

Lecture 1 \Rightarrow The language of probabilities and microstates

Statistical Mechanics \Rightarrow The theory of how nature works
 \Rightarrow How large systems (consisting of a large number of constituents) behave. (e.g. markets, stocks, wealth distribution. -- not just chemical systems)

Stochastics and Dynamics in systems \Rightarrow Resolve system down to molecular states and processes. \Rightarrow for instance molecular binding. meaning of K_d at microscopic level. (see side notes)

Natural chemical systems \Rightarrow consist of large number of molecules. $\nearrow N$
While the trajectory of a single molecule can be described accurately in phase (position, momentum) space

by the laws of classical and quantum mechanics, it is both unfeasible and unnecessary to describe the evolution of the entire system in terms of the exact microscopic trajectory of every single one of its constituents. Just the sheer number of variables one would have to measure makes this almost impossible. $\hookrightarrow 6N$

As $N \rightarrow \infty$, the macroscopic state of the system can be described by a small number of variables, which can be obtained by statistical averaging of the possible states of the microscopic constituents, taking into account the laws of probability

It's the statistics of large numbers at work!!

Coin toss of a fair coin \Rightarrow difficult to accurately predict the outcome of any given toss. But when no. of tosses $\Rightarrow \infty$, one knows with certainty that exactly half lead to "heads" & other half to "tails". That's how probabilities are defined.

For finite number of tosses, there is an error associated with this predictability $\propto \frac{1}{\sqrt{N}} \Rightarrow$ analogy to fluctuations in thermodynamics

$$N \rightarrow \infty \quad \frac{1}{\sqrt{N}} \rightarrow 0 \quad (\text{Thermodynamic limit})$$

It is no longer necessary to know independent outcome of every coin toss. We can accurately predict the "macro" outcome of interest.

Single-molecule system \Rightarrow



Averaging

Thermodynamic system \Rightarrow

Stochastic nature \Rightarrow of outcomes

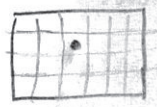
Complete trajectory observable

Deterministic & predictable outcomes

\Rightarrow Microscopic Dynamics is lost

Statistical mechanics approach to process spontaneity (2nd law)
 A large system with a macrostate defined by (N, V, E)

$N \Rightarrow$ no. of molecules
 $V \Rightarrow$ Volume
 $E \Rightarrow$ Total energy



when $N \rightarrow \infty, V \rightarrow \infty \Rightarrow$
 $N/V \rightarrow$ constant (Intensive)
 $E \propto N, V \propto N$ (Extensive)

Thermodynamic limit
 properties uniform across system

No. of possible microscopic configurations

$n_1 \dots \epsilon_1$
 $n_2 \dots \epsilon_2$
 \vdots
 $n_i \dots \epsilon_i$
 i.e. n_1 molecules with energy ϵ_1

$$\sum_i n_i = N ; \quad \sum_i n_i \epsilon_i = E$$

The no. of configurations depends on N of course
 Also of E and V due to quantum mechanics

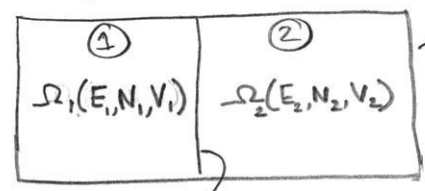
\hookrightarrow constraining potential
 eigenvalue E of the Hamiltonian \Rightarrow possible eigenstates and

Let this be denoted by $\Omega(E, N, V) \Rightarrow$ no. of microstates.

In future we will attempt to calculate this for specific systems.

system \Rightarrow equally likely to be in any of these microstates in the absence of any constraints or any bias. \Rightarrow v. Imp principle.
 "equal a priori probabilities"

Now imagine thermal contact between two systems:



insulating boundary (isolated system)

$$E_1 + E_2 = E \text{ (constant)} \dots 1^{st} \text{ law}$$

let's make this thermally conducting

Two systems exchange energy such that $E_1 + E_2 = \text{constant}$ till equilibrium is reached. At equilibrium $E_1 = \bar{E}_1$ & $E_2 = \bar{E}_2$
 At what value of \bar{E}_1 & \bar{E}_2 is equilibrium reached.

