Statistical Mechanics $\Rightarrow$ The theory of how nature works
$\Rightarrow$ How large systems (consisting of a large number of constituents) behave. (eg. markets, stocks, wealth distribution. -- not just chemical systems).
$\Rightarrow$ Organ of this behavior in terms of microscopic dynamics

Stoichiometry and Dynamics in systems $\Rightarrow$ Resolve system down to molecular states and processes. For instance, molecular binding. Meaning of $K_d$ at microscopic level. (see side note)

Natural chemical systems $\Rightarrow$ 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.

As $N \to \infty$, 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 is the statistics of large numbers at work!!

A coin toss of a fair coin is difficult to accurately predict the outcome of any given toss. But when no. of tosses $\to \infty$, 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

$N \to \infty \quad \frac{1}{\sqrt{N}} \to 0$ (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 trajectory is unobservable

$\downarrow$

Averaging

Thermodynamic system $\Rightarrow$ Deterministic & predictable outcomes

Dynamics is lost
Thermodynamics: page no attention to discrete molecular/ microscopic processes. arrived at empirically even before atoms and molecules were known to exist.

The other extreme = a single molecule. Consider a dimer dissociation process

$$A_2 \rightleftharpoons A + A$$

$$K_d = \frac{[A][A]}{[A_2]}$$

...ratio of dissociated to undissociated species concentrations

Now imagine if you had only one molecule of $A_2$. $K_d$ is just the probability of $A_2$ to be in a dissociated state to that of being in an undissociated state. Averaged over time or large number of molecules. $K_d = \frac{N(A+A)}{N(A_2)}$

(Stochastic at individual level)

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

Objectives: Encourage your to think of processes in terms of microscopic states, their stochastic dynamics and correlations build upwards to explain the stability, equilibrium, and path taken by thermodynamic systems.

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 at end of day)
Problem sets (Once a week \( \Rightarrow \) Due the following week) \( \Rightarrow \) 20%
Midterm \( \Rightarrow \) 20%
Research literature project \( \Rightarrow \) 20%
Final \( (40\%) \)
A large system with a macrostate defined by \((N,V,E)\) when \(N \to \infty\), \(V \to \infty\) \(\Rightarrow\) uniform and constant \(E\) \(\Rightarrow\) intensive

\(N \to \) no. of molecules
\(V \to \) volume
\(E \to \) total energy

\(\frac{E}{N} \to \) constant \(\Rightarrow\) intensive

Exhaustive

No. of possible macroscopic configurations

\[ n_1 \cdots E_1 \]
\[ n_2 \cdots E_2 \]
\[ \vdots \]
\[ n_i \cdots E_i \]

\[ \sum n_i = N \quad \sum n_i E_i = E \]

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

\(\Rightarrow\) constraining potential

eigenvalue \(E\) of the Hamiltonian \(\Rightarrow\) possible eigenstates

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 equally likely to be in any of these microstates in the absence of any constraints or any bias \(\Rightarrow\) v. max principle.

"equal a priori probabilities"

Now imagine thermal contact between two systems:

\[ \Omega_1(E,N_1,V_1) \]
\[ \Omega_2(E_2,N_2,V_2) \]

\[ \Omega_{1,2}(E,N_1,V_1) \]

\(E_1 + E_2 = E\) \(\Rightarrow\) 1st law

Let's make this thermally conducting.

Two systems exchange energy such that \(E_1 + E_2 = \) constant till equilibrium is reached. At equilibrium \(E_1 = E_2\) is equilibrium reached.

At what value \(\bar{E_1} \) and \(\bar{E_2} \) is equilibrium reached.

Note \(N\) and \(V\) are constant.
method of most probable distribution:

Number of possible configurations for the combined system: 

\[ \Omega_1(E_1, N_1, V_1) \cdot \Omega_2(E_2, N_2, V_2) \Rightarrow \] 

related to 

conditional probabilities 

math refresher

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. \( E \):

\[ \frac{\partial \Omega_1}{\partial E_1} \bigg|_{E_1 = E} + \frac{\partial \Omega_2}{\partial E_2} \bigg|_{E_2 = E} \frac{\partial E_2}{\partial E_1} = 0 \]

\[ \therefore \frac{\partial \Omega_1}{\partial E_1} \bigg|_{N_1, V_1, E_1 = E_1} = \frac{\partial \Omega_2}{\partial E_2} \bigg|_{N_2, V_2, E_2 = E_2} \]

At equilibrium:

small transfer 
of energy from 1 

to 2 leads to 

\( \% \) in microstates of 1 

different as \( \% \) in microstates of 2.

