h(x)$  also has maxima at  $x_0$

(Smooth functions)

Let us define,

$$g = \frac{g(x_0)}{g(x)} = \frac{mf(x_0)}{mf(x)} = \frac{f(x_0)}{f(x)} \rightarrow \text{No } m \text{ dependence}$$

Similarly defining,

$$h = \frac{h(x_0)}{h(x)} = \frac{\exp[mf(x_0)]}{\exp[mf(x)]} = \exp[m\{f(x_0) - f(x)\}]$$

④ Proof of Stirling's approximation →

$$T'(N+1) = N! = \int_0^\infty dx x^N e^{-x}$$

→ What is the motivation?  
We try to write this like a Laplace method integral as seen right before.

So,

$$x^N e^{-x} \rightarrow \exp[m\phi(x)]$$

↑ Defined maxima.  
Large no.

$$\Rightarrow \phi(x) = \ln x - \frac{x}{N}$$

$$\Rightarrow \phi'(x_{\max}) = \frac{1}{x_{\max}} - \frac{1}{N} = 0$$

$$\Rightarrow x_{\max} = N$$

Now,

$$\phi''(x) = -\frac{1}{x^2}$$

$$\Rightarrow \phi''(x_{\max} = N) = -\frac{1}{N^2} \rightarrow \text{Clearly, } x_{\max} \text{ is point of global maxima.}$$

$$\begin{aligned}\therefore \Gamma(N+1) = N! &= \int_0^\infty dx x^N e^{-x} \\ &= \int_0^\infty dx \exp\left[N\left\{\phi(x_{\max}) - \frac{1}{2}|\phi''(x_{\max})|(x-x_{\max})^2\right\}\right] \xrightarrow{\text{Taylor exp about maxima.}} \\ &= \int_0^\infty dx \exp\left[N \ln N - N - N \frac{1}{2} \cdot \frac{1}{N^2} (x-N)^2\right] \quad (\text{Gaussian integral}) \\ &= N^N e^{-N \sqrt{2\pi N}}\end{aligned}$$

$$\Rightarrow \ln(N!) = N \ln N - N + \frac{1}{2} \ln(2\pi N)$$

$$\Rightarrow \ln(N!) = \left(N + \frac{1}{2}\right) \ln(N) - N + \frac{1}{2} \ln(2\pi) \rightarrow \text{Stirling's approximation.}$$

① Example →

$$I = \int_0^\infty x^{2n} \exp\left[-\alpha x^2 - 6 \frac{x^6}{2}\right] dx \quad \begin{array}{l} \xrightarrow{\text{decays fast at larger } x} \\ \xrightarrow{\text{grows rapidly at lower } x} \end{array} \quad \begin{array}{l} \text{You may expect a maxima} \\ \text{somewhere in the middle.} \end{array}$$

We do,

$$u = x^2$$

$$\Rightarrow du = 2x dx$$

and,

$$n - \frac{1}{2} = m \gg 1$$

$$\Rightarrow I = \frac{1}{2} \int_0^\infty u^m \exp[-\bar{P}(u)] du = \frac{1}{2} \int_0^\infty e^{-P(u)} du$$

Now,

$$P(u) = \frac{b}{2}u^2 + au - m \log u$$

$$P'(u_0) = bu_0 + a - \frac{m}{u_0} = 0$$

$$\Rightarrow bu_0^2 + au_0 - m = 0$$

$$\therefore u_0 = \frac{-a \pm \sqrt{a^2 - (b)(-m)}}{2b} = \frac{-a \pm \sqrt{a^2 + 4bm}}{2b}$$

Also,

$$P''(u) = b + \frac{m}{u^2}$$

$$\therefore P''(u_0) = b + m \left[ \frac{4b^2}{(-a \pm \sqrt{a^2 + 4bm})^2} \right]$$

Maxima (?)

So we may evaluate the integral using Laplace method.

→ End of Probability Theory for the course.