Note N and V are constant.

Method of most probable distribution:

Number of possible configurations for the combined system \Rightarrow

$$\Omega_1(E_1, N_1, V_1) \cdot \Omega_2(E_2, N_2, V_2) \Rightarrow \text{related to conditional probabilities}$$

math refresher

System \nearrow tends to maximize number of possible microstates.
 Why? Since every microstate is equally likely, a system with more microstates is more probable, higher likelihood of its existence.

So maximizing w.r.t E_1

$$\left. \frac{\partial \Omega_1}{\partial E_1} \right|_{N_1, V_1, E_1 = \bar{E}_1} + \Omega_1 \left. \frac{\partial \Omega_2}{\partial E_2} \right|_{N_2, V_2, E_2 = \bar{E}_2} \frac{\partial E_2}{\partial E_1} = 0$$

$$\therefore E_2 = E - E_1 \quad \frac{\partial E_2}{\partial E_1} = -1$$

$$\therefore \frac{1}{\Omega_1} \left. \frac{\partial \Omega_1}{\partial E_1} \right|_{N_1, V_1, E_1 = \bar{E}_1} = \frac{1}{\Omega_2} \left. \frac{\partial \Omega_2}{\partial E_2} \right|_{N_2, V_2, E_2 = \bar{E}_2}$$

$$\left(\frac{\partial \ln \Omega_1}{\partial E_1} \right) \Big|_{N_1, V_1, E_1 = \bar{E}_1} = \left(\frac{\partial \ln \Omega_2}{\partial E_2} \right) \Big|_{N_2, V_2, E_2 = \bar{E}_2}$$

lets call this $\beta = \frac{\partial \ln \Omega}{\partial E} \Big|_{N, V, E = \bar{E}}$

So $\beta_1 = \beta_2$... at equilibrium.

Does this quantity seem familiar?

When two systems are in thermal contact, they attain equal TEMPERATURE at equilibrium.

So β must be related to temperature. In fact $\beta = \frac{1}{kT}$

At equilibrium small transfer of energy from ② to ① leads to % \uparrow in microstates of ① same as % \downarrow in microstates of ②

② $\Omega_1, \Omega_2 = \text{maximized}$
 Not $\Omega_1 + \Omega_2$ but $\ln \Omega_1 + \ln \Omega_2$ is maximized.

The isolated system is a toy model of the universe. (① \rightarrow system)
 Universe spontaneously tends towards increasing disorder (② \rightarrow surroundings)
 Disorder is simply a manifestation of the largeness of the number of microstates ^{or configurations} the system can have.
 The larger the choice of microstates the lesser the predictability and hence the increased level of disorder.

Did the universe start in a single microstate?!

Let's define a new extensive property that describes the level of disorder. A good choice for such a property is

most fundamental property $\rightarrow S = k \ln \Omega$... k is a constant, Boltzmann constant

For above case: composite system ① + ②

$$S = S_1 + S_2 = k(\ln \Omega_1 + \ln \Omega_2) = k \ln \Omega_1 \Omega_2 = k \ln \Omega$$

We need S to be an extensive property so that $S \propto$ size of system.

This choice of function makes it extensive

Also for a system with only one possible configuration; perfectly ordered $S = k \ln 1 = 0 \Rightarrow$ no disorder. We may talk more about this in the context of the third law.

In any spontaneous process, Ω is maximized; i.e. S of composite system increases.

For any spontaneous process $\therefore \Delta S_{\text{composite}} \geq 0$

The equality is true for reversible processes.

% microstates gained by ① equal % microstates lost by ②
driving force limiting to zero.

A process where the system takes small infinitesimal steps towards final state. At each step, the state of the system is perfectly defined. ^(E, N, V) Therefore, it is possible to reverse this process along this exact same path.

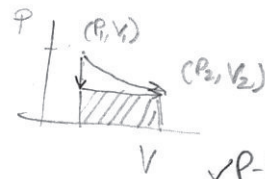
No change in the information content required to define the system. In practice, only infinitesimal steps reversible \rightarrow reversibility is a tool to understand equilibrium properties

Natural processes \Rightarrow irreversible. System takes complex non-equilibrium steps

require lots of variables to define \rightarrow the path so impossible to retrace path.