So \( \Omega_1, \Omega_2 = \text{maximum} \) 

Not \( \Omega_1 + \Omega_2 \)

is maximized.

Let's call this \( \beta = \frac{\partial \ln \Omega}{\partial E} \bigg|_{N, V, E = E} \)

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 \( \beta \) 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 larger number of microstates the universe can have. 

The larger the choice of microstates the lesser the predictability and hence the increased level of disorder.

Is the universe 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 the most fundamental property:

$$S = k \ln \Omega$$

$k$ is a constant, Boltzmann constant.

For the above case: composite system $\text{(1)} + \text{(2)}$

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

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:

$$S = k \ln 1 = 0 \implies \text{no disorder.}$$

We may talk more about this in the context of the third law.

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

For any spontaneous process: $\Delta S > 0$ for reversible processes.

The equality is true for reversible processes.

A process where the system takes small infinitesimal steps towards final state. At each step, the state of the system is perfectly defined. 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.

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

$\Rightarrow$ require lot of variables to define so impossible to retrace path.

Irreversible processes are dissipative $\Rightarrow$ some "energy" permanently lost to 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.
First law: Restated for a system in contact with surroundings

\[ \Delta E = \Delta q - \Delta W \]

- **E** is a state function. Independent of the path taken.
- **Heat gained by the system** (Q from the system)
- **Work done by the system** (W)

\[ \Delta W_{\text{rev}} \to \Delta W \]
\[ \Delta q_{\text{rev}} \to \Delta q \]

Let's connect entropy and energy

\[ \frac{1}{k} \frac{\partial S}{\partial E}_{N,V} = \beta = \frac{1}{kT} \]
\[ \Rightarrow \frac{\partial S}{\partial E}_{N,V} = \frac{1}{T} \]

**S** is also a state function, like **E**.

For reversible processes: \[ \Delta E = \Delta q_{\text{rev}} - p \Delta V + m \Delta N \]

At constant **N, V**

\[ \Rightarrow \Delta S = \frac{\Delta q_{\text{rev}}}{T} \]

**Heat is basically flowing energy.**

\[ \Rightarrow \Delta S > \Delta q_{\text{rev}} / T \]
\[ \Rightarrow \Delta S_{\text{system}} > \frac{\Delta q_{\text{irrev}}}{T} \]

**Entropy gained by the system**

\[ \Rightarrow \Delta S_{\text{system}} > \Delta S_{\text{composite constant}} \]

\[ \Rightarrow \Delta S_{\text{system}} > \Delta S_{\text{composite}} \]

**Entropy lost by the surroundings**

\[ \Rightarrow \Delta E = T \Delta S - p \Delta V + m \Delta N \] ... for a reversible process.

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 \( V_1 \) and \( V_2 \) can change, Total \( V = V_1 + V_2 \) constant

\* Permeable boundary \( N_1 \) and \( N_2 \) can change, Total \( N \) constant.
\[ dE = dq - dW \rightarrow \text{not state func.} \]
\[ dW_{rev} - dW_{nonrev} = dq_{rev} - dq_{nonrev} \]
\[ = T dS_{system} - dq_{nonrev} \]
\[ = T \left( dS_{system} - dq_{nonrev} \right) \]
\[ = T \left( \text{difference in entropy gained by system and lost by the surroundings} \right) \]
\[ \text{increase in}\ T \sigma \text{ (disorder of composite system.)} \]
Maximize number of microstates as a function of $V_1$ (or $V_2$)

$$\frac{d \ln \Omega_1}{dV_1} = \frac{d \ln \Omega_2}{dV_2}$$

Likewise for diffusion:

$$\frac{d \ln \Omega_1}{dN_1} = \frac{d \ln \Omega_2}{dN_2}$$

We have seen $dE = TdS - PdV + udN$ ... $dS = dE/T - PdV - u dN$.

$$\frac{dS}{dE} = \frac{1}{T} \quad \frac{dS}{dN} = -\frac{P}{T} \quad \frac{dS}{dV} = \frac{u}{T}$$

$p, u$ are known as driving forces from empirical experience. These are the microscopic definitions.