## ① Entropy →

Boltzmann Entropy :  $S = \ln \Omega \xrightarrow{\text{No. of microstates corresponding to some macrostate.}}$

When does this hold? When,

$$P_i = \frac{1}{\Omega} \quad \forall i \rightarrow \text{All of these microstates are equally probable.}$$

$$\Rightarrow S = -\ln P_i$$

What if this is not the case? i.e.  $P_i \neq P_j$

$$S = - \sum_i P_i \ln P_i \quad (\text{weighted sum})$$

Note: This reduces to  $-\ln p_i$  if we set  $P_j = P_i \quad \forall j$

We may now write this as,

$$S = - \int dx f(x) \ln(f(x)) \rightarrow \text{Continuum limit}$$

② Coin Toss: H T T ... T H T T ... → Large no. of trials.

What is the no. of possibilities for any given sequence of N trials?

Obviously,  $2^N$

Here, entropy is,

$$S_{\text{bit}} = \frac{1}{N} \log 2^N = \log 2 \rightarrow \text{maximum possible entropy in this experiment.}$$

We extend to random walk problem.

$$\text{Say, } P(H) = p \Rightarrow \# H \text{ has prob} = Np$$

$$P(T) = 1-p \Rightarrow \# T \text{ has prob} = (1-p)N$$

No. of possible microstates corresponding to N tosses.

$$\Omega = \frac{N!}{(Np)!(1-p)^N!}$$

Using Stirling,

$$\begin{aligned} \Omega &= \frac{N^N}{(pN)^{pN} (N-pN)^{(N-pN)}} \\ &= \left[ \frac{1}{(p^p)(1-p)^{1-p}} \right]^N \end{aligned}$$

→ we ignore the  $\sqrt{2\pi}$  thing  
□ Show that it can be ignored.

$$\begin{aligned} \therefore S_{\text{bit}} &= \frac{1}{N} \ln \Omega = -p \ln p - (1-p) \ln (1-p) \\ &= -\sum_i P_i \ln P_i \end{aligned}$$

Again,

$$S_{\text{bit}} \stackrel{\text{defn}}{=} \frac{1}{N} \ln S$$

because,

$B.E = S = \ln \Omega$  is NOT intensive.

Now, another 'take' on this thing.

$$S = - \sum p_i \ln p_i$$

We want a probability distribution for  $P$ , that extremizes  $S$ . We use Lagrange multipliers for this.

$$\Rightarrow S' = - \sum_i p_i \ln p_i - \lambda \left( \sum_i p_i - 1 \right) - \beta \left( \sum_i p_i E_i - E \right)$$

↓ ↓  
 Normalization Energy constraints

We maximize w.r.t ~~total~~<sup>constraint</sup> constraints.

$$\frac{\partial S'}{\partial P_i} = -\ln P_i - P_i \cdot \frac{1}{P_i} - \lambda - \beta E_i = 0$$

$$\Rightarrow \ln p_i = -1 - \lambda - \beta E_i$$

$$\Rightarrow p_i = \exp[-1 - \lambda] \exp[-\beta E_i]$$

Using Normalization,

$$\sum_i p_i = 1$$

$$\Rightarrow \exp[-1-\lambda] \cdot \sum \exp[-\beta E_i] = 1$$

$$\Rightarrow P_i = \frac{\exp[-\beta E_i]}{\sum_j \exp[-\beta E_j]}$$

→ This distribution maximizes entropy and thus is related to equilibrium.