Irreversible processes are dissipative \rightarrow analogy to friction some "energy" permanently lost to ^{thermal disorder} In the natural course, energy content of the universe is becoming less and less available for conversion into work. The energy available for work \Rightarrow free energy. Free energy decreases in spontaneous processes. \rightarrow Second law. \rightarrow more later

First law restated for a system in contact with surroundings



$$dE = dq - dW$$

E is a state function. Independent of the path taken.

heat gained by system (flows into system)

work done by system

$$dW_{rev} > dW$$

$$dq_{rev} > dq$$

✓ P-V work
 ✓ chemical work.
 ✓ other forms of work f-x
 f = force
 x = displacement

Let's connect entropy and energy

We derived $\frac{1}{k} \left(\frac{\partial S}{\partial E} \right)_{N,V} = \beta = \frac{1}{kT} \therefore \left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T}$

S is also a state function, like E.

For reversible process $dE = dq_{rev} - pdV + \mu dN$

μ = chemical potential

At constant N, V no work done

$$\Rightarrow dS = \frac{dq_{rev}}{T}$$

of system

$$\Delta S_{system} = \int_A^B \frac{dq_{rev}}{T} \Rightarrow S_{composite} \text{ constant}$$

$$dS > \frac{dq_{irrev}}{T}$$

of system

$$\Delta S_{system} > \int_A^B \frac{dq_{irrev}}{T} \Rightarrow S_{composite} \uparrow$$

$$\therefore dq_{irrev} < dq_{rev}$$

Heat is basically flowing energy.

entropy gain by system

entropy lost by surroundings

$$\therefore dE = TdS - pdV + \mu dN \dots \text{for a reversible process.}$$

or, for a given state (equilibrium state)

Free Energy available for work

$$A = E - TS \dots \text{Helmholtz free energy}$$

" available for chemical work

$$G = E - TS + PV \dots \text{Gibbs free energy}$$

More on this in Legendre transform discussion (next lecture)

Other types of contact between systems. ① and ②

* Movable boundary between ① and ②
 Volumes V_1 & V_2 can change, Total $V = V_1 + V_2$ constant

* Permeable boundary
 N_1 & N_2 can change. Total N constant.

$dE = dq - dW \rightarrow$ ^{not state fun⁻} _{not state function}

We saw $dq_{rev} > dq_{irrev}$ since E is state funⁿ
 $\Rightarrow dW_{rev} > dW_{irrev}$

$$dW_{rev} - dW_{irrev} = dq_{rev} - dq_{irrev}$$

where is this work lost?

$$= TdS_{system} - dq_{irrev}$$

$$= T \left(dS_{system} - \frac{dq_{irrev}}{T} \right)$$

also $T(dS_{system} + dS_{surrounding})$
 \Downarrow
 > 0 for irreversible process

$$= T(\text{difference in entropy gained by system and that lost by the surroundings})$$

$$= T \times (\text{increase in disorder of composite system.})$$

Expansion
Maximize microstates as a function of V_1 (or V_2)

$$\left. \frac{d \ln \Omega_1}{dV_1} \right|_{N_1, E_1, V_1 = \bar{V}_1} = \left. \frac{d \ln \Omega_2}{dV_2} \right|_{N_2, E_2, V_2 = \bar{V}_2}$$

Likewise for Diffusion

$$\left. \frac{d \ln \Omega_1}{dN_1} \right|_{E_1, V_1, N_1 = \bar{N}_1} = \left. \frac{d \ln \Omega_2}{dN_2} \right|_{E_2, V_2, N_2 = \bar{N}_2}$$

differential form of fundamental entropy law.