Also we get equilibrium criteria for above cases:

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

$$\frac{M_1}{kT_1} = \frac{M_2}{kT_2} \quad \text{or} \quad M_1 = M_2 \quad \Rightarrow \quad T_1 = T_2$$

$T, p, u$ are intensive properties. So $S$ & $E$ are both extensive. Knowing $T$ and calculating $S$ allows $E, P, \text{and} u$ 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 $M_1 = M_2$

We derived this from statistical mechanics (first principles).

More about conditions for equilibrium & stability next lecture.

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

Equilibrium reached when no further Tin 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/moments 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.

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

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

The meaning of temperature

\( \frac{\partial Q}{\partial E} = \frac{1}{kT} \)

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.

Temperature

- Systems release energy to get more disordered.
- Systems absorb energy to get less disordered.

\( T = 0 \) temperature, an infinite increase in disorder with absorption of smallest package of energy

\( T = \infty \), 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, until the incremental ability to increase disorder becomes equal. (equilibrium)

Dynamic equilibrium ⇒ tiny energy packets exchanged back and forth without any increase in disorder.

Energy increase allows increase in multiplicity | configurations

\[
\begin{align*}
\Delta E & \quad \Rightarrow \quad E = \Delta E \quad \Rightarrow \quad E = 2\Delta E \quad \Rightarrow \quad E = 3\Delta E
\end{align*}
\]

Possible distinct configurations

\[
\frac{4!}{0!4!} = 1, \quad \frac{4!}{9!1!} = 4, \quad \frac{4!}{2!2!} = 6, \quad \frac{4!}{11!3!} = 4, \quad \frac{4!}{4!0!} = 1
\]

\[
\begin{align*}
T=\infty & \quad T=\infty \\
T=0 & \quad T=0 \\
\frac{1}{T}=\infty & \quad \frac{1}{T}=\infty \\
\frac{1}{T}=0 & \quad \frac{1}{T}=0
\end{align*}
\]

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

If \( N \) particles, \( n \) in excited state and \( N-n \) in ground state, then
\[
\frac{1}{T} = \frac{k}{\Delta E} \left( -1 - \ln \frac{n}{N} + \ln \frac{(N-n)}{N} + \frac{(N-n)}{(N-n)} \right)
\]

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

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

\[
\text{ground} \Rightarrow \text{fraction of molecules in ground state}
\]

\[
\text{excited} \Rightarrow \text{fraction of molecules in excited state}
\]

The four cases in the two-state model:

\[
\frac{1}{T} = \frac{k}{\Delta E} \frac{\ln (0/4)}{0/4} \Rightarrow T=0
\]

\[
\frac{1}{T} = \frac{k}{\Delta E} \frac{\ln (8/4)}{2/4} = \frac{k}{\Delta E} \ln 3 \Rightarrow T=\frac{\Delta E}{k \ln 3}
\]

\[
\frac{1}{T} = \frac{k}{\Delta E} \frac{\ln (2/4)}{2/4} = 0 \Rightarrow T=\infty
\]

\[
\frac{1}{T} = \frac{k}{\Delta E} \frac{\ln (4/3)}{3/4} = \frac{k}{\Delta E} \ln 3 \Rightarrow T=\frac{-\Delta E}{k \ln 3}
\]

\[
\frac{1}{T} = \frac{k}{\Delta E} \frac{\ln (0/4)}{4/4} = -\infty \Rightarrow T=0
\]
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.

\[
\text{Possible configurations } Y = \frac{3!}{8!0!} = 1 \quad \frac{4!}{8!1!} = 4 \quad \frac{5!}{3!2!} = 10
\]

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.

\[
\Delta \Delta \Delta | 000 \quad \Delta \Delta 0 | 000 \quad \Delta 00 | \Delta 00
\]

No of possible microstates
\[
\frac{3! \times 3!}{0!3!} = 1 \quad \frac{3! \times 3!}{2!1!2!} = 9 \quad \frac{3! \times 3!}{1!2!1!2!} = 9
\]

Mixing between different spatial regions (diffusion) and different phases (chemical reaction or phase change)
Chemical equilibrium: Particles flow from system 1 to 2 if \( H_1 > H_2 \) (until \( H_1 = H_2 \) \( \Rightarrow \) chemical equilibrium (entropy increase)).