## ↳ Partition function.

(\*) How do we see that  $\beta \alpha \frac{1}{f}$ ? (Like we know)

Normally, we associate,

$$E = \frac{p_x^2}{2m} - p_x = mv_x$$

$$\Rightarrow \text{prob}(p_x) = \frac{e^{-\beta p_x^2/2m}}{\sum_{\text{all states}} \exp[-\beta p_x^2/2m]} \xrightarrow{\text{Should be integral}}$$

Now,

$$\bar{E} = \langle E \rangle = \int_{-\infty}^{\infty} \frac{p_x^2}{2m} e^{-\beta p_x^2/2m} dp_x = \frac{1}{2} \beta^{-1} = \frac{1}{2} kT$$

$\frac{\sqrt{2\pi m}}{\beta}$

$$\hookrightarrow \beta \propto \frac{1}{T}$$

□ How exactly do we know that  $\bar{E} = \frac{1}{2} kT$ ?

Consider an atom in contact with a bath of temp T

Here, atom is not isolated. But, "atom + bath"  $\rightarrow$  isolated.

This atom may have microstates  $S_1$  and  $S_2$  with probabilities  $p(S_1)$  and  $p(S_2)$ ,

and energies  $E(S_1)$  and  $E(S_2)$

Now, since atom is coupled to reservoir, any change in atom reflects in reservoir.

So, we associate no. of available microstates of the reservoir to be,

$\Omega_R(S_1)$  and  $\Omega_R(S_2)$

These encode entropy of the reservoir, (only reservoir part)

$$S_R(S_1) \sim \ln(\Omega_R(S_1))$$

$$S_R(S_2) \sim \ln(\Omega_R(S_2))$$

Assumption 1: Atom is equally likely to be in  $S_1$  and  $S_2$ .

# Both  $\Omega_R(S_1)$  and  $\Omega_R(S_2)$  are  $\gg 2$ , because they have many more DOF than the atom here.

So,

$$\frac{p(S_2)}{p(S_1)} = \frac{\Omega_R(S_2)}{\Omega_R(S_1)} = \frac{\exp[S_R(S_1)]}{\exp[S_R(S_2)]}$$

$$= \exp[S_R(S_1) - S_R(S_2)] \rightarrow \text{Small change in atom microstate getting amplified (due to exp)}$$

From thermodynamics,

$$TdS_R = dU_R + \left( \underbrace{PdV_R}_{-} - \underbrace{g_1 dN_p}_{-} \right) = 0 \quad (\text{isolated})$$

$$\Rightarrow S_R(S_1) - S_R(S_2) = \frac{1}{T} [U_R(S_1) - U_R(S_2)]$$

Due to energy conservation of atom + reservoir system,

$$\therefore S_R(S_1) - S_R(S_2) = \frac{1}{T} [E(S_1) - E(S_2)]$$

Then, we write,

$$\frac{P(S_2)}{P(S_1)} = \frac{e^{-E(S_2)/T}}{e^{-E(S_1)/T}}$$

$$\Rightarrow P(S) \sim e^{-E(S)/kT}$$

Next class, we start Kinetic Theory.

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22<sup>nd</sup> January 2025 (Wednesday) →

① Kinetic Theory → (Sourced directly from Kardas' book)

We wish to understand the macroscopic properties of a very large no. of particles.

Thermodynamics → Empirical Laws

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Kinetic Theory → microscopic dynamics

To start, we need a suitable definition of equilibrium.

→ Our systems will be in equilibrium, or will dynamically evolve towards equilibrium.

What do we mean by large?  $N \sim 10^{23}$

Δ Microstate → A complete specification of the type,

$$\{\vec{x}_i, \vec{p}_i\}, i=1, \dots, N$$

Δ Macrostate →  $(E, T)$  → A defined value of the system. Represents a subset of the set of all possible microstates, as many of them may be different but have the same energy, temperature, etc.

The dimension of our phase space is 6-N → Each specification of  $(\vec{x}, \vec{p})$  is a point in this space.

We do have bounds, like the dimensions of the box, or velocity bounds.