We have seen $dE = TdS - PdV + \mu dN \therefore dS = \frac{dE}{T} + \frac{PdV}{T} - \frac{\mu dN}{T}$

$$\therefore \left. \frac{\partial S}{\partial E} \right|_{V, N} = \frac{1}{T} \quad ; \quad \left. \frac{\partial S}{\partial V} \right|_{N, E} = \frac{P}{T} \quad ; \quad \left. \frac{\partial S}{\partial N} \right|_{E, V} = \frac{-\mu}{T}$$

P, μ are known as driving forces from empirical experience. These are the microscopic definitions

generally $\frac{\partial S}{\partial X} = \frac{force}{displacement}$

Also we get equilibrium criteria for above cases

$$\frac{P_1}{KT_1} = \frac{P_2}{KT_2}$$

$$\text{or } P_1 = P_2$$

$\therefore T_1 = T_2$
simultaneous thermal exchange

$$\text{and } \frac{\mu_1}{KT_1} = \frac{\mu_2}{KT_2}$$

$$\text{or } \mu_1 = \mu_2$$

$\therefore T_1 = T_2$

$\frac{1}{T}, \frac{P}{T}, \frac{\mu}{T}$
are driving forces

T, P, μ are intensive properties $\because S$ & E are both extensive
Knowing T and calculating S allows E, P and μ to be calculated.

If systems can exchange

- 1) Energy then $T_1 = T_2$ at equilibrium
- 2) Volume then $P_1 = P_2$ "
- 3) Particles then $\mu_1 = \mu_2$

We derived this from statistical mechanics (first principles)
More about conditions for equilibrium & stability \Rightarrow next lecture

Systems tend towards occupying more microstates.
Usually processes initiated by removing a constraint that introduces additional microstates.

equilibrium reached when no further \uparrow in microscopic states or configurations possible.

E, V, N repartitioned until S maximum.

$$S(E, V, N) \geq S(E, V, N, \text{internal constraint})$$

Some clarifications

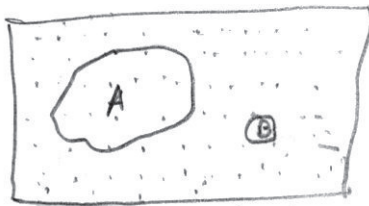
⇒ What do we mean by microstate?

configuration of system in terms of the position/momenta of all particles in the system.
energy associated with each microstate



⇒ Every system, whenever the opportunity, increases its possible microstates or multiplicities.

Why?



universe of all possible microstates.

A is more probable than B since universe would traverse microstates of A more often than B.

Note, here we use the fact that every microstate is equally likely. (equal a priori probabilities) → just like all faces of a dice equally likely.

⇒ The meaning of temperature

how much more "disordered" can you get by absorbing energy.

$\frac{\partial \ln \Omega}{\partial E} = \frac{1}{kT}$ ⇒ The % increase in microstates per unit increase in internal energy. Measures the relative propensity of a system to absorb or release heat.

$\frac{1}{T}$ is the driving force for heat flow.

-ve temperature

systems release energy to get more disordered.

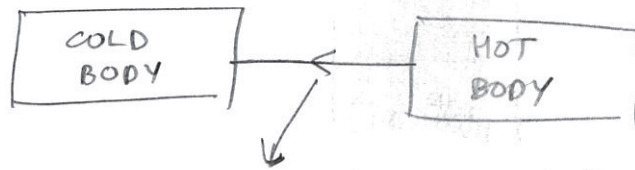
True temperature

systems absorb energy to get more disordered.

$T = 0$ temperature, an infinite increase in disorder with absorption of ^{smallest} packet of energy.
↳ from complete order to finite disorder.

$T = \infty$, no increase in further disorder with absorption of any amount of energy.

Nature prefers to give energy (in the form of heat) to a system with a lower temperature than a system with a higher temperature



energy flows until the incremental ability to increase disorder become equal (equilibrium)

dynamic equilibrium \Rightarrow tiny energy packets exchanged back and forth without any increase in disorder.