\( \Delta H \) is the 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.

**Fundamental Enthalpy equation:**

\[
\frac{dS}{T} = \frac{dE}{T} + \sum \frac{dN}{T} - \sum \frac{dX}{T} \quad \text{(for a given system)}
\]

Reversible processes vs quasi-static processes: reversible processes are 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 of time-dependent quantities such as velocities and friction coefficients.

Quasi-static process \( \Rightarrow \) derive relationship between work and state variables, pressure and volume.

\[
 dw = -pdV
\]

- Enthalpy of an isolated system always increases.
- Enthalpy of a system can decrease but in response the enthalpy of the surroundings has to increase by an amount greater than the work done.
Stirling's approximation:

\[ \ln n! = \ln 1 + \ln 2 + \ldots + \ln n \]

\[ \approx \sum_{m=1}^{n} \ln m \]

For \( n \to \infty \), this becomes an integral:

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

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

For \( n \to \infty \):

\[ \ln n! \approx n \ln n - n = n \ln n - n \ln e = n \ln n/e = \ln (n/e)^n \]

i.e., \( n! \approx (n/e)^n \)
No. of microstates and entropy

N particles distributed into groups of

\[ n_1, n_2, n_3, \ldots, n_r \]

OR N trials with \( n_i \) occurrences of \( i^{th} \) outcome.

Possible ways to do this

\[ \Omega = \frac{N!}{n_1! n_2! \cdots n_r!} \]

\[ = \frac{(N/e)^N}{(n_1/e)^{n_1} (n_2/e)^{n_2} \cdots (n_r/e)^{n_r}} \]

\[ = \frac{N!}{(n_1^{n_1} n_2^{n_2} \cdots n_r^{n_r})} \frac{e^{n_1}}{e^{n_1}} = \frac{1}{p_1^{n_1} p_2^{n_2} \cdots p_r^{n_r}} \]

where \( p_i \) is the probability of being in \( i^{th} \) state.

Entropy

\[ \frac{S}{k} = \ln \Omega = -\ln(p_1^{n_1} p_2^{n_2} \cdots p_r^{n_r}) \]

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

\[ \frac{S}{Nk} = -\sum_{i=1}^{r} \frac{p_i}{N} \ln p_i \Rightarrow \text{Probabilistic interpretation of entropy.} \]

(Entropy per particle or entropy per trial.)

What distribution of probabilities is most likely?

Maximize \( S \)
\( N \) particles distributed over \( i \) levels: \( N = n_1 + n_2 + \ldots + n_i \) such that \( N = \sum_i n_i \)

or \( N \) trials distributed over \( i \) outcomes: \( n_1, n_2, \ldots, n_i \) such that \( N = \sum_i n_i \n
\text{probability of having outcome } i \quad p_i = \frac{n_i}{N} \quad \sum_i p_i = 1

What distribution \( p_1, p_2, \ldots, p_i \) maximizes entropy?

Now \( S = -N k \sum_i p_i \ln p_i \)

Maximize this function subject to constraint \( \sum_i p_i = 1 \)

Method of Lagrange multipliers: \( \n\)

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

at maximum of \( f \quad \frac{\partial f}{\partial x_j} = 0 \) i.e. \( \frac{\partial f}{\partial x_j} = 0 \) for every \( j \)

or equations. This is if all \( x_j \)'s are independent.

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

i.e. \( \frac{\partial g}{\partial x_j} = 0 \)

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

Not let's say \( \lambda = \frac{\frac{\partial f}{\partial x_k}}{\frac{\partial g}{\partial x_k}} \)

Lagrange multiplier.

then \( \frac{\partial f}{\partial x_j} - \lambda \frac{\partial g}{\partial x_j} = 0 \quad \text{for } j \neq k \)

\( \lambda \) is \( g \)'s Lagrange multiplier.

