

Lecture 1 ⇒ The language of probabilities and microstates

Statistical Mechanics ⇒ The theory of how nature works

⇒ how large systems (consisting of a large number of constituents) behave. (e.g. markets, stocks, wealth distribution. -- not just chemical systems)

⇒ origin of this behavior in terms of microscopic dynamics
Stochastics and Dynamics in systems ⇒ resolve system down to molecular states and processes. ⇒ for instance molecular binding. meaning of K_d at microscopic level. (see side note) $\rightarrow N$

Natural chemical systems ⇒ consist of large number of molecules.

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. $\rightarrow 6N$

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 ⇒ 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 $\propto \frac{1}{\sqrt{N}}$ ⇒ 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 Stochastic nature \Rightarrow complete
of outcomes trajectory
observable

Averaging

Thermodynamic system \Rightarrow Deterministic \Rightarrow macroscopic
& predictable outcomes Dynamics is
lost

Thermodynamics \Rightarrow pays no attention to discrete molecular/microscopic processes, arrived at empirically even before atoms and molecules were known to exist.

The other extreme \Rightarrow A single molecule. Consider a dimer dissociation process



$$K_d = \frac{[A][A]}{[A_2]} \quad \dots \text{ratio of dissociated to undissociated species concentrations}$$

Now imagine if you had only one molecule of A_2 .
Kd is just the probability of A_2 to be in dissociated state to that of being in undissociated state.

Averaged over time or large number of molecules. $K_d = \frac{N(A+A)}{N(A_2)}$
(Stochastics at individual level)

The equilibrium is dynamic. Constant exchange between $A+A$ and A_2 states. \Rightarrow (Dynamics).

Objectives \Rightarrow Encourage you to think of processes in terms of microscopic states, their stochastics, ~~dynamics~~ and correlations

Build upwards to explain the stability, equilibrium, and paths towards equilibrium taken by thermodynamic systems.

(methods of ensembles & distributions)

- * Use statistical machinery (methods of ensembles & distributions) to solve problems in physical chemistry, solid-state physics, and materials science. Maybe even biophysics
- * Appreciate the applicability of such an approach to cutting-edge research.

Lectures & office hours — Notes (available @ end of day)

Problem sets (Once a week \Rightarrow Due the following week) \Rightarrow 20%

Midterm \Rightarrow 20%

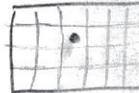
Research literature project \Rightarrow 20%

Final (40%)

Statistical mechanics approach to process Spontaneity (2nd law)

A large system with a macrostate defined by (N, V, E)

$N \Rightarrow$ no. of molecules



when $N \rightarrow \infty, V \rightarrow \infty \Rightarrow$

Thermodynamic limit properties uniform across system

$V \Rightarrow$ Volume

$N/V \rightarrow$ constant (Intensive)

$E \Rightarrow$ Total energy

$E \propto N$

$V \propto N$ (Extensive)

No. of possible microscopic configurations

$$n_1 \dots \varepsilon_1$$

$$n_2 \dots \varepsilon_2$$

:

$$n_l \dots \varepsilon_l$$

i.e. n_1 molecules with energy ε_1

$$\sum_i n_i = N, \quad \sum_i n_i \varepsilon_i = E$$

The no. of configurations depends on N of course

Also of E and V Due to quantum mechanics

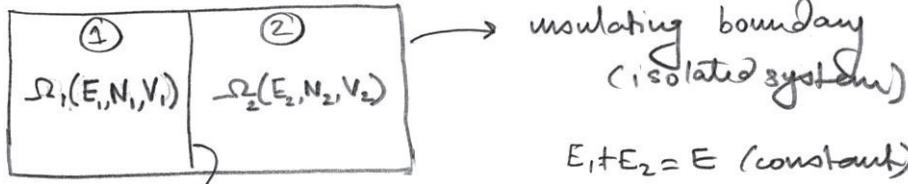
↓
eigenvalues E of the hamiltonian \Rightarrow Possible eigenstates and constraining potential

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 :



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

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

$$\Omega_1(E_1, N_1, V_1) \cdot \Omega_2(E_2, N_2, V_2) \Rightarrow \begin{array}{l} \text{related to} \\ \text{conditional probabilities} \\ \text{Math refresher} \end{array}$$

System 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

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

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

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

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

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

$$\text{so } \beta_1 = \beta_2 \dots \text{at equilibrium.}$$

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 $\beta = \frac{1}{kT}$

The isolated system is a toy model of the universe.
 Universe spontaneously tends towards increasing disorder.
 Disorder is simply a manifestation of the largeness of the number of microstates the system can have.
 The larger the choice of microstates the less predictable and hence the increased level of disorder.