∴ We have the volume of phase space denoted by,

$$V = \prod_{i=1}^N \{x_i, p_i\}$$

We should also have a Hamiltonian for the system,  $H(\vec{q}, \vec{p})$

Where,

$$\frac{\partial q_i}{\partial t} = \frac{\partial H}{\partial p_i}$$

$$\frac{\partial p_i}{\partial t} = - \frac{\partial H}{\partial q_i}$$

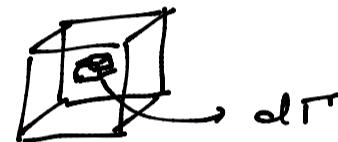
Note: We can look at this system as a snapshot of  $N$  particles,  
or  $\underbrace{N \text{ snapshots of 1 particle}}_{\text{(N - representative points)}}$

↳ When can we do this?

We wait a long time b/w snapshots, so that  
the correlation is lost. Then, we can say that  
the observations are random.

We take a small box volume,  $d\Gamma$ ,

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



We want to count no. of microstates in this  $d\Gamma$  volume.

We define this using,

$$e(p, q, t) = \lim_{N \rightarrow \infty} \frac{dN(p, q, t)}{N}$$

$\rightarrow$  No. of microstates in that volume.

Representative points:  
Sufficiently sample the space

The way that we have defined it,

$$\int e d\Gamma = 1 \rightarrow It \text{ must be conserved}$$

Also, this is a PDF for the probability of finding particle at  $(p, q, t)$

So, we may compute the expectation of any operator,

$$\langle \hat{H} \rangle = \int d\Gamma e(p, q, t) \hat{H}(p, q, t)$$

Say we started from some,  $\{\vec{p}, \vec{q}\}$  which evolves in  $\{\vec{p}', \vec{q}'\}$

We model this as,

→ Ignored.

$$q'_\alpha = q_\alpha + \dot{q}_\alpha \delta t + O(\delta t^2)$$

$$p'_\alpha = p_\alpha + \dot{p}_\alpha \delta t + O(\delta t^2)$$

Taking a differential of these equations,

$$dq'_\alpha = dq_\alpha + \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} \cdot dq_\alpha \cdot \delta t$$

$$dP'_\alpha = dP_\alpha + \frac{\partial \dot{P}_\alpha}{\partial P_\alpha} dP_\alpha \cdot \delta t$$

→ Einstein summation(?)

So, a small volume element,  $dV = dq_\alpha dP_\alpha$

evolves (deforms) to give us,  $dV' = dq'_\alpha dP'_\alpha$

We put in the expressions for the differentials.

$$dV' = dP_\alpha dq_\alpha \left[ 1 + \left\{ \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{P}_\alpha}{\partial P_\alpha} \right\} \delta t \right]$$

↙  
Just look at  
a particle  
slice.

Note,

$$dV = dV'$$

↪ Replace in hamilton eqns  
for  $\dot{q}_\alpha$  and  $\dot{P}_\alpha$  to see that  
this term vanishes. (Exchange of  
partial diff)

Why? Hamiltonian dynamics is conservative. We may  
deform the volume, but cannot change it.

(Liouville's Theorem) □ Try to understand better.

We look at time evolution of  $\rho$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left[ \frac{\partial \rho}{\partial P_\alpha} \cdot \dot{P}_\alpha + \frac{\partial \rho}{\partial q_\alpha} \cdot \dot{q}_\alpha \right]$$

Note:  $\frac{d\rho}{dt} = 0$ , as  $\rho$  is conserved. No number density flows in, or out.

$$\therefore \frac{\partial \rho}{\partial t} = - \sum_{\alpha=1}^{3N} \left[ \frac{\partial \rho}{\partial P_\alpha} \dot{P}_\alpha + \frac{\partial \rho}{\partial q_\alpha} \dot{q}_\alpha \right]$$

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

↓  
Poisson bracket

This could be looked at as a  
consequence of Liouville

This equation dictates the time evolution of  $\rho$ .

We can now define equilibrium.

$$\frac{\partial \rho_{eq}}{\partial t} = 0$$

$$\Rightarrow \{ \rho_{eq}, H \} = 0$$

So, we can say that  $\rho_{eq}$  is conserved.