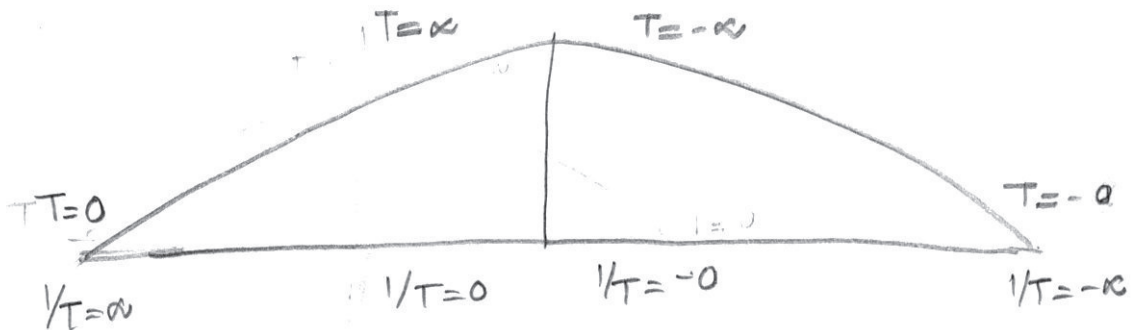
Energy increase allows \overline{x} increase in multiplicity / configurations. The tendency for this is given by $1/T$



Increasing energy \rightarrow

Possible distinct configurations

$$\frac{4!}{0!4!} = 1, \quad \frac{4!}{3!1!} = 4, \quad \frac{4!}{2!2!} = 6, \quad \frac{4!}{1!3!} = 4, \quad \frac{4!}{4!0!} = 1$$



OF N particles n_0 in excited state and $N-n_0$ in ground state then

$$\Omega = \frac{N!}{n! (N-n)!} \Rightarrow \ln \Omega = \ln \left(\frac{N^N}{n^n \cdot (N-n)^{N-n}} \right)$$

$$= -n \ln \frac{n}{N} - (N-n) \ln \left(\frac{N-n}{N} \right)$$

$$\beta = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{V, N}$$

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

$$E = n \Delta E + (N-n) 0 = n \Delta E$$

$$\frac{\partial n}{\partial E} = 1/\Delta E$$

$$\frac{1}{T} = \frac{k}{\Delta E} \left(-1 - \ln \frac{n}{N} + \ln \frac{(N-n)}{N} + \frac{(N-n)}{(N-n)} \right)$$


$$= \frac{k}{\Delta E} \left(-1 - \ln \frac{n}{N} + 1 + \ln \frac{(N-n)}{N} \right)$$


$$= \frac{k}{\Delta E} \left(\ln \frac{(N-n)}{n} \right)$$


$$\frac{1}{T} = \frac{k}{\Delta E} \ln \left(\frac{(1 - \frac{n}{N})}{(n/N)} \right) = \frac{k}{\Delta E} \ln \left(\frac{f_{\text{ground}}}{f_{\text{excited}}} \right)$$


$f_{\text{ground}} \Rightarrow$ fraction of molecules in ground state
 $f_{\text{excited}} \Rightarrow$ fraction of molecules in excited state.


The four cases in the two-state model \Rightarrow


 $\frac{1}{T} = \frac{k}{\Delta E} \ln \left(\frac{4/4}{0/4} \right) = \infty \Rightarrow T = 0$

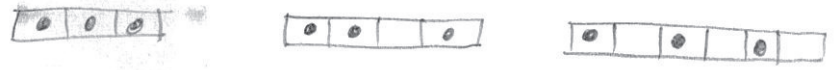

 $\frac{1}{T} = \frac{k}{\Delta E} \ln \left(\frac{3/4}{1/4} \right) = \frac{k}{\Delta E} \ln 3 \Rightarrow T = \frac{\Delta E}{k \ln 3}$


 $\frac{1}{T} = \frac{k}{\Delta E} \ln \frac{2/4}{2/4} = 0 \Rightarrow T = \infty$


 $\frac{1}{T} = \frac{k}{\Delta E} \ln \left(\frac{1/4}{3/4} \right) = \frac{-k}{\Delta E} \ln 3 \Rightarrow T = \frac{-\Delta E}{k \ln 3}$


 $\frac{1}{T} = \frac{k}{\Delta E} \ln \left(\frac{0/4}{4/4} \right) = -\infty \Rightarrow T = -0$

Pressure is the tendency of the system to expand. Expansion \Rightarrow more disorder, more microstates
 High pressure \Rightarrow small expansion leads to large incremental increase in microstates.



possible configurations } $\frac{3!}{3!0!} = 1$ $\frac{4!}{3!1!} = 4$ $\frac{5!}{3!2!} = 10$

This is a better explanation than particles bouncing against the wall! Derived from concept of maximum multiplicities.