(1) \rightarrow system
 (2) \rightarrow surroundings

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.

$$S = k \ln \Omega, \quad \dots \quad k \text{ is a constant, Boltzmann constant}$$

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 $S = k \cdot \ln 1 = 0 \Rightarrow$ 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
wanting 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
impossible to retrace path.

In reversible processes are dissipative \rightarrow some "energy" ^{available} \rightarrow analogy to friction
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 decreases in spontaneous processes. \Rightarrow Second law. \rightarrow more later

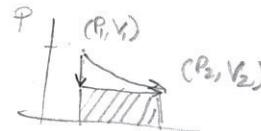
First law restated for a system in contact with surroundings

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

$$dE = dq - dW$$

heat gained by system (flow into system)

work done by system



$\checkmark P-V$ work
 \checkmark chemical work.
 \checkmark other forms of work $f \cdot x$
 f = force
 x = displacement

Let's connect entropy and energy

We derived

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

S is also a state function, like E .

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

At constant N, V
no work done

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

β = chemical potential

$$\Delta S > \frac{dq_{irrev}}{T}$$

of system

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

Heat is basically flowing energy.

entropy gain by system

$$\Delta S_{\text{system}}$$

$$\int_A^B \frac{dq_{irrev}}{T} \Rightarrow S_{\text{composite}} \uparrow$$

entropy lost by surroundings

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

or, for a given state (equilibrium state)

Free Energy available for work $A = E - TS$ Helmholtz free energy

" available for chemical work $G = E - TS + PV$ 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.

$$dE = dq - dW \xrightarrow{\text{not state func}} \text{We saw } dq_{\text{rev}} > dq_{\text{irrev}} \text{ since } E \text{ is state func}^{\Rightarrow} dW_{\text{rev}} > dW_{\text{irrev}}$$

where is this work lost

$$\begin{aligned} dW_{\text{rev}} - dW_{\text{irrev}} &= dq_{\text{rev}} - dq_{\text{irrev}} \\ &= TdS_{\text{system}} - dq_{\text{irrev}} \\ &= T\left(dS_{\text{system}} - \frac{dq_{\text{irrev}}}{T}\right) \quad \text{also } T(dS_{\text{system}} + dS_{\text{surrounding}}) \\ &= T(\text{difference in entropy gained by system and that lost by the surroundings}) \\ &= Tx (\text{disorder in composite system.}) \end{aligned}$$

\downarrow
 >0 for irreversible process

Expansion

Maximize microstates as a function of V_1 (or V_2)

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

Likewise for Diffusion

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

differential form of fundamental entropy law.

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

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

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

Also we get equilibrium criteria for above cases

$$\frac{P_1}{kT_1} = \frac{P_2}{kT_2} \quad \text{or} \quad P_1 = P_2 \quad \therefore T_1 = T_2$$

simultaneous thermal exchange

$$\text{and} \quad \frac{N_1}{kT_1} = \frac{N_2}{kT_2} \quad \text{or} \quad N_1 = N_2 \quad \therefore T_1 = T_2$$

$\frac{1}{T}, \frac{P}{T}, \frac{\mu}{T}$
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.
 \hookrightarrow from knowledge of microstates
If systems can exchange

- 1) Energy then $T_1 = T_2$ at equilibrium
- 2) Volume then $P_1 = P_2$
- 3) Particles then $N_1 = N_2$

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?

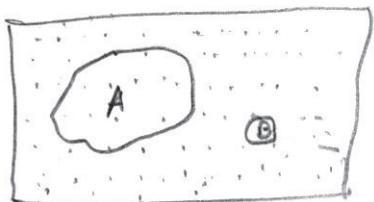
configuration of system in terms of the positions/momenta of all particles in the system.
energy associated with each microstate

classical
continuous distribution

quantum
discrete allowed

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

Why?



universe of all possible microstates.

microstates of A more often than B. A is more probable than B since universe would traverse 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. $\frac{\partial \ln \Omega}{\partial E} = \frac{1}{kT}$ → The % increase in microstates per unit increase in internal energy measures the 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.

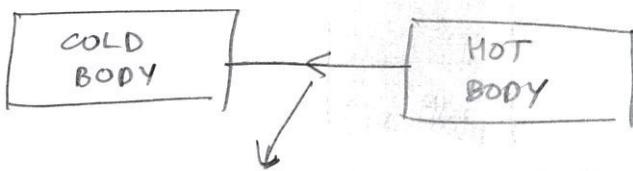
the temperature

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=∞, no increase in further disorder with absorption of any amount of energy.