So,

$$\sum_{a=1}^{3N} \left[ \frac{\partial \rho_{eq.}}{\partial p_a} \dot{p}_a + \frac{\partial \rho_{eq.}}{\partial q_a} \dot{q}_a \right] = 0$$

All components must satisfy, no component form. (Why? all comp are independent here)

$$\Rightarrow \frac{\partial \rho_{eq.}}{\partial p} \cdot \dot{p} + \frac{\partial \rho_{eq.}}{\partial q} \dot{q} = 0$$

How can this hold?

① Trivially,  $\rho_{eq}$  is independent of  $p$  and  $q$ .

$$\Rightarrow \frac{\partial \rho_{eq.}}{\partial p} = \frac{\partial \rho_{eq.}}{\partial q} = 0$$

→ This directly implies that finding the particle at any ( $p, q$ ) has equal probability. (A priori prob may now be defined)

(Microcanonical)

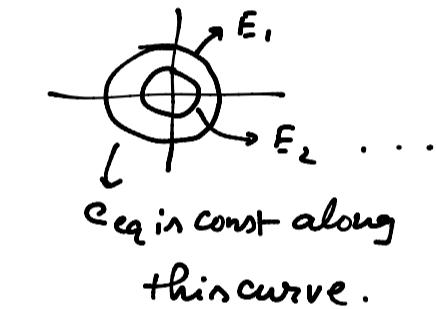
②  $\rho_{eq}$  is constant on a fixed energy surface.

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

(Canonical Ensemble)

Note:  $\rho_{eq} \sim e^{-\frac{H(p, q)}{k_B T}}$  → Boltzmann form

satisfies this canonical condition.



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23<sup>nd</sup> January 2025 (Thursday) →

Reminder:  $\frac{\partial \rho_{eq.}}{\partial t} = 0 \Rightarrow \{ \rho_{eq.}, H \} = 0$

So we have our system going  $\rightarrow$  flow to equilibrium.  
time reversal

If  $\rho$  is far on phase space from  $\rho_{eq}$ , time reversal symmetry of eq state implies large fluctuations -

So, we restrict ourselves to a small region around  $\rho_{eq}$ .

We average over time here — time average

• Ergodic Hypothesis: Time average = Ensemble average.

□ Read upon this.

This may not work well for non-eq systems.

Let's look at one particle  $\rightarrow$

$$f_i(\mathbf{r}_i, \mathbf{p}_i, t) = \text{prob}[\text{Particle at } (\mathbf{r}_i, \mathbf{p}_i, t)] \xrightarrow{\text{Note: particles are indistinguishable}} f_i(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) \prod_{i=1}^N d^3\mathbf{r}_i d^3\mathbf{p}_i$$

Why? Particles are identical, so we get  $N$  times the marginal PDF.

Also,  $\int d^3\mathbf{r} d^3\mathbf{p} f_i(\mathbf{p}, \mathbf{r}, t) = N$

Clearly, we may use this to derive some average density.

$$\eta(\mathbf{r}, t) = \int d^3\mathbf{p} f_i(\mathbf{r}, \mathbf{p}, t) \rightarrow \text{Integrate over momentum info.}$$

Also, average velocity.

$$\bar{\mathbf{v}}(\mathbf{r}, t) = \int d^3\mathbf{p} \frac{\vec{\mathbf{p}}}{m} f_i(\mathbf{r}, \mathbf{p}, t) \rightarrow \text{1st moment of } \frac{\vec{\mathbf{p}}}{m} = \vec{\mathbf{v}}$$

Now, we investigate how  $\frac{\partial f_i}{\partial t}$  evolves with time.

$$\begin{aligned} \frac{\partial f_i}{\partial t} &= N \int \prod_{i=2}^N d^3\mathbf{r}_i d^3\mathbf{p}_i \frac{\partial f}{\partial t} \xrightarrow{\text{Now, this satisfies Liouville.}} \\ &= N \int \prod_{i=2}^N d^3\mathbf{r}_i d^3\mathbf{p}_i \{H, f\} \end{aligned}$$