Chemical potential is the ability of a system to exchange particles. Diffusion and mixing result because it leads to increase in possible configurations.

	$\Delta\Delta\Delta \mid 000$	$\Delta 0 \Delta \mid 00\Delta$	$\Delta 00 \mid \Delta 0 \Delta$
No of possible microstates }	$\frac{3!}{0!3!} \times \frac{3!}{0!3!}$	$\frac{3!}{2!1!} \times \frac{3!}{2!1!}$	$\frac{3!}{1!2!} \times \frac{3!}{1!2!}$
	$= 1$	$= 9$	$= 9$
		$\xrightarrow{\text{mixing}}$	$\xrightarrow{\text{no further mixing}}$
	Mixing bet ^z diff spatial regions (diffusion)		and different phases (chemical reaction or phase change)

Classifications & Review

→ gradient

defined in terms of entropy/microstates

$\nabla(\frac{1}{T}, \frac{\mu}{T}, \frac{p}{T}) \Rightarrow$ driving forces \Rightarrow also known as thermodynamic fields.

Chemical equilibrium \Rightarrow Particles flow from system ① to ② if $\mu_1 > \mu_2$ (small X -fer dN_i from ① to ② increases dS_{total}) until $\mu_1 = \mu_2 \Rightarrow$ chemical equilibrium (no further entropy increase)

$\frac{\mu}{T}$ is driving force for mass exchange. also known as escaping tendency from one "phase" to another.

E, N, V are the conjugate variables which flow in response to the driving forces.
 one for each type of particle.

fundamental entropy equation. $\Rightarrow dS = \frac{dE}{T} + \frac{p}{T}dV - \sum_j \frac{\mu_j}{T}dN_j - \frac{f}{T}dX$ (for a given system)

Reversible processes or Quasi-static processes \Rightarrow

slower than relaxation time of a system.

i.e. at each step, the system is in equilibrium.

Only quasi-static processes can be represented on state diagrams, because non-quasi-static processes involve more variables than those that define state points.

Non-quasi static processes also depend on gradients or time-dependent quantities such as velocities and friction coefficients

Quasi-static process \Rightarrow allow us to derive relationship between work dw and state variables, pressure and volume.

not a state property. depends on path.

$dw = -p dV$

\Rightarrow Entropy of an isolated system always increases.

\Rightarrow Entropy of a system can decrease but in response the entropy of the surroundings has to increase by an amount greater. only for a reversible process are these two equal.

Stirling's approximation:

$$\ln n! = \ln 1 + \ln 2 + \dots + \ln n$$

$$= \sum_{m=1}^n \ln m$$

For $n \rightarrow \infty$

↓ this becomes an integral

$$\approx \int_{m=1}^n \ln m \, dm$$

$$\approx \left[m \ln m - m \right]_{m=1}^n = n \ln n - n - (-1)$$

For $n \gg 1$

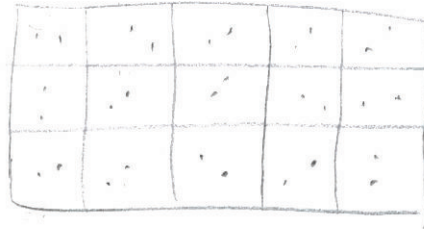
$$\ln n! \approx n \ln n - n = n \ln n - n \ln e = n \ln n/e = \ln \left(\frac{n}{e} \right)^n$$

$$\text{i.e. } n! \approx \left(\frac{n}{e} \right)^n$$

No. of microstates and entropy

N particles distributed into groups of

n_1
 n_2
 n_3
 \vdots
 n_r



$$N = \sum_{i=1}^r n_i$$

$$1 = \sum p_i \text{ where } p_i = \frac{n_i}{N}$$

one example

N molecules of a gas distributed among r sub-volumes $\Rightarrow \omega(n_1, n_2, \dots, n_r)$

p_i is the probability of finding a molecule in the i^{th} subsection

OR N trials with n_i occurrences of i^{th} outcome.
Possible ways to do this

$$\Omega = \frac{N!}{n_1! n_2! \dots n_r!}$$

$$= \frac{(N/e)^N}{(n_1/e)^{n_1} (n_2/e)^{n_2} \dots (n_r/e)^{n_r}}$$

$$= \frac{N^N}{(n_1^{n_1} n_2^{n_2} \dots n_r^{n_r})} \frac{e^N}{e^N} = \frac{1}{p_1^{n_1} p_2^{n_2} \dots p_r^{n_r}}$$