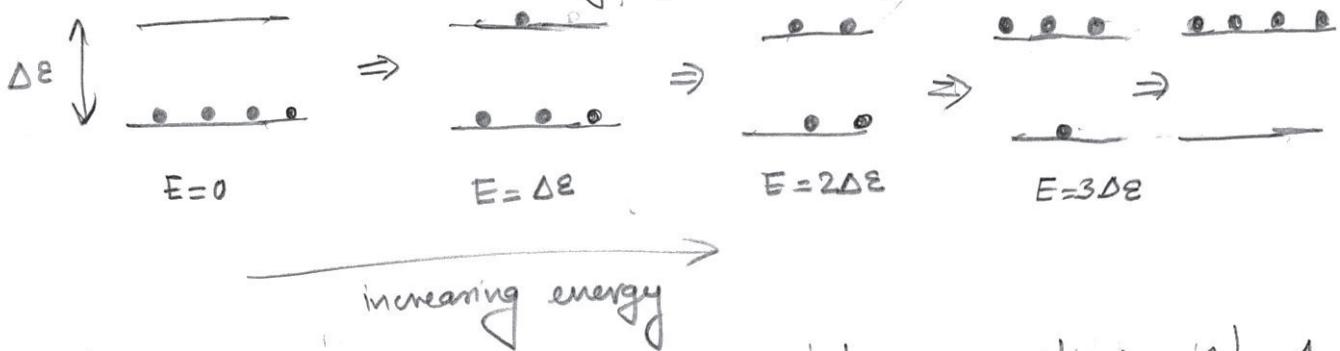
Nature prefers to give energy (in the form of heat) to a system with a lower temperature than a system with a higher temperature



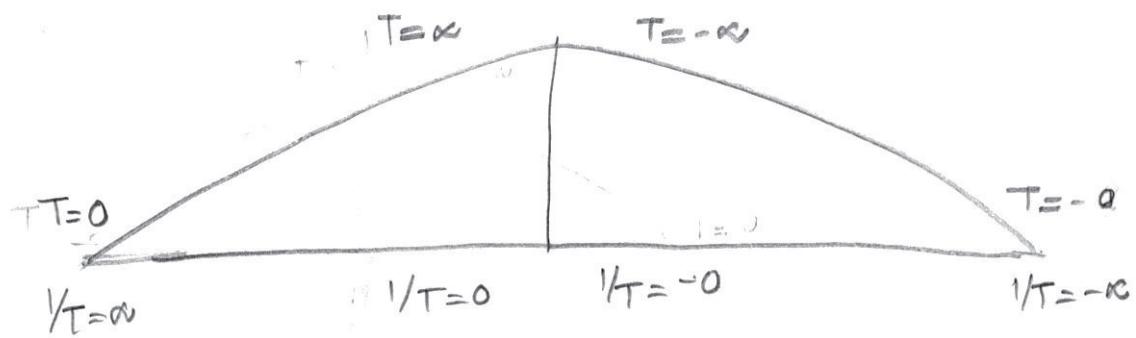
energy flows until the incremental ability to increase disorder become equal. (equilibrium)

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

Energy increase allows increase in multiplicity / configuration. The tendency for this is given by $1/T$



Possible distinct configurations $\frac{4!}{0!4!} = 1$, $\frac{4!}{3!1!} = 4$, $\frac{4!}{2!2!} = 6$, $\frac{4!}{1!3!} = 4$, $\frac{4!}{0!4!} = 1$



If N particles n in excited state and $N-n$ in ground state

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

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

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

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

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

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

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

$f_{\text{ground}} \Rightarrow$ 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

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

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

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

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

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

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

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Dimensional analysis
 Possible configurations } $\xrightarrow{\text{increasing volume}}$ $\frac{3!}{3!0!} = 1$ $\frac{4!}{3!1!} = 4$ $\frac{5!}{3!2!} = 10$

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

Chemical potential is $\xrightarrow{-\chi}$ the ability of a system to exchange particles. Diffusion and mixing result because it leads to increase in possible configurations.

$\Delta\Delta\Delta | 000$

$\Delta\Delta\Delta | 00\Delta$

$\Delta\Delta\Delta | \Delta\Delta\Delta$

No of possible microstates } $\frac{3!}{0!3!} \times \frac{3!}{0!3!} = 1$

$$\frac{3!}{0!3!} \times \frac{3!}{0!3!} = 1$$

$$\frac{3!}{2!1!} \times \frac{3!}{2!1!} = 9$$

$$\frac{3!}{1!2!} \times \frac{3!}{1!2!} = 9$$

$\xrightarrow{\text{mixing}}$

$\xrightarrow{\text{no further mixing}}$

Mixing betⁿ diff spatial regions and different phases
 (diffusion) (chemical reaction or phase change)

Classifications & Review

gradient

defined in terms of entropy/microstates

$\nabla\left(\frac{U}{T}\right), \nabla\left(\frac{M}{T}\right), \nabla\left(\frac{P}{T}\right) \Rightarrow$ driving forces \Rightarrow also known as thermodynamic fields.