Reminder:

$$\{H, f\} = \sum_i \left[ \frac{\partial H}{\partial \mathbf{r}_i} \frac{\partial f}{\partial \mathbf{p}_i} - \frac{\partial H}{\partial \mathbf{p}_i} \frac{\partial f}{\partial \mathbf{r}_i} \right] \quad (2\text{-body})$$

Let's take a Hamiltonian:  $H = \frac{1}{2m} \sum_{i=1}^N \mathbf{p}_i^2 + \sum_{i=1}^N V(\mathbf{r}_i) + \underbrace{\sum_{i < i'} U(\mathbf{r}_{i'} - \mathbf{r}_i)}$

All particles independent here.

Interaction term.

Going back,

$$\begin{aligned} \frac{\partial f_i}{\partial t} &= N \int \prod_{i=2}^N d^3\mathbf{r}_i d^3\mathbf{p}_i \left[ - \sum_{j=1}^N \left( \frac{\mathbf{p}_j}{m} \frac{\partial f}{\partial \mathbf{r}_j} \right) + \sum_{j=1}^N \left( \frac{\partial V}{\partial \mathbf{r}_j} \frac{\partial f}{\partial \mathbf{p}_j} \right) \right. \\ &\quad \left. + \sum_{j=1}^N \sum_{k < j} \frac{\partial U(\mathbf{r}_k - \mathbf{r}_{i'})}{\partial \mathbf{r}_j} \cdot \frac{\partial f}{\partial \mathbf{p}_j} \right] \end{aligned}$$

? will it  
be  $j$ ?

for  $N=2$ ,

$$\frac{\partial f_1}{\partial t} = 2 \int d^3 r_1 d^3 p_1 \left[ -\frac{p_1}{m} \frac{\partial f_1}{\partial r_1} - \frac{p_2}{m} \frac{\partial f_1}{\partial r_2} + \frac{\partial V}{\partial r_1} \frac{\partial f_1}{\partial p_1} + \frac{\partial V}{\partial r_2} \frac{\partial f_1}{\partial p_2} + \frac{\partial U(r_1, -r_2)}{\partial r_1} \cdot \frac{\partial f_1}{\partial p_1} \right]$$

( $\hookrightarrow$  why no other term?)

I Think about this - central force assumption?

$$\Rightarrow \frac{\partial f_1}{\partial t} = \left[ -\frac{p_1}{m} \frac{\partial f_1}{\partial r_1} + \frac{\partial V}{\partial r_1} \frac{\partial f_1}{\partial p_1} \right] + \frac{\partial U(r_1, -r_2)}{\partial r_1}$$

Ah screw it, something is wrong here.

Redo  $\rightarrow$

$$\frac{\partial f_1}{\partial t} = 2 \int d^3 r_1 d^3 p \left[ \frac{\partial H}{\partial p} \frac{\partial f_1}{\partial r_1} + \frac{\partial H}{\partial r_1} \frac{\partial f_1}{\partial p} \right]$$

$$\text{Let, } \frac{\partial H}{\partial r_1} = F_2(r)$$

$$\text{We use IBP, } \int u v dx = u \int v dx - \int u' \{ v dx \} dx$$

So, we note,

$$\int \left[ \int d^3 r_1 F_2 \right] \frac{\partial f_1}{\partial p} dp = \left[ \int d^3 r_1 F_2 \right] \int \frac{\partial f_1}{\partial p} dp \xrightarrow{\text{Vanishes at both boundaries.}}$$
$$- \int \left[ d^3 r_1 \frac{\partial F_2}{\partial p} \left\{ \int \frac{\partial f_1}{\partial p} dp \right\} \right] dp$$

$\rightarrow$  Each of these  $r_2$  dependent term integrals vanish.

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