where p_i is the probability of being in i^{th} state

$$\text{Entropy } S/k = \ln \Omega = -\ln(p_1^{n_1} p_2^{n_2} \dots p_r^{n_r})$$

$$= -\sum_{i=1}^r n_i \ln p_i$$

$$\frac{S}{Nk} = -\sum p_i \ln p_i$$

\Rightarrow Probabilistic interpretation of entropy.

\downarrow
entropy per particle
or entropy per trial.

what distribution of probabilities is most likely?
Maximize S

N particles distributed over i levels : $\{n_1, n_2, \dots, n_i\}$ such that $N = \sum_i n_i$
 or N trials distributed over i outcomes : $\{n_1, n_2, \dots, n_i\}$ such that $N = \sum_i n_i$

probability of having outcome i $p_i = \frac{n_i}{N}$ $\sum p_i = 1$

What distribution of $\{p_1, p_2, \dots, p_i\}$ maximizes entropy.

Now $S = -Nk \sum_i p_i \ln p_i$ → collection of probabilities

Maximize this funⁿ subject to constraint $\sum p_i = 1$

Method of Lagrange multipliers ⇒

For a multivariable function $f(x_1, x_2, \dots, x_r)$

at maximum of f $\delta f = \sum_{j=1}^r \left(\frac{\partial f}{\partial x_j} \right)_{\max} \delta x_j = 0$ i.e. $\frac{\partial f}{\partial x_j} = 0$ for every j

r equations. This is ^{only} if all x_j 's are independent.

But if you have a constraint given by $g(x_1, x_2, \dots, x_r) = \text{constant}$

i.e. $\delta g = \sum_{j=1}^r \left(\frac{\partial g}{\partial x_j} \right)_{\max} \delta x_j = 0$

One of the x_j 's is dependent. Let's call it x_k .

Not let's say $\lambda = \left(\frac{\partial f}{\partial x_k} \right)_{\max} / \left(\frac{\partial g}{\partial x_k} \right)_{\max}$
 Lagrange multiplier.

then $\delta f - \lambda \delta g = \sum_{\substack{j=1 \\ \text{except} \\ j=k}}^r \left(\frac{\partial f}{\partial x_j} \right)_{\max} - \lambda \left(\frac{\partial g}{\partial x_j} \right)_{\max} \delta x_j = 0$

Now all x_j 's above eqⁿ are independent $\therefore x_k$ is no longer present

Thus we have (r-1) eqⁿ $\left(\frac{\partial f}{\partial x_j} \right)_{\max} - \lambda \left(\frac{\partial g}{\partial x_j} \right)_{\max} = 0$

get x_j values that satisfy above expression in terms of λ

for multiple constraints $g_1(x_1, x_2, \dots, x_r) = 0, g_2(x_1, x_2, \dots, x_r) = 0, \dots$

$\left(\frac{\partial f}{\partial x_j} \right)_{\max} - \lambda \left(\frac{\partial g_1}{\partial x_j} \right)_{\max} - \beta \left(\frac{\partial g_2}{\partial x_j} \right)_{\max} - \dots = 0$

obtained from experiment

$$S = -Nk \sum_{i=1}^r p_i \ln p_i$$

$$\frac{S}{Nk} = - \sum_{i=1}^r p_i \ln p_i$$

Maximizing $\frac{S}{Nk}$ w.r.t. (p_1, p_2, \dots, p_r) subject to $\sum_{i=1}^r p_i = 1$

$$\therefore \sum_{i=1}^r \delta p_i = 0$$

$$\sum_{i=1}^r \left[\left(\frac{\partial S}{\partial p_i} \right)_{p_j \neq i} - \alpha \right] \delta p_i = 0$$

$$- \left(p_i \frac{1}{p_i} - \ln p_i \right) - \alpha = 0 \quad \text{for all } i$$

$$(-1 - \ln p_i - \alpha) = 0 \quad \text{for all } i$$

$$p_i = e^{-(1+\alpha)} \quad \text{for all } i$$

$$\sum_{i=1}^r p_i = \sum_{i=1}^r e^{-(1+\alpha)} = 1$$

$$\Rightarrow r e^{-(1+\alpha)} = 1$$

$$\therefore e^{-(1+\alpha)} = \frac{1}{r}$$

$$\boxed{p_i = \frac{1}{r}}$$

\Rightarrow Uniform (flat) probability distribution in the absence of constraints.