Chemical equilibrium \Rightarrow Particles flow from system ① to ② if $M_1 > M_2$
 (small X -grad N_i from ① to ② increases d_{total}) until $M_1 = M_2 \Rightarrow$ chemical equilibrium (no further entropy increase)

$\frac{M}{T}$ 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. \rightarrow one for each type of particle.

Fundamental entropy equation. $\Rightarrow dS = \frac{dE}{T} + \frac{P}{T} dV - \sum_j \frac{M_j}{T} dN_j - \frac{f}{T} dX$ (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 & time-dependent quantities such as velocities and friction coefficients

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

$$d\omega = -P dV$$

$\cancel{\text{not a state property}}$
 $\cancel{\text{depends on path}}$

\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.

Stirlings' approximation:

$$\ln n! = \ln 1 + \ln 2 + \dots + \ln n$$
$$= \sum_{m=1}^n \ln m$$

For $n \rightarrow \infty$

↓ this becomes an integral

$$\approx \int_{m=1}^n \ln m dm$$
$$\approx \int_{m=1}^n (m \ln m - m) = n(\ln n - 1) - (-1)$$

For $n \gg 1$

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

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

No. of microstates and entropy

N particles distributed into groups of

$$\begin{matrix} n_1 \\ n_2 \\ n_3 \\ \vdots \\ n_r \end{matrix}$$

n_1	\cdot	\cdot	\cdot	\cdot	\cdot
\cdot	\cdot	\cdot	\cdot	\cdot	\cdot
\cdot	\cdot	\cdot	\cdot	\cdot	\cdot
\cdot	\cdot	\cdot	\cdot	\cdot	\cdot

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

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

one example

N molecules of a gas distributed among r sub-volumes \Rightarrow (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

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

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

$$= \frac{N^N}{(n_1^{n_1} n_2^{n_2} \dots n_r^{n_r})} \frac{e^N}{e^{n_1} e^{n_2} \dots e^{n_r}} = \frac{1}{P_1^{n_1} P_2^{n_2} \dots P_r^{n_r}}$$

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

$$\begin{aligned} \text{Entropy } S/k &= \ln \Omega = -\ln(p_1^{n_1} p_2^{n_2} \dots p_r^{n_r}) \\ &= -\sum_{i=1}^r n_i \ln p_i \end{aligned}$$

$$\frac{S}{Nk} = -\sum_i p_i \ln p_i \Rightarrow \text{probabilistic interpretation of entropy.}$$

↓
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 $p_i = \frac{n_i}{N} \quad \sum p_i = 1$

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

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

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

Method of Lagrange multipliers \Rightarrow

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 $g(x_1, x_2, \dots, x_r) = \text{constant}$.

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

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

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

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

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

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

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

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

Maximizing $\frac{S}{Nk}$ w.r.t. (p_1, p_2, \dots, p_r) subject to $\sum_{i=1}^r p_i = 1$
 $\therefore \sum_{i=1}^r \delta p_i = 0$

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

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

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

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

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

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

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

$\therefore \boxed{p_i = \frac{1}{r}}$ \Rightarrow Uniform (flat) probability distribution
 in the absence of constraints.

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

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

like our two-level system

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

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

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

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

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

$$\therefore \boxed{p_i = \frac{e^{-\beta \varepsilon_i}}{\sum e^{-\beta \varepsilon_i}}} \quad \dots \text{Boltzmann distribution}$$

p_i distributions \Rightarrow Multinomial distribution

Binomial \leftarrow discrete Gaussian

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

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

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

$$\ln \Omega(n) = \ln \Omega\left(\frac{N}{2}\right) + \frac{d \ln \Omega}{dn} \Big|_{n=\frac{N}{2}} \left(n - \frac{N}{2}\right) + \frac{1}{2} \frac{d^2 \ln \Omega}{dn^2} \Big|_{n=\frac{N}{2}} \left(n - \frac{N}{2}\right)^2 + \dots$$

$\stackrel{0}{\text{(maximum cond.)}}$

higher order terms neglected for small fluctuations

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

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

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

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

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

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

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

plot this. a gaussian with center at $\frac{N}{2}$ and width $\sim \sqrt{N}$

$$\text{Gaussian } f(x) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left(-\frac{(x-x_c)^2}{2\sigma^2}\right)$$

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