Now all \( x_j \)'s above eq\( \# \) are independent if \( x_k \) is no longer present.

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

get \( x_j \) values that satisfy above expression in terms of \( \lambda \)

for multiple constraints \( g_1(x_1, x_2, \ldots, x_r) = 0, \quad g_2(x_1, x_2, \ldots, x_r) = 0, \ldots \)

\( \frac{\partial f}{\partial x_j} - \lambda \left( \frac{\partial g_1}{\partial x_j} \right)_{\text{max}} - \beta \left( \frac{\partial g_2}{\partial x_j} \right)_{\text{max}} = 0 \)
\[ S = -Nk \sum_{i=1}^{r} p_i \ln p_i \quad \frac{S}{Nk} = - \sum_{l=1}^{r} p_i \ln p_i \]

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

\[ \sum_{i=1}^{r} \left[ \frac{\partial S}{\partial p_i} - \alpha \right] \delta p_i = 0 \]

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

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

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

\[ \sum_{l=1}^{r} p_i = \sum_{l=1}^{r} e^{- (1+\alpha)} = 1 \]

\[ \Rightarrow \quad e^{- (1+\alpha)} = \frac{1}{r} \]

\[ \Rightarrow \quad \boxed{p_i = \frac{1}{r}} \]

\[ \Rightarrow \quad \text{Uniform (flat) probability distribution in the absence of constraints.} \]

\[ \Rightarrow \quad \text{Uniform probability of finding particle is equal for any sub-volume in the absence of any bias.} \]

\[ \Rightarrow \quad \text{Introduce a constraint in addition } \sum_{l=1}^{r} \delta p_i = \frac{E}{N} \]

\[ \sum_{l=1}^{r} (1 - \ln p_i - \alpha - \beta \delta) \delta p_i = 0 \]

\[ p_i = e^{- (1+\alpha + \beta \delta)} \]

\[ \sum_{l=1}^{r} p_i = \sum_{l=1}^{r} e^{- (1+\alpha)} = 1 \]

\[ e^{- (1+\alpha)} = \frac{1}{\sum_{l=1}^{r} e^{- \beta \delta}} \]

\[ p_i = \frac{e^{- \beta \delta}}{\sum_{l=1}^{r} e^{- \beta \delta}} \]

\[ \Rightarrow \quad \text{Boltzmann distribution.} \]
\( q \text{ distributions } \Rightarrow \text{ Multinomial distribution} \)

Special case \( \Rightarrow \text{ Binomial distribution} \)

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

\( q \text{ or } \ln \Omega = -\frac{n \ln \frac{n}{N} + (N-n) \ln \frac{N-n}{N}}{N} \) \( \quad \text{for large numbers} \)

It follows from general case that most likely distribution is \( n = \frac{N}{2} \) in the absence of constraints. What is the likelihood of a distribution deviating from this point? Expand \( \ln \Omega(n) \) about this point.

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

\( \ln \Omega \left( \frac{N}{2} \right) = -\left( \frac{N}{2} \ln \frac{1}{2} + \frac{N}{2} \ln \frac{1}{2} \right) \]

\( = -N \ln \frac{1}{2} = N \ln 2 \)

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

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

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

At \( n = \frac{N}{2} \) ; \( \frac{d^2 \ln \Omega}{dn^2} = \frac{-N}{N \cdot N/2} = \frac{-4}{N} \)

\[
\therefore \ln \Omega(n) = N \ln 2 - \frac{2}{N} \frac{(n-N)^2}{2}
\]

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

\( q \text{ Gaussian } f(x) = \frac{1}{(2\pi \sigma^2)^{1/2}} \exp \left( -\frac{(x-x_0)^2}{2\sigma^2} \right) \)

plot this. a gaussian with center \( \frac{N}{2} \) and width \( \sqrt{N} \)

relative fluctuations \( \sim \frac{\sigma}{N} \)

relative fluctuations \( \sim \frac{1}{\sqrt{N}} \)