\Rightarrow probability of finding particle in equal for any sub-volume in the absence of any bias.

Let's introduce a constraint in addition $\sum_{i=1}^r \epsilon_i p_i = E/N$

like our two-level system

$$\text{or } \sum_{i=1}^r \epsilon_i \delta p_i = 0$$

$$\sum_{i=1}^r (-1 - \ln p_i - \alpha - \beta \epsilon_i) \delta p_i = 0$$

$$\therefore p_i = e^{-(1+\alpha+\beta \epsilon_i)}$$

$$\sum_{i=1}^r p_i = \sum_{i=1}^r e^{-(1+\alpha)} \cdot e^{-\beta \epsilon_i} = 1$$

$$\therefore e^{-(1+\alpha)} = 1 / \sum_{i=1}^r e^{-\beta \epsilon_i} =$$

$$\boxed{p_i = \frac{e^{-\beta \epsilon_i}}{\sum_{i=1}^r e^{-\beta \epsilon_i}}}$$

... Boltzmann distribution

p_i distributions \Rightarrow Multinomial distribution

binomial \leftarrow discrete Gaussian
 \uparrow

Special case \Rightarrow Binomial distribution

$$\Omega(n) = \frac{N!}{n!(N-n)!}$$

$$\text{or } \ln \Omega = -\left(n \ln \frac{n}{N} + (N-n) \ln \left(\frac{N-n}{N}\right)\right)$$

for large numbers

It follows from general case, that most likely distribution is

$n = \frac{N}{2}$ in the absence of constraints.

What is likelihood of a distribution deviating from this
Expand $\ln \Omega(n)$ about this point.

$$\ln \Omega(n) = \ln \Omega\left(\frac{N}{2}\right) + \left. \frac{d \ln \Omega}{dn} \right|_{n=\frac{N}{2}} (n - \frac{N}{2}) + \left. \frac{d^2 \ln \Omega}{2 dn^2} \right|_{n=\frac{N}{2}} (n - \frac{N}{2})^2 + \dots$$

\parallel
 0
(maximum condⁿ)

higher order terms neglected for small fluctuations

$$\begin{aligned} \ln \Omega\left(\frac{N}{2}\right) &= -\left(\frac{N}{2} \ln \frac{1}{2} + \frac{N}{2} \ln \frac{1}{2}\right) \\ &= -N \ln \frac{1}{2} = N \ln 2 \end{aligned}$$

$$\frac{d \ln \Omega}{dn} = -\left(\frac{\ln n}{N} + 1 - \ln\left(\frac{N-n}{N}\right) - 1\right)$$

$$\frac{d \ln \Omega}{dn} = -\left(\ln\left(\frac{n}{N-n}\right)\right) = \ln\left(\frac{N-n}{n}\right)$$

$$\frac{d^2 \ln \Omega}{dn^2} = \frac{-1}{N-n} - \frac{1}{n} = \frac{-N}{n(N-n)}$$

$$\text{At } n = \frac{N}{2} ; \frac{d^2 \ln \Omega}{dn^2} = \frac{-N}{\frac{N}{2} \cdot \frac{N}{2}} = -\frac{4}{N}$$

$$\therefore \ln \Omega(n) = N \ln 2 - \frac{2}{N} (n - N/2)^2$$

$$\Omega(n) = 2^N \cdot \exp\left(-\frac{(n - N/2)^2}{N/2}\right)$$

plot this. a gaussian with center at $\frac{N}{2}$ and std deviation $\sigma \sim \sqrt{N}/2$

Gaussian $f(x) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right)$ relative fluctuations $\sim \frac{\sigma}{N/2}$

relative fluctuations $\sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$